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TAILORING ELECTROLYTE SOLVATION AND ELECTRODE-ELECTROLYTE INTERPHASES FOR HIGH-PERFORMANCE SODIUM METAL BATTERIES

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Tailoring Electrolyte Solvation and Electrode-Electrolyte Interphases for High-Performance Sodium Metal Batteries

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A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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<u>Hu Liang</u> (Name of student)

Abstract

Lithium-ion batteries (LIBs) have dominated the global market of consumer electronics, electric vehicles, and grid-scale energy storage because of their high energy/power density, long cycle life, and safety. However, limited reserves and geographical distribution of lithium have intensified the search for alternatives. Sodium-ion batteries (SIBs) have emerged as a promising one, because of their low cost, abundant existence, and compatible technologies with existing LIB production. Nevertheless, gaps still exist between state-of-the-art SIBs and commercial LIBs, particularly in terms of energy density and stability. Employing sodium metal anode presents a promising pathway to bridge this gap, because of its high theoretical capacity of 1166 mAh g^{-1} and low electrochemical potential (-2.71 V vs. reversible hydrogen electrode). The reversible and durable operation of sodium metal batteries (SMBs) at low temperatures is essential for cold-climate applications but is plagued by dendritic Na plating and unstable solid-electrolyte interphase (SEI) formation. Current Coulombic efficiencies (CE) of sodium plating/stripping at low temperatures fall significantly below 99.9%, representing a substantial barrier to practical implementation.

In this research, the challenges stated above were addressed strategically first by modifying the solvation structure of a conventional 1M NaPF₆ in diglyme (G2) electrolyte through facile cyclic ether (1,3-dioxolane, DOL) dilution. This DOL diluent helps achieve an impressive Na⁺ ion conductivity, 5.46 mS cm⁻¹ at 25 °C, and facilitates the desolvation of Na⁺ through weakening the chelation by G2, leading to a decrease in the Na⁺ ion desolvation energy from 282.7 to 245.1 kJ mol⁻¹. More importantly, this modification promotes concentrated electron cloud distribution around PF₆⁻ in the solvates, favoring their preferential decomposition, and an inorganic-rich SEI with compositional uniformity, high ionic conductivity, and high Young's modulus of 1.1 Gpa. As a result, a record-high CE exceeding 99.9% is achieved at an ultralow temperature of -55 °C, and a 1-Ah capacity pouch cell employing an initial anode-free sodium metal battery (AFSMB) configuration retains 95% of the initial discharge capacity over 100 cycles at -25 °C.

High-voltage cathodes of SMBs are promising for increasing energy density. However, the elevated charging cut-off voltage necessitates better oxidation stability of the electrolyte. Although ether-based electrolytes are highly compatible with Na metal anodes, their applications in high-voltage SMBs remain limited because of their relatively low value of highest occupied molecular orbital (HOMO) energy levels. High-concentration electrolytes have proven effective in

decreasing solvent activity and enhancing the electrolyte oxidative stability of electrolytes. However, concentrating ether electrolytes based on fluorine-rich sodium salts is challenging because of their high lattice energies and limited solubility in ether solvents. The next part of the work reveals a unique solubilization effect of cyclic ethers for enhanced solubility of NaPF₆ in G2. The introduction of solubilizing DOL co-solvent into the NaPF₆–G2 electrolyte promotes the coordination of G2 solvent with Na⁺ and decreases the free G2 solvent ratio from 35 to 24%. The ratio of contact ion pair (CIP) and aggregate (AGG) solvates increases from 23 to 32%, promoting the formation of stable NaF-rich cathode electrolyte interphase (CEI). Both factors significantly eliminate the decomposition reaction at high-voltage battery operation, enabling an average charge/discharge CE of 99.7% for the Na₃V₂O₂(PO₄)₂F cathode. More intriguingly, the asobtained electrolytes retain a relatively low viscosity of 10.83 mPa·s at 25 °C, ensuring fast Na⁺ ion mobility with a diffusion coefficient of 1.17×10^{-10} m² s⁻¹ and thus smooth charge transfer kinetics during charge/discharge. Consequently, the as-fabricated Na//Na₃V₂O₂(PO₄)₂F cell retains 89.9% capacity over 2000 cycles at a high operation voltage of 4.4 V.

Solvent engineering involves molecular structure regulation of solvents, such as optimizing the structure of alkyl groups in solvent molecules, decreasing the ether oxygen atom content in solvent molecules, and substituting atoms of the solvent molecules with halogen atoms or halogen groups. While improving oxidative stability, these modifications weaken the salt dissociation ability of solvents and decrease electrolyte ionic conductivity. Furthermore, fluorinated solvents have high costs and pose potential environmental hazards. In the last part of the research, the stabilization of the ether electrolyte at high operation voltages by forming a crown-like solvation structure is demonstrated. It enables the coordination of active oxygen atoms in the ether solvent with Na⁺ ions. Unlike the above-mentioned solvent engineering strategies, this new approach promotes an oxidatively stable electrolyte, achieving a 55% ratio of solvent-separated ion pair solvates, favorable salt dissociation up to 2.5 M, and ensuring a Na⁺ ion conductivity of 1.13 mS cm⁻¹ at 25 °C. The high-voltage reversibility of the cathode can be enhanced by using NaBF₄ to replace NaPF₆, which produces more favorable B-containing CEIs. Moreover, further concentrating the electrolyte results in more crown-like solvates and boosts the charge/discharge CE to a record-high 99.9%. In consequence, the high-voltage $Na_3V_2O_2(PO_4)_2F$ cathode delivers 95.5% capacity over 1000 cycles. Fabricated AFSMB shows a superior cycling performance of 94% capacity retention over 200 cycles at 1 C.

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Table of Contents

Abstract	i
Acknowledgements	iii
List of Figures	X
List of Tables	xxi
Abbreviations	xxii
Chapter 1 Introduction	1
1.1 Background	1
1.1.1 Worldwide ubiquitous utilization of batteries in modern life	1
1.1.2 Success of lithium-ion batteries	2
1.1.3 Progress in alternative rechargeable sodium batteries	4
1.1.4 Overview of cathode materials for SMBs	6
1.1.5 Challenges in sodium metal batteries	
1.1.6 Advancements in sodium metal battery research	
1.2 Research objectives and strategies	15
Chapter 2 Literature Review	16
2.1 Overview of electrolyte formulations for sodium metal batteries	16
2.1.1 Commonly used sodium salts	16
2.1.2 Commonly used organic solvents	19
2.1.3 Various additives	
2.1.4 Impact of electrolyte concentrations	
2.2 Fundamental properties of electrolytes	
2.2.1 Dissociation of salts	
2.2.2 Electrochemical stability window	
2.2.3 Na ⁺ ion conducting mechanisms	

2.3 Na ⁺ ion solvation structures adjustment	. 36
2.3.1 Coordination of Na ⁺ ions	. 38
2.3.2 Solvating power evaluation	. 39
2.3.3 Other solvation structures	. 43
2.4 Tuning electrolyte-electrode interphases	. 45
2.4.1 Formation of electrode-electrolyte interphases	. 45
2.4.2 Engineering of sodium metal-electrolyte interphase	. 45
2.4.3 Minimizing the dissolution of SEI	. 47
2.4.4 Engineering of CEI	. 48
2.5 Advancements in low-temperature sodium metal batteries	. 49
2.5.1 Developing electrolytes with high ionic conductivity	. 50
2.5.2 Engineering weakly solvating electrolytes	. 51
2.5.3 Tailoring SEI formation	. 52
2.6 Advancements in high-voltage sodium metal batteries	. 53
2.6.1 High-voltage electrolyte additives	. 54
2.6.2 High concentration electrolytes	. 54
2.6.3 Solvent engineering	. 55
2.7 Summary	. 56
Chapter 3 Materials and Experimental Methods	. 58
3.1 Materials	. 58
3.1.1 Pre-treatment of solvents and salts	. 58
3.1.2 Electrode preparation	. 58
3.2 Battery fabrication	. 60
3.2.1 Coin cell fabrication	. 60
3.2.2 Pouch cells fabrication	. 60
3.3 Characterization methodsvi	. 61

3.3.1 Characterization of electrolyte properties	61
3.3.2 Electrochemical measurement	63
3.3.3 Solvation structure characterization by spectroscopy techniques	67
3.3.4 Morphology, structure, and composition of electrode analysis	68
3.3.5 Theoretical calculations	70
Chapter 4 Highly Reversible Sodium Metal Anodes at Ultralow Temperatures Boosted Restructured Electrolyte Solvation	by 74
4 1 Introduction	74
4.2 Screening and characterization of electrolytes	76
4.2.1 Electrolyte formulation	76
4.2.2 Physicochemical property characterization of selected electrolytes	78
4.3 Evaluation of Na reversibility at low temperatures	82
4.3.1 Na plating/stripping CE test	82
4.3.2 Morphology observation of the deposited Na metal	85
4.3.3 Analysis of internal resistance change over Na plating/stripping cycles	86
4.4 Characterization of electrolyte solvation structure	86
4.4.1 Computational characterization	87
4.4.2 Spectroscopic characterization	91
4.5 Na metal anode-electrolyte interphase characterizations	. 93
4.5.1 Study on the SEI-formation pathways	. 93
4.5.2 Surface analysis of as-formed SEI	. 95
4.5.3 Analysis of interfacial kinetics	100
4.6 Electrochemical performance evaluation	103
4.6.1 Coin cells 1	103
4.6.2 Pouch cells 1	105
4.7 Summary	109

Chapter 5 High Voltage Sodium Metal Batteries Induced by Cyclic Ether Solubilization 110
5.1 Introduction
5.2 Physicochemical properties of cyclic ether solubilized electrolyte 111
5.2.1 Measurement of electrolyte viscosity 112
5.2.2 Evaluation of Na ⁺ ion conductivity 113
5.2.3 Simulation of Na ⁺ diffusion coefficient
5.2.4 Evaluation of oxidation stability116
5.3 Solvation structure analysis 116
5.3.1 Free solvent ratio and solvation structures ratio
5.3.2 Coordination numbers
5.3.3 Raman spectroscopy 121
5.4 Electrode-electrolyte interphase characterization
5.4.1 Cathode-electrolyte interphase characterization
5.4.2 Analysis of exchange current density 125
5.5 Electrochemical performance evaluation
5.5.1 Na plating/stripping reversibility 127
5.5.2 Electrochemical performances of high-voltage SMBs 128
5.6 Summary
Chapter 6 Highly Reversible High Voltage Anode-Free Sodium Metal Batteries Enabled by
Crown-like Electrolyte Solvation
6.1 Introduction
6.2 Characterization of crown-like solvation structure
6.3 Physicochemical and electrochemical properties of the as-formulated electrolytes 137
6.4 Further improvement of high-voltage reversibility and mechanistic study 142
6.4.1 Improvement of high-voltage reversibility by electrolyte optimization
6.4.2 Solvation structures and ion-conducting properties of electrolytes

6.4.3 Characterization of electrode-electrolyte interphases	145
6.5 High-performance AFSMBs	147
6.6 Summary	150
Chapter 7 Conclusions	151
7.1 Contributions to knowledge	151
7.2 Suggestions for future research	152
Reference	154
Appendix List of Publications	176

List of Figures

- Figure 1.1 Global primary energy consumption by energy source (2010–2050). Image 1 from https://www.eia.gov/todayinenergy.
- Figure 1.2Estimated gravimetric energy densities based on various battery chemistries.3Reproduced with permission: Copyright 2018, American Chemical Society.
- Figure 1.3 Schematic illustrations of two different battery configurations. Reproduced 6 with permission: Copyright 2021, American Chemical Society.
- Figure 1.4 Crystal structure of NASICON-type Na₃V₂(PO₄)₃: 3D framework Na-1 site 8 (a, b), and Na-2 site (c, d). Reproduced with permission: Copyright 2020, John Wiley & Sons, Inc.
- Figure 1.5 Intercalation and deintercalation of Na⁺ ions in N₃VP within a potential range 8 from 0 to 3 V vs. Na⁺/Na. Reproduced with permission: Copyright 2015, The Royal Society of Chemistry.
- Figure 1.6 The illustration of the crystal structure of Na₃V₂O₂(PO₄)₂F in the a-b plane 9 and the a-c plane. Reproduced with permission: Copyright 2023, John Wiley & Sons, Inc.
- Figure 1.7 Electrochemical charge/discharge curves of Na₃V₂(PO₄)₂FO₂//Na half-cells 10 in different voltage ranges of 2–4.4 V and 1.1–4.4 V vs. Na⁺/Na. Reproduced with permission: Copyright 2017, John Wiley & Sons, Inc.
- Figure 1.8 Schematic illustration of Na dendrite formation based on a sequential growth 12 mechanism. Reproduced with permission: Copyright 2019, John Wiley & Sons, Inc.
- Figure 2.1 Geometric configuration of the commonly used sodium salts. Reproduced 17 with permission: Copyright 2022, John Wiley & Sons, Inc.
- Figure 2.2 Lattice energies and decomposition temperatures of the commonly used 18 sodium salts. Reproduced with permission: Copyright 2022, John Wiley & Sons, Inc.
- Figure 2.3 (a) Schematic representation of the in situ Raman test condition. Raman 23 spectrum evolutions of the super-concentrated electrolytes (LAV: LiFSI– acetonitrile (AN)–vinylene carbonate (VC)), (b), and baseline carbonate

electrolytes (c) at 1 and 4 mA cm⁻². Reproduced with permission: Copyright 2020, John Wiley & Sons, Inc.

- Figure 2.4 Viscosity (a) and ionic conductivity (b) of the dilute electrolyte, HCE, and 24
 LHCEs. Reproduced with permission: Copyright 2018, American Chemical Society.
- Figure 2.5 Schematic illustration of the high-concentration electrolytes and localized 24 high-concentration electrolytes. Reproduced with permission: Copyright 2018, American Chemical Society.
- Figure 2.6 Cyclic capability of NIBs using electrolytes with different concentrations. 25 Reproduced with permission: Copyright 2020, American Chemical Society.
- Figure 2.7 The energy change during the dissociation process of salts. Reproduced with 26 permission: Copyright 2022, John Wiley & Sons, Inc.
- Figure 2.8 Schematic illustration of the relative electron energies in the electrodes and 28 electrolyte of a thermodynamically stable battery. Reproduced with permission: Copyright 2010, American Chemical Society.
- Figure 2.9 LUMO energy levels of the commonly used sodium salts. Reproduced with 29 permission: Copyright 2022, John Wiley & Sons, Inc.
- Figure 2.10 LUMO and HOMO energy levels of ether solvents and carbonate solvents 30 and their corresponding Na⁺ complexes. Reproduced with permission: Copyright 2022, The Royal Society of Chemistry.
- Figure 2.11 Summary of the parameters determining the structural and vehicular 31 transport of the metal cations in the electrolytes. Reproduced with permission: Copyright 2023, Springer Nature.
- Figure 2.12 Schematic illustration of cation transport behaviors based on three different 32 mechanisms: (a) vehicular mechanism, (b) structural mechanism, and (c) ligand-channel-facilitated mechanism. Reproduced with permission: Copyright 2024, Springer Nature.
- Figure 2.13 Bruce–Vincent method of measuring ion transference number from the 35 steady state in the DC polarization curve. Reproduced with permission: Copyright 2022, Springer Nature.

- Figure 2.14 Possible solvation structures present in the electrolytes. Reproduced with 38 permission: Copyright 2023, American Chemical Society.
- Figure 2.15 Optimized structures of isolated DME, DEGDME, and TEGDME solvent 39 molecules and corresponding Na⁺ complexes containing n glyme molecules by DFT simulations. Reproduced with permission: Copyright 2020, Elsevier.
- Figure 2.16 (a) The solvent diagram of DN versus dielectric constant (log ε). Solvents 40 located in zone IV are denoted as soft solvents. (b) Illustration of the soft solvation between the soft solvent and Li⁺ ions, rapid Li⁺ ion transport, and wide-temperature range (±60 °C) stability. Reproduced with permission: Copyright 2023, Springer Nature.
- Figure 2.17 Schematic illustrations of the interfacial model of less polar ether-based 41 electrolyte (a) and polar ether-based electrolyte (b). Reproduced with permission: Copyright 2023, Springer Nature.
- Figure 2.18 Schematic illustration of Li⁺ solvation structure in DME and BME-based 42 electrolytes. Reproduced with permission: Copyright 2023, John Wiley & Sons, Inc.
- Figure 2.19 Schematic of local solvation structures (a) and nanometric aggregates (b). 43 Reproduced with permission: Copyright 2022, American Chemical Society.
- Figure 2.20 Visual representation of the ligand exchange process in a 4.12 M NaFSI 44 DME electrolyte. Initially, a single Na⁺ ion is coordinated by two DME molecules and two FSI⁻ ions. Within approximately 60–120 ps, one of the FSI⁻ ions from the initial solvation shell dissociates, while another DME molecule enters. Reproduced with permission: Copyright 2018, American Chemical Society.
- Figure 2.21 (a) Schematics illustration of the conventional understanding of LHCE. (b) 44
 Schematics illustration of the micelle-like structure of LHCE. (c) A real micelle electrolyte formed by lithiophilic/phobic hydrofluoroether-based solvent in a LiTFSI–TTE electrolyte. Reproduced with permission: Copyright 2023, Springer Nature.
- Figure 2.22 Time-of-flight secondary ion mass spectrometry (TOF-SIMS) three- 47 dimensional views of the SEI and CEI films, the two three-dimensional

views are for B^+ and P^- secondary ions. Reproduced with permission: Copyright 2022, Springer Nature.

- Figure 2.23 (a) Schematic illustration of SEI dissolution in conventional electrolyte and 48
 (b) suppressed SEI dissolution in low-solvation electrolyte. Reproduced with permission: Copyright 2022, Springer Nature.
- Figure 2.24 (a) Conductivity of the electrolytes in the temperature range from 25 to 50 -20 °C. (b) Aurbach CE test with Cu//Na half batteries at -20 °C.
 Reproduced with permission: Copyright 2021, John Wiley & Sons, Inc.
- Figure 2.25 (a) Desolvation energy of Na⁺–OTF, Na⁺–THF, and Na⁺–DME. (b) Aurbach 51
 CE test with Cu//Na half batteries at -20 °C. Reproduced with permission: Copyright 2022, Elsevier.
- Figure 2.26 Binding energy of EA–Na⁺, EDFA–Na⁺, and DFEA–Na⁺. Reproduced with 52 permission: Copyright 2024, John Wiley & Sons, Inc.
- Figure 2.27 (a) Cryo-TEM investigation of the structure of the SEI formed at -40 °C. (b) 52
 CE measurements at 20 °C and -40 °C. Reproduced with permission:
 Copyright 2021, The Royal Society of Chemistry.
- Figure 2.28 Illustration of a high-voltage anode-free Na battery constructed by 55 optimizing the electrolyte aggregation through using a 3A zeolite molecular sieve. Reproduced with permission: Copyright 2022, John Wiley & Sons, Inc.
- Figure 2.29 (a) Molecule structure of HFME. (b) HOMO and LUMO energy levels of 56 HFME, HFE, and G2.solvents. Reproduced with permission: Copyright 2024, John Wiley & Sons, Inc.
- Figure 3.1Schematic illustration of the symmetric stainless-steel cell.61

63

- Figure 3.2 Equivalent circuit of symmetric Na//Na cell.
- Figure 3.3 Tafel plots of Li//Li symmetrical cells using the LAV (LiFSI-acetonitrile 65 (AN)-vinylene carbonate (VC)) and baseline carbonate electrolytes recorded at different current densities. Reproduced with permission: Copyright 2020, John Wiley & Sons, Inc.
- Figure 3.4 Tafel plots obtained from cyclic voltammetry measurements. Reproduced 66 with permission: Copyright 2017, John Wiley & Sons, Inc.

- Figure 4.1 Optical images of four diluted electrolytes in a customized low-temperature 77 chamber under -40 (a) and -55 °C (b): 1) 0.4 M NaPF₆ G2 electrolyte, 2)
 0.4 M NaPF₆ G2/DOL electrolyte, 3) 0.4 M NaPF₆ G2/DBE electrolyte, and 4) 0.4 M NaPF₆ G2/TTE electrolyte.
- Figure 4.2 (a) Voltage profile at the beginning of initial discharge of Na//Al cells with 77 the 0.4 M NaPF₆ G2/TTE electrolyte at RT (RT = 25 °C). (b) Cycling stability of Na//Al cells with the 0.4 M NaPF₆ G2/DBE electrolyte at RT (RT = 25 °C). (c) Voltage profile at the beginning of initial discharge of Na//Al cells with the 0.4 M NaPF₆ G2/DBE electrolyte at -25 °C.
- Figure 4.3 Cycling stability of Na//Al cells at 0.5 mA cm⁻² and 1.0 mAh cm⁻² under 78 -25 °C. The inset shows the corresponding voltage profiles.
- Figure 4.4 Wettability test of a–c) 0.4 M NaPF₆ G2 and d–f) 0.4 M NaPF₆ G2/DOL 79 electrolytes on Na metal, Celgard 2500, and Whatman glass fiber.
- Figure 4.5 Temperature-dependent viscosity of 0.4 M NaPF₆ G2 and 0.4 M NaPF₆ 79 G2/DOL electrolytes.
- Figure 4.6 Temperature-dependent ionic conductivity of 0.4 M NaPF₆ G2, 1 M NaPF₆ 80 G2, and 0.4 M NaPF₆ G2/DOL electrolytes.
- Figure 4.7 Nyquist plots for (a) 0.4 M NaPF₆ G2 electrolyte and (b) 0.4 M NaPF₆ 81 G2/DOL electrolytes. (c) Polarization curves for two electrolytes.
- Figure 4.8 Polarization curve for the 1 M NaPF₆ G2 electrolyte. Insets are Nyquist plots 81 before and after polarization.
- Figure 4.9 (a) Voltage profiles of Na//Al cells with two electrolytes at 1 mA cm⁻² and 82 1.0 mAh cm⁻² under -25°C. (b) Cycling stability of Na//Al cells with 0.4 M NaPF₆ G2/DOL electrolyte at 2 mA cm⁻² and 1.0 mAh cm⁻² under -25 °C.
- Figure 4.10 Cycling stability of Na//Al cells with NaPF₆–G2/DOL electrolytes of 83 different concentrations at 0.5 mA cm⁻² and 1.0 mAh cm⁻² under -25 °C (a) and 1 mA cm⁻² and 1.0 mAh cm⁻² under -40 °C (b).
- Figure 4.11 Cycling stability of Na//Al cells at different current densities in 0.4 M NaPF₆ 83
 G2/DOL under -40 °C. The insets show the corresponding voltage profiles at the 1st, 50th, and 100th plating/stripping cycles at 2 mA cm⁻².

- Figure 4.12 Cycling stability of Na//Al cells with 0.4 M NaPF₆ G2/DOL electrolyte under 84 ultralow temperatures of -55 °C and -65 °C.
- Figure 4.13 Aurbach measurement of Na plating/stripping CE in Na//Al cells at -25 °C 84 and -40 °C.
- Figure 4.14 Comparison of LT Na plating/stripping CEs in the 0.4 M NaPF₆ G2/DOL 85 electrolyte with those in the reported electrolytes.
- Figure 4.15 SEM images of the deposited Na metal on Al/C current collectors in (a) 0.4 85
 M NaPF₆ G2 and (b) 0.4 M NaPF₆ G2/DOL electrolytes after 200 cycles of Na plating/stripping at 0.5 mA cm⁻², 0.5 mAh cm⁻² under -25 °C.
- Figure 4.16 Nyquist plots of Na//Al cells with (a) 0.4 M NaPF₆ G2 and (b) 0.4 M NaPF₆ 86 G2/DOL electrolytes after 3, 100, and 200 Na plating/stripping cycles at 0.5 mA cm⁻², 0.5 mAh cm⁻² under -25 °C.
- Figure 4.17 The force field types and the corresponding atomic charges of ions and 87 molecules in the 0.4 M NaPF₆ G2 and 0.4 M NaPF₆ G2/DOL electrolytes.
- Figure 4.18 Snapshots obtained from classical molecular dynamics simulations of (a) 0.4 88 M NaPF₆ G2 and (b) 0.4 M NaPF₆ G2/DOL electrolytes.
- Figure 4.19 The mean-squared displacements of Na⁺ in two investigated electrolytes at 88 RT (RT = 25 °C), (a), and -25 °C (b).
- Figure 4.20 Na⁺ radial distribution function (RDF) and the coordination number in two 89 investigated electrolytes obtained from MD simulations at RT (RT = 25 °C).
- Figure 4.21 Na⁺ RDF and the coordination number in two investigated electrolytes 90 obtained from MD simulations at -25 °C.
- Figure 4.22 Solvation structure of two electrolytes and the corresponding distances 91 between Na⁺ and the O atoms of G2 molecules calculated by DFT.
- Figure 4.23 Desolvation energy of Na⁺ in 0.4 M NaPF₆ G2 and 0.4 M NaPF₆ G2/DOL 91 electrolytes.
- Figure 4.24 Raman spectra of various electrolytes and components. 92
- Figure 4.25 ²³Na NMR spectra of the 0.4 M NaPF₆ G2/DOL and NaPF₆ G2 electrolytes 93 with different concentrations.
- Figure 4.26 Reduction reaction site prediction of (a) CIP complexes in the 0.4 M NaPF₆ 94 G2 electrolyte, (b) CIP complexes in the 0.4 M NaPF₆ G2/DOL electrolyte,

and c) SSIP complexes in the 0.4 M NaPF₆ G2 and 0.4 M NaPF₆ G2/DOL electrolytes via Fukui function analysis. The yellow color regions represent electron-rich regions, and the blue color regions represent electron-deficient regions.

- Figure 4.27 LUMO of solvent molecules, sodium salts, and solvate complexes in 95 electrolytes.
- Figure 4.28 The in-depth XPS F 1s spectra of SEI formed in two electrolytes at -25 °C. 96
- Figure 4.29 The in-depth XPS P 2p spectra of SEI formed in two electrolytes at -25 °C. 97
- Figure 4.30 The in-depth XPS Na 1s spectra of SEI formed in two electrolytes at -25 °C. 98
- Figure 4.31 The in-depth XPS O 1s spectra of SEI formed in two electrolytes at -25 °C. 99
- Figure 4.32 Schematic illustration of the SEI composition/microstructures formed in two 99 electrolytes at -25 °C.
- Figure 4.33 AFM surface profiling of SEI formed in the (a) G2/DOL and (b) G2 100 electrolytes at -25 °C. Young's modulus mapping of SEI formed in the (c) G2/DOL and (d) G2 electrolytes at -25 °C.
- Figure 4.34 EIS results of symmetric Na//Na cells with (a) 0.4 M NaPF₆ G2 and (b) 0.4 101 M NaPF₆ G2/DOL electrolytes at different temperatures.
- Figure 4.35 The R_{SEI} and R_{ct} values at different evaluation temperatures for the G2 and 101 G2/DOL electrolytes system.
- Figure 4.36 The CV curves of symmetric Na//Na cells in investigated electrolytes at (a) 102 RT (RT = 25 °C), (b) -25 °C, and (c) -40 °C.
- Figure 4.37 Tafel plots in two investigated electrolytes under (a) RT (RT = 25 °C), (b) 102 -25 °C, and (c) -40 °C.
- Figure 4.38 Schematic illustration of the mechanism of improved LT Na reversibility by 103 the DOL-diluted electrolyte.
- Figure 4.39 Rate performance and long-term galvanostatic cycling performance of 104 $Na/Na_3V_2(PO_4)_3$ half-cells at -25 °C (a, c) and -40 °C (b, d).
- Figure 4.40 Temperature-dependent galvanostatic cycling of AFSMBs at 0.2C. 104
- Figure 4.41 Long-term galvanostatic cycling performance of AFSMBs at 1C under -25 105 °C and -40 °C.
- Figure 4.42 Long-term cycling performances of AFSMBs at a) -55 °C and b) -65 °C. 105

- Figure 4.43 The schematic diagram and optical image of the Ah-level anode-free pouch 106 cell using the G2/DOL electrolyte.
- Figure 4.44 Galvanostatic charge/discharge curves of the as-fabricated pouch cell at -25 106 °C.
- Figure 4.45 Cyclability of the as-fabricated pouch cell at -25 °C. 107
- Figure 5.1 Optical images of the three electrolytes: (a) 2.5 M NaPF₆ G2, (b) 0.1 M 112
 NaPF₆ DOL, and (c) 2.5 M NaPF₆ G2/DOL. The white substance at the bottom of the bottle in (a) and (b) is undissolved NaPF₆.
- Figure 5.2 Temperature-dependent viscosity of 2.5 M NaPF₆ G2 and 2.5 M NaPF₆ 112 G2/DOL electrolytes.
- Figure 5.3 Temperature-dependent ionic conductivity of 2.5 M NaPF₆ G2 and 2.5 M 113 NaPF₆ G2/DOL electrolytes.
- Figure 5.4 Nyquist plots before (a) and after (b) the polarization process, and the 114 polarization curves (c) of the symmetric Na//Na cells with the 2.5 M NaPF₆
 G2 and 2.5 M NaPF₆ G2/DOL electrolytes.
- Figure 5.5 The force field types and the corresponding atomic charges of ions and 115 molecules in the 2.5 M NaPF₆ G2 and 2.5 M NaPF₆ G2/DOL electrolytes.
- Figure 5.6 Snapshots obtained from classical molecular dynamics simulations of (a) 2.5 115M NaPF₆ G2 and (b) 2.5 M NaPF₆ G2/DOL electrolytes.
- Figure 5.7 The mean-squared displacements of Na⁺ ions in 2.5 M NaPF₆ G2 and 2.5 M 115 NaPF₆ G2/DOL electrolytes.
- Figure 5.8 Oxidation stability of 2.5 M NaPF₆ G2 and 2.5 M NaPF₆ G2/DOL 116 electrolytes evaluated by linear sweeping voltammetry at a scanning rate of $50 \,\mu\text{V s}^{-1}$.
- Figure 5.9 Content of free G2 solvent in 1 M NaPF₆ G2, 2.5 M NaPF₆ G2, and 2.5 M 117 NaPF₆ G2/DOL electrolytes calculated from MD simulations.
- Figure 5.10 SSIP, CIP, and AGG solvate ratios in 1 M NaPF₆ G2, 2.5 M NaPF₆ G2, and 118
 2.5 M NaPF₆ G2/DOL electrolytes calculated from MD simulations.
- Figure 5.11 HOMO and LUMO energy levels of the solvents, Na^+ ion, PF_6^- anion, and 118 solvated complexes in three studied electrolytes.

- Figure 5.12 Na⁺ radial distribution functions (a–c) and the coordination numbers (d–f) in 120 three investigated electrolytes obtained from MD simulations.
- Figure 5.13 The interatomic distances of Na⁺-solvent in the SSIP, CIP, and AGG 121 solvates.
- Figure 5.14 Raman spectra of 1 M NaPF₆ G2, 2.5 M NaPF₆ G2, and 2.5 M NaPF₆ 122 G2/DOL electrolytes and their components.
- Figure 5.15 The fitted Raman peaks of free G2 solvent (purple and cyan peaks) and 123 solvating G2 (yellow and orange peaks) in three electrolytes and G2 solvent.
- Figure 5.16 The in-depth XPS F 1s spectra of CEI formed in two electrolytes. 124
- Figure 5.17 The in-depth XPS C 1s spectra of CEI formed in two electrolytes. 125
- Figure 5.18 The in-depth XPS spectra (Na 1s) of CEI formed in two electrolytes. 125
- Figure 5.19 The cyclic voltammogram curves of symmetric Na//Na cells using 2.5 M 126 NaPF₆ G2 and 2.5 M NaPF₆ G2/DOL electrolytes.
- Figure 5.20 Tafel plots in the 2.5 M NaPF₆ G2 and 2.5 M NaPF₆ G2/DOL electrolytes. 126
- Figure 5.21 Voltage profiles of Na//Al cells with 2.5 M NaPF₆ G2 electrolyte (a) and 2.5 127 M NaPF₆ G2/DOL electrolyte (b) at 0.25 mA cm⁻².
- Figure 5.22 (a) Cycling stability of Na//Al cells with 2.5 M NaPF₆ G2/DOL electrolyte. 128 The corresponding plating and stripping voltage profiles at the 1st cycle (b) and 200th cycle (c) at 0.5 mA cm⁻².
- Figure 5.23 CE comparison of SMBs with 2.5 M NaPF₆ G2 and 2.5 M NaPF₆ G2/DOL 128 electrolytes.
- Figure 5.24 Long-term galvanostatic cycling performances of SMB with 2.5 M NaPF₆ 129 G2/DOL electrolyte.
- Figure 5.25 Rate performance of SMBs with 2.5 M NaPF₆ G2 and 2.5 M NaPF₆ G2/DOL 130 electrolytes.
- Figure 5.26 Temperature-dependent galvanostatic cycling performances of SMB with 130 2.5 M NaPF₆ G2 and 2.5 M NaPF₆ G2/DOL electrolytes at 0.5C.
- Figure 5.27 Long-term galvanostatic cycling performances of Na//Na₃V₂O₂(PO₄)₂F full 131 cells with limited Na anode at 1C using 2.5 M NaPF₆ G2/DOL electrolyte.
- Figure 6.1 The force field types and the corresponding atomic charges of ions and 133 molecules in the 1 M NaPF₆ DEGDBE and 1 M NaPF₆ G4 electrolytes.

- Figure 6.2 Snapshots obtained from classical molecular dynamics simulations of (a) 1 134 M NaPF₆ DEGDBE and (b) 1 M NaPF₆ G4 electrolytes.
- Figure 6.3 The Na⁺ radial distribution functions of (a) 1 M NaPF₆ DEGDBE and (b) 1 135
 M NaPF₆ G4 electrolytes. The corresponding coordination numbers of (c) 1
 M NaPF₆ DEGDBE and (d) 1 M NaPF₆ G4 electrolytes.
- Figure 6.4 Typical solvation structures in (a) 1 M NaPF₆ DEGDBE and (b) 1 M NaPF₆ 136 G4 electrolytes.
- Figure 6.5 SSIP, CIP, and AGG solvation ratios in 1 M NaPF₆ DEGDBE and 1 M NaPF₆ 136
 G4 electrolytes calculated from MD simulation results.
- Figure 6.6 (a) Raman spectra of the studied electrolytes and corresponding components. 137
 Enlarged view of the characteristic peaks of (b) DEGDBE and (c) G4
 solvents.
- Figure 6.7 Temperature-dependent ionic conductivity of 1 M NaPF₆ DEGDBE and 1 M 138 NaBF₄ G4 electrolytes.
- Figure 6.8 Nyquist plots and the variation in current during the voltage bias process for 139 the (a) 1 M NaPF₆ DEGDBE and (b) 1 M NaBF₄ G4 electrolytes.
- Figure 6.9 Electrostatic potential maps of DEGDBE and G4 molecules. 139
- Figure 6.10 (a) The charge-discharge curves and (b) long-term galvanostatic cycling 140 performance of the $Na_3V_2O_2(PO_4)_2F//Na$ cells with the 1 M NaPF₆ DEGDBE and the 1 M NaPF₆ G4 electrolytes.
- Figure 6.11 HOMO and LUMO energy levels of solvent molecules, Na⁺ ion, PF₆⁻ anion, 141 and solvated complexes in 1 M NaPF₆ DEGDBE and 1 M NaPF₆ G4 electrolytes.
- Figure 6.12 Oxidation reaction site prediction of solvation structures in 1 M NaPF₆ 142 DEGDBE (a) and 1 M NaPF₆ G4 electrolytes (b) via Fukui function analysis.
- Figure 6.13 The Coulombic efficiency of SMBs within the first 50 cycles using 1 M 143 NaPF₆ G4 and 2.5 M NaBF₄ G4 electrolytes.
- Figure 6.14 (a) Raman spectra of the studied electrolytes and corresponding 144 components. (b) Enlarged view of the characteristic peaks of G4 solvent.
- Figure 6.15 Temperature-dependent ionic conductivity of 1 M NaBF₄ G4 and 2.5 M 144 NaBF₄ G4 electrolytes.

- Figure 6.16 Nyquist plots and the variation in current during the voltage bias process for 145 the 1 M NaBF₄ G4 (a) and 2.5 M NaBF₄ G4 (b) electrolytes.
- Figure 6.17 The in-depth XPS F 1s spectra of CEI formed in two electrolytes. 146
- Figure 6.18 The in-depth XPS B 1s spectra of CEI formed in 2.5 M NaBF₄ G4 electrolyte. 146
- Figure 6.19 The in-depth XPS C 1s spectra of CEI formed in two electrolytes. 147
- Figure 6.20 Long-term galvanostatic cycling performance of SMBs with (a) 1 M NaPF₆ 148 G4 and (b) 2.5 M NaBF₄ G4 electrolytes.
- Figure 6.21 Cycling stability of Na//Al cells 1 M NaPF₆ G4 and 2.5 M NaBF₄ G4 149 electrolytes.
- Figure 6.22 Long-term galvanostatic cycling performance of AFSMBs with 1 M NaPF₆ 150 G4 and 2.5 M NaBF₄ G4 electrolytes.

List of Tables

Table 3.1	Chemicals and reagents used in this research.	59
Table 4.1	Physicochemical properties of the solvents of interest. ^[151, 167, 229]	76
Table 4.2	The calculated LUMO and HOMO energy levels for salt (PF ₆), solvents	95
	(G2 and DOL), and solvation complexes in the 0.4 M NaPF $_6$ G2 and 0.4 M	
	NaPF ₆ G2/DOL electrolytes.	
Table 4.3	Specific energy density comparison between the AFSMB pouch cell in our	108
	work and commercial LiFePO ₄ //graphite (G) cell at 25 °C and -25 °C.	
Table 6.1	Physicochemical properties of DEGDBE and G4 solvents. ^[151]	138
Table 6.2	Comparison of average long-cycling CE values of the SMBs using the 2.5	148
	M NaBF ₄ G4 electrolyte with those using reported electrolytes.	

List of Abbreviations

AFM	Atomic force microscopy
AFSMBs	Anode-free sodium metal batteries
AGG	Aggregate
AN	Acetonitrile
BME	Bis(2-methoxyethoxy) methane
BTFE	Bis(2,2,2-trifluoroethyl) ether
CD	Contact dimer
CE	Coulombic efficiency
CEI	Cathode electrolyte interphase
CIP	Contact ion pair
CN	Coordination numbers
DEC	Diethyl carbonate
DEE	1,2-diethoxyethane
DEGDBE	Diethylene glycol dibutyl ether
DFT	Density functional theory
DME	Dimethyl ether
DN	Donor number
DNP	Double Numerical plus Polarization
DOL	1,3-dioxolane
DPE	Dipropyl ether
DSC	Differtial Scanning Calorimetery
EC	Ethylene carbonate
EDFA	Ethyl difluoroacetate
Eg	Energy separation
ESW	Electrochemical stability window
eV	Electron volts
FAN	Fluoroacetonitrile
FEC	Fluoroethylene carbonate
FTIR	Fourier-transform infrared

G2/diglyme/DEGDME	Diethylene glycol dimethyl ether
GGA	Generalized gradient approximation
HCEs	High-concentration electrolytes
HFE	1,1,2,2-tetrafluoroethyl-2,2,2-trifluoroethyl ether
НОМО	Highest occupied molecular orbital
ICE	Initial Coulombic efficiency
LHCE	Localized high-concentration electrolytes
LIBs	Lithium-ion batteries
LiDFBOP	Lithium difluorobis(oxalato) phosphate
LSV	Linear scanning voltammetry
LUMO	Lowest unoccupied molecular orbital
M4FP	Methyl 2,3,3,3-tetrafluoro propionate
MD	Molecular dynamics
MDFA	Methyl difluoroacetate
MDFSA	Methyl 2,2-difluoro-2 (fluorosulfonyl)acetate
MSD	Mean square displacement
NaBOB	Sodium bisoxalato borate
NaDFOB	Sodium difluoro(oxalato) borate
n-AGGs	Nanometric aggregates
NaPDI	Sodium 4,5-dicyano-2-(pentafluoroethyl)imidazolate
NaTDI	Sodium 4,5-dicyano-2-(trifluoromethyl)imidazolate
NMP	N-methyl-2-pyrrolidone
NMR	Nuclear magnetic resonance
N/P ratio	Negative electrode capacity/positive electrode capacity ratio
NPT	Constant number, pressure, and temperature
NVOPF	$Na_3V_2O_2(PO_4)_2F$
NVP	$Na_3V_2(PO_4)_3$
NVPF	$Na_3V_2(PO_4)_2F_3$
NVT	Constant number, volume, and temperature
PBE	Perdew-Burke-Ernzerhof function
PC	Propylene carbonate

PEO	Polyethylene oxide
PFG-NMR	Pulsed-field gradient nuclear magnetic resonance
RDF	Radial distribution function
SAXS	Small-angle X-ray scattering
SEI	Solid electrolyte interphase
SEM	Scanning electron microscopy
SIBs	Sodium-ion batteries
SIP	Solvent-shared ion pair
SL	Sulfolane
SMBs	Sodium metal batteries
SSD	Solvent-shared dimer
SSIP	Solvent-separated ion pair
TEGDME	Tetraethylene glycol dimethyl ether
TEP	Triethyl phosphate
TFP	Tris(2,2,2-trifluoroethyl) phosphate
THF	1,3-dioxane, tetrahydrofuran
TMP	Trimethyl phosphate
ТОР	Tris(2-ethylhexyl) phosphate
TPrP	Tripropyl phosphate
TTE	1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether
VC	Vinylene carbonate
V _{OC}	Open circuit voltage
WAXS	Wide-angle X-ray scattering
XPS	X-ray photoelectron spectroscopy

Chapter 1 Introduction

1.1 Background

1.1.1 Worldwide ubiquitous utilization of batteries in modern life

Electrochemical batteries play a critical role in modern life by storing and delivering energy, from powering portable electronics and driving electric vehicles to enabling grid-scale energy storage.^[1, 2] As we transit towards a more sustainable future, this pivotal role is poised to become even more crucial. After over two centuries of dominance by gasoline-powered vehicles, the automotive industry, is experiencing a paradigm shift towards electrification.^[3, 4] This transformation is driven by the rapid advancement in battery technology and, thus, the increasing availability and affordability of electric vehicles. It holds immense potential for decreasing fossil fuel utilization and greenhouse gas emissions to combat climate change, a defining challenge of our time.^[4, 5]

Electrochemical batteries are also essential for effectively harnessing renewable energy sources. As global energy demands continue escalating, projections indicate that renewable energy consumption will increase to the level of petroleum and other liquid energy sources by 2050 (Figure 1.1).^[6] However, unlike centralized large-scale facilities that dominate current electrical grids, renewable sources such as solar, wind, tidal, biomass, and geothermal energy are inherently intermittent and geographically dispersed. Efficient energy storage solutions are paramount to leverage these renewable energy sources fully. They are critical for balancing supply and demand, stabilizing the grid, and ensuring a reliable electricity supply.^[7]



Figure 1.1 Global primary energy consumption by energy source (2010–2050). Image from https://www.eia.gov/todayinenergy.

1.1.2 Success of lithium-ion batteries

The advancement of electrochemical batteries has involved substantial technological progress to establish a durable structural framework, guaranteeing consistent functionality across a wide range of devices. The major components of an electrochemical battery include a positive electrode (cathode), a negative electrode (anode), and an electrolyte that facilitates ionic connectivity between the two electrodes.^[8] In order to prevent internal short circuit, a separator is usually placed between the cathode and the anode which allows for ion transportation but not electrons. The complex interplay among these components, however, makes developing new battery chemistries an arduous endeavor, often relying on serendipity.^[9, 10] Key performance metrics, such as energy and power densities, efficiency, safety, cycle life, calendar life, and cost, necessitate simultaneous optimization through meticulous design, selection, and integration.

The history of electrochemical batteries can be traced back to Alessandro Volta's groundbreaking invention of the Voltaic Pile in 1800, a rudimentary battery consisting of stacked copper and zinc plates (coins) separated by brine-soaked paper.^[8, 11]. However, despite over two centuries of research and development, fewer than two dozen battery systems, encompassing both primary and rechargeable types, have achieved successful commercialization.^[10] As Figure 1.2 illustrates, the highest energy density of commercially available batteries has only witnessed a modest improvement rate of approximately 5% per year since 1970. This sluggish pace contrasts sharply with the exponential advancements in semiconductors and electronics driven by "Moore's Law" since the 1960s. This disparity stems from the fundamental difference in charge carriers: while semiconductors and electronics rely on the rapid movement of electrons, batteries are inherently limited by the slower ionic transportation within their electrochemical systems. And the energy density stems from the amount of ions that can be stored in the system, and the power derives from how fast a given amount of ions are transported.

The evolutionary trajectory of lithium-ion batteries (LIBs) has been marked by groundbreaking discoveries and persistent challenges. The first primary lithium battery, a result of a collaboration between NASA and Panasonic, emerged in 1970.^[12] A significant breakthrough followed in 1973 when Whittingham demonstrated the ability of transition metal dichalcogenides, such as TiS₂, to accommodate Li⁺ ions with high mobility within their crystal lattices reversibly.^[13] However, the path to commercially viable rechargeable lithium metal batteries was hindered by safety concerns,

particularly the uncontrolled growth of lithium dendrites. This led to a shift in focus towards the more promising dual-intercalation LIBs in the 1990s.^[9, 14]



Figure 1.2 Estimated gravimetric energy densities based on various battery chemistries. Reproduced with permission: Copyright 2018, American Chemical Society.^[10]

In 1972, Michel Armand proposed the "rocking chair" model of LIBs, characterized by intercalation mechanisms in both electrodes for reversible Li^+ ion shuttling during chargedischarge cycles.^[15, 16] Subsequently, Goodenough and his colleagues reported the remarkable stability of layered LiCoO₂ at high oxidation states in 1980.^[17] Building upon these breakthroughs, Akira Yoshino and his co-workers developed the world's first LIB prototype in 1986. This prototype LIB incorporated a LiCoO₂ cathode and a non-graphitic carbonaceous anode, such as petroleum coke or vapor-grown carbon fiber, alongside a porous polyolefin separator soaked with a nonaqueous electrolyte containing LiClO₄ dissolved in propylene carbonate (PC).^[18] Following years of refinement, Sony achieved the milestone of mass-producing the first commercially available LIBs in 1991, utilizing a LiCoO₂ cathode, a petroleum coke anode, and an electrolyte comprising LiPF₆ dissolved in PC.

Early attempts to incorporate layered graphite as the anode faced challenges because of the instability of the widely used solvent PC against the reduction, resulting in graphite exfoliation.^[10] In 1983, Yazami and Touzain demonstrated reversible Li⁺ intercalation/deintercalation of graphite without solvent co-intercalation using a solid polymer electrolyte comprising LiClO₄ dissolved in polyethylene oxide (PEO).^[19] That same year, Dahn and his co-workers achieved the first

documented electrochemical synthesis of LiC_6 in an electrolyte comprising LiAsF_6 dissolved in a mixture of ethylene carbonate (EC) and $\text{PC}^{[20]}$. They established a clear correlation between the reversibility of Li^+ intercalation in the graphitic anode and the presence of EC in the electrolyte. The passivation layer formed on the graphite surface during the initial lithiation in the EC-based electrolyte prevents further irreversible reactions in subsequent cycles while facilitating reversible Li^+ intercalation/deintercalation. Because of the meticulously refined electrochemical dynamics and interactions between the electrolytes and the electrodes over the years, the EC-based commercial electrolytes now enable extraordinary Coulombic efficiency (CE) surpassing 99.98% and a lifespan extending beyond 1000 cycles when paired with LiCoO_2 cathode and graphite anode, which is widely used in portable applications nowadays.^[21, 22]

Goodenough and his colleagues first demonstrated the electrochemical activity of olivine LiFePO₄ as the cathode for LIBs in 1997.^[22] Its abundance, environmental benignity, low cost, and high chemical/thermal stability have propelled its widespread adoption in LIBs for electric vehicles targeting the mid-to-low-range range market, as well as in grid-scale energy storage systems. Layered oxide cathodes, particularly nickel–cobalt–manganese (NCM) and nickel– cobalt–aluminum (NCA), represent another prominent class of cathodes utilized in commercial LIBs. These cathodes offer high specific capacity exceeding 200 mAh g⁻¹ and an elevated working potential of 3.8 voltage *vs*. Li/Li⁺, making them particularly attractive for high-end electric vehicles and other applications requiring high power and energy densities.^[23]

1.1.3 Progress in alternative rechargeable sodium batteries

The rising need for LIBs in electronics, electric vehicles, and grid storage has put a significant strain on lithium resources. Given the limited and geographically concentrated availability of lithium reserves, such high demand has caused a steep rise in lithium salt prices and severe concerns on the supply chain stability of LIBs.^[23, 24] It has thus stimulated extremely active research into alternative battery technologies. Sodium-ion batteries (SIBs) stand out among them because of the abundance of sodium resources, cost-effectiveness, and similarity with lithium battery electrochemistry. Furthermore, the non-alloying nature of sodium with aluminum allows for using cost-inexpensive and lightweight aluminum current collectors in both electrodes, favoring more cost-efficient manufacturing of batteries with improved energy densities.

Despite these great advantages, the practical implementation of SIBs remains hindered by the limited energy density.^[25] Like in LIBs, Na-insertion cathodes have witnessed great success in SIBs.^[26, 27] However, the development of anode materials is still in its infancy. The intercalation-based graphite anode used in commercial LIBs exhibits significantly decreased sodium storage capability because of the much larger size of Na⁺. Alternative anode materials, such as hard carbon, phosphorus, metal oxides/sulfides, and organic compounds, while demonstrating higher capacities, fail to achieve a sufficiently low working potential or high CE for practical applications.^[28] Consequently, SIBs generally exhibit limited energy densities of less than 160 Wh kg⁻¹, only 50% to 80% of that offered by commercial LIBs.^[29]

Utilizing sodium metal as the anode offers a compelling pathway to enhance energy density because of its high theoretical capacity (1166 mAh g^{-1}) and low electrochemical potential (-2.71 V *vs.* reversible hydrogen electrode). Rechargeable sodium metal batteries (SMBs) utilizing conventional insertion-type cathodes could achieve energy densities comparable to the current state-of-the-art LIBs. Furthermore, employing conversion-type cathodes in rechargeable SMBs offers the potential for even higher energy densities and more cost-effective energy storage systems.^[30, 31] However, research on Na metal anodes remains nascent. The great challenges of forming an unstable solid electrolyte interphase (SEI) and uncontrolled growth of sodium dendrites during charge-discharge cycles hinder their practical implementation.

Initial anode-free sodium metal batteries (AFSMBs) comprising a sodium-containing cathode and a bare current collector as the anode have gained significant research interest in recent years.^{[32-^{35]} As illustrated in Figure 1.3, the absence of a pre-existing sodium reservoir in AFSMBs offers substantial advantages in gravimetric/volumetric energy densities compared to conventional SIBs.^[36, 37] It also enhances operation safety by eliminating highly reactive metallic sodium during cell fabrication and enables compatibility with LIB production lines. The battery manufacturers, including Contemporary Amperex Technology Co. Ltd (CATL), have made a lot of effort in AFSMB research, revealing the great potential of AFSMBs for commercialization.^[38]}

However, inhomogeneous sodium deposition and parasitic reactions between the plated sodium and the electrolyte inevitably consume active sodium during charge-discharge cycles.^[39] The limited sodium inventory in AFSMBs makes them highly sensitive to sodium loss. For instance, a CE of 99.9% sustains 223 cycles at 80% capacity retention, drastically dropping to

merely 44 and 22 cycles when CE values slightly decrease to 99.5% and 99%, respectively.^[40] Therefore, achieving high Na plating/stripping CE beyond 99.9% is crucial for extending the cycle life of anode-free cells.



Sodium-ion battery

Anode-free sodium metal battery

Figure 1.3 Schematic illustrations of two different battery configurations. Reproduced with permission: Copyright 2021, American Chemical Society.^[36]

1.1.4 Overview of cathode materials for SMBs

Cathode materials for rechargeable sodium batteries can be generally categorized into insertion type and conversion type. The former includes layered transition metal oxides, polyanionic compounds, and Prussian blue analogs. Typical examples of the latter are sulfur and oxygen cathodes, which promise higher theoretical capacities, but their intricate multistep charge storage and uncontrollable parasitic reactions impede their practical applications.^[41] Therefore, insertion-type cathodes are discussed in detail below.

a) Layered transition metal oxides

The typical chemical formula of layered transition metal oxides is Na_xMO₂, where M represents transition metals, such as Mn, Ni, Fe, Co, Cr, and Ti. They generally exhibit more intricate crystal chemistry than their Li⁺ ion counterparts because Na occupies both octahedral and prismatic spaces while Li only resides in octahedral spaces.^[42] This structural difference not only leads to changes in Na-stoichiometry and the capacity but also makes them susceptible to Na-driven structural phase

transition. Consequently, Na-based layered oxides suffer from fast capacity decay during long-term cycling at high voltages.^[43]

b) Prussian blue analogues

Prussian blue analog cathodes are promising for large-scale applications because of their open framework, facile synthesis process, and cost-effectiveness. A variety of Prussian blue analogs with the chemical formula $Na_xM[Fe(CN)_6]_{1-y}X_y \cdot nH_2O$ ($0 \le x \le 2, 0 \le y \le 1$) have been synthesized, where M represents transition metals and X stands for the vacancy induced by the loss of Fe(CN)₆ group.^[44] The applications of Prussian blue analogs in SMBs have been severely hindered because of the deleterious side reactions between the inherent bound water and the reactive sodium metal anode.

c) Sodium vanadium phosphates

The polyanionic compounds mainly include orthophosphates, pyrophosphates, sodium superionic conductors (NASICON), sulfates, and silicates.^[45, 46] Among these, NASICON-type sodium vanadium phosphate (Na₃V₂(PO₄)₃) and sodium-vanadium fluorophosphate have attracted extensive attention as promising SMB cathodes because of their remarkable structural and thermodynamic stability.

 $Na_3V_2(PO_4)_3$ could accommodate three Na^+ ions when V is in the trivalent state. One Na^+ ion resides in the Na-1 site and the other two occupy the Na-2 sites, as elucidated in Figure 1.4. During the charging process, two Na^+ ions deintercalated from the Na-2 sites at a potential of 3.4 V *vs*. Na^+/Na , accompanied by the oxidation of V^{3+} to V^{4+} . The Na^+ ion at the Na-1 site is immobilized, which prevents further oxidation of V^{4+} to V^{5+} . As a result, the work voltage is relatively low and the specific energy density of as-fabricated batteries is unsatisfactory. Efforts to enhance the performance of $Na_3V_2(PO_4)_3$ have involved the partial substitution of vanadium with other transition metals such as Cr^{3+} or Al^{3+} .^[47, 48] It facilitates the utilization of the $V^{4+}/^{5+}$ redox couple at about 4 V *vs*. Na^+/Na , thereby increasing the discharge potential and enhancing the energy density of SMBs.^[49]

During the discharging process, $NaV_2(PO_4)_3$ transforms to $Na_3V_2(PO_4)_3$ when the two Na^+ ions intercalate back into the Na-2 site at 3.37 V vs. Na^+/Na , providing a discharge capacity of 117.6 mAh g⁻¹. Na⁺ ions can be further inserted, causing the electrode material to change from $Na_3V_2(PO_4)_3$ to $Na_4V_2(PO_4)_3$ at 1.6 V vs. Na^+/Na with a capacity of 60 mAh g⁻¹ delivered. This insertion can continue, resulting in a change from $Na_4V_2(PO_4)_3$ to $Na_5V_2(PO_4)_3$ at an even lower potential of 0.3 V vs. Na^+/Na , as shown in Figure 1.5.^[50] However, because of its relatively low discharge plateau transitioning from $Na_3V_2(PO_4)_3$ to $Na_5V_2(PO_4)_3$, this capacity minimally enhances energy density for practical battery applications. Nevertheless, the capability to stably incorporate additional Na^+ ions facilitates the straightforward pre-sodiation of $Na_3V_2(PO_4)_3$ to either $Na_4V_2(PO_4)_3$ or $Na_5V_2(PO_4)_3$. The stored Na^+ ions can effectively compensate for the inevitable sodium loss over charge-discharge cycles.



Figure 1.4 Crystal structure of NASICON-type $Na_3V_2(PO_4)_3$: 3D framework Na-1 site (a, b), and Na-2 site (c, d). Reproduced with permission: Copyright 2020, John Wiley & Sons, Inc.^[49]



Figure 1.5 Intercalation and deintercalation of Na^+ ions in N_3VP within a potential range from 0 to 3 V *vs.* Na^+/Na . Reproduced with permission: Copyright 2015, The Royal Society of Chemistry.^[50]
d) Sodium vanadium fluorophosphates

The relatively low voltage plateau of the Na₃V₂(PO₄)₃ cathode has ignited interest in investigating alternative cathode materials with higher working voltages. Sodium vanadium fluorophosphate (Na₃V₂(PO₄)₂F₃) stands out among these materials. By replacing one PO₄³⁻ in the Na₃V₂(PO₄)₃ cathode with three F⁻, elevated working voltage plateaus at 3.7 V and 4.2 V *vs*. Na⁺/Na are obtained because of the strong electronegativity of fluorine and more pronounced inductive effect of the (PO₄)³⁻ polyanion.^[51] Similar to Na₃V₂(PO₄)₃, Na₃V₂(PO₄)₂F₃ is also capable of de-intercalating two Na⁺ ions with a specific capacity of 128 mAh g⁻¹ delivered.^[41]

However, its poor electronic conductivity (~ 10^{-12} S cm⁻¹) retards the sodium storage kinetics and necessitates composition/structure modifications, including compositing with conductive materials, micro-nano structure regulation, and element doping.^[52] Furthermore, the large content of highly electronegative F⁻ in Na₃V₂(PO₄)₂F₃ hampers the migration of Na⁺ ions, leading to sluggish interfacial reaction kinetics. To counteract this, the Na₃V₂O_{2-2x}(PO₄)₂F_{1+2x} (0 ≤ *x* < 1) materials family was synthesized by replacing some F⁻ with O²⁻ to weaken the inductive effect and facilitate Na⁺ diffusion. The Na₃V₂O₂(PO₄)₂F cathode is a representative one in this family, which exhibits a high theoretical capacity of 130 mA h g⁻¹ and possesses two high working plateaus at about 3.6 V and 4.0 V *vs.* Na⁺/Na.^[52] The low intrinsic electronic conductivity (~ 10^{-7} S cm⁻¹) has yet to be improved for practical use.^[53]

Figure 1.6 illustrates the lattice structure of $Na_3V_2O_2(PO_4)_2F$, where octahedra [VO₅F] and tetrahedra [PO₄] layer structures are stacked along the a-b planes, forming two different sites for Na⁺ ion insertion. The Na-1 site is coordinated by six O atoms and one F atom, whereas Na-2 is coordinated by six O atoms. The partially occupied Na-2 site ensures the vacancies for Na⁺ ion diffusion, while interstitial channels along the a and b axes also provide extra-large cavities for Na⁺ ion movement.^[54]



Figure 1.6 The illustration of the crystal structure of $Na_3V_2O_2(PO_4)_2F$ in the a-b plane and the a-c plane. Reproduced with permission: Copyright 2023, John Wiley & Sons, Inc.^[52]

During the reversible insertion/extraction process, Na⁺ ions migrate between these sites following a typical two-step single solid solution reaction mechanism with the voltage range of 2.5–4.4 V vs. Na⁺/Na. Bianchini and co-workers reported that further Na insertion into Na₃V₂O₂(PO₄)₂F produces Na₄V₂O₂(PO₄)₂F at ~1.6 V vs. Na⁺/Na, which provides an additional specific capacity of ~60 mAh g⁻¹ (Figure 1.7).^[55] Moreover, the crystal structure of Na₃V₂O₂(PO₄)₂F maintains very stable after Na insertion. Thus, it offers a facile pre-sodiation strategy for Na₃V₂O₂(PO₄)₂F cathodes, which can effectively compensate for inevitable sodium loss over charge-discharge cycles.



Figure 1.7 Electrochemical charge/discharge curves of $Na_3V_2(PO_4)_2FO_2//Na$ half-cells in different voltage ranges of 2–4.4 V and 1.1–4.4 V *vs.* Na⁺/Na. Reproduced with permission: Copyright 2017, John Wiley & Sons, Inc.^[55]

1.1.5 Challenges in sodium metal batteries

A primary challenge hindering the development of rechargeable SMBs is how to achieve high reversibility during Na plating/stripping cycles.^[39] This reversibility can be quantified by the CE value, which is defined as the ratio of the amount of Na that can be electrochemically stripped from the negative electrode to that plated in the preceding step. A CE above 99.95% represents a performance benchmark for 80+% capacity retention over 1,000 cycles.^[56, 57] Accurate CE determination requires a working electrode devoid of excess sodium and a counter electrode with a sodium reservoir, typically realized by assembling Na//Al half cells. The CE values can be calculated using the following equation:^[58]

$$CE = \frac{\text{Stripping capacity}}{\text{Depositing capacity}} = \frac{N_{e^{-}}(\text{stripping Na}) + N_{e^{-}}(\text{IER})}{N_{e^{-}}(\text{depositing Na}) + N_{e^{-}}(\text{IER})}$$
(1.1)

where N_{e-} is the number of electrons and IER represents the irreversible electrochemical reactions.

While widely used to evaluate sodium inventory loss during Na plating/stripping cycles, CE measurement is encumbered by inherent limitations. Ideally, a CE value of 100% indicates a complete Na plating/stripping reversibility without parasitic reactions. Practical cells inevitably encounter both chemical and electrochemical side reactions.^[56, 59] Chemical parasitic reactions, typically not involving electron transfer through the current collectors, are undetectable by CE measurements. Only electrochemical side reactions involving electron transfer at the current collectors reflect the deviation from the ideal 100% CE.^[10, 60] Besides, it is assumed that sodium inventory loss occurs solely in either the charge or discharge process, but not both. If that occurs, the CE value will not accurately reflect the total sodium loss.^[40, 61]

The first parameter that affects the CE is the unstable SEI. The high reactivity and negative electrochemical potential of sodium metal anodes pose a significant challenge in battery design, as most organic solvents are prone to degradation upon contact with the Na metal. This degradation typically results in the forming of a thick film via chemical reactions, and this film serves as an initial SEI layer. However, such SEI layer continuously deteriorates over the charge/discharge cycles because of the electrochemical side reactions. This process usually leads to an unstable, organic-rich, and heterogeneous SEI layer on the sodium metal, compromising its efficacy as a protective barrier.^[62, 63]

The "hostless" plating/stripping mechanism inherent to sodium metal anodes presents another significant challenge for SEI. Substantial interfacial fluctuations between the sodium metal anode and the SEI layer during cycling lead to mechanical stress, which induces cracking within the SEI and exposes fresh Na metal to the electrolyte. Consequently, further side reactions are accelerated, depleting both the limited sodium metal and the electrolyte.^[64] Additionally, undesirable gas evolution is inevitable during SEI formation, compromising the safety and performance of the battery. Zhang and his co-workers demonstrated that the complexation of organic solvents with Na⁺ ions significantly facilitates electrolyte decomposition and gas evolution compared to the pure solvent because of the decreased lowest unoccupied molecular orbital (LUMO) energy level.^[65]

The next factor affecting the CE is the dendrite growth. Extensive research has focused on elucidating the mechanisms underlying dendrite formation because it greatly hinders the safe and stable operation of SMBs. As illustrated in Figure 1.8, the initial stage of sodium deposition is often characterized by non-uniformity because of the inherently uneven SEI layer. Such uneven

deposition is further exacerbated after further Na plating since the SEI with poor elasticity fails to accommodate the volumetric expansion, leading to crack formation. These cracks then act as preferential pathways for Na⁺ ion flux, amplifying the uneven deposition and ultimately forming detrimental Na dendrites.^[39, 66]



Figure 1.8 Schematic illustration of Na dendrite formation based on a sequential growth mechanism. Reproduced with permission: Copyright 2019, John Wiley & Sons, Inc.^[39]

The growth of Na dendrites presents a multifaceted threat to both battery performance and safety. First, dendrites can propagate through the separator and reach the cathode, leading to internal short circuits and potentially catastrophic thermal runaway. Second, during the subsequent stripping process, these dendrites are prone to detachment from the anode because of the preferential dissolution at their base. This detachment results in electrically isolated "dead" Na, accompanied by the formation of new SEI layers. It decreases the CE and contributes to an overall impedance increase, ultimately accelerating cell failure. Repeated cycles of sodium plating and stripping exacerbate these issues, leading to the accumulation of "dead" Na, excessive SEI formation, increased Na metal anode porosity, and electrolyte depletion. These factors collectively contribute to the poor cycling stability of SMBs.^[39, 64]

In addition to the above general challenges faced by SMBs, specific application scenarios such as low-temperature and high-voltage operations introduce further complexities. At low temperatures, the formation of fragile SEI layers and the growth of Na dendrite impair the reversibility of Na plating/stripping. Those issues are further compounded by the sluggish transfer kinetics of Na⁺ ions, which slow down the desolvation process at the electrode/electrolyte interface and make it the rate-limiting step during sodium deposition.^[67, 68]

Operating SMBs at high voltages, while promising for enhancing energy density, also introduces significant challenges. The higher redox potential of sodium, which is +0.3 V compared to lithium, requires electrolytes with superior anti-oxidation potential to achieve comparable cutoff voltage.^[25] The high potential readily induces progressive electrolyte oxidative decomposition at the cathode surface, leading to the formation of an unstable cathode electrolyte interphase (CEI) layer.^[69] In addition, high-voltage conditions can cause severe cathode degradation, including structural reconstruction, transition metal dissolution, and mechanical degradation, which significantly impact the cycle stability of SMBs.^[70]

1.1.6 Advancements in sodium metal battery research

Extensive research efforts have been devoted to enhancing the reversibility of sodium plating/stripping, suppressing the growth of detrimental Na dendrites, and improving the oxidative stability of electrolytes. These efforts focus on two key strategies: sodium metal anode engineering ^[71-74] and electrolyte engineering.^[75-80]

a) Na anode engineering

3D sodium metal anodes can be constructed by using metallic/carbonaceous materials as sodium hosts, which effectively accommodate the significant volume expansion/contraction during repeated Na plating/stripping cycles. Moreover, by providing high surface area and electrically conductive hosts, these 3D architectures enable decreased local current densities and promote homogeneous and dendrite-free sodium deposition.^[34, 37, 81-83] For instance, Liu and co-workers demonstrated the efficacy of replacing commercial Al foil with a 3D porous Al current collector in providing ample surface area for Na nucleation, leading to significantly improved homogeneity in Na plating/stripping.^[84]

Given the highly reactive nature of sodium metal and its susceptibility to inducing unstable SEI formation, engineering an artificial SEI layer on the sodium anode surface has been considered an efficient strategy to address the above-mentioned issues. It is normally achieved by chemical reactions, atomic/molecular layer deposition, and coating of 2D materials such as graphene^[85] and MXene^[86]. Archer and co-workers demonstrated the effectiveness of an artificial SEI layer composed of NaBr in suppressing the formation of porous dendrites in a carbonate electrolyte.^[87]

Luo and co-workers developed a low-temperature plasma-enhanced atomic layer deposition technology to deposit an ultrathin Al_2O_3 film on Na metal to passivate the sodium metal in the carbonate electrolyte.^[88]

b) Electrolyte engineering

The electrochemical performances of sodium metal anodes and high-voltage cathodes are significantly influenced by the electrolyte composition. The primary objective of electrolyte engineering is to bolster the stability of SEI and CEI layers for mitigated dendrite formation on the anode and enhance the oxidative stability of the electrolyte at the cathode.^[89-92] Extensive research efforts have thus been directed toward optimizing the electrolyte composition, including solvents, salts, and additives, and they are discussed in detail below.

1.2 Research objectives and strategies

According to the above discussions, the practical application of SMBs is still hindered, especially in low-temperature and high-voltage operations. Investigations in these directions remain in a nascent stage. This research therefore focuses on electrolyte formulation to address the key challenges confronting low-temperature and high-voltage SMBs. The research objectives are as below:

- a. Enabling low-temperature AFSMB operation down to -65 °C. This study will explore the solvation structure reconfiguration of a conventional glyme-based electrolyte to improve the sluggish Na⁺ mobility and poor-quality SEI at low temperatures.
- Enhancing the electrochemical oxidative stability of electrolytes for high-voltage SMBs up to 4.4V. The solubilizing agent will be explored in the electrolyte to decrease the content of oxidation-sensitive free solvents and to form a more stable CEI.
- c. Realizing high-voltage SMBs in an anode-free configuration with high capacity retention > 90% over 200 cycles. A crown-like solvation structure will be investigated to stabilize the ether electrolyte at both high-voltage cathode and Na metal anode toward high CE.

Chapter 2 Literature Review

2.1 Overview of electrolyte formulations for sodium metal batteries

Electrolytes serve as a bridge to connect two electrodes by enabling the movement of ions from the cathode to the anode on charge and in reverse on discharge. In SMBs, the Na⁺ transportation facilitates the charge and mass transfer across the cell.^[2, 10] The electrolyte formulation in SMBs not only determines the transport behavior of Na⁺ ions but also dramatically affects the formation of electrolyte-electrode interphases. Therefore, it significantly influences battery performance regarding accessible capacity, rate capability, lifespan, and operation safety. An ideal electrolyte for SMBs must meet various requirements, including high Na⁺ ion conductivity in a wide temperature range, environment benignity, low cost, ease of processibility, and good stability against the positive and negative electrodes.^[93]

Current commercially available electrolytes are primarily liquid-based since liquid electrolytes promote smooth ion transport and wet the electrodes well. To date, the investigation of liquid electrolytes for SMBs remains nascent. While carbonate-based electrolytes are extensively used in commercial LIBs, they fail to form a stable SEI on the sodium metal surface, resulting in poor Na plating/stripping reversibility. In contrast, ether-based electrolytes have emerged as the preferred choice because of their low reactivity with sodium anode and high CE of Na plating/stripping; their high-voltage electrochemical stability has yet to be improved.

2.1.1 Commonly used sodium salts

Electrolytes for SMBs typically consist of one or more sodium salts dissolved in a single or multiple solvents. Salts are essentially composed of Na⁺ cations and various anions, which serve as the charge carriers in the electrolyte for smooth ion transportation. Generally, ideal sodium salt should possess the following pivotal characteristics:

- (i) high solubility to ensure a sufficient concentration of charge carriers in the electrolyte;
- (ii) good thermal stability to enhance battery safety by mitigating thermal runaway risks;
- (iii) robust chemical stability to prevent undesirable side reactions;
- (iv) sufficient electrochemical stability to maintain a wide electrochemical stability window (ESW) of electrolytes;

 (v) cost-effectiveness and low toxicity to enable practical, sustainable, and mass production of electrolytes.

Figure 2.1 illustrates the compositions and crystal structures of commonly investigated sodium salts for SMBs, including NaOTf, NaFSI, NaTFSI, NaClO₄, NaPF₆, and NaBF₄. These salts all own a central atom coordinated with electron-withdrawing ligands.^[94, 95] Such configuration effectively delocalizes the negative charge, weakening cation-anion interactions.



Figure 2.1 Geometric configuration of the commonly used sodium salts. Reproduced with permission: Copyright 2022, John Wiley & Sons, Inc.^[96]

Lattice energy refers to the energy released when sodium ions and the respective anions combine to form a crystalline lattice structure of a sodium salt. The lattice energy of sodium salts can be lowered by electron-withdrawing functional groups of the anion. These groups delocalize the electron density, decreasing the electrostatic attraction between the sodium cation and the anion. As depicted in Figure 2.2, NaBF₄ exhibits the highest lattice energy among the six salts, while NaPF₆ possesses the lowest value. Notably, the lattice energies across the six salts do not differ significantly.

Figure 2.2 provides insights into the thermal stability of various salts by presenting their decomposition temperatures. Generally, they are positively correlated with the lattice energy and also significantly influenced by the inherent stability of the anion. Ponrouch and co-workers utilized differential scanning calorimetry (DSC) measurements to investigate the thermal stability of electrolytes containing different sodium salts.^[97] NaClO₄ demonstrated the highest thermal stability among the six investigated salts.^[29]



Figure 2.2 Lattice energies and decomposition temperatures of the commonly used sodium salts. Reproduced with permission: Copyright 2022, John Wiley & Sons, Inc.^[96]

Developing new anions for sodium-based electrolytes is crucial for advancing battery technology. One successful strategy involves modifying the ligands coordinated to a central boron atom. This approach led to the synthesis of sodium bisoxalato borate (NaBOB) by Whittingham and co-workers in 2003.^[98] Younesi and co-workers then demonstrated the efficacy of 0.66 M NaBOB in N-methyl-2-pyrrolidone (NMP) electrolyte. It achieves an impressive ionic conductivity of 8.83 mS cm⁻¹, superior to that of the commonly used 1 M NaPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC) electrolyte (6.44 mS cm⁻¹).^[99]

Subsequently, sodium difluoro(oxalato) borate (NaDFOB) was developed, which combines the advantages of NaBOB and NaBF₄ salts. The presence of electron-withdrawing fluorine atoms in NaDFOB enhances its solubility compared to NaBOB. Additionally, the LUMO energy level for DFOB⁻ anion is lower than that of BF_4^- anion; therefore, it is readily reduced on the Na metal surface and enables the formation of borate- and fluoride-rich SEI layer.^[72, 100]

Beyond borate-based anions, incorporating heterocyclic rings in the anion represents another promising approach for developing new salts. For instance, sodium 4,5-dicyano-2-(trifluoromethyl)imidazolate (NaTDI) and sodium 4,5-dicyano-2-(pentafluoroethyl)imidazolate (NaPDI) are two imidazolium anions featuring five-membered rings. Electrolytes composed of NaTDI and NaPDI salts dissolved in propylene carbonate solvent exhibited ionic conductivities of approximately 4 mS·cm⁻¹ at 20 °C at 0.5 M and 1 M concentrations, respectively. Importantly, both NaTDI and NaPDI salts demonstrate excellent thermal stability exceeding 300 °C and high

electrochemical stability with an upper voltage limit of over 4.5 V and 4.2 V vs. Na⁺/Na, respectively.^[101]

2.1.2 Commonly used organic solvents

Solvents dissociate salts in the electrolytes, determining their physicochemical and electrochemical properties. For SMBs, the selection of proper organic solvents is critical for formulating optimized electrolytes and achieving high battery performances. However, the ideal solvent must fulfill a demanding set of criteria as below:

- (i) suitable polarity and dielectric constant to facilitate salt dissociation and minimize ion pairing;
- (ii) low viscosity to ensure rapid ion mobility;
- (iii) electrochemical stability to ensure the inertness of solvents at the electrochemically active cathode and anode surfaces during battery operation;
- (iv) wide liquid range, characterized by a low melting point and a high boiling point, to ensure that the electrolyte remains liquid over a wide temperature range;
- (v) safety, non-toxicity, and economic viability for mass production.

Meeting the diverse and sometimes contradictory requirements by a single solvent can be very challenging, necessitating the use of solvent mixtures in SMB electrolytes.

The hyperreactivity of Na metal with moisture precludes the utilization of nonaqueous solvents in SMBs. Ester solvents are widely used in rechargeable lithium batteries and SIBs mainly because of their high salt solubility and resulting high ionic conductivity. However, the formation of a soluble and continuously thickening carbonate-derived SEI layer on the Na metal surface leads to low Na plating/stripping reversibility and restricted application in SMBs. In contrast, ether solvents demonstrate superior compatibility with Na metal, making them promising candidates for SMB electrolytes. Ether solvents can be broadly categorized into cyclic ethers, such as 1,3dioxolane (DOL), 1,3-dioxane, tetrahydrofuran (THF), and linear ethers such as dimethyl ether (TEGDME). As a typical example, Seh and co-workers reported a remarkably high average CE of 99.9% for Na plating/stripping over 300 cycles at 0.5 mA cm⁻² using a glyme-based electrolyte of 1 M NaPF₆ in G2 at room temperature.^[75] Tang and co-workers showed that a weakly solvating electrolyte of 1 M NaPF₆ THF achieves both low Na⁺ ion desolvation energy and fast ion transport, enabling the battery to work at $-25^{\circ}C.^{[102]}$ Phosphate solvents, such as trimethyl phosphate (TMP), triethyl phosphate (TEP), and tripropyl phosphate (TPrP), have gained intensive research interest because of their non-flammable properties for enhanced safety of SMBs. For instance, Jin and co-workers demonstrated that a NaFSI-TEP electrolyte enabled a long-term cycling capacity retention of 89% after 500 cycles at 0.5 C for a Na//NaNi_{0.68}Mn_{0.22}Co_{0.10}O₂ half-cell.^[103] However, one challenge with TEP-based electrolytes is their chemical stability against Na metal.^[104] Fluorinated TEP derivatives, such as tris(2,2,2-trifluoroethyl) phosphate (TFP), exhibit improved stability against Na metal while retaining excellent flame-retardant properties. However, TEP-based electrolyte is known for its low ionic conductivity (0.43 mS cm⁻¹) and poor compatibility with sodium metal.^[105]

The physicochemical properties of solvents significantly influence the overall properties of the electrolyte. For instance, the dielectric constant (ε) is a crucial indicator, directly influencing the ease with which it dissociates ion pairs of salts and forms Na⁺-solvent solvation complexes. On the one hand, a high dielectric constant of solvent promotes salt dissociation and ion conduction. On the other hand, strong solvent-Na⁺ coordination hinders smooth desolvation at the electrode interface. This slowed desolvation process adversely impacts charge transfer kinetics. It also decreases the Na⁺ ion transference number and weakens the rate capability of the battery. Moreover, high dielectric constant solvents typically possess strong dipole-dipole forces with elevated freezing points and compromised low-temperature performances.^[106]

Lewis basicity reflects the ability of a solvent to donate electron pairs.^[107] It is often characterized by Gutmann donor number (DN), derived from the enthalpy of the reaction between the solvent and the Lewis acid antimony pentachloride. A high DN signifies a strong tendency for cation solvation, as the solvent readily coordinates with the electron-accepting Na⁺ ions. Solvents with high DN values exceeding 10 typically dissociate salts well. Conversely, those with low DN values, tend to be poor solvating agents.^[108]

2.1.3 Various additives

Electrolyte additives are crucial components for enhancing battery performance in spite of their low content. They can act as film-forming agents, preferentially being oxidized on the cathode surface or reduced on the anode surface. High-quality electrode/electrolyte interphases can be formed for stable battery operation. For instance, Seok and co-workers demonstrated that incorporating fluoroethylene carbonate (FEC) into a NaClO₄–PC electrolyte significantly

improves the uniformity of sodium plating and enhances cycling stability by forming a stable NaFrich SEI layer.^[109] Jiang and co-workers introduced N, O-bis(trimethylsilyl) trifluoroacetamide (BSTFA) additives to a 0.3 M NaPF₆ in EC/PC electrolyte to enhance its performance in SMBs.^[110] BSTFA effectively scavenges H₂O and HF within the electrolyte, preventing the decomposition of NaPF₆. Furthermore, it preferentially decomposes to form organic-dominated, NaF-rich interfacial films on both the cathode and anode surfaces.

Besides boosting the interfacial stability, additives can also enhance battery safety. For instance, Zheng and co-workers introduced temperature-sensitive perfluoro-2-methyl-3-pentanone (PFMP) to a 1.0 M NaPF₆ in FEC/PC/HFE electrolyte.^[111] During a potential thermal runaway event, PFMP undergoes a prior endothermic evaporation process, dissipating surrounding heat, effectively suppressing thermal runaway, and extinguishing the potential fire.

2.1.4 Impact of electrolyte concentrations

The selection of appropriate electrolyte concentrations requires a meticulous balance between the number of available charge carriers and their mobility within the electrolyte. Classical theories that describe electrolyte behavior are typically based on the ideal diluted electrolyte model. It assumes complete dissociation of salts, independent migration of ions, and negligible interactions between ions. SSIP solvates dominate the solvation structure, with anions largely unpaired and a substantial portion of solvents remaining uncoordinated.^[112, 113] Nevertheless, practical electrolytes deviate from this ideal model, even at low concentrations below 0.1 M. Electrolytes at moderate concentrations, such as 1M, are conventionally used because of considerations of production cost and the balance between the number and mobility of Na⁺ ions. While increasing electrolyte concentrations can enhance ionic conductivity by providing a larger amount of Na⁺ ions for charge transfer, this approach is often limited by the sharply increased viscosity at higher concentrations, which significantly hinders ionic mobility.

a) High-concentration electrolytes

High-concentration electrolytes (HCEs) are gaining significant attention because of their potential to unlock superior electrochemical performance for SMBs by forming special solvation structures. There is no definitive criterion to classify high-concentration and moderate-concentration regimes distinctly. A promising approach involves utilizing the ion-solvation shell as a criterion: HCEs are

characterized by a predominant proportion of anions residing within the primary solvation shell, with few free solvent molecules, typically at concentrations exceeding 3 M.^[114]

In HCEs, CIP and AGGs solvates are dominated, facilitating the preferential decomposition of anions to form inorganic interphases. These formed interphases have been reported to effectively protect the electrolytes from further decomposition and enhance the stability of electrodes.^[115] Lu and co-workers constructed a beyond-concentrated electrolyte through the size effect of a 3A zeolite molecular sieve film. It suppresses the trace but continuous oxidative decomposition and extends the oxidative stability to 4.5 V without sacrificing the Na reversibility of the anode (99.91%).^[89]

Furthermore, HCEs exhibit lower concentration gradients during the charging and discharging process than moderate-concentration electrolytes. This has been confirmed in lithium-based electrolytes and applied to sodium-based electrolytes. Peng and co-workers monitored the vibrational band evolutions of the super-concentrated electrolytes and baseline carbonate electrolytes at different current densities through in-situ Raman spectroscopy. They discovered that the Raman peak corresponding to the symmetrical stretching band of FSI⁻ in the super-concentrated electrolyte only shows a slight shift. In contrast, the Raman peak corresponding to the symmetrical stretching band of FSI⁻ in the super-concentrated electrolyte only shows a slight shift. In contrast, the Raman peak corresponding to the symmetrical stretching ball of FSI⁻ in the super-concentrated electrolyte only shows a slight shift. In contrast, the Raman peak corresponding to the symmetrical stretching ball of FSI⁻ anion concentration gradient, as illustrated in Figure 2.3.^[116]

While highly concentrated electrolytes (HCEs) offer several advantages, they are characterized by increased viscosity and larger solvated sodium ions, presenting a challenge to ion transport. The decrease in ionic mobility in HCEs is a result of the inverse relationship between ion mobility and viscosity, as well as ionic radius. This aligns with the conventional understanding of charged particle behavior in electrical fields, where ion movement is principally driven by the force of the electric field. Recent research has revealed that the presence of AGG solvates in HCEs plays a significant role in the overall transport process by introducing structural diffusion. In contrast to conventional vehicle transport significantly affected by intermolecular attractions, such structural transport can be quite smooth even in viscous electrolytes.^[113, 117] Besides the Na⁺ mobility issue, high cost and poor wettability toward electrodes and separators also hinder the practical application of HCEs.



Figure 2.3 (a) Schematic representation of the in situ Raman test condition. Raman spectrum evolutions of the super-concentrated electrolytes (LAV: LiFSI–acetonitrile (AN)–vinylene carbonate (VC)), (b), and baseline carbonate electrolytes (c) at 1 and 4 mA cm⁻². Reproduced with permission: Copyright 2020, John Wiley & Sons, Inc.^[116]

b) Localized high-concentration electrolytes

The concept of localized high-concentration electrolytes (LHCE) was first introduced by Zheng and co-workers in 2018 to tackle the issues of high viscosity and high cost associated with HCEs.^[118] Their approach involved using polyfluorinated ether bis(2,2,2-trifluoroethyl) ether (BTFE) to dilute a 5.2 M NaFSI/DME HCE. By Incorporating BTFE as a diluent, they achieved a significant decrease in viscosity and an enhancement in the ionic conductivity of the electrolyte, as depicted in Figure 2.4.

The weakly interacting solvents are widely used as diluents, these "inert" diluent has minimal or negligible impact on the AGGs solvates present in HCEs, as shown in Figure 2.5. Hydrofluoroethers are identified as meeting the "inert" requirements because of their low dielectric constant and low donor number. These properties ensure that hydrofluoroethers are ineffective in dissolving salts but exhibit great miscibility with the salt/solvent complexes. This strategy not only

decreases the overall cost and viscosity of electrolytes but preserves the local coordination environment of HCEs.



Figure 2.4 Viscosity (a) and ionic conductivity (b) of the dilute electrolyte, HCE, and LHCEs. Reproduced with permission: Copyright 2018, American Chemical Society.^[118]



Figure 2.5 Schematic illustration of the HCE and LHCE. Reproduced with permission: Copyright 2018, American Chemical Society.^[118]

c) Low-concentration electrolytes

The exploration of the low-concentration regime for SMB electrolytes remains limited because of the prevailing assumption that both ionic conductivity and electrolyte stability are compromised below a salt concentration of 1 M. This paradigm was challenged by Li and co-workers in 2020, who demonstrated the feasibility of a low-concentration electrolyte (0.3 M NaPF₆ in EC/PC) for SIBs. Remarkably, this electrolyte achieved an impressive average CE of 99.9% in full cells

pairing a disordered carbon anode with a layered O3–Na[Cu_{1/9}Ni_{2/9}Fe_{1/3}Mn_{1/3}]O₂ cathode. This performance significantly surpasses the 98–99% CE typically observed in SIBs using 1M electrolyte (Figure 2.6).^[119] The utilization of low-concentration electrolytes presents numerous significant advantages. It significantly decreases the cost and expands the operational temperature range of SIBs. The lower viscosity favors the interfacial wettability and decreases the risk of corrosive HF attack caused by the decomposition of NaPF₆ salt. Furthermore, the formation of stable organic-dominated SEI/CEI layers with superior kinetics facilitates the stable operation of NIBs at extreme temperatures.^[115]



Figure 2.6 Cyclic capability of NIBs using electrolytes with different concentrations. Reproduced with permission: Copyright 2020, American Chemical Society.^[118]

2.2 Fundamental properties of electrolytes

2.2.1 Dissociation of salts

A typical electrolyte is a homogeneous solution produced by dissociating salts in the solvent. The salt dissolution process involves two individual steps: lattice dissociation determined by lattice energy (U) and solvation by solvents determined by solvation energy (ΔH_h). The simplified Born–Haber cycle of the dissolution process is shown in Figure 2.7.



Figure 2.7 The energy change during the dissociation process of salts. Reproduced with permission: Copyright 2022, John Wiley & Sons, Inc.^[96]

$$\Delta H = -U + \Delta H_{\rm h} \tag{2.1}$$

$$\Delta S = \Delta S_1 + \Delta S_2 \tag{2.2}$$

Based on this thermodynamic cycle, a more negative Gibbs free energy (ΔG) signifies a more favorable dissociation process. Considering the entropy change for the salt dissolution is extremely low, the Gibbs free energy of dissolution is approximate to the enthalpy change, which is determined by the lattice energy and the solvation energy. Consequently, for specific salts and solvents, a higher lattice energy of the salt corresponds to a lower solubility, whereas a higher solvation energy results in a higher solubility.^[120]

Recall that NaBF₄ exhibits the highest lattice energy, and NaPF₆ possesses the lowest among the six commonly used Na salts (NaOTf, NaFSI, NaTFSI, NaClO₄, NaPF₆, and NaBF₄). Lower lattice energy benefits enhanced solubility. Experimentally, NaPF₆ readily dissolves in DEGDME solvent at concentrations exceeding 2 M, whereas the NaBF₄ system reaches saturation at approximately 0.64 M in the same solvent.^[91] Moreover, salts such as NaCl and NaF, characterized by strong ionic bonds and consequently high lattice energies, are practically insoluble in nonaqueous solvents.^[121]

According to the simplified Born–Haber cycle, the solvation ability of solvents also profoundly affects the dissociation of salts. Polar solvents weaken the electrostatic forces within crystal lattices, facilitating salt dissociation. Solvents with high dielectric constant also facilitate salt dissociation by diminishing the attractive forces between dissolved ions.^[122]

2.2.2 Electrochemical stability window

The stability of an electrolyte is measured by the voltage range between its oxidative and reductive decomposition limits, known as the "electrochemical stability window" (ESW). The upper limit

of this window is determined by the oxidative stability of the electrolyte, which is the highest potential at which electrolyte molecules can resist oxidation without decomposition. And the lower limit is determined by how well the electrolyte can resist reduction without decomposition. Given the extreme potential at which the electrodes of modern batteries operate, achieving electrochemical stability purely through thermodynamics is usually not feasible. Instead, the electrochemical stability is often achieved through a passivation process. This involves the sacrificial decomposition of electrolyte components, such as salts, solvents, and additives to form a SEI and a CEI. These thin films separate the electrolyte from the highly reductive anode and the highly oxidative cathode, respectively.

Figure 2.8 illustrates the relative electron energies within the electrodes and the electrolyte of a thermodynamically stable battery. In the molecular orbital theory, the HOMO represents the highest energy orbital containing electrons, and the LUMO refers to the lowest energy orbital available to accept electrons. HOMO typically functions as the electron donor in chemical reactions, while LUMO acts as the electron acceptor. The energy separation (E_g) between LUMO and HOMO reflects the ESW of the electrolyte to some extent. The higher the HOMO energy level, the easier it is for the electrolyte to be oxidized, thereby lowering the upper limit of the ESW, and vice versa. The μ_A and μ_C in Figure 2.8 represent the electrochemical potentials of the anode and cathode, respectively. The Φ_A and Φ_C represent the work functions of the anode and cathode, and their difference determines the open circuit voltage (V_{OC}) of a battery system. When μ_A is lower than LUMO, and μ_C is higher than HOMO, the electrolyte remains stable even without the formation of two interphases.^[123] Therefore, a thermodynamic stable battery needs to meet the following equation,

$$eV_{\rm OC} = \mu_{\rm A} - \mu_{\rm C} \le E_{\rm g} \tag{2.3}$$

where e is the magnitude of the electron charge.

When the μ_A value of the anode is higher than the LUMO energy level of the electrolyte, the anode spontaneously transfers electrons to the electrolyte. This situation occurs with the Na metal anode because of its low potential. The Na metal anode spontaneously reduces the electrolyte through parasitic corrosion reactions when it contacts the electrolyte. During the later charge/discharge process, the Na metal further reduces the electrolyte until a passivating SEI layer forms on its surface.^[124] Similarly, when the μ_C of the cathode is lower than the HOMO energy

level of the electrolyte, the electrolyte undergoes oxidation. Decomposition products form a passivating CEI layer, which blocks the interaction between the electrolyte and the cathode. The formation and modification of SEI and CEI layers are dynamic processes throughout the charging/discharging cycles. The stability of these interphases during battery cycling is crucial for achieving a stable cycling.

Notably, the unit of the energy here is electron volt (eV), and the energy states of electrodes are reversely related to their voltages according to the equation:

$$\Delta G = -n F E \tag{2.4}$$

where ΔG is the Gibbs free energy change, *n* is the number of electrons transferred in the reaction, F is the Faraday constant, and *E* is the potential of the electrode.



Figure 2.8 Schematic illustration of the relative electron energies in the electrodes and electrolyte of a thermodynamically stable battery. Reproduced with permission: Copyright 2010, American Chemical Society.^[123]

Peljo and co-workers argued that HOMO and LUMO concepts, derived from approximated electronic structure theory for isolated molecules, do not directly indicate species involved in redox reactions. Redox potentials are directly related to the Gibbs free energy difference of the reactants and products. Although redox potentials can sometimes be strongly correlated with HOMO/LUMO energies, there can be significant discrepancies of several eVs in some cases. Therefore, they proposed the thermodynamic representation for the electrochemical stability of the electrolyte should be based on redox potentials and the Fermi level of the electron in the electrolyte.^[125]

a) The impact of sodium salts on the electrochemical stability

Recent research emphasizes the significant role of salt anions, rather than solvents, in determining the ESW of electrolytes.^[126] This influence is demonstrated through two primary modalities. First, the LUMO energy level of the anion determines reduction reactions at the electrolyte-anode interface. Different anions produce unique reduction products, which affect the composition and properties of SEI, and in turn, the Na reversibility.^[77, 78, 127] Second, the HOMO energy level of anions dictates the upper limit of the ESW in the electrolyte. Figure 2.9 illustrates the HOMO energy level at -11.67 eV, demonstrates high resistance to oxidative decomposition. In contrast, NaOTf and NaClO₄, with HOMO levels at -7.5 eV and -7.89 eV, respectively, exhibit poor anti-oxidation stability. The stability of salts against oxidation and reduction is relative due to interactions with solvents within the electrolyte, which can modify their actual HOMO and LUMO energy levels.



Figure 2.9 HOMO energy levels of the commonly used sodium salts. Reproduced with permission: Copyright 2022, John Wiley & Sons, Inc.^[96]

b) The impact of solvent on the electrochemical stability

The electrochemical stability of electrolytes is inherently related to the electronic states of free and solvated solvents. Figure 2.10 illustrates that ether solvents, including DME, DEGDME, and TEGDME, exhibit higher LUMO and HOMO levels compared to carbonate solvents (EC, PC, and DEC). This difference indicates the superior reductive stability but inferior oxidative stability of ether solvents. Their enhanced reductive stability suggests a lower susceptibility to decomposition during the discharging process, avoiding the formation of solvent-derived organic-rich SEI. Notably, the formation of the Na⁺ ion solvation complex significantly lowers both the HOMO and

LUMO energy levels for all solvents, which can be attributed to the altered electronic states upon complexation. Consequently, the solvation complexes possess lower reductive and higher oxidative potentials than their corresponding bare solvents.^[127]



Figure 2.10 LUMO and HOMO energy levels of ether solvents and carbonate solvents and their corresponding Na⁺ complexes. Reproduced with permission: Copyright 2022, The Royal Society of Chemistry.^[127]

2.2.3 Na⁺ ion conducting mechanisms

Ionic conduction in liquid electrolytes arises from the movement of solvated ion complexes. While solvent molecules in the primary solvation shell exhibit stronger binding affinities than those in the secondary and bulk regions, the stability of this sheath structure is transient, persisting only on picosecond to nanosecond timescales. This dynamic behavior is evidenced by the characterization results of ultrafast spectroscopic techniques, which can differentiate between solvent molecules in different solvation shells.^[114, 128] Moreover, molecular dynamics (MD) simulations reveal that the residence time of Na⁺-solvent coordination can be longer or shorter than the residence times of Na⁺-anion coordination in different electrolyte systems, highlighting the complex interplay between Na⁺ ions, and solvents.^[114, 129]

a) Vehicular and structural ion motions

Na⁺ ion transfer in the electrolyte can be based on two primary mechanisms: vehicular and structural motions, as illustrated in Figure 2.11. Vehicular motion with cations moving with a solvation shell of neighboring solvent molecules dominates in dilute electrolytes. This mechanism is exemplified by Na⁺ ions in ethereal solutions, where strong chelation by multiple ether oxygens results in predominantly vehicular transport of the Na⁺-ether complex.^[130] In contrast, structural motion entails the "hopping" of Na⁺ ions between solvation shells through a series of dissociation

and association events, breaking and forming bindings with solvent molecules and anions, respectively.^[114]

The relative contributions of vehicular and structural motions to cation diffusion can be quantified by analyzing the average distance that a solvent (or anion) travels alongside a cation relative to its size. Vehicular transport is primarily characterized by a cation traversing distances exceeding multiple solvent diameters before exchanging its coordinating molecules. Factors favoring vehicular mechanisms include strong cation-solvent interactions, low solvent viscosity, and small solvent size. Although strong chelation of Li⁺-ether results in predominantly vehicular transport for Li⁺ ions in ether-based electrolytes, the weaker binding affinity of Na⁺-ether, coupled with the larger size of the Na⁺ solvation sheath, leads to a shift from primarily vehicular to structural in the transport mechanism. In addition, a transition to structural diffusion is often observed as the salt concentration increases.^[114]



Figure 2.11 Summary of the parameters determining the structural and vehicular transport of the metal cations in the electrolytes. Reproduced with permission: Copyright 2023, Springer Nature.^[21]

Conventional electrolytes with dominant vehicular motion typically exhibit high ionic conductivities. However, this ion transport mechanism often leads to high desolvation energies and organic-rich SEI formation because of the prevalence of SSIP solvation structures. In contrast, HCEs, LHCEs, and weakly solvating electrolytes with higher CIP/AGG solvate ratios promote the formation of anion-derived, inorganic-rich SEIs. However, these electrolytes often suffer from lower ionic conductivity because cation diffusion primarily occurs through structural diffusion

involving sequential hopping of cations between solvent molecules and anions via multidentate ligation.

Recently, Lu and co-workers proposed a novel mechanism for enhanced Li⁺ ions transport in electrolytes containing small-sized solvents to overcome this limitation.^[131] As shown in Figure 2.12, the small fluoroacetonitrile (FAN) molecules in the secondary solvation sheath interact with Li⁺ ions in the primary solvation shell, effectively "pulling" them out and facilitating the formation of fast ion-conducting ligand channels. Moreover, the low solvation energy of these small solvents allows anions to penetrate the first Li⁺ solvation shell, promoting the formation of an inorganic-rich interphase. Consequently, a 1.3 M LiFSI FAN electrolyte exhibits high ionic conductivities of 40.3 mS cm⁻¹ at 25 °C and 11.9 mS cm⁻¹ even at -70 °C while also facilitating the formation of a desirable LiF-Li_xN-rich SEI at the graphite electrode surface.^[131]



Figure 2.12 Schematic illustration of cation transport behaviors based on three different mechanisms: (a) vehicular mechanism, (b) structural mechanism, and (c) ligand-channel-facilitated mechanism. Reproduced with permission: Copyright 2024, Springer Nature.^[131]

b) Ionic conductivity

Ionic conductivity (σ) is a crucial property of electrolytes, reflecting their ability to conduct electric current through the movement of ions. An ionic conductivity higher than 1 mS cm⁻¹ is essential for the fast ion transportation in the electrolyte. A comprehensive understanding of ionic conductivity is paramount for designing novel electrolytes. Mathematically, it can be expressed as the sum of the contributions from all individual ionic species:

$$\sigma = F \sum (z_i \ c_i \ \mu_i) \tag{2.5}$$

where z_i is the valence of the ion i, c_i represents its concentration, μ_i denotes its ion mobility, and F is the Faraday constant.

Ion mobility (μ) quantifies the ease with which an ion migrates within the electrolyte under an electric field. Solvent properties, such as dielectric constant and viscosity, significantly influence the migration velocity of both cations and anions. Additionally, ionic valence also influences their mobility. Without an electric field, the ion self-diffusion coefficient (D) quantifies the random motion of individual ions within a macroscopically equilibrated solution. The relationship between ion mobility and ion self-diffusion coefficient can be calculated through the Einstein relation:

$$\mu = \frac{D}{k_{\rm B} T} \tag{2.6}$$

where $k_{\rm B}$ is the Boltzmann constant, and T is the absolute temperature.

For an ion with a hydrodynamic radius $r_{\rm H}$ in an electrolyte, its self-diffusion coefficient can be calculated by the Stokes–Einstein equation:

$$D = \frac{k_{\rm B} T}{6 \pi \eta r_{\rm H}} \tag{2.7}$$

where η is the viscosity of the electrolyte. Experimentally, the ion self-diffusion coefficient can be determined using the pulsed-field gradient nuclear magnetic resonance (PFG-NMR). In the MD theoretical simulations, the ion self-diffusion coefficient within a specific electrolyte model can be calculated from the mean square displacement curve of the ion.

Based on the self-diffusion coefficients of cations and ions in the electrolyte, the molar electrical conductivity (Λ) can be calculated using the Nernst–Einstein equation:

$$\Lambda = \frac{F^2}{R T} (v_+ z_+^2 D_+ + v_- z_-^2 D_-)$$
(2.8)

where v_+ and v_- are the stoichiometric numbers of the cation and anion per formula unit of the electrolyte, respectively. z_+ and z_- are their respective valences, and D_+ and D_- represent their respective diffusion coefficients. *R* is the universal gas constant.

Note that the Nernst–Einstein equation relies on the assumption of the ideal electrolyte, i.e., complete salt dissociation into free ions, full participation of all free ions in diffusion and migration processes, and independent motion of each solvated ion without influence from neighboring ions.

These conditions stem from classical dilute electrolyte theory. However, numerous species coexist in practical electrolytes. The movement of one species is inevitably influenced by the neighboring mobile ones, thus deviating from the above-mentioned ideal conditions.

The Stefan–Maxwell equation provides a more precise description of species transport within multi-component systems, especially HCE, by explicitly considering inter-species interactions.^[132] The Stefan–Maxwell approach relates the ionic conductivity to three diffusion coefficients, D_{0+} , D_{0-} , and D_{+-} for an electrolyte comprising cations (+), anions (-), and solvents (0). This relationship is represented by:

$$\sigma = -\frac{z_{-} z_{+} F^{2} c_{T}}{RT} \frac{\left(c_{-} D_{0+} + c_{+} D_{0-}\right) D_{+-}}{c_{-} D_{0+} + c_{+} D_{0-} + c_{0} D_{+-}}$$
(2.9)

where z_+ and z_- represent the valences of the cation and anion (negative for anions), respectively; c_+ , c_- , and c_0 represent the concentrations of the cations, anions, and solvents, respectively, and c_T is the total concentration ($c_T = c_+ + c_- + c_0$); D_{0+} and D_{0-} are the Stefan–Maxwell diffusion coefficients of cations and anions relative to the solvent, respectively, reflecting their individual self-diffusion capabilities within the solvent; D_{+-} represents the Stefan–Maxwell diffusion coefficient of cations relative to anions, which captures the relative diffusion behavior between cations and anions based on their interactions.^[132]

At low concentrations, the ionic conduction primarily depends on the independent diffusion coefficient of cations D_{0+} , and anions D_{0-} because of the abundant solvent molecules surrounding them. However, the interplay between cations and anions becomes increasingly significant in high-concentration electrolytes. Consequently, D_{+-} , which includes both self-diffusion and interaction effects, emerges as the dominant factor governing ionic conduction.

c) Na⁺ ion transference number

The Na⁺ ion transference number (t_{Na+}) is an important descriptor for ion transport, quantifying the contribution of Na⁺ ion movement to the total current. A high bulk electrolyte conductivity (σ_{bulk}) does not necessarily imply a high sodium ion conductivity (σ_{Na+}), which limits the achievable current density in the SMBs.^[133] σ_{Na+} is calculated as the product of σ_{bulk} and t_{Na+} : $\sigma_{Na+} = \sigma_{bulk} \times t_{Na+}$.^[112] A high t_{Na+} value signifies high-efficiency charge transfer, while excessively low values exacerbate concentration polarization.

However, accurately measuring t_{Na+} presents a significant challenge. The widely employed Bruce–Vincent method relied on the combination of AC impedance and DC polarization. It involves monitoring the current decay in a symmetric Na//Na cell under constant DC polarization until a steady state is reached, as shown in Figure 2.13.^[134] At the initial state, both cation and anion migration contribute to the current (I_0). At the steady state, only cation migration contributes to the current (I_{SS}) because the anion is blocked by the electrodes. Besides, the presence of interphases on the Na metal and the evolution of interphase resistance with time must be taken into consideration; thus, the t_{Na+} is calculated as:

$$t_{+} = \frac{I_{\rm ss}}{I_0} = \frac{I_{\rm ss} \left(\Delta V - I_0 R_0\right)}{I_0 \left(\Delta V - I_{\rm ss} R_{\rm ss}\right)} \tag{2.10}$$

where ΔV is the applied bias, R_0 and R_{SS} represent the interphase resistance at the initial and the steady state, respectively. However, this method, initially developed for polyethylene oxide-based polymer electrolytes, operates under the assumption of an ideal electrolyte with no complex speciation or convection disrupting the linear concentration gradient. PFG-NMR offers an alternative approach to determine the t_{Na+} according to the following equation:^[135]

$$t_{\rm Na+} = \frac{D_+}{D_+ + D_-} \tag{2.11}$$

where D_+ and D_- represent the cationic and anionic diffusion coefficients, which can be directly measured by using PFG-NMR.



Figure 2.13 Bruce–Vincent method of measuring ion transference number from the steady state in the DC polarization curve. Reproduced with permission: Copyright 2022, Springer Nature.^[112]

Because this method is based on the Nernst–Einstein relation, it holds true only for fully dissociated salt. In partially dissociated systems, the Haven Ratio is commonly used to correct deviations from the fully dissociated case by accounting for correlated motions of undissociated salt molecules or ionic clusters.^[136]

It is noteworthy that the calculated t_{Na+} represents an idealized value. Because an anion concentration gradient would be built when the ions in the electrolyte start the migration driven by an external field, this anion concentration gradient induces opposing diffusion, leading to a higher t_{Na+} during the operation of a cell. Nonetheless, the calculated t_{Na+} remains a vital parameter for evaluating electrolyte capability. It defines the steady-state current limit under anion-blocking conditions, indicating the maximum current an electrolyte can sustain. Therefore, electrolytes with higher t_{Na+} are better choices for supporting high charge/discharge rates.

2.3 Na⁺ ion solvation structures adjustment

Within an electrolyte, Na⁺ ions do not exist in isolation but rather coordinate with solvent molecules or anions. These coordinated solvent molecules and anions create a solvation sheath consisting of one or multiple layers around the Na⁺ ions. This intricate structure arises from various interactions between the Na⁺ ions, anions, and solvent molecules, including Coulombic interactions, van der Waals forces, electrostatic interactions, hydrogen bonding, and other ion-molecule interactions. Furthermore, external factors such as temperature and electric fields can influence the solvation structures.

Elucidating and manipulating the Na⁺ ion solvation structure in the electrolyte is paramount as it significantly influences various electrolyte properties, including the ionic conductivity, Na⁺ ion transference number, liquid temperature range, and the desolvation process. Moreover, the reduction or oxidation sequence of the solvated complex differs from that of individual solvent molecules and ions. Therefore, the formation pathway of the electrode-electrolyte interface is significantly affected.^[29]

The study of solvation started by Miertus and co-workers in the 1980s, who proposed a continuum model based on electrostatic interactions.^[137] Up to date, various characterization methods and theoretical calculations have been employed to elucidate the solvation structures of electrolytes. Vibrational spectroscopy techniques, such as Raman and Fourier-transform infrared

(FTIR) spectroscopy, provide insights into the local vibrational modes of molecules. By analyzing shifts in specific band wavenumbers, researchers can identify variations in the bending, twisting, or stretching vibrations of free solvent molecules, coordinated solvent molecules, and anions, thereby gaining valuable information on local coordination environments. Nuclear magnetic resonance (NMR) spectroscopy offers complementary insights by detecting chemical shifts in specific elements, revealing details about the chemical surroundings, and aiding in the analysis of solvation structures. However, both vibrational spectroscopy and NMR techniques primarily provide local and short-range information (below 1 nm). To probe larger-scale structural features, small-angle X-ray scattering (SAXS) offers an efficient approach. SAXS can probe intermolecular spacing, cluster size, and inhomogeneity domains ranging from 1 to 150 nm, providing valuable insights into the arrangement of clusters or networks within the electrolyte.^[138]

While experimental methods are powerful tools for studying solvation structures, limitations exist when they are used for characterizing complex of multi-component electrolytes. Deconvoluting overlapping spectral peaks from solvents with similar functional groups can be particularly challenging. Theoretical calculations offer a powerful complementary approach, enabling the prediction of electrolyte solvating behavior across a wide range of temporal and spatial scales. MD simulations, by numerically solving Newton's equations of motion, simulate the dynamic features of ions and molecules in the electrolytes. Density functional theory (DFT) investigates changes in the electronic structure of ions and solvent molecules by solving the equations of motion for electrons, providing insights into the nature of bonding and interactions within the electrolyte.

Up to date, the common solvation structures in the electrolyte include SSIP, solvent-shared ion pair (SIP), CIP, AGG, solvent-shared dimer (SSD), and contact dimer (CD), as shown in Figure 2.14. Among them, SSIP, CIP, and AGG are the most extensively studied solvation structures. Moderate- and low-concentration electrolytes predominantly feature SSIP solvation structures. This prevalence of SSIP structures in the solvation sheath often leads to the formation of a solvent-derived, organic-rich SEI and a high Na⁺ ions desolvation energy barrier. As salt concentration increases, the dominant ion-pairing configuration gradually transitions from SSIP to CIP and AGG. In HCEs and LHCEs, CIP and AGG are the dominant solvation structures. This facilitates the preferential decomposition of anions, leading to an inorganic-rich SEI. Furthermore, the decreased

content of free solvent molecules in HCEs and LHCEs enhances the oxidative stability of the electrolyte.^[139]



Figure 2.14 Possible solvation structures present in the electrolytes. Reproduced with permission: Copyright 2023, American Chemical Society.^[140]

2.3.1 Coordination of Na⁺ ions

The solvation structure of Na⁺ ions arises from the competitive coordination of solvent molecules and anions. This intricate interplay is governed by several factors, including the solvent's dielectric constant, polarity, donor number, and steric effects, as well as the structure and size of the anions. A key parameter for describing the geometrical configuration of the cationic solvation structure is the coordination number. This number, typically calculated from the radial distribution function (RDF) curve obtained from MD simulations, represents the number of coordinating atoms from solvent molecules or anions within the first solvation sheath surrounding a single Na⁺ ion.

Na⁺ ions, having lost their outermost electron, possess empty 2s orbitals and readily accept electron pairs from electron-rich species. Consequently, Na⁺ ions preferentially coordinate with oxygen atoms in organic solvent molecules, particularly those with carbonyl or ether functionalities. Shakourian and co-workers demonstrated that carbonate solvents interact with Na⁺ ions primarily through their carbonyl oxygen atoms within the primary solvation sphere.^[141] Vitoriano and co-workers investigated Na⁺ ions solvation in ether-based electrolytes, the lone pairs of polar oxygen atoms act as binding sites for Na⁺ ions through electrostatic interaction.^[142] Their findings revealed that Na⁺ ions favor coordination with DEGDME molecules, exhibiting a coordination number of 4–6 with the ether oxygen atoms (Figure 2.15).



Figure 2.15 Optimized structures of isolated DME, DEGDME, and TEGDME solvent molecules and corresponding Na⁺ complexes containing n glyme molecules by DFT simulations. Reproduced with permission: Copyright 2020, Elsevier.^[142]

The coordination binding between Na⁺ ions and the electronegative atoms of anions are also present within the electrolyte. The electron-withdrawing nature of certain functional groups in the anions can delocalize electron density within the anions. This delocalization weakens the electrostatic interaction between anions and the Na⁺ ions in the salts, effectively lowering the lattice energy of the salt and facilitating salt dissociation. However, this effect also diminishes the strength of the coordination binding and lowers the ratio of coordination number between the Na⁺ ions and the anions, hindering the formation of the ion pairs and aggregates.

2.3.2 Solvating power evaluation

The solvating power of a solvent in SMB electrolytes refers to the strength of the interactions between Na⁺ ions and solvent molecules. Weakly solvating solvents are widely used for low-temperature SMBs because weak interactions between Na⁺ and solvents facilitate a moderate desolvation process at low temperatures. Moreover, electrolytes with weakly solvating solvents exhibit a higher proportion of CIP/AGG solvates, which promotes the formation of an anion-derived inorganic SEI.^[112]

Stronger interactions between Na⁺ and solvents generally lead to a higher proportion of SSIP solvates. For instance, a high dielectric constant weakens the Coulombic interactions between cations and anions, promoting the formation of solvated ions. Consequently, solvents with large ε , such as EC and water, typically exhibit high solvating power. However, the dielectric constant alone does not fully determine the ability of a solvent to solvate Na⁺ ions. The solvent molecules

must also possess sufficient electron-donating ability to interact favorably with Na⁺ ions. The Lewis basicity of a solvent molecule, often characterized by its DN, can be used to assess such electron-donating capability. Solvents with higher DN values, such as glymes containing ethereal oxygen groups, tend to form stronger coordinate binding with Na⁺ ions.^[143]

Taking both ε and DN into consideration, Xu and co-workers proposed a design principle for "soft solvating" solvents characterized by relatively low DN values (less than 10) and high ε (greater than 5).^[108] As illustrated in Figure 2.16, a series of fluorinated esters falling within zone IV, including ethyl difluoroacetate (EDFA), methyl 2,3,3,3-tetrafluoro propionate (M4FP), methyl difluoroacetate (MDFA) and methyl 2,2-difluoro-2 (fluorosulfonyl)acetate (MDFSA), meet the criteria of "soft solvating". These solvents minimize the Li⁺-solvent binding energy while still facilitating salt dissociation, intrinsically favoring the formation of ion pairs and aggregates in solution, which is beneficial for forming anion-derived, LiF-rich interphases. Notably, a 1 M LiTFSI MDFA/MDFSA-1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE) electrolyte enabled stable operation of the NMC811//graphite full cells over a wide temperature range (-60 °C to 60 °C).



Figure 2.16 (a) The solvent diagram of DN versus dielectric constant (log ε). Solvents located in zone IV are denoted as soft solvents. (b) Illustration of the soft solvation between the soft solvent and Li⁺ ions, rapid Li⁺ ion transport, and wide-temperature range (±60 °C) stability. Reproduced with permission: Copyright 2023, Springer Nature.^[108]

Solvent polarity significantly influences the coordination environment of cations in the electrolyte, ultimately affecting the formation and properties of electrode-electrolyte interphases. A primary indicator of solvent polarity is the dipole moment, defined as the product of charge magnitude and the distance between charges.^[144] Low-polarity or non-polar ether solvents effectively weaken cation-solvent interactions by decreasing the charge density on the ligand

atoms, thus hindering the formation of strong solvation shells around the cations. Consequently, the proportion of CIP/AGG solvates in the electrolyte increases.^[145, 146]

Li and co-workers demonstrated a typical example by formulating a non-polar dipropyl ether (DPE)-based electrolyte of 1.8 M LiFSI DPE. The weak coordination ability of DPE towards Li⁺ facilitated the formation of AGG-rich solvation structures.^[144] This altered solvation environment impacted the decomposition pathway of the electrolyte at the cathode surface. Specifically, the preferential degradation of ion aggregates, driven by their modified HOMO energy levels, superseded the oxidation of free DPE molecules, leading to a robust, anion-derived CEI layer. Furthermore, as illustrated in Figure 2.17, lower polarity solvents like DPE and diethyl ether promote the accumulation of aggregated Li solvation structures at the electrode interface, displacing free solvent molecules. This results in a solvent-deficient interfacial regime, effectively enhancing ion transport compared to electrolytes utilizing higher polarity solvents like DME and DIG (diglyme).



Figure 2.17 Schematic illustrations of the interfacial model of less polar ether-based electrolyte (a) and polar ether-based electrolyte (b). Reproduced with permission: Copyright 2023, Springer Nature.^[144]

Beyond polarity, the molecular structure of the solvent, particularly its denticity and steric hindrance, also plays a crucial role in determining its ion-solvating ability. While the molecular structure does not drastically alter bulk solvent properties like dielectric constant and DN, it significantly regulates the interactions between solvent molecules and ions. For instance, DME exhibits superior solvation properties compared to DOL because of its ability to chelate Na⁺ ions although they have similar ε and DN values.^[143]

Steric hindrance has also been manipulated to tune the solvation structure of Li⁺ ions. Chen and co-workers substituted the methoxy groups in DME with bulkier ethoxy groups to produce 1,2-diethoxyethane (DEE).^[147] The increased steric hindrance of the ethoxy groups weakened the interaction between DEE and Li⁺ ions, resulting in a lower average coordination number than DME. This weaker solvation enhanced Li⁺ ion transference numbers and improved high-voltage stability when the DEE solvent was paired with LiFSI salt.

Furthermore, the influence of multidentate coordination on solvation structure was reported. For instance, Wu and co-workers proposed the formation of bidentate and tridentate chelates between Li⁺ ions and bis(2-methoxyethoxy) methane (BME) was observed in a 1 M LiFSI BME electrolyte.^[148] As shown in Figure 2.18, while DME solvent coordinates to Li⁺ ion in a bidentate chelate through its two oxygen atoms separated by 1, 2-ethylidene, with a Li–O interatomic distance of 1.80 Å. BME solvent exhibits a more complex behavior. In its linear conformation, BME coordinates to Li⁺ ion through its two central oxygen atoms with a slightly longer interatomic distance (1.88 Å) than DME. Interestingly, BME can adopt a bent conformation, enabling tridentate coordination to Li⁺ ion via all three oxygen atoms. This tridentate coordination results in even longer Li–O interatomic distances (1.89 Å, 1.91 Å, and 2.04 Å), signifying weaker Li⁺solvent interactions and promoting an anion-rich solvation structure.



Figure 2.18 Schematic illustration of Li⁺ solvation structure in DME (a) and BME-based (b) electrolytes. Reproduced with permission: Copyright 2023, John Wiley & Sons, Inc.^[148]

While solvent properties can provide insights into solvating power, they often fail to fully capture the complexity of the solvation process. A more accurate approach involves establishing a direct solvating power series for various solvents. This is crucial because no single solvent property can accurately and comprehensively describe solvating power. Su and co-workers demonstrated this by defining the relative solvating power of individual solvents.^[149] Their method

involved calculating the ratio between the coordination percentage of a test solvent and a reference solvent (ethyl methyl carbonate) using internally referenced diffusion-ordered spectroscopy and diffusion coefficient-coordination ratio analysis. This approach revealed fluoroethylene carbonate as a superior cyclic carbonate co-solvent compared to difluoroethylene carbonate in a methyl (2,2,2-trifluoroethyl) carbonate-based electrolyte, highlighting its significantly higher Li⁺ ion solvation ability.

2.3.3 Other solvation structures

Beyond the well-characterized local solvation structures surrounding dissolved ions, recent studies have unveiled the presence of nanometric aggregates (n-AGGs) in various electrolyte systems. These aggregates emerge under specific conditions, including super-concentrated salt solutions, weak solvents, and the introduction of multivalent ions. The formation of n-AGGs is governed by a complex interplay of intermolecular interactions, including electrostatic forces, hydrogen bonding, solvophobic effects, π - π stacking, and steric/volume exclusion. Unlike smaller aggregates composed of a few ions, n-AGGs are significantly larger, comprising tens to hundreds of ions and exceeding 1 nm in size (Figure 2.19).^[150]



Figure 2.19 Schematic of local solvation structures (a) and nanometric aggregates (b). Reproduced with permission: Copyright 2022, American Chemical Society.^[150]

The presence of n-AGGs significantly influences ionic transport in salt-concentrated electrolytes. MD simulations of a 4.12 M NaFSI DME electrolyte revealed that Na⁺ ion diffusion within n-AGGs occurs primarily through coordinated ligand exchange on a timescale of tens of picoseconds.^[151] This suggests that structural motion within the n-AGG governs ionic diffusion,

as illustrated in Figure 2.20. Similarly, the equimolar NaFSI sulfolane (SL) electrolytes exhibit high Na⁺ ion transference numbers of 0.8 because of the ligand exchange (solvent and anion) facilitated by structural rearrangements.^[152]



Figure 2.20 Visual representation of the ligand exchange process in a 4.12 M NaFSI–DME electrolyte. Initially, a single Na⁺ ion is coordinated by two DME molecules and two FSI⁻ ions. Within approximately 60–120 ps, one of the FSI⁻ ions from the initial solvation shell dissociates, while another DME molecule enters. Reproduced with permission: Copyright 2018, American Chemical Society.^[151]



Figure 2.21 (a) Schematics illustration of the conventional understanding of LHCE. (b) Schematics illustration of the micelle-like structure of LHCE. (c) A real micelle electrolyte formed by lithiophilic/phobic hydrofluoroether-based solvent in a LiTFSI–TTE electrolyte. Reproduced with permission: Copyright 2023, Springer Nature.^[153]

Efaw and co-workers elucidated a unique micelle-like structure within a LHCE using a multifaceted approach combining small-angle and wide-angle X-ray scattering (SAXS-WAXS), Raman characterization, and MD simulations.^[153] Specifically, in a LiTFSI in TTE electrolyte, the amphiphilic nature of hydrofluoroether TTE drives the formation of distinct micellar structures, as
shown in Figure 2.21c.^[154] This amphiphilicity arises from both lithiophilic and lithiophobic groups within the TTE molecule. Similar micelle-like structures were observed in a LiFSI–DME–tris(2,2,2-trifluoroethyl) orthoformate (TFEO) LHCE, as shown in Figure 2.21b.^[153] In this system, the formation of micelles is attributed to the interplay between solvent-diluent miscibility and salt solubility of the solvent. In the LiFSI–1.2DME–2TFEO electrolyte, increased coordinated AGG structures suggest a correlation with micelle formation, contributing to the inorganic-rich SEI formation.

2.4 Tuning electrolyte-electrode interphases

2.4.1 Formation of electrode-electrolyte interphases

Ideally, electrolytes should remain chemically unchanged throughout battery operation, confining Faradaic reactions strictly to the electrodes.^[155] However, liquid electrolytes inevitably undergo degradation when exposed to highly oxidizing or reducing electrode materials.^[156] This challenge is particularly pronounced in SMBs. The reduction potentials of most nonaqueous solvents are higher than that of Na⁺/Na, making them prone to degradation upon contact with the sodium metal anode.

During electrochemical cycling, both solvents and anions near the Na metal anode may undergo reduction, forming a SEI layer. Conversely, these components tend to oxidize at the cathode to form a CEI layer. Notably, although formed through degradation reactions, these interphases play a critical role in expanding the ESW of the electrolyte. These formed interphases enable practical battery operation with strongly oxidative cathodes and strongly reductive sodium metal anodes.^[157]

2.4.2 Engineering of sodium metal-electrolyte interphase

The SEI layer greatly affects the performance of SMBs. An ideal SEI should function as a robust barrier, electrically insulating the Na metal anode from the electrolyte while remaining permeable to Na⁺ ions. This interphase must possess a unique set of properties of:

- (i) high chemical and electrochemical stability to resist decomposition and unwanted side reactions;
- (ii) an efficient and homogeneous Na⁺ ions permeability for achieving high rate capability and inhibiting dendrite formation;

 (iii) good mechanical toughness combining strength and ductility to withstand the significant volume changes over sodium plating/stripping cycles.

However, it remains a great challenge to fabricate such high-quality SEIs because natural SEIs are inherently heterogeneous, comprising a complex and dynamic mixture of organic and inorganic components. For instance, Schafzahl and co-workers demonstrated the potential of the NaFSI-DME electrolyte for advanced SMBs. While the FSI⁻ anion facilitated the formation of an inorganic-rich interphase on Na metal anodes, the CE values of Na plating/stripping after prolonged 300 cycles remained moderate at approximately 97.7%.^[158] Seh and co-workers achieved a remarkable breakthrough using a simple 1 M NaPF₆ glyme electrolyte, demonstrating long-term dendrite-free sodium plating/stripping with a CE of 99.9% over 300 cycles.^[75] This exceptional performance was attributed to the formation of a stable, inorganic-rich SEI primarily composed of Na₂O and NaF.

Li and co-workers achieved high-performance anode-free sodium batteries using 0.9 M NaPF₆ and 0.1 M NaBF₄ in diglyme electrolyte. Their work revealed a distinct distribution of B–O and P-containing species within the SEI and CEI layers, as shown in Figure 2.22. Crucially, B-containing species, originating from BF_4^- anion decomposition, played a significant role in both interphases. The sheet-like B–O species within the SEI effectively suppressed dendrite formation, repaired cracks during Na plating/stripping cycles, and protected the structural integrity of cathode. These beneficial interphase properties contributed to the impressive performance of their anode-free Na battery, achieving an energy density exceeding 200 Wh kg⁻¹.^[159]



Figure 2.22 Time-of-flight secondary ion mass spectrometry (TOF-SIMS) three-dimensional views of the SEI and CEI films, the two three-dimensional views are for B⁺ and P⁻ secondary ions. Reproduced with permission: Copyright 2022, Springer Nature.^[159]

2.4.3 Minimizing the dissolution of SEI

The dissolution of the SEI presents a more significant challenge for SMBs than the Li counterpart primarily because of the higher solubility of sodium-based SEI. Sustained SEI breaking and reformation proceeded during battery operation, resulting in accelerated electrolyte consumption, decreased CE, and ultimately, a shortened lifespan for SMBs.^[64]

Extensive research has delved into understanding and mitigating this challenge. Ma and coworkers investigated SEI formation and dissolution in three distinct electrolytes: NaPF₆–PC, NaPF₆–EC/PC, and NaPF₆–EC/DEC systems. Their findings highlighted the influence of electrolyte chemistry, encompassing solvent, salt, and additive composition, on SEI dissolution. Specifically, they observed that the capacity consumed during SEI formation, the composition of the SEI itself, and the capacity loss attributed to SEI dissolution depended on the electrolyte used. ^[160] Strategies employing low-solvation electrolytes have shown promise in minimizing SEI dissolution. Jin and co-workers demonstrated that incorporating the low-polar TFP into a NaFSI– DMC electrolyte effectively inhibits SEI dissolution. The electron-withdrawing fluorine atoms in TFP weaken its interaction with Na⁺ ions, promoting the formation of insoluble SEI components on the hard carbon anode, as shown in Figure 2.23.^[27] Similarly, Liu and co-workers achieved suppressed SEI dissolution by employing tris(2-ethylhexyl) phosphate (TOP) with lengthened phosphate backbones. This modification decreased the solvation ability of the electrolytes, leading to an anion-enriched primary Na⁺ ion solvation sheath and a compact, low-solubility interphase, effectively mitigating continuous SEI dissolution and parasitic reactions.^[161]



Figure 2.23 (a) Schematic illustration of SEI dissolution in conventional electrolyte and (b) suppressed SEI dissolution in low-solvation electrolyte. Reproduced with permission: Copyright 2022, Springer Nature.^[27]

2.4.4 Engineering of CEI

An ideal CEI should exhibit a high Na⁺ diffusivity for efficient Na⁺ ions transfer, robust chemical, electrochemical, and mechanical stability to withstand the harsh electrochemical environment, and low electronic conductivity to prevent self-discharge. However, achieving this delicate balance remains a significant challenge, primarily because of the complexities associated with the formation, morphology, and dynamic evolution of the CEI.

Battery operation at high voltages often compromises the CEI stability because of inevitable electrolyte decomposition, transition metal dissolution from the cathode, and undesirable surface reconstruction. To mitigate these issues, considerable research efforts have been devoted to doping the cathode material with functional metal elements or applying protective surface coatings to enhance its structural integrity and electrochemical stability.^[162] Another efficient approach is electrolyte engineering, which employs HCE or incorporates electrolyte additives to enhance the stability of the electrode/electrolyte interface and suppress unwanted side reactions.

Conventional carbonate-based electrolytes, although widely used in rechargeable lithium batteries, suffer from inherent limitations of poor compatibility with Na metal anodes and stable

operations at high potentials (> 4V vs. Na⁺/Na). Their poor passivation capability and strong dissolution for CEI hinder the formation of a stable and robust CEI.^[27] Liu and co-workers introduced the intrinsically oxidation-stable succinonitrile (SN) solvent to a NaClO₄-DEC electrolyte containing FEC additives. This electrolyte formulation facilitated the formation of an ultra-thin, uniform, and nitrogen-rich inorganic/organic CEI layer on a Na₃V₂O₂(PO₄)₂F cathode. The strong coordination between SN and surface vanadium, combined with the enhanced mechanical stability of the resulting CEI, effectively suppressed vanadium and phosphorus dissolution. Consequently, $Na_3V_2O_2(PO_4)_2F$ half-cells exhibited exceptional cycling stability, retaining over 90% of their initial capacity after 3000 cycles with an average CE of over 99.6% at 1C.^[163] The application of layered transition metal oxide cathodes in SMBs faces challenges because of their significant volume changes during cycling. These changes, larger than their lithium counterparts because of the larger Na⁺ ionic radius and phase transitions, lead to interfacial instability, exacerbating unwanted side reactions, transition metal dissolution, surface reconstruction, and the formation of intragranular cracks.^[162] Fan and co-workers demonstrated that introducing SA solvent as a synergistic filming additive to an FEC-containing carbonate-based electrolyte improves the lifespan of Na//Na_{0.6}Li_{0.15}Ni_{0.15}Nn_{0.55}Cu_{0.15}O₂ cells.^[164] The high HOMO value of SA promotes its preferential oxidation, forming a uniform and stable CEI that protects the electrolyte and cathode structure.

Ether solvents have rarely been used for high-voltage SMBs, mainly because of their relatively low HOMO energy levels. A 1 M NaBF₄ G4 electrolyte was reported by Le and co-workers to achieve Na plating/stripping CE of 99.9%, but the as-fabricated Na//P2-Na_{2/3}Co_{1/3}Mn_{2/3}O₂ cells achieved only 70% capacity retention after 100 cycles with an upper voltage limit of 4.2 V *vs*. Na⁺/Na.^[165] Polyanionic cathodes have demonstrated promising compatibility with ether solvents. Westman and co-workers showed that stabilized cycling of Na₃V₂(PO₄)₂F₃ over tens of cycles in a 1 M NaPF₆-diglyme electrolyte without significant capacity degradation.^[166] Qin and co-workers further revealed that as-produced CEI comprises a polymer matrix embedded with inorganic NaF particles.^[167]

2.5 Advancements in low-temperature sodium metal batteries

Developing rechargeable SMBs that can operate effectively at low temperatures is of important scientific and practical value, especially for applications in extreme environments.^[168, 169] However,

at low temperatures, challenges such as fragile SEI layers and Na dendrite growth—which impair Na plating/stripping reversibility—are exacerbated. Moreover, the sluggish transfer kinetics of Na⁺ ions at low temperatures render the desolvation process at the electrode/electrolyte interface a rate-limiting step during sodium deposition, resulting in significant capacity fading.^[67, 68] Additionally, the high freezing/melting points of most conventional electrolytes cause increased resistance and decreased salt solubility at low temperatures, further hindering the performance of SMBs.^[79]

2.5.1 Developing electrolytes with high ionic conductivity

To address these challenges, extensive research has explored novel electrolyte formulations for low-temperature SMBs. Electrolyte design strategies typically fall into three main categories. The first category emphasizes achieving high ionic conductivity at low temperatures. For instance, Hu and co-workers developed an ether–ionic liquid composite electrolyte containing 1 M NaPF₆ in a mixture of 1-butyl-3-methylimidazolium tetrafluoroborate and diglyme. Figure 2.24a shows that this electrolyte maintains a high ionic conductivity of 42 mS cm⁻¹ at -20 °C. The Cu//Na half batteries with this composite electrolyte realized an average Na plating/stripping CE of 99.5% using the Aurbach method, with a current density of 0.5 mA cm⁻² and a capacity of 1 mAh cm⁻² at -20 °C (Figure 2.24b).^[76]



Figure 2.24 (a) Conductivity of the electrolytes in the temperature range from 25 to -20 °C. (b) Aurbach CE test with Cu//Na half batteries at -20 °C. Reproduced with permission: Copyright 2021, John Wiley & Sons, Inc.^[76]

2.5.2 Engineering weakly solvating electrolytes

The second strategy involves engineering weakly solvating electrolytes to facilitate the Na⁺ ions desolvation at low temperatures. Zhou et. al. demonstrated that a binary solvent electrolyte of 0.8 M NaOTf in THF/DME achieved a decreased Na⁺ desolvation kinetic barrier, because of the introduction of THF, a weak Na⁺ solvating co-solvent. DFT calculations indicated that Na⁺–THF possesses the lowest desolvation energy of -63.29 kJ mol⁻¹ among the components in the electrolyte, as shown in Figure 2.25a. The Cu//Na half batteries with the electrolyte realized an average Na plating/stripping CE of 99.29% at -20 °C using the Aurbach method, as shown in Figure 2.25b.^[79] Similarly, Yang and co-workers introduced weak solvating THF solvent into the NaPF₆–G2 conventional electrolyte system, enabling low-temperature application.^[170]



Figure 2.25 (a) Desolvation energy of Na⁺–OTF, Na⁺–THF, and Na⁺–DME. (b) Aurbach CE test with Cu//Na half batteries at -20 °C. Reproduced with permission: Copyright 2022, Elsevier.^[79]

Fluorinated solvents generally exhibit weak solvation ability with Na⁺ ions. Gao et. al. modified the ethyl acetate (EA) molecule by introducing a difluorination group at various sites, developing ethyl difluoroacetate (EDFA) and 2,2-difluoroethyl acetate (DFEA) solvents. As shown in Figure 2.26, EDFA–Na⁺ shows a binding energy of -38.38 kcal mol⁻¹, slightly higher than that of EA–Na⁺, because of the chelating interaction between the Na⁺ ion and O/F atoms in the EDFA molecule. In contrast, DFEA–Na⁺ exhibits the lowest binding energy, only -30.46 kcal mol⁻¹, which enables faster Na⁺ transport and enhanced desolvation ability in DFEA-based electrolytes. Although the weakly solvating electrolytes allow decreased coordination of Na⁺ to the solvent and enable decreased desolvation battier at low temperatures, they concurrently limit the ionic conductivity of electrolytes because of the weakened salt dissociation ability.



Figure 2.26 Binding energy of EA–Na⁺, EDFA–Na⁺, and DFEA–Na⁺. Reproduced with permission: Copyright 2024, John Wiley & Sons, Inc.^[171]

2.5.3 Tailoring SEI formation

The third design strategy focuses on electrolyte formulations that promote the formation of anionderived, inorganic-rich SEI layer. Thenuwara and co-workers developed a dual-salt electrolyte containing 0.8 M NaOTf and 0.2 M NaBF₄ in diglyme.^[77] As shown in Figure 2.26a, cryo-TEM results revealed that the SEI, formed at -40 °C, is rich in inorganic species such as Na₂CO₃, Na₂O, and Na₂SO₄. The half-cells with a sodium metal counter electrode and a stain-less-steel working electrode using the dual-salt electrolyte achieved an average CE of 97.4% over 50 cycles with a current density of 0.5 mA cm⁻² and a capacity of 0.5 mAh cm⁻² at -40 °C (Figure 2.26b). Zhong et. al. introduced ethylene sulfate (ES) as an additive to a carbonate-based electrolyte of 1 M NaFSI in EC/PC/DEC (1:1:4, v/v) for low-temperature SMB. The ES additive helps to form a Na₃N, Na₂S, and Na₂SO₃-rich SEI with a high mechanical strength of about 7.0 GPa. The fabricated Cu//Na half batteries using the electrolyte realized an average Na plating/stripping CE of 95.5% at -40 °C using the Aurbach method.^[80]



Figure 2.27 (a) Cryo-TEM investigation of the structure of the SEI formed at -40 °C. (b) CE measurements at 20 °C and -40 °C. Reproduced with permission: Copyright 2021, The Royal Society of Chemistry.^[77]

In addition to modifying the SEI formation via electrolyte formulation engineering, artificial SEI engineering has also been reported to facilitate the Na⁺ ions transfer at the Na metal/electrolyte interface. For example, Zheng and co-workers developed an ionic-conductive Na₁₅Sn₄/NaF biphasic SEI layer that facilitates Na⁺ ion transfer at the Na metal/electrolyte interface. It results in a remarkable 25-fold decrease in cell impedance from ~2.8 × 10⁴ Ω to ~1100 Ω at -20 °C, promoting spherical Na deposition and achieving exceptional cycling stability in Na//Na symmetric cells.^[73] Xia and co-workers developed a Na₂Se/V hybrid interphase layer with exceptional mechanical toughness, sodiophilicity, and fast ion transport kinetics. Its inherently fast desolvation capability contributed to the superior performance of the Na@Na₂Se/V electrode at -40 °C with a remarkable cycle life exceeding 1500 hours at 0.5 mA cm⁻² and 0.5 mAh cm⁻².^[172]

Despite extensive advancements, achieving beyond 99.9% CE for low-temperature Na plating/stripping remains a huge challenge to date, because of the stringent prerequisites, including sufficient ion mobility, fast desolvation kinetics, and formation of beneficial SEI. Current unsatisfactory CEs below 99.5% plague the sustainable low-temperature operation of initial anode-free SMBs, limiting the lifespan to only a few tens of cycles.

2.6 Advancements in high-voltage sodium metal batteries

Employing high-voltage cathodes to elevate the working potential presents a direct strategy for enhancing the energy density of SMBs. However, this approach presents significant challenges. First, the higher redox potential of sodium (+0.3 V) compared to lithium necessitates electrolytes with a higher anti-oxidation potential to achieve comparable cutoff voltage.^[25] The high potential readily induces progressive electrolyte oxidative decomposition at the cathode surface. Second, the decomposition reactions lead to an unstable CEI layer.^[69] Last, high-voltage conditions can cause severe cathode degradation, including structural reconstruction, transition metal dissolution, and mechanical degradation, which significantly impact the cycle stability of SMBs.^[70]

Inhibiting oxidative decomposition of the electrolyte and forming protective CEI is critical for addressing the above challenges in SMBs employing high-voltage cathodes. Electrolyte solvents are generally considered more susceptible to high-voltage oxidation at the cathode surface.^[173, 174] Carbonate-based electrolytes own excellent high-voltage stability against oxidation and have been widely employed in commercial LIBs. Nonetheless, their high reactivity with sodium metal poses a significant challenge for SMBs.^[175, 176] This reactivity results in the continuous generation of

flammable gases and the formation of unstable SEI layers with low Na plating/stripping CE of < 90%.^[65, 177, 178] Ether-based electrolytes are highly compatible with Na metal anodes,^[75, 165] but their relatively high highest occupied molecular orbital (HOMO) energy levels make them inappropriate for high-voltage SMB applications.^[165, 167] To address these challenges, various electrolyte modification strategies have been explored to improve the high-voltage performance of SMBs.

2.6.1 High-voltage electrolyte additives

Film-forming cathode additives preferentially decompose on the cathode surface because of their lower HOMO level compared to solvent molecules. This allows them to form a high-quality protective film on the cathode surface, inhibiting electrolyte decomposition and decreasing parasitic reactions. For example, Chen et. al. introduced lithium difluorobis(oxalato) phosphate (LiDFBOP) as an additive to a 1 M NaPF₆ in FEC/DEC electrolyte for high-voltage SMBs.^[179] Using this electrolyte, a Na//Na₃V₂(PO₄)₂F₃ full cell with a N/P ratio of 4/1 realized a high average CE of 99.5% over 220 cycles, with a cut-off voltage of 4.5 V *vs.* Na⁺/Na. Liu and co-workers found that 3-Trimethylsilyl-2-oxazolidinone (TMSO) as an additive enhances the stability of FEC-containing electrolytes.^[180] TMSO forms a stable CEI layer on the NVP cathode surface, alleviating cracking and structural pulverization of the NVP cathode. The Na//NVP cell exhibits a capacity retention of 93.1% over 1400 cycles. While sacrificial additives can form a protective layer and effectively inhibit the oxidative decomposition of the electrolyte, they often lead to significant side reactions with the sodium metal anode, limiting their practical application.

2.6.2 High concentration electrolytes

Beyond additives, there are two primary strategies for boosting the oxidative stability of ether electrolytes: improving electrolyte concentration and solvent engineering. Concentrating the electrolyte decreases the proportion of free ether solvents, which are normally most susceptible to oxidation. It also induces more anion participation in the solvation sheath toward more stable inorganic-rich CEI. Lu and co-workers leveraged the size-selective properties of a zeolite molecular sieve film to manipulate the solvation structure of the electrolyte.^[89] As shown in Figure 2.28, the well-defined pore size of the zeolite (3.2 Å) facilitated a unique desolvation process, effectively trapping highly aggregated solvation structures within its pores. This confinement suppressed the trace yet persistent oxidative decomposition typically observed in a conventional 1

M NaPF₆ G2 electrolyte, extending the oxidative stability to 4.5 V without compromising the reversibility of the sodium metal anode.



Figure 2.28 Illustration of a high-voltage anode-free Na battery constructed by optimizing the electrolyte aggregation by using a 3A zeolite molecular sieve. Reproduced with permission: Copyright 2022, John Wiley & Sons, Inc.^[89]

2.6.3 Solvent engineering

Solvent engineering to boost the oxidative stability of ether electrolytes involves molecular structure regulation of solvents, such as optimizing the structure of alkyl groups in solvent molecules,^[181,182] decreasing the ether oxygen atom content in solvent molecules,^[144,183] and atom substitution of the solvent molecules with halogen atoms or halogen groups.^[184-186] For instance, Li and co-workers proposed a diluent-participated solvate in diglyme-based electrolytes by introducing weakly coordinating diluent hexafluoroisopropyl methyl ether (HFME), as shown in Figure 2.29a.^[187] The electron-withdrawing effect of F substituents in HFME lowers the HOMO energy level of the Na⁺ solvation structure, promoting preferential decomposition of the anions and diluent molecules (Figure 2.29b). This selective decomposition facilitates the formation of a robust, inorganic-rich CEI layer on the cathode surface. Consequently, the Na//P'2-Na_{0.67}MnO₂ cell delivers a high capacity retention of 87.3% with a high average CE of 99.7% after 350 cycles. While improving oxidative stability, these modifications essentially weaken the dissociation ability of solvents and decrease the ionic conductivities of electrolytes. Furthermore, fluorinated solvents have high costs and pose potential environmental hazards.^[188] Therefore, improving the

high-voltage stability of ether electrolytes without sacrificing the ionic conductivity of the electrolyte is of urgent need.



Figure 2.29 (a) Molecule structure of HFME. (b) HOMO and LUMO energy levels of HFME, HFE, and G2.solvents. Reproduced with permission: Copyright 2024, John Wiley & Sons, Inc.^[187]

2.7 Summary

Although extensive research has focused on designing electrolytes for low-temperature AFSMBs, including weakly solvating solvents and LHCE with fluorinated diluents, achieving CE exceeding 99.9% for Na plating/stripping at low-temperature remains a significant challenge. This difficulty arises from the stringent prerequisites, including sufficient ion mobility, fast desolvation kinetics, and the formation of beneficial SEI. Unsatisfactory CEs below 99.5% plague the sustainable low-temperature operation of AFSMBs, limiting their lifespan to only a few tens of cycles.

Boosting the work potential is an effective strategy for enhancing the energy density of SMBs. However, the elevated charging cut-off voltage necessitates better oxidation stability of the electrolyte. While sacrificing additives could be considered, they often introduce significant side reactions with the sodium metal anode, limiting their practical application. Therefore, research has focused on two primary strategies for intrinsically enhancing the oxidative stability of ether-based electrolytes. The first is increasing the salt concentration to form a high-concentration electrolyte, a method that has been proven to effectively improve the oxidative stability of electrolytes. However, achieving high concentrations with ether electrolytes using fluorine-rich sodium salts is challenging because of their limited solubility. The second strategy, solvent engineering, aims to modify the molecular structure of the solvent to enhance its oxidative stability. This encompasses approaches such as regulating the molecular structure of solvents, decreasing the ether oxygen atom content in the solvent molecules, and substituting atoms in the solvent molecules with halogen atoms or halogen groups. It is crucial to note that while these modifications can improve oxidative stability, they often compromise salt solubility and decrease the ionic conductivity of electrolytes.

Therefore, this research aims to overcome the challenges for SMBs operating at lowtemperature conditions and with high-voltage cathodes. This work aims to enable the AFSMB operation down to -65 °C by enhancing sluggish Na⁺ mobility and improving the quality of SEI at low temperatures. For high-voltage applications, two distinct approaches are explored to enhance the electrochemical oxidative stability of electrolytes for SMBs operating at voltages up to 4.4V. These approaches involve investigating the use of a solubilizing agent to enhance salt solubility and the strategic design of a crown-like solvation structure within the electrolyte.

Chapter 3

Materials and Experimental Methods

The chemicals and reagents utilized in this study will be presented in this chapter. The characterization techniques employed will be discussed for the investigation of the physical, chemical, and electrochemical properties of the electrolytes, electrodes, and assembled cells. The general experimental procedures, encompassing chemical pre-treatment and electrode preparation, will also be described. The detailed methodologies for specific experiments will be elaborated in subsequent chapters.

3.1 Materials

The purity and suppliers of the chemicals and reagents utilized in the experiment are listed in Table 3.1.

3.1.1 Pre-treatment of solvents and salts

To eliminate trace water, solvents were treated with 4 Å molecular sieves before electrolyte preparation. Each solvent was added to a glass bottle containing an appropriate amount of molecular sieves. The bottles were sealed and left overnight in an argon-filled glovebox (MBRAUN, oxygen < 0.1 ppm, water < 0.1 ppm). Sodium salts were dried before electrolyte preparation. Each salt was transferred to an aluminum bottle and heated on a stirring hotplate at 80° C overnight within an argon-filled glovebox.

3.1.2 Electrode preparation

Commercial sodium foils with 15.6 mm diameter and 0.4 mm thickness were used as Na metal anodes, which were adhered to an aluminum foil and protected by a plastic film. The plastic film was removed immediately before the use of sodium foils. Double-sided conductive carbon-coated aluminum (Al/C) foils were utilized as current collectors for both the $Na_3V_2(PO_4)_3$ and $Na_3(VO)_2(PO_4)_2F$ cathodes, as well as the anode in anode-free cells. The carbon coating layer and Al foil thicknesses are 1 µm and 16 µm, respectively. The Al/C foils were used as received without further treatment.

 $Na_3V_2(PO_4)_3$ powder was used directly to prepare the cathode electrode without additional treatment. For the cathode film preparation, a slurry was prepared by mixing $Na_3V_2(PO_4)_3$ powder,

acetylene black, and polyvinylidene fluoride (PVDF) in a mass ratio of 90:5:5 in N-methyl-2pyrrolidone (NMP) solvent. The mixture was homogenized in a glass bottle via gentle magnetic stirring. The resulting slurry was then cast onto an Al/C foil using a doctor blade and dried for eight hours at 110°C in a blast oven and twelve hours at 110°C in a vacuum oven. For the $Na_3(VO)_2(PO_4)_2F$ cathode fabrication, the mass ratio of active material, super P, and PVDF were controlled to be 70:20:10. All other synthesis procedures are the same.

Chemicals	Formula	Purity	Supplier	
Diethylene glycol dimethyl ether (G2)	(CH ₃ OCH ₂ CH ₂) ₂ O	(CH ₃ OCH ₂ CH ₂) ₂ O 99.5%		
Tetraethylene glycol dimethyl ether (G4)	CH ₃ O(CH ₂ CH ₂ O) ₄ CH ₃	99%	Sigma-Aldrich	
1,3-dioxolane (DOL)	$C_3H_6O_2$	99.5% Sigma-Aldric		
1,1,2,2-tetrafluoroethyl 2,2,3,3- tetrafluoropropyl ether (TTE)	$C_5H_4F_8O$	99.8% Dodochem		
Dibutyl ether (DBE)	$[CH_{3}(CH_{2})_{3}]_{2}O$	99.3%	Sigma-Aldrich	
Diethylene glycol dibutyl ether (DEGDBE)	(CH ₃ CH ₂ CH ₂ CH ₂ OCH ₂ CH ₂) ₂ O	99%	Sigma-Aldrich	
1-Methyl-2-pyrrolidinone (NMP)	C ₅ H ₉ NO	99.5%	Sigma-Aldrich	
Sodium hexafluorophosphate	NaPF ₆	99.8%	Dodochem	
Sodium tetrafluoroborate	NaBF ₄ 98%		Sigma-Aldrich	
Acetylene black	С	/	Alfa Aesar	
Super P Li	С	/	TIMCAL	
4 Å molecular sieves	Na ₁₂ [(AlO ₂) ₁₂ (SiO ₂) ₁₂] \cdot xH ₂ O	/	Sigma-Aldrich	
Polyvinylidene fluoride (PVDF)	$-(C_2H_2F_2)_n-$	99.5	MTI	
Sodium metal foil	Na	99.7%	MTI	
Conductive carbon-coated aluminum foil	Al/C	Al/C 99.9%		
Sodium Vanadium Phosphate	$Na_3V_2(PO_4)_3$	/	Hubei Energy Technology	
Sodium vanadium fluorophosphate	Na ₃ (VO) ₂ (PO ₄) ₂ F	/	Heshi New Materials	

 Table 3.1 Chemicals and reagents used in this research.

3.2 Battery fabrication

3.2.1 Coin cell fabrication

CR2025-type coin cells were assembled in an argon-filled glovebox for all electrochemical tests except for symmetric Na//Na cells. The Na//Na cells were made using CR2032-type coin cells, because of the increased total thickness using two Na metal electrodes. All coin cells employed a sandwich-structured separator consisting of a Whatman glass fiber separator sandwiched between two Celgard 2500 films and 120 μ L of electrolyte was filled in each cell. The following coin cell configurations were used:

- Na//Al cells: Sodium metal foil (ϕ 15.6 mm) is paired with Al/C foil (ϕ 16 mm).
- Na//Na cells: Two sodium metal foils (ϕ 15.6 mm) are used as the working electrodes.
- Stainless steel//stainless steel cells: Two CR20 stainless steel spacers (\$\$\phi\$15.8 mm, thickness of 1 mm) are used as the working electrodes.
- Na₃V₂(PO₄)₃//Na half cells: Na₃V₂(PO₄)₃ cathode (φ 12 mm) is paired with sodium metal anode (φ 15.6 mm). The typical mass loading of Na₃V₂(PO₄)₃ active material is ~ 7 mg cm⁻².
- Na₃V₂(PO₄)₃//Al anode-free cells: Na₃V₂(PO₄)₃ cathode (φ 12 mm) is paired with Al/C foil anode (φ 16 mm). The typical mass loading of Na₃V₂(PO₄)₃ active material is ~ 7 mg cm⁻².
- Na₃(VO)₂(PO₄)₂F//Na half cells: Na₃(VO)₂(PO₄)₂F cathode (\$\$\phi\$ 10 mm\$) is paired with sodium metal anode (\$\$\$\phi\$ 15.6 mm\$). The typical mass loading of Na₃(VO)₂(PO₄)₂F active material is ~ 2 mg cm⁻².
- Na₃(VO)₂(PO₄)₂F//Al anode-free cells: Na₃(VO)₂(PO₄)₂F cathode (φ 10 mm) is paired with Al/C foil anode (φ 12 mm). The typical mass loading of Na₃(VO)₂(PO₄)₂F active material is ~ 2 mg cm⁻².

3.2.2 Pouch cells fabrication

Anode-free Na₃V₂(PO₄)₃//Al pouch cells were assembled using a multilayer electrode configuration. The cathode comprised six double-layer coated Na₃V₂(PO₄)₃ films, each with dimensions of 12.1 cm × 6.1 cm and a mass loading of ~ 30 mg cm⁻² (based on double-layer coating). These were interleaved with seven layers of Al/C foil current collectors, each measuring 12.3 cm × 6.2 cm. The same sandwich-structured separators as those in coin cells were incorporated between each electrode layer. The assembled electrode stack was then encased in an aluminum-plastic film pouch and filled with 30 mL of electrolyte.

3.3 Characterization methods

3.3.1 Characterization of electrolyte properties

a) Viscosity of electrolytes

The viscosities of the electrolytes were measured across a range of temperatures using a Haake Mars 60 rheometer equipped with a double-gap cylinder. Kinetic viscosity measurements were conducted in the rotational mode at a constant shear rate of 300 s⁻¹, cooling at 5 °C min⁻¹ to specified temperatures and maintaining for a period of time.

b) Ionic conductivity of electrolytes

Electrolyte ionic conductivity was determined using electrochemical impedance spectroscopy (EIS) measurements conducted in symmetric stainless steel cells. A standard solution of 1 M NaPF6 G2 electrolyte (ionic conductivity: 7.34 mS cm⁻¹ at 25 °C, provided by the electrolyte supplier) was used to calibrate the cell constant. EIS measurements were performed using the customized two-electrode cell (shown in Figure 3.1) connected to a Metrohm Autolab potentiostat/galvanostat instrument. Data points were collected over a frequency range of 1 MHz to 10 mHz at temperatures ranging from 25°C to -40 °C. The ionic conductivity was calculated using the following equation:

$$\delta = \frac{L}{A \times R} \tag{3.1}$$

where R is the resistance obtained from the EIS measurement, A is the area of the stainless steel electrodes, and L is the distance between two stainless steel electrodes.



Figure 3.1 Schematic illustration of the symmetric stainless-steel cell.

c) Na⁺ ion transference number of electrolytes

Na⁺ ion transference number (t_{Na+}) quantifies the contribution of Na⁺ transport to the total ionic current. In this research, t_{Na+} values for the studied electrolytes were determined by using the Bruce–Vincent method.^[189] It involves applying a constant voltage bias of 5 mV to a symmetric Na/Na cell containing the studied electrolyte and monitoring the resulting current response over 2 hours using a Metrohm Autolab potentiostat/galvanostat instrument.

Immediately upon applying the voltage bias, the initial current (I_0) reflects the movement of both anions and cations, as their distribution within the electrolyte is initially homogeneous. However, the applied bias creates a driving force that compels anions to migrate, establishing a concentration gradient that intensifies over time. Eventually, this concentration gradient counterbalances the electrochemical driving force, halting further anion migration. The steadystate current (I_{SS}) is attributed solely to the Na⁺ ions transfer since no concentration gradient exists between the identical sodium metal electrodes. Ideally, t_{Na+} can be simply obtained from the I_{SS}/I_0 ratio. However, passivating layers on the electrode surfaces introduce a time-dependent contact resistance. To account for this, impedance measurements were conducted before and after the voltage bias application to determine the evolving contact resistance and enable a more accurate estimation of t_{Na+} .

Figure 3.2 presents a typical equivalent circuit model for symmetric Na//Na cells. Here, *Rs* represents the overall ohmic resistance, integrating contributions from the electrolyte, current collector, sodium metal, and their interfaces. Considering the potential influence of electrode roughness and surface phenomena such as dendrite formation, the electrode behavior is modeled using a constant phase element (CPE) in conjunction with a resistance. $R_{interphase}$ and CPE₁ characterize the Na⁺ diffusion process at the electrolyte-electrode interfaces, while R_{ct} and CPE₂ represent the charge transfer process, primarily governed by Na⁺ ion desolvation. The Warburg impedance (W) is included to account for diffusional processes within the cell. Based on this equivalent circuit model, the t_{Na+} can be calculated using Equation 2.10.



Figure 3.2 Equivalent circuit of symmetric Na//Na cell.

3.3.2 Electrochemical measurement

a) Electrochemical impedance spectroscopy analysis

EIS offers a powerful tool for probing the intricate dynamics of electrochemical systems. This method involves utilizing frequency-dependent measurements of current and potential to unveil insights that surpass the capabilities of steady-state techniques. Note that EIS alone is insufficient for definitive model identification. Complementary experimental observations are essential for robust interpretation and validation of the proposed model. In this study, EIS measurements were conducted on Na//Al and Na//Na cells using a Metrohm Autolab potentiostat/galvanostat instrument. The impedance response was recorded across a frequency range of 100 mHz to 1 MHz with a perturbation amplitude of 10 mV.

b) Coulombic efficiency evaluation

Two primary methods were employed to assess the reversibility of the Na plating/stripping process: long-term cycling CE tests and Aurbach CE tests. For the long-term cycling tests, Na//Al half cells were initially cycled between 0 and 1 V at a low current density of 50 μ A to electrochemically clean the Al/C electrode surface. Subsequently, repeated cycles of Na plating and stripping were performed, depositing and removing a controlled amount of Na (1 mAh cm⁻²) in each cycle. Plating was controlled by the discharge current density and time, while stripping was performed at the same current density until a cut-off voltage of 1 V was reached to ensure complete Na removal. The CE for each cycle was determined by the ratio of the plating and stripping capacities recorded by a Land (CT3001A) battery testing system. Long-term cycling CE values were then calculated by averaging the individual cycle CEs. This evaluation was performed at various current densities (0.5, 1, and 2 mA cm⁻²) to provide a comprehensive assessment of the Na plating/stripping reversibility.^[58] For the Aurbach CE test, a conditioning cycle was implemented prior to the standard protocol to facilitate stable SEI formation.^[190-193] This involved depositing 5 mAh cm⁻² of Na onto the Al/C substrate at 0.5 mA cm⁻², followed by complete stripping to 1 V. Subsequently, a fixed charge of 5 mAh cm⁻² (Q_T) of Na was plated and then subjected to n cycles of Na stripping/plating at a constant capacity of 1 mAh cm⁻² (Q_C) and a current density of 0.5 mA cm⁻². Finally, the cells were charged to 1 V (Q_S). The Aurbach CE was then calculated using the following equation:

Average
$$CE = \frac{nQ_c + Q_s}{nQ_c + Q_T}$$
 (3.2)

The two CE evaluation methods differ in the substrate for Na plating/stripping. The long-term cycling CE test probes these processes directly on the bare Al/C substrate, while the Aurbach CE test examines them on a pre-plated Na metal surface, simulating cycling on a pre-formed Na electrode.

c) Exchange current density analysis

Anodic and cathodic reactions occur simultaneously at any electrode surface. Equilibrium is established when these opposing reactions proceed at equal rates, resulting in a net zero current flow. The absolute current density at this equilibrium point, representing either the anodic or cathodic reaction rate, is termed the exchange current density (j_0) .^[194-196] This crucial parameter serves as a cornerstone in electrochemical kinetics. It appears in key expressions like the Tafel equation and Butler–Volmer equation and offers valuable insights into the inherent charge transfer rate at the electrode-electrolyte interface.^[196-198]

For SMBs, j_0 provides crucial insights into the anodic interfacial reaction kinetics.^[199] This process involves four intertwined steps:

- i) solvated Na⁺ transport in the bulk electrolyte,
- ii) desolvation of these Na⁺ ions at the Na anode surface,
- iii) migration of desolvated Na⁺ through SEI, and
- iv) reduction of Na⁺ into Na⁰.^[200]

Notably, the diffusion behavior of Na⁺ ions within the SEI differs from that in the bulk electrode or electrolyte, adding complexity to understanding the Na⁺ diffusion process.^[40]

To study the intrinsic electrolyte properties and circumvent the complexities brought by the SEI, Boyle and co-workers developed a transient ultramicroelectrode voltammetry technique. It enables the kinetics analysis of the electrode-electrolyte interface before significant SEI formation by using an ultrafast scan rate of 10 V s⁻¹.^[201, 202] As the measurement timescale of < 1 s is shorter than the typical passivation time by an SEI, the obtained j_0 values reflect the inherent charge transfer kinetics at pristine metal-electrolyte interfaces. To date, this method has been employed to investigate the interfacial charge transfer kinetics of various lithium battery electrolytes.^[202] However, Na⁺ diffusion through SEI in practical battery systems contributes significantly to the overall j_0 value. Consequently, practical current exchange processes in most reported papers involve all the four charge transfer processes stated above.^[194, 198-200] Two methods are primarily employed for determining j_0 . The first one is based on the rate performance test of symmetric metal cells. By plotting the logarithm of current density against the overpotential (μ), a linear Tafel region emerges at high overpotentials of typically above 150 mV or below –150 mV (see Figure 3.3). This linearity arises from the Tafel equation:

$$\mu = A \left(\log j - \log j_0 \right) \tag{3.3}$$

where μ represents the overpotential, A is the Tafel slope, j is the current density, and j_0 is the exchange current density. This equation allows for the extraction of j_0 from the linear Tafel region of the plot.



Figure 3.3 Tafel plots of Li//Li symmetrical cells using the LAV (LiFSI-acetonitrile (AN)vinylene carbonate (VC)) and baseline carbonate electrolytes recorded at different current densities. Reproduced with permission: Copyright 2020, John Wiley & Sons, Inc.^[198]

Alternatively, j_0 can be extracted from linear sweep voltammetry or cyclic voltammetry measurements of symmetric metal cells. In this approach, j_0 is calculated from the following Tafel equation:

$$\eta = \mathbf{a} + \mathbf{b} \, \lg(j) \tag{3.4}$$

where η represents the applied bias voltage, *a* and *b* are constants. The current density at $\eta = 0$ corresponds to the desired j_0 value. In practice, j_0 is typically determined by linear fitting of the Tafel plot within a certain overpotential range, as shown in Figure 3.4. The intercept of at $\eta = 0$ corresponds to j_0 . This study determined the j_0 values of various electrolyte systems using the cyclic voltammetry method with symmetric Na//Na cells. The voltage range is -100 mV to 100 mV and the scan rate is 1 mV s⁻¹.



Figure 3.4 Tafel plots obtained from cyclic voltammetry measurements. Reproduced with permission: Copyright 2017, John Wiley & Sons, Inc.^[196]

The relationship between the exchange current density and Li/Na reversibility has not yet been fully understood. Liu and co-workers observed that a lower exchange current density induces a larger critical radius for Li nucleation toward higher CE and dendrite-free Li deposition.^[194] Several other studies found that higher exchange current densities are correlated with faster interfacial charge transfer kinetics.^[198, 199] Hobold and co-workers offered a nuanced view, suggesting that the relationship between CE and j₀ hinges on the ratio between the local current density (*j*) and the exchange current density (*j*/*j*₀). Specifically, they proposed distinct relationships

for scenarios where j/j_0 is greater than or less than 10.^[40] Further investigation is required to fully elucidate the complex interplay between exchange current density and overall battery performance.

d) Linear scanning voltammetry studies

Linear scanning voltammetry (LSV) is a powerful tool for delineating the electrochemical stability window of each electrolyte. This study performed LSV tests with all studied electrolytes using the Na//Al coin cells on a Metrohm Autolab potentiostat/galvanostat instrument at a scan rate of 0.05 mV s⁻¹. The voltage was swept from the open circuit potential up to 6 V, identifying the potential limits within which the electrolyte remains electrochemically inert.

e) Long-term galvanostatic cycling of SMBs

The long-term galvanostatic cycling tests of half-cells and full cells with $Na_3V_2(PO_4)_3$ cathode were tested with a voltage range of 2.5–3.8 V. The theoretical capacity is based on 110 mAh g⁻¹ for different rate calculations. The specific capacities were calculated based on the weight of active $Na_3V_2(PO_4)_3$ material. The long-term galvanostatic cycling tests of half-cells and full cells with $Na_3(VO)_2(PO_4)_2F$ cathode were tested with a voltage range of 2.5–4.4 V. The theoretical capacity is based on 130 mAh g⁻¹ for different rate calculations. The specific capacities were calculated based on the mass of active $Na_3(VO)_2(PO_4)_2F$ material.

3.3.3 Solvation structure characterization by spectroscopy techniques

a) Raman Spectroscopy

Raman spectroscopy is a powerful vibrational spectroscopic technique that provides insights into molecular structure, composition, and chemical bonding. It exploits the inelastic scattering of photons, known as Raman scattering, which occurs when a small fraction of incident laser light interacts with the molecular vibrations of the sample. The energy difference between the incident and scattered photons corresponds to specific vibrational modes of the molecules, resulting in a unique spectral fingerprint.^[203]

Raman spectroscopy offers valuable information on the solvation structure of the electrolytes by reflecting the complex interactions between solvent molecules and ions. Specifically, the interactions between solvent molecules, Na⁺ ions, and anions, influence their respective vibrational modes. This leads to characteristic shifts in the Raman peaks corresponding to the solvent and the anions. By analyzing these shifts, the solvating power of the solvent in the electrolytes can be determined. For instance, strongly solvating solvents exhibit a more pronounced blue shift in their characteristic peaks than pure solvents, indicating strong interactions with Na⁺ ions. Additionally, the characteristic peaks associated with anion-cation interactions experience a redshift as Na⁺ ions are more coordinated with solvent molecules. The magnitude of this redshift provides a measure of the solvating power of the solvent.

In this research, the Raman spectra of the studied electrolytes and their component were acquired using a micro-laser confocal Raman spectrometer (Horiba LabRAM HR800, France) with a 532 nm laser. The Raman microscope has a 50 times objective magnification and a 600 lines/mm grating. The spectral resolution of the Raman data gathered is 2 cm^{-1} .

b) Nuclear Magnetic Resonance

Nuclear Magnetic Resonance (NMR) spectroscopy is a powerful analytical technique that provides detailed insights into the local chemical environment surrounding atomic nuclei. This technique exploits the phenomenon of nuclear spin transitions induced by radiofrequency radiation when a sample is placed within a strong magnetic field. By analyzing the frequencies at which different nuclei absorb and emit energy, NMR spectroscopy can reveal subtle variations in electron density, offering valuable information about molecular structure and dynamics.^[204] One key parameter derived from NMR spectra is the chemical shift, which is sensitive to the electron density around a nucleus.

In electrolyte, the Na⁺ ions are solvated by the solvent molecules. These interactions influence the chemical shifts of the Na⁺ ions. Therefore, the solvating ability of different solvents can be directly inferred from the chemical shifts of Na⁺ ions in the corresponding electrolytes. In this study, ²³Na-NMR analysis of the electrolytes was performed using a Jeol ECZ500R 500 MHz Solid-State NMR spectrometer. Before the test, dimethyl sulfoxide (DMSO-d6), as a deuterium reagent, was thoroughly mixed with the electrolyte.

3.3.4 Morphology, structure, and composition of electrode analysis

a) Scanning Electron Microscopy

Scanning electron microscopy (SEM) is a powerful technique employed to investigate the surface morphology and composition of materials. In SEM, a focused beam of electrons is systematically scanned across a sample, generating various signals because of electron-sample interactions. These signals, including low-energy secondary electrons, which provide topographical information, and higher-energy backscattered electrons, which reveal compositional contrast, are captured by

specialized detectors. High-resolution images are produced by mapping the intensity of these signals, enabling the visualization of surface features and elemental analysis with nanometer-scale precision.^[205] In this study, the morphologies of the deposited Na on Al/C current collectors after Na plating/stripping cycles were examined using SEM (Tescan VEGA3). The electrodes were washed with 1,2-dimethoxyethane (DME) solvent in an argon-filled glove box and transferred to the SEM chamber using a customized Ar-filled container before observation.

b) Atomic Force Microscopy

Atomic Force Microscopy (AFM) is a powerful technique capable of producing high-resolution, three-dimensional images of surface topography. It operates by measuring the minute forces that arise between a sharp tip, attached to a sensitive cantilever, and the sample surface. As the tip scans across the sample, attractive and repulsive forces, such as Van der Waals, electrostatic, and capillary forces, cause the cantilever to deflect. These deflections are precisely measured using a laser beam reflected off the back of the cantilever. By systematically raster scanning the tip and recording its deflection at each point, AFM constructs a detailed map of the surface, revealing features at the nanometer scale.^[206]

In this study, AFM (Bruker, DIMENSION ICON) was employed to characterize the surface fluctuation and Young's modulus of the SEI. Measurements were conducted within an Ar-filled glovebox using PeakForce tapping mode. The Young's modulus was determined using quantitative nanomechanics mode (QNM) and the Derjaguin-Muller-Toropov (DMT) model. To prepare samples for AFM analysis, Na//Al cells were disassembled in the plating state, and the electrode surfaces were rinsed with DME solvent within an argon-filled glovebox. Samples were then directly transferred from the glovebox to the AFM instrument using a customized transfer vessel to prevent air exposure.

c) X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive analytical technique that provides valuable information about the elemental composition and chemical states of a material by exploiting the photoelectric effect. When a sample is irradiated with X-rays, core-level electrons are ejected with kinetic energies dependent on their binding energies and the incident X-ray energy. By measuring these kinetic energies, XPS can identify the elements present in the sample based on their unique core-level binding energies. Moreover, shifts in these binding energies, referred to

as chemical shifts, provide insights into the chemical environment of each element, including its oxidation state and bonding interactions. Because of the short escape depth of photoelectrons, XPS is highly surface-sensitive, typically probing the outermost 10 nanometers of a material.^[207]

In this study, XPS (PHI5000 VersaProbe II, Al K α irradiation of 1,486.6 eV) was employed to investigate the chemical compositions of the CEI on the cycled cathode and the SEI formed on the Na metal anode. Similar to the AFM sample preparation, electrode surfaces were rinsed with DME in an argon-filled glovebox and transferred to the XPS instrument using a customized transfer vessel to avoid air exposure.

3.3.5 Theoretical calculations

Computational modeling and simulations provide invaluable tools for unraveling the concurrent microscopic processes within a battery. These simulations empower researchers to predict electrochemical system behavior across expansive temporal and spatial scales, offering insights inaccessible through experimental means alone.

Molecular dynamics (MD) simulations, rooted in classical mechanics principles and interatomic potentials, numerically solve Newton's equations of motion to model the dynamic behavior of ions and molecules within electrolytes. MD simulations illuminate key phenomena such as ion diffusion and migration, providing a dynamic perspective on electrolyte behavior.

Density functional theory (DFT) delves into the electronic realm, solving equations governing electron motion to unveil the electronic structure of ions and solvent molecules. DFT calculations are instrumental in determining the electrochemical stability window of electrolytes and identifying reactive sites involved in redox reactions. By synergistically employing MD and DFT, one can gain a comprehensive understanding of electrolyte behavior from dynamic and electronic perspectives.

a) Molecular Dynamics Simulations

This study performed all the classical MD simulations using the Forcite module within Materials Studio 2018. Simulations commenced with constructing an amorphous simulation cell containing randomly packed solute and solvent molecules at the desired ratios. Specific electrolyte models employed in each chapter are detailed below:

- Chapter 4: 0.4 M NaPF₆ G2 electrolyte (16 NaPF₆ and 280 G2 molecules); 0.4 M NaPF₆ G2/DOL electrolyte (10 NaPF₆, 70 G2 molecules, and 215 DOL molecules).
- Chapter 5, 2.5 M NaPF₆ G2 electrolyte (100 NaPF₆ and 280 G2 molecules); 2.5 M NaPF₆ G2/DOL electrolyte (100 NaPF₆, 210 G2 molecules, and 143 DOL molecules).
- Chapter 6, 1 M NaPF₆ G4 electrolyte (60 NaPF₆ and 243 G4 molecules); 1 M NaPF₆ DEGDBE electrolyte (60 NaPF₆ and 243 DEGDBE molecules); 2.5 M NaBF₄ G4 electrolyte (150 NaBF₄ and 273 G4 molecules).

The utilization of fixed partial charges on atomic sites, typically with integer ionic charges, to represent Coulomb interactions is a common practice in atomistic force fields. This approach has yielded accurate predictions of thermodynamic properties. However, a significant discrepancy arises when comparing simulated dynamics to experimental observations, with the former exhibiting notably slower dynamics.^[208] To accurately capture ion-ion and ion-dipole interactions and achieve agreement with experimental diffusivity and ionic conductivity values, ionic charges were scaled from their default values. In Chapter 4, the charges of Na⁺ and PF₆⁻ were scaled by a factor of 0.83; in Chapter 5, the charges of Na⁺ and PF₆⁻ were scaled by a factor of 0.8.^[153, 209, 210]

After the electrolyte models were constructed, they were first subjected to a structural optimization process. The COMPASS II force field was employed to optimize all electrolyte models.^[211] All simulation cells underwent an equilibration process to obtain the equilibrium structure. In Chapter 4, this process entailed two stages: first, a constant number, pressure, and temperature (NPT) simulation under 1 atm; followed by a constant number, volume, and temperature (NVT) simulation. Both NPT and NVT simulations lasted for 1 ns, with the radial distribution function and coordination number based on the final 0.5 ns of the NVT simulation. In Chapters 5 and 6, MD simulations proceeded through three stages of NPT simulations under 1 atm and 25 °C. These stages encompassed a 2 ns pre-equilibrium run, a 4 ns equilibrium run, and a 4 ns production run. Structural analyses were performed on the last 4 ns production run trajectories.

For all the simulation processes, the timestep was set to be 1 fs, and the Ewald summation method^[212] was used for the electrostatic with an accuracy of 1×10^{-4} kcal mol⁻¹ and a buffer width of 0.5 Å. The atom-based summation method was used for the van der Waals interaction with a cutoff distance of 15.5 Å, a cubic spline width of 1.0 Å, and a buffer width of 0.5 Å.

Nose method^[213] and Berendsen method^[214] were used to control the temperature and pressure, respectively.

The diffusion coefficient was calculated according to the mean square displacement (MSD) on the production simulation:

$$D = \frac{1}{6N_{\rm a}} \lim_{\tau \to \infty} \frac{\mathrm{d}}{\mathrm{d}\tau} \sum_{t=0}^{t-\tau} \sum_{i}^{N_{\rm a}} \left[r_{\rm i}(t+\tau) - r_{\rm i}(t) \right]^2 = \frac{1}{6} \lim_{\tau \to \infty} \frac{\mathrm{d}}{\mathrm{d}\tau} \mathrm{MSD}(\tau)$$
(3.5)

where *t* is the simulation time, τ represents the time interval, N_a is the total number of atoms in a given species, $r_i(t + \tau)$ and $r_i(t)$ are the position vectors of atom i at different time $(t + \tau \text{ and } t)$.

Radial distribution functions (RDF) and coordination numbers (CN) within the solvation sheath of the electrolyte can be evaluated from the MD simulation results. The RDF elucidates the probability of finding an atom at a specific distance from a reference Na⁺ ion. The CN, determined from the RDF, quantifies the average number of atoms directly coordinating with the Na⁺ ion. Specifically, the first minimum following the initial peak in the RDF plot defines the cutoff radius, signifying the boundary of the first solvation shell surrounding the Na⁺ ions. By integrating the RDF curve of a particular atom type around the Na⁺ ion within this cutoff radius, the CN for that specific atom-Na⁺ ion pair can be obtained.

b) Density Functional Theory Calculations

Frontier molecular orbitals, particularly the HOMO and LUMO, play a crucial role in dictating a molecule's electronic properties and reactivity. The HOMO typically acts as the electron donor, while the LUMO functions as the electron acceptor in chemical reactions.^[215-217] This study extended these concepts to solvation complexes within the electrolyte to understand the relative preference for electron loss or gain among different complexes. This analysis provides insights into the preferential order of reduction reactions at the anode and oxidation reactions at the cathode.

Fukui functions offer a powerful tool for analyzing and predicting molecular reactivity. These functions describe the sensitivity of a molecule's electron density to changes in the total number of electrons, effectively mapping the propensity for electron addition or removal at specific sites within the molecule. Three main types of Fukui functions exist, corresponding to nucleophilic attack, electrophilic attack, and radical attack.^[218] This study employed Fukui functions to pinpoint reactive sites within the solvation complexes. Specifically, the Fukui function for nucleophilic

attack was used to identify reduction sites, while the function for electrophilic attack highlighted potential oxidation sites.

The HOMO, LUMO, and Fukui functions of each Na⁺-coordinated cluster (typically containing three to five solvent molecules and anions) and free species (anion or solvent) were obtained by the DFT calculations. Each Na⁺-coordinated cluster and free species were considered an independent electron-capturing center that can be reduced or oxidized. These localized molecular structures served as input for DFT calculations, followed by molecular geometry optimization and subsequent determination of reduction potentials or oxidation potentials using an implicit solvation model.

DFT calculations were performed utilizing the Dmol3 module^[219] within Materials Studio. These calculations included all electrons and employed a local basis set of Double Numerical plus Polarization (DNP).^[220] The exchange-correlation effects were accounted for using the Perdew-Burke-Ernzerhof (PBE) functional with the generalized gradient approximation (GGA).^[221] Ion positions were relaxed during energy minimization until one of the three convergence criteria was met: 3×10^{-4} eV/system for energy change, 0.05 eV/Å for force, and 0.005 Å for displacement. All DFT calculations were conducted within the COSMO solvation model,^[222] treating the solvent as a dielectric continuum. The dielectric constant was set according to the specific solvent properties; for instance, it was set to 7.4 for the G2 solvent in Chapter 4 and Chapter 5, and to 7.5 for the G4 solvent in Chapter 6.

Chapter 4

Highly Reversible Sodium Metal Anodes at Ultralow Temperatures Boosted by Restructured Electrolyte Solvation

4.1 Introduction

Developing rechargeable batteries with high power delivery at LT is significant for coldclimate applications.^[108, 168, 169] Commercial LIBs suffer severe energy loss at temperatures below 0 °C.^[223] Moreover, the sharply rising price of lithium has driven the research community to explore emerging technologies beyond LIBs.^[224] Rechargeable sodium batteries are promising alternatives because of the abundant natural resources of Na, its similar electrochemical characteristics to Li,^[127, 225, 226] lower desolvation energy, and smaller Stokes radius of Na⁺ for improved LT battery performance.^[79, 115, 227] Among them, the initial AFSMB delivers the maximized energy density. It pairs a Na-containing cathode with a bare anode current collector, upon which Na metal is plated in the initial charging process and then serves as the Na source over subsequent charge/discharge cycles. Removing reactive metallic sodium during cell fabrication makes it much safer, attracting extensive research attention from academia and industry.^[32, 33]

The limited Na inventory in AFSMBs imposes steep requirements for reversibility, mandating Na plating/stripping CE above 99.9% for 80+% capacity retention over 200 cycles.^[40, 228] Glymebased electrolytes are highly compatible with Na metal anodes,^[37, 61, 75, 89, 159, 165] making them an excellent option for long-term cycling of AFSMBs at room temperature (RT, RT = 25 °C).^[34, 71, 229, 230] However, the kinetics of the anodic charge transfer reaction is drastically decreased at LT because of the complex multistep process involving the transportation of Na⁺ in bulk electrolyte, desolvation of Na⁺-based solvates, subsequent diffusion of Na⁺ through SEI, and final reduction of Na⁺ to Na^{0, [2, 194]} Specifically, the multiple oxygen atoms of glyme molecules render strong intermolecular interaction and thus slow migration of solvated Na⁺ at LT. They also form strong chelation with Na⁺ ions.^[148, 191] The large binding energy not only retards the kinetics of desolvation but induces more solvent molecules in the solvation sheath to participate in forming SEI.^[231] Unstable organic-rich SEI is thus produced with high adhesion to the metal surface, small Young's modulus, and low interfacial energy.^[190] Therefore, sluggish Na plating kinetics, low Na reversibility, and poor cycling stability are presented at LT.^[77, 80]

Novel electrolytes are urgently required to overcome the obstacles mentioned above. In recent years, those formulations enabling anion-derived, inorganic-rich SEI have attracted particular interest for reversible Na plating/stripping.^[232, 233] High-concentration electrolytes represent typical examples, which facilitate enhanced involvement of anions in the solvation sheath, minimizing the presence of SSIP solvates and increasing the content of CIP and AGG solvates.^{[118,} ²³⁴] Their applications in LT batteries are yet infeasible because of the tremendously increased viscosity. Fluorinated diluents, such as 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether (TTE), are popular diluents in concentrated electrolytes for decreasing viscosity, but their reductive decomposition at Na metal surface accelerates electrolyte dry-up.^[73, 235] Furthermore, the strong chelation of Na⁺ by glyme oxygen is not regulated by these non-solvating diluents, maintaining high desolvation energy barriers. Very recently, non-fluorinated weakly solvating solvents have been utilized in electrolytes for facilitated desolvation.^[78, 79] The weakly solvating electrolytes allow decreased coordination of Na⁺ to the solvent and enhanced anion participation in the solvation sheath. Nonetheless, the simultaneously weakened dissociation of sodium salts results in limited ionic conductivities. The stringent prerequisites, including sufficient ion mobility, fast desolvation kinetics, and formation of beneficial SEI, make it a huge challenge to realize beyond 99.9% CE of LT Na plating/stripping to date. Current unsatisfactory CEs below 99.5% plague the sustainable LT operation of AFSMBs, limiting the lifespan to only a few tens of cycles.

In this research, the solvation structure of a conventional glyme-based electrolyte (1M NaPF₆ in diglyme (G2)) has been reconfigured by facile cyclic ether (1,3-dioxolane, DOL) dilution for high Na reversibility at LT. DOL molecules alleviate the Na⁺–PF₆⁻ Coulombic interaction and intermolecular forces of G2 solvents, generating a remarkably high Na⁺ mobility. DOL also participates in the solvation sheath and weakens the chelation of Na⁺ by G2 toward a decreased energy barrier of desolvation. Moreover, it effectively alters the energy level distribution in the solvates, inducing an electron cloud concentrated around PF₆⁻ anions and thus their preferential decomposition. A desired SEI with compositional uniformity, high ionic conductivity, and high Young's modulus is generated, and ultrahigh Na plating/stripping CE beyond 99.9% is achieved even at -55 °C. A practical Ah-level AFSMB pouch cell delivers 95% of the initial capacity over 100 cycles at -25 °C. This study provides new opportunities to improve the LT Na reversibility, and is expected to pave the way for practically viable AFSMBs with boosted power output and durability at LT.

4.2 Screening and characterization of electrolytes

4.2.1 Electrolyte formulation

Four low-melting-point diluents, including 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropylether (TTE), dibutyl ether (DBE), diethylene glycol dimethyl ether (G2), and 1,3-dioxolane (DOL), were added into the conventional 1M NaPF₆ G2 electrolyte, the properties of those solvents were shown in Table 4.1. All the diluted electrolytes remain liquid at -40 °C and -55 °C. As shown in Figure 4.1, the electrolytes maintain level states when the glass bottle is tilted. The Na plating/stripping reversibility utilizing the four diluted electrolytes was investigated using Na//Al cells. The cells with 0.4 M NaPF₆ G2/TTE electrolyte failed to operate at RT (RT = 25 °C) because of the severe side reactions between TTE and Na metal anode, as shown in Figure 4.2a. The 0.4 M NaPF₆ G2/DBE electrolyte shows an average Na plating/stripping CE of 99.6% at RT (RT = 25 °C), (Figure 4.2b). Still, Na deposition failed to occur at -25° C because of the large internal resistance (Figure 4.2c).

Solvent	Melting	Boiling	Viscosity	Donor number	Dielectric
	point (°C)	point (°C)	(mPa·s)	$(kJ mol^{-1})$	constant (ε)
Diglyme (G2)	-64	162	1.06	19.5	7.4
1,3-Dioxolane (DOL)	-95	75	0.531	18	7.1
Dibutyl ether (DBE)	-95	141	0.602	19.0	3.06
1,1,2,2-Tetrafluoroethyl- 2,2,3,3-tetrafluoropropyl ether (TTE)	-94	92	/	/	6.2

Table 4.1 Physicochemical properties of the solvents of interest.^[127, 143, 236]



Figure 4.1 Optical images of four diluted electrolytes in a customized low-temperature chamber under -40 (a) and -55 °C (b): 1) 0.4 M NaPF₆ G2 electrolyte, 2) 0.4 M NaPF₆ G2/DOL electrolyte, 3) 0.4 M NaPF₆ G2/DBE electrolyte, and 4) 0.4 M NaPF₆ G2/TTE electrolyte.



Figure 4.2 (a) Voltage profile at the beginning of initial discharge of Na//Al cells with the 0.4 M NaPF₆ G2/TTE electrolyte at RT (RT = 25 °C). (b) Cycling stability of Na//Al cells with the 0.4 M NaPF₆ G2/DBE electrolyte at RT (RT = 25 °C). (c) Voltage profile at the beginning of initial discharge of Na//Al cells with the 0.4 M NaPF₆ G2/DBE electrolyte at -25 °C.

Figure 4.3 shows that the 0.4 M NaPF₆ G2 electrolyte exhibits an initial CE of 98.7% at -25° C, slowly increasing to 99.5% after about 40 cycles. In stark contrast, the 0.4 M NaPF₆ G2/DOL electrolyte demonstrates a high initial CE of 99.3%, reaching 99.9% within three cycles and maintaining this CE value over the subsequent 200 cycles. From the voltage profiles in the inset of Figure 4.3, a low plating/stripping overpotential of ~19 mV can be observed for the G2/DOL system. It is only half that of the G2 counterpart, revealing the accelerated redox reaction kinetics in the G2/DOL system.



Figure 4.3 Cycling stability of Na//Al cells at 0.5 mA cm⁻² and 1.0 mAh cm⁻² under -25 °C. The inset shows the corresponding voltage profiles.

4.2.2 Physicochemical property characterization of selected electrolytes

The wettability testing of 0.4 M NaPF₆ G2 and 0.4 M NaPF₆ G2/DOL electrolytes was conducted within an Argon-filled glove box at RT (RT = 25 °C). Both the G2 and the G2/DOL electrolyte systems can achieve rapid and complete wetting on the surface of the Na metal and separators, as shown in Figure 4.4. This suggests that the performance disparities primarily originate from the intrinsic properties of the electrolytes.

The viscosities of 0.4 M NaPF₆ G2 and 0.4 M NaPF₆ G2/DOL electrolytes at various temperatures were investigated, and the results are shown in Figure 4.5. The 0.4 M NaPF₆ G2 electrolyte shows a sharp viscosity increase with a decrease in temperature, from 1.73 mPa·s at 25 °C to 9.58 mPa·s at -40 °C. The DOL-diluted electrolyte displays a comparable viscosity to G2 at RT (RT = 25 °C) but increases much less to only 3.92 mPa·s at -40 °C.



Figure 4.4 Wettability test of a–c) 0.4 M NaPF₆ G2 and d–f) 0.4 M NaPF₆ G2/DOL electrolytes on Na metal, Celgard 2500, and Whatman glass fiber.



Figure 4.5 Temperature-dependent viscosity of 0.4 M NaPF₆ G2 and 0.4 M NaPF₆ G2/DOL electrolytes.

The ionic conductivities of the electrolytes were also evaluated, and the values at various temperatures are shown in Figure 4.6.^[237] The DOL-diluted electrolyte possesses an 80% higher ionic conductivity than 0.4 M NaPF₆ G2 at RT (RT = 25 °C). Surprisingly, it surpasses the 1 M NaPF₆ G2 electrolyte before dilution. At -40 °C, a high ionic conductivity of 3.62 mS cm⁻¹ is maintained for the DOL-diluted electrolyte, far superior to 1.41 mS cm⁻¹ of 0.4 M NaPF₆ G2. Such impressive enhancement in ion-conducting capability could be ascribed to the DOL-regulated structure, which will be discussed in detail in the following section.



Figure 4.6 Temperature-dependent ionic conductivity of 0.4 M NaPF₆ G2, 1 M NaPF₆ G2, and 0.4 M NaPF₆ G2/DOL electrolytes.

To evaluate the Na⁺ ion conductivities of investigated electrolytes, Na⁺ ion transference numbers (t_{Na+}) were measured according to the method described in Chapter 2.^[191] Figures 4.7 a,b show the Nyquist plots of 0.4 M NaPF₆ G2 and 0.4 M NaPF₆ G2/DOL electrolytes before and after the polarization process. Figure 4.7c depicts the polarization curves of two electrolytes, through which the t_{Na+} values of the DOL-diluted electrolyte and G2 electrolyte were determined to be 0.711 and 0.556, respectively. An elevated t_{Na+} yields substantial improvements in terms of materials utilization, power and energy densities, particularly when operating at high discharge rates.^[238] The corresponding Na⁺ ion conductivity of the DOL-diluted electrolyte was thus calculated to be 5.46 mS cm⁻¹. It can be seen that the DOL-diluted electrolyte outperforms 0.4 M NaPF₆ G2 and even 1 M NaPF₆ G2 (Figure 4.8). It can be anticipated that the DOL diluent shields the Coulombic interaction between Na⁺ and PF₆⁻ and intermolecular forces of G2 solvent, leading to remarkably accelerated Na⁺ ion conductivity.


Figure 4.7 Nyquist plots for (a) 0.4 M NaPF₆ G2 electrolyte and (b) 0.4 M NaPF₆ G2/DOL electrolytes. (c) Polarization curves for two electrolytes.



Figure 4.8 Polarization curve for the 1 M $NaPF_6$ G2 electrolyte. Insets are Nyquist plots before and after polarization.

4.3 Evaluation of Na reversibility at low temperatures

4.3.1 Na plating/stripping CE test

As shown in Figure 4.9a, at a Na plating/stripping current density of 1 mA cm⁻², the Na//Al cells with DOL-diluted electrolyte show reversible and durable plating/stripping. However, those with the 0.4 M NaPF₆ G2 electrolyte experience progressive voltage polarization, leading to failure by the third cycle. When the current density increases to 2 mA cm⁻², the cells with DOL-diluted electrolyte maintain an impressive average CE value of 99.9% over 400 cycles, manifesting its superior high-rate performance (Figure 4.9b).



Figure 4.9 (a) Voltage profiles of Na//Al cells with two electrolytes at 1 mA cm⁻² and 1.0 mAh cm⁻² under -25° C. (b) Cycling stability of Na//Al cells with 0.4 M NaPF₆ G2/DOL electrolyte at 2 mA cm⁻² and 1.0 mAh cm⁻² under -25° C.

The Na reversibility of NaPF₆–G2/DOL electrolytes with different concentrations was also explored. The 0.33 M NaPF₆ G2/DOL, 0.4 M NaPF₆ G2/DOL, and 0.5 M NaPF₆ G2/DOL systems all show similarly high CE values over prolonged cycling at 0.5 mA cm⁻² and 1 mAh cm⁻², with the 0.4 M system demonstrating the least fluctuation among the three (Figure 4.10a). When the current density is further increased to 1 mA cm⁻², the 0.4 M system still shows a high average CE of 99.9% over 200 cycles with little fluctuation (Figure 4.10b), while 0.33 M and 0.5 M systems display lower CE values of 99.8% and 99.7% with more obvious fluctuations. The selection of 0.4 M NaPF₆ G2/DOL as the working electrolyte was justified by its optimal CE and cyclic stability.

The Na plating/stripping reversibility at even lower temperatures was further estimated. Figure 4.11 shows Na plating/stripping CE of the DOL-diluted electrolyte over prolonged cycling at -40 °C. At 0.5 and 1 mA cm⁻², the CE value increases very fast to 99.9% after several cycles and then

remains very stable over the following 200 cycles. And it takes about 20 cycles to reach the stabilized CE value of 99.9% at 2 mA cm⁻². The corresponding voltage profiles in the inset of Figure 4.11 also keep very steady during prolonged cycling.



Figure 4.10 Cycling stability of Na//Al cells with NaPF₆–G2/DOL electrolytes of different concentrations at 0.5 mA cm⁻² and 1.0 mAh cm⁻² under -25 °C (a) and 1 mA cm⁻² and 1.0 mAh cm⁻² under -40 °C (b).



Figure 4.11 Cycling stability of Na//Al cells at different current densities in 0.4 M NaPF₆ G2/DOL under -40 °C. The insets show the corresponding voltage profiles at the 1st, 50th, and 100th plating/stripping cycles at 2 mA cm⁻².

When the temperature is further decreased to -55 °C, the cells with DOL-diluted electrolyte still display ultrahigh average CE values of 99.9% and 99.8% at 0.25 and 0.5 mA cm⁻², respectively. Even under -65 °C, the cell shows a high average CE of 99.4% over 150 cycles at 0.25 mA cm⁻² and 0.5 mAh cm⁻², as shown in Figure 4.12. This highlights the superior Na reversibility at ultralow temperatures.



Figure 4.12 Cycling stability of Na//Al cells with 0.4 M NaPF₆ G2/DOL electrolyte under ultralow temperatures of -55 °C and -65 °C.

Aurbach CE tests were carried out to provide another efficient evaluation of the Na plating/stripping reversibility on Na metal substrates.^[192, 193] Figure 4.13 shows that high CE values of 99.9% were obtained at -25 °C and -40 °C. Such excellent performance is far superior to those reported to date (see Figure 4.14),^[76-79] especially considering the applied ultralow temperature of -40 °C and high current density of 2 mA cm⁻².



Figure 4.13 Aurbach measurement of Na plating/stripping CE in Na//Al cells at -25 °C and -40 °C.



Figure 4.14 Comparison of LT Na plating/stripping CEs in the 0.4 M NaPF₆ G2/DOL electrolyte with those in the reported electrolytes.^[76-79]

4.3.2 Morphology observation of the deposited Na metal

The Na plating/stripping reversibility is highly correlated with the uniformity of deposited Na. Therefore, the morphology of the deposited Na metal after 200 cycles was obtained by scanning electron microscopy (SEM), which was obtained by disassembling the cell in the Na plating state (Figures 4.15). For the 0.4 M NaPF₆ G2 system, the Na metal shows irregular surfaces filled with cracks and pores. In contrast, the G2/DOL system exhibits a uniform and smooth surface, which accords well with the high Na plating/stripping CE in the previous discussion.



Figure 4.15 SEM images of the deposited Na metal on Al/C current collectors in (a) 0.4 M NaPF₆ G2 and (b) 0.4 M NaPF₆ G2/DOL electrolytes after 200 cycles of Na plating/stripping at 0.5 mA cm⁻², 0.5 mAh cm⁻² under -25 °C.

4.3.3 Analysis of internal resistance change over Na plating/stripping cycles

Electrochemical impedance spectroscopy (EIS) tests were performed further to examine the internal resistance change over 200 cycles. The plotted Nyquist curves of the G2 system exhibited a gradual increase in resistance throughout the cycling. Specifically, the ohmic resistance shows an increase from 20 to 24.7 ohms, and the charge transfer resistance escalated from 0.4 to 3 ohms. This increase in impedance indicates the gradual accumulation of irreversible reactions within the G2 electrolyte system. In stark contrast, the G2/DOL counterparts show remarkable stability over 200 cycles, with their ohmic resistance steadfast around 8.3 ohms and charge transfer resistance consistently at 0.4 ohms. This exceptional stability demonstrates the superior cycling stability of the G2/DOL electrolyte system (Figure 4.16).



Figure 4.16 Nyquist plots of Na//Al cells with (a) 0.4 M NaPF₆ G2 and (b) 0.4 M NaPF₆ G2/DOL electrolytes after 3, 100, and 200 Na plating/stripping cycles at 0.5 mA cm⁻², 0.5 mAh cm⁻² under -25 °C.

4.4 Characterization of electrolyte solvation structure

Electrolyte solvation structure plays a critical role in regulating the ionic conducting behavior in the bulk electrolyte and the desolvation kinetics at the sodium metal surface. It also determines the electrolyte decomposition pathway and, thus, the component, structure, and electrochemical property of the electrode/electrolyte interphases. Here, theoretical simulations and experimental techniques were combined to gain detailed kinetic and thermodynamic insights into the properties of studied electrolytes.

4.4.1 Computational characterization

Classical MD simulations were first performed on 0.4 M NaPF₆ G2 and 0.4 M NaPF₆ G2/DOL electrolytes using the COMPASS II force field with optimized atom types and charges (Figures 4.17 and 4.18). To properly account for the ion-ion and ion-dipole interactions, the charges of Na⁺ and PF₆⁻ from the salts were scaled by 0.83 in this study. Both simulation cells underwent a comprehensive equilibration process to achieve their equilibrium structures. This process comprises two distinct stages: initially, a constant number, pressure, and temperature (NPT) simulation, followed by a constant number, volume, and temperature (NVT) simulation. Considering that the freezing point of aqueous solution models often deviates from experimental values because of the presence of hydrogen bonds,^[239] the density changes of two electrolyte models from 25 °C to -25 °C and further to -40 °C were investigated. For 0.4 M NaPF₆ G2 electrolyte, the density increases from 1.065 to 1.119 and further to 1.142 g cm⁻³ when temperature decreasing. The slight increase in density indicates that both electrolyte models remain in the liquid state within the investigated temperature range.



Figure 4.17 The force field types and the corresponding atomic charges of ions and molecules in the 0.4 M NaPF₆ G2 and 0.4 M NaPF₆ G2/DOL electrolytes.



Figure 4.18 Snapshots obtained from classical MD simulations of (a) 0.4 M NaPF₆ G2 and (b) 0.4 M NaPF₆ G2/DOL electrolytes.

By tracking the mean-squared displacements as a function of the time interval for 100 ps, the Na⁺ diffusion coefficient of the G2/DOL electrolyte was calculated to be 4.33×10^{-10} m² s⁻¹ at RT (RT = 25 °C), higher than that of 0.4 M NaPF₆ G2. And this gap further widens at -25 °C, the Na⁺ diffusion coefficient of G2/DOL electrolyte still maintains 1.49×10^{-10} m² s⁻¹, while that of 0.4 M NaPF₆ G2 drops to 6.2×10^{-11} m² s⁻¹ (see Figure 4.19). Such calculation results reveal the rapid mobility of Na⁺ charge carriers in the G2/DOL electrolyte, especially at low temperatures.



Figure 4.19 The mean-squared displacements of Na⁺ in two investigated electrolytes at RT (RT = 25 °C), (a), and -25 °C (b).

Radial distribution functions (RDF) and coordination numbers (CN) within the solvation sheath were further evaluated. Both two electrolytes show strong Na–O (G2) peaks in RDF curves and high CN of Na–O (G2) at RT (RT = 25 °C), (Figure 4.20), indicating that the SSIP solvates are the dominant species. For the DOL-diluted electrolyte, the ratio of SSIP to CIP/AGG solvates was quantitatively determined to be 72:28, and a tiny Na-O (DOL) peak can be detected with a small CN value. When the temperature decreases to -25 °C, this peak becomes stronger, and the as-derived CN increases to 0.34 (Figure 4.21), suggesting a considerable involvement of DOL in the solvation sheath. Additionally, CN values of Na–F are 0.08 and 0.69 for the G2 electrolyte and G2/DOL electrolyte at -25 °C, predicting more anion participation in the solvates. While the calculated ratio of SSIP to CIP/AGG slightly decreases to 70:30, the DOL-diluted electrolyte still maintains a SSIP-dominated solvation structure. For the 0.4 M NaPF₆ G2 electrolyte, the ratio of SSIP to CIP/AGG solvates was quantitatively determined to be 79:21 at RT (RT = 25 °C). This ratio changed to 93:7 as the temperature decreased to -25 °C, indicating a distinct trend compared to the DOL-diluted electrolyte. The different change in the DOL-diluted electrolyte may be attributed to the higher incorporation of DOL at lower temperatures, which could hinder the incorporation of more G2 solvents into the solvation sheath.



Figure 4.20 Na⁺ radial distribution function (RDF) and the coordination number in two investigated electrolytes obtained from MD simulations at RT (RT = 25 °C).



Figure 4.21 Na⁺ RDF and the coordination number in two investigated electrolytes obtained from MD simulations at -25 °C.

The three oxygen atoms of G2 molecules constitute the coordination sites for Na⁺ binding. Density functional theory (DFT) was employed to calculate the interatomic distance (Figure 4.22) and their binding energies (Figure 4.23). Notably, these calculations are based on the most stable CIP or SSIP complexes. The 0.4 M NaPF₆ G2 shows the same interatomic distance of 2.53 Å for all three oxygen atoms, indicating the highly bent state of the linear G2 molecule with a significant elastic potential. In contrast, 0.4 M NaPF₆ G2/DOL presents distinct interatomic distance of 2.52 Å, 2.74 Å, and 3.06 Å, respectively. It suggests that the incorporation of DOL into the solvation sheath helps release part of the elastic potential energy in the bent G2 molecular, enabling it to partially recover to its original linear state. Moreover, the strong chelation of Na⁺ by G2 oxygen in 0.4 M NaPF₆ G2/DOL. Therefore, the DOL dilution could decrease the energy barrier for Na⁺ desolvation.



Figure 4.22 Solvation structure of two electrolytes and the corresponding distances between Na⁺ and the O atoms of G2 molecules calculated by DFT.



Figure 4.23 Desolvation energy of Na⁺ in 0.4 M NaPF₆ G2 and 0.4 M NaPF₆ G2/DOL electrolytes.

4.4.2 Spectroscopic characterization

Raman spectroscopy was performed to further validate the solvation structures. Figure 4.24a displays the Raman spectra of two electrolytes and their components, along with 1 M NaPF₆ G2 for reference. A prominent fingerprint peak at 850 cm⁻¹ corresponding to the C–O stretching vibration was detected in the G2 solvent.^[240, 241] It is blue-shifted by 20 cm⁻¹ in the electrolytes, indicating the strong coordination between G2 and Na⁺. In contrast, DOL displays a slight blue shift from 938 to 941 cm⁻¹ in the DOL-diluted electrolyte, owing to its weak binding with Na⁺.^[237, 242] The symmetric stretching vibration (a_{1g}) mode of PF₆⁻ is also shifted from 765 cm⁻¹ in NaPF₆ to ~740 cm⁻¹ in three electrolytes, which should be ascribed to the decreased coordination between PF₆⁻ and Na⁺ after dissociation.^[243]



Figure 4.24 Raman spectra of various electrolytes and components.

Nuclear Magnetic Resonance (NMR) measurements provide more intricate details regarding the participation of PF_6^- in the solvates. Figure 4.25 illustrates the ²³Na NMR spectra of the DOLdiluted electrolyte and NaPF₆ G2 electrolytes with various concentrations. As the concentration increased from 0.1 M to 2 M, the ²³Na shift of NaPF₆ G2 electrolytes became progressively more negative, from -2.1 ppm to -4.5 ppm. This shift indicates the enhanced ion pairing between Na⁺ and PF₆⁻ and the gradual transformation of the SSIP solvates into CIP/AGGs.^[244, 245] It has been widely acknowledged that SSIP dominates the solvation structure in super-diluted electrolytes like 0.1 M NaPF₆ G2.^[113] It can be observed that the characteristic peak of 0.4 M NaPF₆ G2/DOL is close to that of 0.1 M NaPF₆ G2, again confirming the SSIP-dominated solvation structure in the DOL-diluted electrolyte.



Figure 4.25 ²³Na NMR spectra of the 0.4 M NaPF₆ G2/DOL and NaPF₆ G2 electrolytes with different concentrations.

4.5 Na metal anode-electrolyte interphase characterizations

4.5.1 Study on the SEI-formation pathways

The composition and microstructure of SEI play a critical role in determining the reversibility of Na plating/stripping. Although extensive research has been undertaken to understand the formation mechanism of SEI,^[89, 165, 246] it remains a subject of considerable debate, particularly concerning the reduction pathways. To obtain more comprehensive information in this direction, DFT calculations were employed to analyze the Fukui function and the LUMO of the solvation structures. The Fukui functions offer insight into the electron density distributions around investigated atoms, with higher values indicating stronger electron gain.^[218, 247] It is noteworthy that the CIP complexes in both electrolytes show higher tendencies toward electron gain and reduction than SSIP (Figure 4.26).



Figure 4.26 Reduction reaction site prediction of (a) CIP complexes in the 0.4 M NaPF₆ G2 electrolyte, (b) CIP complexes in the 0.4 M NaPF₆ G2/DOL electrolyte, and c) SSIP complexes in the 0.4 M NaPF₆ G2 and 0.4 M NaPF₆ G2/DOL electrolytes via Fukui function analysis. The yellow color regions represent electron-rich regions, and the blue color regions represent electron-deficient regions.

LUMO energy levels of PF_6^- and G2/DOL solvents and the distribution in solvation complexes are summarized in Figure 4.27 and Table 4.2. The solvation complexes in the DOL-diluted electrolyte show a lower LUMO energy level of -0.36 eV than that of -0.01 eV in the 0.4 M NaPF₆ G2 electrolyte, favoring the preferential anion decomposition. More importantly, it can be observed that LUMO is mainly distributed around PF_6^- in the solvation complex. All results indicate that the introduction of DOL effectively regulates the solvation structure, not only reducing the LUMO energy level of the solvation complex but enabling concentrated LUMO distribution around PF_6^- anions. The reduction reaction of PF_6^- anions is thus facilitated, which may promote the formation of favorable inorganic components in SEI.



Figure 4.27 LUMO of solvent molecules, sodium salts, and solvate complexes in electrolytes.

Table 4.2 The calculated LUMO and HOMO energy levels for salt (PF ₆), solvents (G2 and DOL)
and solvation complexes in the 0.4 M $NaPF_6$ G2 and 0.4 M $NaPF_6$ G2/DOL electrolytes.

LUMO	НОМО
1.06	-7.5
0.72	-6.1
0.38	-6
-0.36	-6.23
-0.01	-6.03
	LUMO 1.06 0.72 0.38 -0.36 -0.01

4.5.2 Surface analysis of as-formed SEI

The electronic states of composition elements in as-formed SEI were studied using depth-profiling X-ray photoelectron spectroscopy (XPS). Normalized XPS fitting results of high-resolution F 1s, P 2p, O 1s, and Na 1s spectra were obtained at different Ar⁺ sputtering times, as shown in Figure 4.28–4.31. The surface of SEI formed in the G2/DOL system shows a strong F–P peak at 687.6 eV in the F 1s spectrum and a prominent P–F peak at 137.5 eV in the P 2p spectrum. These peaks correspond to Na_xPO_yF_z and Na_xPF_y derived from the reduction of PF₆^{-.[248, 249]} The strength of the F–P peak decreased continuously throughout the in-depth etching, while that of the F–Na peak

at 684.5 eV showed a gradual increase followed by a slight decrease. It indicates a gradient inorganic structure in SEI with rich $Na_xPO_yF_z/Na_xPF_y$ species at the top and abundant NaF at the bottom. In contrast, no discernible signals were detected in the F 1s and P 2p spectra at the surface of SEI formed in the G2 system, and only a weak signal began to emerge after 24 s of etching.



Figure 4.28 The in-depth XPS F 1s spectra of SEI formed in two electrolytes at -25 °C.



Figure 4.29 The in-depth XPS P 2p spectra of SEI formed in two electrolytes at -25 °C.

For the SEI formed in the G2/DOL system, the Na 1s spectra reveal the presence of inorganic Na compounds at the surface. The content of NaF reached its highest level at an etching time of 48 seconds, which has been reported to possess multiple merits in SEI, including electronic insulation to limit subsequent parasitic reactions, high Young's modulus to suppress Na dendrite growth, and large surface energy to facilitate surface Na⁺ diffusion.^[91, 250] A peak corresponding to Na⁰ at 1070.6 eV^[251] began to appear at 48 s of etching and became intensified afterward, suggesting penetration of the SEI. In contrast, the Na 1s spectra for the G2 system mainly showed Na₂CO₃,^[252] and the characteristic Na⁰ peak did not appear until 118 s of deep profiling. These findings manifest the formation of very thin and NaF-dominant SEI in the G2/DOL system. Additionally, the peak associated with the organic R–O–Na at 533.5 eV^[102] in O 1s spectra disappeared for the G2/DOL system at an etching time of 48 s, which existed even after 118s of etching for the G2 system. Such XPS characterizations thus accord well with the above simulation results. The introduction of DOL indeed promotes the formation of anions-derived SEI, as shown in Figure 4.32.



Figure 4.30 The in-depth XPS Na 1s spectra of SEI formed in two electrolytes at -25 °C.



Figure 4.31 The in-depth XPS O 1s spectra of SEI formed in two electrolytes at -25 °C.



Figure 4.32 Schematic illustration of the SEI composition/microstructures formed in two electrolytes at -25 °C.

To further examine the surface morphologies and mechanical properties of as-formed SEI, atomic force microscope (AFM) imaging and nanoindentation measurements were carried out. The sodium metal surface after the first cycle in the DOL-diluted electrolyte shows a quite smooth texture with an average roughness of as low as 3.25 nm (Figure 4.33a), indicating the extraordinarily uniform Na deposition and reversible Na stripping. In contrast, the topography image of the G2 counterpart presents a much larger average roughness of 17.1 nm (Figure 4.33b), evidencing more heterogeneous Na plating/stripping. Young's modulus mapping was used to

study the mechanical strength of as-formed SEI (Figure 4.33c–d). The average Young's modulus was determined to be 1.1 GPa in the G2/DOL system, much higher than 0.3 GPa in the G2 system. The improved mechanical strength may be derived from the as-generated NaF in SEI, which owns a high Young's modulus of 76 GPa.^[83] It can efficiently inhibit potential dendrite growth and penetration, thus favoring high Na reversibility.



Figure 4.33 AFM surface profiling of SEI formed in the (a) G2/DOL and (b) G2 electrolytes at -25 °C. Young's modulus mapping of SEI formed in the (c) G2/DOL and (d) G2 electrolytes at -25 °C.

4.5.3 Analysis of interfacial kinetics

Charge transfer kinetics plays a key role in determining the efficiency and reversibility of Na plating/stripping.^[253] EIS of symmetric Na//Na cells were thus analyzed to evaluate the interfacial resistances. The resulting Nyquist plots of two electrolytes at different temperatures are depicted in Figure 4.34. The Nyquist plots of two electrolytes at different temperatures all consist of a straight line in the low-frequency region and two connected semicircles in the medium-to-high-frequency region. The mid-frequency semicircle corresponds to the charge transfer process dominated by Na⁺ desolvation (R_{ct}), the other one can be related to Na⁺ diffusion across SEI (R_{SEI}), and the intercept of the merged semicircle with the real axis represents the ohmic resistance (R_s).

The R_s increases much more rapidly in the G2 system with decreasing temperature than in G2/DOL, consistent with the above-mentioned ionic conductivity change.^[254, 255]



Figure 4.34 EIS results of symmetric Na//Na cells with (a) 0.4 M NaPF₆ G2 and (b) 0.4 M NaPF₆ G2/DOL electrolytes at different temperatures.

The resistance values corresponding to the R_{SEI} and the R_{ct} were further quantitatively analyzed and summarized in Figure 4.35. The R_{ct} value in G2/DOL is much smaller than in G2, confirming the accelerated Na⁺ desolvation by the introduction of DOL. As for R_{SEI} , it presents a minor increase in G2/DOL but a tremendous escalation in G2 when temperature gradually decreases. The Na⁺ diffusion resistance across SEI is highly related to the compositional distribution. Na⁺ desolvation at the interface is sluggish at LT in the G2 system. Therefore, more solvent molecules are anticipated to participate in SEI formation before desolvation, generating more organic species unfavorable for smooth Na⁺ transport. In contrast, SEI formation is dominated by PF₆⁻ anions in the DOL-diluted electrolyte even at LT, resulting in more Na⁺-conductive inorganic species.



Figure 4.35 The R_{SEI} and R_{ct} values at different evaluation temperatures for the G2 and G2/DOL electrolytes system.

The cyclic voltammograms of symmetric Na//Na cells are shown in Figure 4.36. Based on the data from Figure 4.36, the exchange current density (j_0) was also examined to understand the intrinsic kinetics of the electron-transfer activity at interfaces during Na plating/stripping. The j_0 values of G2 and G2/DOL systems at different temperatures were evaluated by linear fitting of Tafel plots (Figure 4.37). They are determined to be 2.39, 0.83, and 0.57 mA cm⁻² in the G2/DOL system at RT (RT = 25 °C), -25°C, and -40°C, respectively, 2–3 times those obtained from the G2 system. Such high j_0 values indicate adequate Na⁺ ions beneath SEI to achieve uniform Na deposition.^[256]



Figure 4.36 The CV curves of symmetric Na//Na cells in investigated electrolytes at (a) RT (RT = 25 °C), (b) -25 °C, and (c) -40 °C.



Figure 4.37 Tafel plots in two investigated electrolytes under (a) RT (RT = 25 °C), (b) -25 °C, and (c) -40 °C.

Based on the above experimental results and theoretical analyses, a potential mechanism for high Na reversibility at LT is proposed as shown in Figure 4.38. The DOL dilution efficiently reconfigures the solvation structure. It not only alleviates the Na⁺–PF₆⁻ Coulombic interaction and intermolecular forces of G2 solvents for accelerated Na⁺ ion conductivity but weakens the chelation of Na⁺ by G2 for facilitated desolvation. Although anion-involved CIP/AGG solvates are not the dominant species in the diluted electrolyte, DOL-participated solvates allow

preferential anion decomposition because of the lowered LUMO energy level and concentrated electron cloud distribution around PF_6^- . A desired inorganic-rich SEI is thus generated with high Na⁺ ion conductivity and compositional homogeneity for uniform Na deposition. Additionally, its high Young's modulus efficiently suppresses uneven Na growth. Consequently, highly reversible Na plating/stripping at LT can be realized.



Figure 4.38 Schematic illustration of the mechanism of improved LT Na reversibility by the DOLdiluted electrolyte.

4.6 Electrochemical performance evaluation

4.6.1 Coin cells

To check the feasibility of the DOL-diluted electrolyte for practical applications, full cells were assembled with Na₃V₂(PO₄)₃ at the cathode side and carbon-coated aluminum current collector at the anode side (without sodium preloading initially). Before that, the low-temperature performances of the Na₃V₂(PO₄)₃ cathode were investigated. As shown in Figure 4.39, the Na/Na₃V₂(PO₄)₃ half-cell exhibits superior rate capability at -25 °C, maintaining a capacity of 57.8 mAh g⁻¹ at 3 C, 60% of its capacity at 0.2 C. At -40 °C, the capacity decreases, showing 44.3 mAh g⁻¹ at 2 C, 58% of its capacity at 0.2 C. Additionally, Na/Na₃V₂(PO₄)₃ half-cell demonstrated excellent long-term cycle stability at both temperatures. At -25 °C with a current density of 1 C, it retains a capacity of 76.1 mAh g⁻¹ with a retention rate of 99.1% over 300 cycles. At -40 °C, it maintains a capacity of 54.3 mAh g⁻¹ with a retention rate of 98.7% over 300 cycles at 1 C.



Figure 4.39 Rate performance and long-term galvanostatic cycling performance of Na//Na₃V₂(PO₄)₃ half-cells at -25 °C (a, c) and -40 °C (b, d).

Temperature-dependent galvanostatic cycling of Al//Na₃V₂(PO₄)₃ anode-free cells was then studied, which presents decreased discharge capacities as the cells are sequentially cooled (Figure 4.40). At 0 °C, it delivers a high specific capacity of 97.2 mAh g⁻¹ at 0.2C and retains 90% at -25 °C, 63% at -40 °C, and ~40% even at an ultralow temperature of -65 °C, respectively. When it reheats to RT (RT = 25 °C), the specific capacity can be fully recovered, demonstrating superior resilience to dramatic temperature variations.



Figure 4.40 Temperature-dependent galvanostatic cycling of AFSMBs at 0.2C.

The long-term cycling stability of AFSMBs at LT was further evaluated at a current rate of 1C, as depicted in Figure 4.41. An initial discharge capacity of 59.7 mAh g⁻¹ and capacity retention of 93.3% over 400 cycles at -25 °C were achieved. A capacity retention of 82.5% over 400 cycles at -40 °C and 91% over ~140 cycles at -55 °C were also realized. Even under -65 °C, the anode-free cell can still smoothly operate with a capacity retention of 69% over 50 cycles(Figure 4.42).



Figure 4.41 Long-term galvanostatic cycling performance of AFSMBs at 1C under -25 °C and -40 °C.



Figure 4.42 Long-term cycling performances of AFSMBs at a) -55 °C and b) -65 °C.

4.6.2 Pouch cells

The gap between material/component properties and the achievable large-format cell-level performance is one key challenge for practical applications of rechargeable alkali metal batteries.^[257] To verify the feasibility of the G2/DOL electrolyte in practical AFSMBs, a 1-Ah capacity pouch cell was fabricated with double-side-coating and high-mass-loading (~30 mg cm⁻²) Na₃V₂(PO₄)₃ cathode films employed (Figure 4.43).



Figure 4.43 The schematic diagram and optical image of the Ah-level anode-free pouch cell using the G2/DOL electrolyte.

The charge-discharge voltage profiles of the as-assembled cells at various current rates under -25 °C are illustrated in Figure 4.44. As the current rates increase from 0.1C, 0.2C to 0.5C, little depression of voltage plateaus can be observed, and high discharge capacities of 82.5 mAh g⁻¹ (1.06 Ah), 78.3 mAh g⁻¹ (1.0 Ah), and 67.3 mAh g⁻¹ (0.86 Ah) are delivered, respectively. The long-term cycling stability of the pouch cell at -25 °C is depicted in Figure 4.45. It maintains 95% of the initial capacity over 100 cycles at 0.2C and remains as high as 86% at a higher discharge rate of 0.5C (~0.5 A) over subsequent 100 cycles.



Figure 4.44 Galvanostatic charge/discharge curves of the as-fabricated pouch cell at -25 °C.



Figure 4.45 Cyclability of the as-fabricated pouch cell at -25 °C.

Development of AFSMBs at the pouch cell level has rarely been reported in previous literature,^[159] especially operating at LT. Although the cell fabrication parameters like the electrolyte amount have yet to be optimized in the present study, such pioneering and encouraging results have demonstrated the great potential of G2/DOL in practical AFSMBs. The energy density is further estimated to be about 219 Wh kg⁻¹ (based on the total mass of electrodes including current collectors), which rivals 191 Wh kg⁻¹ of a commercial LiFePO₄//graphite LIB (see Table 4.3 for details). At a low temperature of -25 °C, as-fabricated AFSMBs still deliver a high energy density of 185 Wh kg⁻¹, almost twice that of the LiFePO₄//graphite cell (99.8 Wh kg⁻¹). Therefore, this work is expected to pave the way for practical high-energy and long-life rechargeable Na batteries that are durably operating at LT.

	LiFePO ₄ //G ¹	LiFePO ₄ //G	AFSMB	AFSMB –25
	25 °C	−25 °C	25 °C	°C
Capacity (Ah)	1.56	0.87 ²	1.22	1.06
Discharge volage plateau (V)	3.2	3.0	3.36	3.30
Active material mass of cathode (g)	11.58 ³		12.8	
Mass of cathode (g)	14.28 4		16.55	
Active material mass of anode (g)	6.93		0	
Mass of anode (g)	11.8	36 ⁵	2	2.36
Specific energy density (Wh kg ⁻¹) ⁶	191.0	99.8	219.4	185.0

Table 4.3 Specific energy density comparison between the AFSMB pouch cell in this work and commercial LiFePO₄//graphite (G) cell at 25 °C and -25 °C.

Notes:

1) The commercial LiFePO₄//G cell consists of six layers of double-layer-coated LiFePO₄ electrode (areal mass loading of 28 mg cm⁻²), five layers of the double-layer-coated graphite electrode (areal mass loading of 14.56 mg cm⁻²) and two layers of the single-layer-coated graphite electrode (mass loading of 7.28 mg cm⁻²). The N/P ratio of this cell is controlled to be 1.33.

2) The capacity retention of LiFePO₄//G cells at -25 °C was calculated based on the literature reported by Ouyang's group.^[258]

3) The calculation of electrode mass, capacity, and energy density of LiFePO₄//G cells was based on commercial LiFePO₄ cathode and graphite anode films from MTI Co., Ltd. (see the details in https://www.szkejing.com/detail-4144.html, https://www.szkejing.com/detail-4138.html).

4) Aluminum foil with an areal mass loading of 4.15 mg cm^{-2} is used as the cathode current collector.

5) Copper foil with an areal mass loading of 8.7 mg cm^{-2} is used as the anode current collector.

6) The specific energy was calculated based on the total mass of electrodes including current collectors.

4.7 Summary

In this part of the research, a record-high Na plating/stripping CE beyond 99.9% at ultralow temperatures has been achieved by restructuring the solvation of the conventional NaPF₆–G2 electrolyte with a versatile diluent of DOL. The DOL dilution in the glyme-based electrolyte boosts remarkably high Na⁺ ion conductivity and decreases the energy barrier for desolvation. The LUMO energy level distributions in the solvates have also been efficiently altered with an electron cloud concentrated around PF_6^- for their preferential decomposition. An inorganic-rich SEI with compositional uniformity, high ionic conductivity, and high Young's modulus is thus generated. High exchange current densities at anodic interfaces have been realized and well maintained at LT, rendering uniform Na deposition and highly reversible Na plating/stripping. A practical 1-Ah level pouch cell delivers 95% of the initial capacity over 100 cycles at -25 °C and a high energy density almost twice that of the commercial LiFePO₄/graphite cell. It thus sheds new light on solvation structure regulation toward ultrahigh Na reversibility for practically viable AFSMBs operating at LT.

Chapter 5

High Voltage Sodium Metal Batteries Induced by Cyclic Ether Solubilization

5.1 Introduction

The energy density of a rechargeable battery system is determined by both the charge storage capacity of the positive/negative electrodes and their work potential difference.^[259] For SMBs, the Na metal anode operates at the lowest potential versus Na⁺/Na. Therefore, boosting the work potential of the positive electrode could be effective in improving the energy density of SMBs.^[259] The Na₃V₂(PO₄)₃ cathode employed in Chapter 4 possesses a relatively low voltage plateau at 3.4 V *vs.* Na⁺/Na, achieving an energy density of 219 Wh kg⁻¹. The Na₃V₂O₂(PO₄)₂F cathode is reported to possess higher voltage plateaus at 3.6 V and 4.0 V *vs.* Na⁺/Na is utilized.^[52] However, the elevated charging cut-off voltage necessitates better oxidation stability of the electrolyte.

Carbonate-based electrolytes own excellent high-voltage stability against oxidation and have been widely employed in commercial LIBs. Nonetheless, their high reactivity with sodium metal poses a significant challenge for SMBs.^[175, 176] It results in the formation of unstable SEI and thus low Na plating/stripping CE of below 90%.^[65, 177, 178] Ether-based electrolytes are highly compatible with Na metal anodes,^[75, 165]. However, their applications in high-voltage SMBs remain limited because of the relatively low HOMO energy levels.^[165, 167]

Increasing salt concentration to form a high-concentration electrolyte has been proven effective in decreasing solvent activity and enhancing the oxidative stability of electrolytes in rechargeable Li/Na batteries.^[237, 260-264] However, concentrating ether electrolytes based on fluorine-rich sodium salts, such as NaPF₆ and NaBF₄, is extremely challenging because of their high lattice energies and, thus, limited solubility in ether solvents.^[96] This study reveals a unique solubilization effect of cyclic ethers, which significantly enhances the solubility of NaPF₆ in a conventional linear ether solvent of diethylene glycol dimethyl ether (G2). The introduction of solubilizing DOL co-solvent into the NaPF₆–G2 electrolyte promotes the coordination of G2 solvent with Na⁺ and decreases the free G2 solvent ratio. It also induces the formation of abundant CIP and AGG solvates toward stable NaF-rich CEI generation. Both factors significantly eliminate the decomposition reaction at high-voltage battery operation. More intriguingly, the as-obtained

electrolyte shows a relatively low viscosity, ensuring fast Na^+ ion mobility and thus smooth charge transfer kinetics during charge/discharge. The as-fabricated $Na/Na_3V_2O_2(PO_4)_2F$ cell can retain 89.9% capacity over 2000 cycles at a high operation voltage of 4.4 V as discussed subsequently.

5.2 Physicochemical properties of cyclic ether solubilized electrolyte

Fluorine-rich sodium salts, such as NaPF₆ and NaBF₄, when paired with proper ether solvents, could obtain advanced electrolytes with high Na plating/stripping CE.^[75, 165] To further improve their high-voltage stability, increasing the electrolyte concentration could be an efficient approach. However, NaPF₆ and NaBF₄ salts show limited solubility in the ether solvents. Specifically, as shown in Figure 5.1a, 2.5 mol NaPF₆ salt cannot be fully dissolved in 1 mL G2 solvent. As a typical example, NaPF₆ can be dissolved in G2 until a saturation concentration of slightly less than 2.5 M. NaPF₆ salt cannot dissolve in a cyclic ether of DOL (less than 0.1 M, as shown in Figure 5.1b).

To overcome this solubility limit, a co-solvent with DOL and G2 was introduced. It can be observed that a 2.5 M of NaPF₆ G2/DOL electrolyte can be formed (v/v=3:1) with NaPF₆ salt fully dissolved in the mixed solvent (Figure 5.1c). Such observation reveals that the addition of DOL significantly enhances the solubility of NaPF₆ in G2 from slightly less than 2.5 M to nearly 3.3 M. To elucidate the mechanism behind DOL solubilization, a systematic investigation of the physicochemical properties of 2.5 M NaPF₆ G2 and 2.5 M NaPF₆ G2/DOL electrolytes was conducted.



Figure 5.1 Optical images of the three electrolytes: (a) $2.5 \text{ M NaPF}_6 \text{ G2}$, (b) $0.1 \text{ M NaPF}_6 \text{ DOL}$, and (c) $2.5 \text{ M NaPF}_6 \text{ G2/DOL}$. The white substance at the bottom of the bottle in (a) and (b) is undissolved NaPF₆.

5.2.1 Measurement of electrolyte viscosity

Figure 5.2 depicts the temperature-dependent viscosity of 2.5 M NaPF₆ G2 and 2.5 M NaPF₆ G2/DOL electrolytes. Notably, the viscosity of the 2.5 M NaPF₆ G2/DOL electrolyte (10.83 mPa·s) is only about one-third of the 2.5 M NaPF₆ G2 electrolyte (30.95 mPa·s) at 25 °C, despite that the two electrolytes have nearly the same concentration. This difference in viscosity becomes even more pronounced as temperature decreases. The 2.5 M NaPF₆ G2 electrolyte experiences a dramatic viscosity increase to over 200 mPa·s at 17 °C, probably because of recrystallization of the NaPF₆ salt. In contrast, the concentrated 2.5 M NaPF₆ G2/DOL electrolyte exhibits a much slower viscosity increase, reaching only 37.95 mPa·s at -10 °C. Such moderate viscosity allows for rapid Na⁺ ion mobility, which is important for high-rate and cold-climate battery applications.



Figure 5.2 Temperature-dependent viscosity of 2.5 M NaPF₆ G2 and 2.5 M NaPF₆ G2/DOL electrolytes.

5.2.2 Evaluation of Na⁺ ion conductivity

Na⁺ ion conductivity limits the current density achievable in a given SMB electrolyte. Here the ionic conductivities and Na⁺ ion transference numbers of 2.5 M NaPF₆ G2 and 2.5 M NaPF₆ G2/DOL electrolytes were tested according to the method described in Chapter 3. Figure 5.3 presents the ionic conductivities of 2.5 M NaPF₆ G2 and 2.5 M NaPF₆ G2/DOL electrolytes across a temperature range from -20 °C to 60 °C. Benefiting from its lower viscosity, the 2.5 M NaPF₆ G2/DOL electrolyte demonstrates superior ionic conductivities to 2.5 M NaPF₆ G2, especially at lower temperatures. At 20 °C the 2.5 M NaPF₆ G2/DOL electrolyte shows a high ionic conductivity of 6.21 mS cm⁻¹, higher than 5.58 mS cm⁻¹ of 2.5 M NaPF₆ G2. As it cools down to

0 °C and -20 °C, 2.5 M NaPF₆ G2 shows negligible ionic conductivities. In contrast, the 2.5 M NaPF₆ G2/DOL electrolyte maintains considerable ionic conductivities of 3.45 mS cm⁻¹ at 0 °C and 1.43 mS cm⁻¹ at -20 °C.



Figure 5.3 Temperature-dependent ionic conductivity of 2.5 M NaPF₆ G2 and 2.5 M NaPF₆ G2/DOL electrolytes.

The Na⁺ ion transference numbers (t_{Na+}) of two electrolytes were further estimated based on the Nyquist plots of symmetric Na//Na cells (Figures 5.4a–b) and the corresponding polarization curves (Figure 5.4c).^[191] According to Equation 2.10, t_{Na+} of the 2.5 M NaPF₆ G2/DOL electrolyte was determined to be 0.592, notably larger than 0.462 of the 2.5 M NaPF₆ G2 electrolyte. Correspondingly, the room temperature (RT = 25 °C) Na⁺ ion conductivity of 2.5 M NaPF₆ G2/DOL electrolyte was calculated to be 3.68 mS cm⁻¹, 43% higher than 2.58 mS cm⁻¹ of 2.5 M NaPF₆ G2 electrolyte. It reveals the significant role of DOL in improving the Na⁺ ion conductivity of the electrolytes.



Figure 5.4 Nyquist plots before (a) and after (b) the polarization process, and the polarization curves (c) of the symmetric Na//Na cells with the 2.5 M NaPF₆ G2 and 2.5 M NaPF₆ G2/DOL electrolytes.

5.2.3 Simulation of Na⁺ diffusion coefficient

Classical molecular dynamics (MD) simulations of 2.5 M NaPF₆ G2 and 2.5 M NaPF₆ G2/DOL electrolytes were conducted using the COMPASS II force field with optimized atom types and charges, as shown in Figure 5.5. The snapshots of these two electrolyte models after the equilibrium process are shown in Figure 5.6. By analyzing the mean-squared displacements of Na⁺ ions over a time interval of 3000 ps during the production run, the diffusion coefficient of Na⁺ ions in the 2.5 M NaPF₆ G2/DOL electrolyte was determined to be 1.17×10^{-10} m² s⁻¹, which is nearly twice that of the 2.5 M NaPF₆ G2 electrolyte (Figure 5.7). Such enhancement can be attributed to the shielding of the intermolecular attractions among linear G2 solvents by the cyclic DOL, which facilitates the rapid mobility of Na⁺-based solvates.



Figure 5.5 The force field types and the corresponding atomic charges of ions and molecules in the 2.5 M NaPF₆ G2 and 2.5 M NaPF₆ G2/DOL electrolytes.



Figure 5.6 Snapshots obtained from classical MD simulations of (a) 2.5 M NaPF₆ G2 and (b) 2.5 M NaPF₆ G2/DOL electrolytes.



Figure 5.7 The mean-squared displacements of Na^+ ions in 2.5 M NaPF₆ G2 and 2.5 M NaPF₆ G2/DOL electrolytes.

5.2.4 Evaluation of oxidation stability

The electrochemical oxidative stability of 2.5 M NaPF₆ G2 and 2.5 M NaPF₆ G2/DOL electrolytes was investigated through linear sweep voltammetry (LSV) tests of Na//Al cells. As Figure 5.8 shows, the onset of a significant increase in oxidation current density is observed at approximately 4.8 V for the G2 electrolyte. In contrast, the G2/DOL electrolyte maintains a low current density smaller than 1 μ A cm⁻² until 5.1 V. This difference demonstrates the enhanced oxidative stability of the G2/DOL electrolyte. The phenomenon that the decomposition current reaches a certain value and does not increase further may be because of the decomposition products covering the electrode surface.



Figure 5.8 Oxidation stability of 2.5 M NaPF₆ G2 and 2.5 M NaPF₆ G2/DOL electrolytes evaluated by linear sweeping voltammetry at a scanning rate of 50 μ V s⁻¹.

5.3 Solvation structure analysis

5.3.1 Free solvent ratio and solvation structures ratio

The solvation structures of 1 M NaPF₆ G2, 2.5 M NaPF₆ G2, and 2.5 M NaPF₆ G2/DOL electrolytes were analyzed quantitatively according to the coordination environments of Na⁺ ions within the final trajectory of the electrolyte models in MD simulations. Note that 1 M NaPF₆ G2, a benchmark electrolyte system for SMBs, was included to understand the impact of increased salt concentration on solvation structures. As the salt concentration increases, there is a noteworthy decrease in the free G2 solvent content from 69% in 1 M NaPF₆ G2 to 34.6% in 2.5 M NaPF₆ G2
(Figure 5.9), which further decreases to 23.8% in the 2.5 M NaPF₆ G2/DOL electrolyte. Elimination of free G2 in the G2/DOL electrolyte would attenuate the oxidative decomposition, thereby enhancing the high-voltage stability. Furthermore, the increased participation of G2 in solvation structures contributes to enhanced NaPF₆ solubility in the G2/DOL electrolyte compared to the G2 electrolyte with the same concentration.



Figure 5.9 Content of free G2 solvent in 1 M NaPF₆ G2, 2.5 M NaPF₆ G2, and 2.5 M NaPF₆ G2/DOL electrolytes calculated from MD simulations.

Figure 5.10 presents the proportion of solvent-separated ion pairs (SSIP), CIPs, and AGGs in three electrolytes. The 1 M NaPF₆ G2 electrolyte exhibits a predominance of SSIP solvates (92.5%) and negligible proportions of CIP/AGG solvates. Increasing the salt concentration to 2.5 M leads to a decrease in SSIP (77%) and a concomitant rise in CIP/AGG species. The elevation of salt concentration to 2.5 M precipitates a reduction in SSIP content to 77% and a simultaneous escalation in CIP/AGG proportions. This trend becomes even more pronounced in the 2.5 M NaPF₆ G2/DOL electrolyte, where the SSIP content further decreases to 68%. The higher ratio of anion-paired solvates induces anion-derived electrolyte-electrode interphases with inorganic-rich components and improved high-voltage stability.^[163] Moreover, the types of CIP solvates differ in the 2.5 M NaPF₆ G2 electrolyte (Na⁺–PF₆⁻–2G2), and the 2.5 M NaPF₆ G2/DOL electrolyte (Na⁺–PF₆⁻–1G2–1DOL). The involvement of DOL in the CIP ion pairs would alter the electronic structure and electrochemical stability, which will be discussed in detail subsequently.



Figure 5.10 SSIP, CIP, and AGG solvate ratios in 1 M NaPF₆ G2, 2.5 M NaPF₆ G2, and 2.5 M NaPF₆ G2/DOL electrolytes calculated from MD simulations.

To gain further insight into the formation pathway of electrolyte electrode interphases, the HOMO and LUMO energy levels of the solvated complexes, free solvents, and anion were evaluated through DFT calculations (Figure 5.11). It is well known that as the HOMO energy level increases, the electrolyte component becomes more susceptible to oxidation.^[215] Free G2 solvent can be found to possess the highest HOMO energy level (-5.88 eV), indicating the importance of coordinating more G2 solvents in the solvates for improved oxidative stability of electrolytes. Moreover, the Na⁺-PF₆⁻-1G2-1DOL complex in the 2.5 M NaPF₆ G2/DOL electrolyte shows a lower HOMO energy level of -6.37 eV than -6.07 eV of the Na⁺-PF₆⁻-2G2 complex in the 2.5 M NaPF₆ G2 electrolyte. It suggests that the participation of DOL in the CIP solvate alters the electronic structure and enhances its stability against oxidation.



Figure 5.11 HOMO and LUMO energy levels of the solvents, Na^+ ion, PF_6^- anion, and solvated complexes in three studied electrolytes.

5.3.2 Coordination numbers

To realize quantitative analysis of the electrolyte solvation structures, the Na⁺ ion coordination numbers (CN) within the solvation sheath were determined by integrating the radial distribution function (RDF), as described in Section 3.3.5. Figure 5.12 presents the RDF curves and corresponding CN values for 1 M NaPF₆ G2, 2.5 M NaPF₆ G2, and 2.5 M NaPF₆ G2/DOL electrolytes. The prominent Na–O (G2) peaks identified in all three electrolytes reveal the prevalence of SSIP species. The elevation of NaPF₆ G2 concentration from 1 M to 2.5 M induces a decrease in the Na–O (G2) coordination number from 5.9 to 5.4. Simultaneously, it leads to an increase in the CN value of Na–F from 0.2 to 1.1. It accords well with the above MD simulation results of decreasing SSIP content and increasing CIP/AGG content at higher concentrations.

The 2.5 M NaPF₆ G2/DOL electrolyte exhibits a higher Na–F CN of 1.6 than 1.1 of the 2.5 M NaPF₆ G2 electrolyte, which should arise from its higher CIP/AGG ratios and the unique CIP solvation structure. In the NaPF₆ G2 electrolyte, the dominant CIP structure is Na⁺–PF₆⁻–2G2, with a Na–F CN of 2. In contrast, the NaPF₆ G2/DOL electrolyte favors a Na⁺–PF₆⁻–1G2–1DOL CIP structure with a Na–F CN of 3. The weakly solvating DOL in the solvation sheath facilitates the coordination between Na⁺ and PF₆⁻.

To gain further insights into the coordination strength, the Na⁺–solvent interatomic distance in the SSIP, CIP, and AGG solvates were estimated (Figure 5.13). The average Na–O (G2) interatomic distance for typical SSIP (Na⁺–2G2), CIP (Na⁺–1PF₆⁻–2G2), and AGG (Na⁺–2PF₆⁻– 1G2) solvates are determined to be 2.44 Å, 2.45 Å, and 2.53 Å, respectively. It reveals the weakened Na⁺–solvent interactions upon anion participation in the solvation sheath. Notably, the CIP solvate involving DOL (Na⁺–PF₆⁻–1G2–1DOL) exhibits an average interatomic distance of 2.92 Å for Na–O (DOL), revealing the weak coordination of DOL with Na⁺ ions.



Figure 5.12 Na⁺ radial distribution functions (a–c) and the coordination numbers (d–f) in three investigated electrolytes obtained from MD simulations.



Figure 5.13 The interatomic distances of Na⁺-solvent in the SSIP, CIP, and AGG solvates.

5.3.3 Raman spectroscopy

Raman spectroscopy was employed to provide further information of the electrolyte solvation structures. Figure 5.14 displays the Raman spectra of 1 M NaPF₆ G2, 2.5 M NaPF₆ G2, and 2.5 M NaPF₆ G2/DOL electrolytes, along with their components. The G2 solvent exhibits two characteristic peaks at 805 cm⁻¹ and 850 cm⁻¹, representing the CH₂ rocking and C–O stretching vibration, respectively.^[240, 241] This peak at 850 cm⁻¹ undergoes a significant blue shift of 20 cm⁻¹ in all three electrolytes, indicative of strong coordination between G2 molecules and Na⁺ ions. In contrast, DOL displays a smaller blue shift from 938 cm⁻¹ for the free solvent to 941 cm⁻¹ for the coordinated solvent in the NaPF₆ G2/DOL electrolyte. It suggests a weaker binding between the DOL molecules and Na⁺ ions, corroborating the relatively large Na–O interatomic distance.^[237, 242] Both findings underscore the weaker solvating ability of the DOL solvent compared to G2. Furthermore, the symmetric stretching vibration (a_{1g}) mode of PF₆⁻ anion shifts from 765 cm⁻¹ in three electrolytes, attributed to the decreased coordination between PF₆⁻ and Na⁺ ions upon salt dissociation.^[243]



Figure 5.14 Raman spectra of 1 M NaPF₆ G2, 2.5 M NaPF₆ G2, and 2.5 M NaPF₆ G2/DOL electrolytes and their components.

Figure 5.15 presents the fitted Raman peaks of G2 in three electrolytes and the bare G2 solvent. The peaks at 805 cm⁻¹ and 850 cm⁻¹ correspond to free G2 molecules, while the peaks at 840 cm⁻¹ and 870 cm⁻¹ correspond to the solvated G2 molecules. The ratio of free to solvated G2 molecules in the three electrolytes can be determined by the area ratio of the characteristic peaks at 850 cm⁻¹ and 870 cm⁻¹. The calculated percentage of free G2 molecules in the 2.5 M NaPF₆ G2/DOL electrolyte is 21.7%, significantly lower than the 42% in the 2.5 M NaPF₆ G2 electrolyte and 56% in the 1 M NaPF₆ G2. These results align with the findings from MD simulations. The decrease of free G2 in the G2/DOL electrolyte attenuates its decomposition, thereby enhancing the overall oxidative stability of the electrolyte.



Figure 5.15 The fitted Raman peaks of free G2 solvent (purple and cyan peaks) and solvating G2 (yellow and orange peaks) in three electrolytes and G2 solvent.

5.4 Electrode-electrolyte interphase characterization

5.4.1 Cathode-electrolyte interphase characterization

The surface chemistry and compositional depth profile of the as-formed CEI on the $Na_3V_2O_2(PO_4)_2F$ cathode were studied using X-ray photoelectron spectroscopy (XPS) with Ar⁺ sputtering. Figures 5.16–5.18 present the normalized high-resolution F 1s, Na 1s, and C 1s XPS spectra obtained at various sputtering depths. Notably, the CEI formed in the NaPF₆ G2/DOL electrolyte exhibited a more pronounced NaF peak at 684.5 eV in the F 1s spectra compared to that in the NaPF₆ G2 electrolyte, both at the surface and after 10 s and 120 s of sputtering. This finding indicates a higher concentration of NaF within the CEI formed in the NaPF₆ G2/DOL system. NaF is known to be a beneficial CEI component because of its electrolyte. Moreover, its high Young's modulus helps suppress volume changes, while its large surface energy facilitates Na⁺ ion diffusion. The P–F peak at 688.4 eV can be attributed to Na_xPO_yF_z/Na_xPF_y species from PF₆⁻ decomposition.^[75] The intensity continuously decreases with increasing sputtering time in both electrolytes, suggesting its surface-enriched distribution within the CEI.



Figure 5.16 The in-depth XPS F 1s spectra of CEI formed in two electrolytes.

The C 1s XPS spectra of the CEI surface in two electrolytes exhibited similar patterns. The deconvoluted C1s spectra are shown in Figure 5.17 with fitted C–C (284.8 eV), C–H (285.4 eV), C–O–C (286.9 eV), –COOR (288.4 eV), and C–F (291.5 eV) peaks. These organic species are consistent with the decomposition products of the ether electrolytes as reported in the literature.^[265] Interestingly, the relative intensities of the C–C and C–H peaks evolved differently with increasing sputtering depth for the CEI formed in the two studied electrolytes. In the NaPF₆ G2 electrolyte, the C–C peak intensity decreased while the C–H peak intensity increased quickly, reaching almost the same value after 10 s of sputtering. As sputtering continues, the C–H peak becomes dominant. For the NaPF₆ G2/DOL electrolyte, this evolution was significantly slower with the C–C and C–H peak intensities reaching the same level after 120 s of sputtering. Such differences should come from the distinct solvation structures and solvent-derived organic species in CEI.

The Na 1s XPS spectra at the CEI surface (0 s of sputtering) revealed the presence of both organic (RCOONa) and inorganic (Na₂O, NaF) sodium species (Figure 5.18). In both electrolytes, the NaF peak intensity increased with sputtering depth, while the Na₂O peak intensity decreased. This suggests a gradient distribution of these inorganic species within the CEI film. In addition, the NaPF₆ G2/DOL electrolyte consistently exhibited a higher NaF peak intensity compared to the NaPF₆ G2 electrolyte at all depths, confirming the enhanced presence of NaF in the formed CEI.



Figure 5.17 The in-depth XPS C 1s spectra of CEI formed in two electrolytes.



Figure 5.18 The in-depth XPS spectra (Na 1s) of CEI formed in two electrolytes.

5.4.2 Analysis of exchange current density

To further elucidate the difference between the two studied electrolytes on the interfacial electrontransfer kinetics during Na plating/stripping, the exchange current density (j_0) was evaluated using symmetric Na//Na cells. Note that accurate j_0 determination relies on obtaining a well-defined linear region in the cyclic voltammetry (CV) curve. However, the Na//Na cell using the 2.5 M NaPF₆ G2 electrolyte did not exhibit a typical linear CV response within a voltage window of -100mV to 100 mV (Figure 5.19). A peak current was observed at approximately 60 mV, followed by a decrease in current with increasing voltage. This non-linear behavior suggests significant mass transport resistance within the 2.5 M NaPF₆ G2 electrolyte at overpotentials exceeding 60 mV, probably owing to the limited Na⁺ ion conductivity in this electrolyte.^[112, 266, 267] Consequently, the voltage range for Tafel analysis was constrained within -50 mV to 50 mV to ensure a reliable linear CV response. Based on this analysis, the j_0 values for the NaPF₆ G2 and NaPF₆ G2/DOL electrolytes were determined to be 0.36 mA cm⁻² and 0.44 mA cm⁻², respectively (Figure 5.20). The higher j_0 value observed in the NaPF₆ G2/DOL electrolyte suggests that the introduction of DOL solvent in the NaPF₆–G2 electrolyte system facilitates faster interfacial charge transfer kinetics.



Figure 5.19 The cyclic voltammogram curves of symmetric Na//Na cells using 2.5 M NaPF₆ G2 and 2.5 M NaPF₆ G2/DOL electrolytes.



Figure 5.20 Tafel plots in the 2.5 M NaPF₆ G2 and 2.5 M NaPF₆ G2/DOL electrolytes.

5.5 Electrochemical performance evaluation

5.5.1 Na plating/stripping reversibility

High Na plating/stripping reversibility at high current rates is a prerequisite for practical applications of SMBs. To investigate the Na reversibility in 2.5 M NaPF₆ G2 and 2.5 M NaPF₆ G2/DOL electrolytes, Na//Al cells were assembled and tested. As depicted in Figure 5.21a, the 2.5 M NaPF₆ G2 system exhibits a quick voltage drop when the Na plating capacity is less than 0.25 mAh even at a small plating current density of 0.25 mA cm⁻², indicating failure of the Na//Al cells. It is most probably attributed to the low Na⁺ ion conductivity in the electrolyte and thus large internal impedance upon discharge. In contrast, the 2.5 M NaPF₆ G2/DOL system showed a smooth Na plating/stripping with low polarization voltages of 13 mV (Figure 5.21b), suggesting its relatively fast charge transfer kinetics.



Figure 5.21 Voltage profiles of Na//Al cells with 2.5 M NaPF₆ G2 electrolyte (a) and 2.5 M NaPF₆ G2/DOL electrolyte (b) at 0.25 mA cm⁻².

It can also be seen that the NaPF₆ G2/DOL system demonstrated exceptional cycling stability, maintaining an impressive average CE value of 99.9% over 200 cycles at 0.5 mA cm⁻², 1 mAh cm⁻² (Figure 5.22a). The corresponding plating/stripping profiles at the 1st and 200th cycles (Figures 5.22b–c) reveal a minor increase in plating (from 22 mV to 25 mV) and stripping (from 20 mV to 27 mV) overpotentials. It again confirms the excellent Na plating/stripping reversibility with long cycling stability.



Figure 5.22 (a) Cycling stability of Na//Al cells with 2.5 M NaPF₆ G2/DOL electrolyte. The corresponding plating and stripping voltage profiles at the 1^{st} cycle (b) and 200th cycle (c) at 0.5 mA cm⁻².

5.5.2 Electrochemical performances of high-voltage SMBs

Na//Na₃V₂O₂(PO₄)₂F half-cells with 2.5 M NaPF₆ G2 and 2.5 M NaPF₆ G2/DOL electrolytes were assembled to evaluate the comprehensive electrochemical performances. The cells were cycled at 1 C after three formation cycles at 0.5 C with an upper voltage limit of 4.4 V *vs.* Na⁺/Na. Remarkably, the SMBs with NaPF₆ G2/DOL electrolyte realized an initial CE of 91.8% and an average CE of 99.7% over 500 cycles.



Figure 5.23 CE comparison of $Na/Na_3V_2O_2(PO_4)_2F$ half-cells with 2.5 M $NaPF_6$ G2 and 2.5 M $NaPF_6$ G2/DOL electrolytes.

In contrast, the SMBs with NaPF₆–G2 electrolyte exhibited a lower initial CE of 89.6% and a lower average CE of 99.5% (Figure 5.23). Figure 5.24 demonstrates the excellent long-term galvanostatic cycling performances of SMB with 2.5 M NaPF₆ G2/DOL electrolyte, achieving an

average CE of 99.7%, an initial capacity of 111.2 mAh g^{-1} , and a capacity retention of 89.9% over an extended 2000 cycles at 1C with a high charging cut-off voltage of 4.4 V.



Figure 5.24 Long-term galvanostatic cycling performances of $Na//Na_3V_2O_2(PO_4)_2F$ half-cells with 2.5 M NaPF₆ G2/DOL electrolyte.

The rate performances of two SMB systems were conducted at varying rates from 0.5 C to a high rate of 9 C (Figure 5.25). At lower C-rates of 0.5 C and 1 C, both cells with two electrolytes demonstrated comparable capacities. However, a significant divergence emerged at higher C-rates. At 3C, the cells with NaPF₆ G2 electrolyte experienced a drastic capacity decline, dropping to less than 40 mAh g⁻¹ with substantial fluctuations. It can be attributed to the higher viscosity and lower Na⁺ ion conductivity of the NaPF₆ G2 electrolyte, which hinders efficient ion transport at high rates. In contrast, the cells with the NaPF₆ G2/DOL electrolyte delivered a significantly higher capacity of 66.6 mAh g⁻¹ at 3C. Even at a high rate of 9C, the NaPF₆ G2/DOL system delivered a notable capacity of 31.9 mAh g⁻¹, revealing its great capability for high power output.

Figure 5.26 compares the temperature-dependent galvanostatic cycling performances of two SMB systems with 2.5 M NaPF₆ G2 and 2.5 M NaPF₆ G2/DOL electrolytes. At 25 °C and 0.5C, the two systems deliver comparable initial capacities of 104.9 mAh g^{-1} and 100.8 mAh g^{-1} , respectively. Decreased discharge capacities are shown as the cells are sequentially cooled. As the temperature is decreased to 10 °C, the NaPF₆ G2/DOL system maintains 90% of the initial capacity, significantly higher than 68% of the NaPF₆ G2 system. At an even lower temperature of 0 °C, the NaPF₆ G2/DOL system still retains 50% capacity, over twice that of the NaPF₆ G2 system. When

it reheats to 25 °C, the specific capacity can be fully recovered, showcasing the superior resilience to drastic temperature change.



Figure 5.25 Rate performance of Na//Na₃V₂O₂(PO₄)₂F half-cells with 2.5 M NaPF₆ G2 and 2.5 M NaPF₆ G2/DOL electrolytes.



Figure 5.26 Temperature-dependent galvanostatic cycling performances of $Na/Na_3V_2O_2(PO_4)_2F$ half-cells with 2.5 M NaPF₆ G2 and 2.5 M NaPF₆ G2/DOL electrolytes at 0.5C.

To evaluate the practical feasibility of the 2.5 M NaPF₆ G2/DOL electrolyte, full cells were assembled using Na₃V₂O₂(PO₄)₂F cathodes and limited Na anodes. The Na anodes were prepared in advance by depositing sodium metal on Al/C current collectors in Na//Al cells, with the amount of deposited sodium metal precisely controlled by adjusting current density and deposition time. The resulting negative/positive areal capacity ratio (N/P ratio) was 7.68:1. After three formation

cycles at 0.5C, the full cells were cycled at 1 C with an upper voltage limit of 4.4 V *vs*. Na⁺/Na. As shown in Figure 5.27, an average CE of 99.6% and a capacity retention of 89.9% were achieved over 300 cycles.



Figure 5.27 Long-term galvanostatic cycling performances of Na//Na₃V₂O₂(PO₄)₂F full cells with limited Na anode at 1C using 2.5 M NaPF₆ G2/DOL electrolyte.

5.6 Summary

This part of the research boosted the high-voltage stability of SMBs through DOL solubilization. The introduction of solubilizing DOL co-solvent into the NaPF₆–G2 electrolyte effectively regulates the solvation structure. First, it promotes the coordination of G2 solvent with Na⁺, increasing the solubility of NaPF₆ salt and decreasing the free G2 solvent ratio. Second, it induces more anion participation in the solvation sheath toward forming stable NaF-rich CEI. Both factors benefit electrochemical stability against high-voltage oxidation at the cathode interface. Third, the introduction of DOL in the solvation sheath helps shield the intermolecular attractions of G2, leading to a moderate electrolyte viscosity even at a high concentration of 2.5 M. Rapid Na⁺ ion mobility has thus been realized to ensure smooth charge transfer kinetics during charge/discharge cycles. Consequently, the as-fabricated Na//Na₃V₂O₂(PO₄)₂F cell using the 2.5 M NaPF₆ G2/DOL electrolyte maintains 89.9% capacity over 2000 cycles at a high charging cut-off voltage of 4.4 V. The results offer new insights for ether electrolyte formulation toward practical high-voltage SMBs.

Chapter 6

Highly Reversible High Voltage Anode-Free Sodium Metal Batteries Enabled by Crown-like Electrolyte Solvation

6.1 Introduction

The initial anode-free sodium metal batteries (AFSMB) pairing a Na-containing cathode and a bare Al current collector promise a maximized energy density among rechargeable sodium batteries. Ether-based electrolytes have demonstrated great potential for Na plating/stripping CE exceeding 99.9%,^[75, 165, 268] which is a prerequisite for practical applications of AFSMB. However, their high-voltage operation is severely hindered by the relatively low HOMO energy levels of ether solvents. For instance, a 1 M NaBF₄ G4 electrolyte was reported by Le and co-workers to achieve Na plating/stripping CE of 99.9%, but the as-fabricated Na//P2-Na_{2/3}Co_{1/3}Mn_{2/3}O₂ cells retained only 70% capacity after 100 cycles with an upper voltage limit of 4.2 V vs. Na⁺/Na.^[165]

Beyond sacrificing additives, there are two primary strategies for boosting the oxidative stability of ether electrolytes: increasing the electrolyte concentration and solvent engineering. Concentrating the electrolyte decreases the proportion of free ether solvents, which are normally most susceptible to oxidation. It also induces more anion participation in the solvation sheath toward a more stable inorganic-rich CEI. For instance, it has been demonstrated in the previous chapter that the solubilizing DOL increases electrolyte concentration and improves the charge/discharge reversibility of the cathode at high operation voltages. Solvent engineering involves molecular structure regulation of solvents, such as optimizing the structure of alkyl groups in solvent molecules,^[181, 182] decreasing the ether oxygen atom content in solvent molecules,^[184, 183] and atom substitution of the solvent molecules with halogen atoms or halogen groups.^[184-186] While improving oxidative stability, these modifications weaken the ability of solvents to dissolve salts and decrease electrolyte ionic conductivity. Furthermore, fluorinated solvents have high costs and pose potential environmental hazards.^[188]

This part of the work demonstrates the stabilization of the ether electrolyte at high operation voltages by forming a crown-like solvation structure. It enables the coordination of active oxygen atoms in the ether solvent with Na⁺ ions. Unlike the above-mentioned solvent engineering strategies, this new approach avoids the weakened salt dissociation and assures smooth Na⁺

mobility. Its efficacy in high-voltage stabilization has been showcased by a comparative study of two electrolytes, 1M NaPF₆ in tetraethylene glycol dimethyl ether (G4) with abundant crown-like solvates and 1M NaPF₆ in diethylene glycol dibutyl ether (DEGDBE) with none. The high-voltage reversibility of the cathode can be enhanced by using NaBF₄ to replace NaPF₆, which produces more favorable B-containing CEIs. Moreover, further concentrating the electrolyte to 2.5 M NaBF₄ in G4 results in more crown-like solvates and boosts the charge/discharge CE to a record-high 99.9%. Consequently, the high-voltage Na₃V₂O₂(PO₄)₂F cathode delivers 95.5% capacity over 1000 cycles. Fabricated AFSMB shows a superior cycling performance of 94% over 200 cycles at 1 C. More details will be presented and discussed in this chapter.

6.2 Characterization of crown-like solvation structure

Electrolyte solvation structure plays a critical role in regulating the ionic conducting property in the bulk electrolyte and the desolvation kinetics at the sodium metal surface. It also determines the electrolyte decomposition pathway and the electrode/electrolyte interphases in terms of the component, structure, and electrochemical property. Experimental techniques and theoretical simulations are combined to gain detailed kinetic and thermodynamic insights into the properties of electrolytes studied.

Classical molecular dynamics (MD) simulations were employed to investigate the solvation structures of 1 M NaPF₆ DEGDBE and 1 M NaPF₆ G4 electrolytes first. Electrolyte models were constructed using the COMPASS II force field with optimized atom types and charges (Figures 6.1 and 6.2). To accurately represent ion-ion and ion-dipole interactions, the charges of Na⁺ and PF_6^- ions were scaled by a factor of 0.8.^[208, 269, 270] All simulation cells underwent an equilibration process to obtain the equilibrium structure. It includes three stages of constant number, volume, and temperature (NVT) simulations for the pre-equilibrium, equilibrium, and production run.



Figure 6.1 The force field types and the corresponding atomic charges of ions and molecules in the 1 M NaPF₆ DEGDBE and 1 M NaPF₆ G4 electrolytes.



Figure 6.2 Snapshots obtained from classical MD simulations of (a) 1 M NaPF₆ DEGDBE and (b) 1 M NaPF₆ G4 electrolytes.

Radial distribution functions (RDF) and coordination numbers (CN) between the Na⁺ ions and coordinated atoms in the studied electrolyte were evaluated based on the equilibrium electrolyte models (Figure 6.3). In the 1 M NaPF₆ DEGDBE electrolyte, prominent Na–F and Na–P peaks in the RDF can be observed with corresponding high CN values of 3.9 and 1.3, respectively. It indicates the strong interaction in Na⁺-PF₆⁻ ion pairs. And the CN value of Na–O (DEGDBE) was 3.6. In contrast, the NaPF₆ G4 electrolyte exhibited a significantly higher Na–O (G4) CN value of 5.9. The weaker Na–F and Na–P peaks also correspond to lower CN values of 1.4 and 0.5, respectively, indicating less involvement of anion in the solvation sheath.



Figure 6.3 The Na⁺ radial distribution functions of (a) 1 M NaPF₆ DEGDBE and (b) 1 M NaPF₆ G4 electrolytes. The corresponding coordination numbers of (c) 1 M NaPF₆ DEGDBE and (d) 1 M NaPF₆ G4 electrolytes.

This disparity in the solvation structure stems from the larger number of ether oxygen atoms in G4 compared to DEGDBE, which facilitates coordination with Na⁺ ions and promotes the formation of crown-like structures, as shown in Figure 6.4. Consequently, a significant difference in solvation structure distribution arises between the two electrolytes. The 1 M NaPF₆ DEGDBE electrolyte exhibits a SSIP, CIP, and AGG ratio of 22:15:63. In contrast, the 1 M NaPF₆ G4 electrolyte demonstrates much more SSIP and less AGG with the corresponding SSIP/CIP/AGG ratio of 55:43:2 (Figure 6.5). Note that CIPs are neutrally charged and do not transfer charge. AGGs, although being charged, their large solvate size typically leads to sluggish ionic conduction. Therefore, the high proportion of SSIPs in the NaPF₆ G4 electrolyte, compared to the dominant CIP and AGG solvates in the NaPF₆ DEGDBE electrolyte, correlates with the observed superior Na⁺ ion conductivity.



Figure 6.4 Typical solvation structures in (a) 1 M NaPF₆ DEGDBE and (b) 1 M NaPF₆ G4 electrolytes.



Figure 6.5 SSIP, CIP, and AGG solvation ratios in 1 M NaPF₆ DEGDBE and 1 M NaPF₆ G4 electrolytes calculated from MD simulation results.

Raman spectroscopy was further employed to probe the electrolyte solvation structures. Figure 6.6a presents the Raman spectra of the electrolytes and their individual components. The broad peaks observed between 780–870 cm⁻¹ in the NaPF₆–G4 electrolyte and pure G4 solvent are attributed to –CH₂ rocking, the –CH₂OCH₂– stretching, and terminal –CH₂OCH₃ vibrations of the G4 solvent. Similarly, the broad peaks between 790–855 cm⁻¹ in the NaPF₆ DEGDBE electrolyte and pure DEGDBE solvent correspond to the –CH₂ rocking and the –CH₂OCH₂– stretching modes of DEGBDE solvent. Notably, the symmetric stretching vibration (a_{1g}) mode of PF₆⁻ anion undergoes a red shift from 765 cm⁻¹ in pure NaPF₆ salts to ~740 cm⁻¹ in both electrolytes. This shift indicates decreased coordination between PF₆⁻ and Na⁺ ions upon electrolyte dissociation.^[243]



Figure 6.6 (a) Raman spectra of the studied electrolytes and corresponding components. Enlarged view of the characteristic peaks of (b) DEGDBE and (c) G4 solvents.

Figures 6.6 b,c provide enlarged views of the characteristic peaks for DEGDBE and G4 solvents, respectively. The dominance of these peaks in the Raman spectra reveals the existence of abundant free solvents in two electrolytes. Notably, a new peak emerged at ~867.9 cm⁻¹ in the NaPF₆ G4 electrolyte, aligning with the characteristic Raman band at ~870 cm⁻¹ in binary mixtures of crown ethers and alkali metal salts. This band, attributed to the "ring breathing mode" arising from the combination of $-CH_2$ rocking and $-CH_2OCH_2$ - stretching modes of the coordinated ether molecules, signifies the formation of crown ether-alkali metal ion complexes.^[271, 272] Therefore, it can be concluded that a crown-like Na⁺-G4 solvate is formed in the NaPF₆ G4 electrolyte.^[273, 274] In contrast, the absence of this peak in the NaPF₆ DEGDBE electrolyte indicates that the decreased number of ether oxygen atoms in DEGDBE solvent (three compared to five in G4 solvent) hinders the formation of such crown-like coordination complex.

6.3 Physicochemical and electrochemical properties of the as-formulated electrolytes

Figure 6.7 presents the ionic conductivities of both electrolytes across a temperature range of -20 °C to 60 °C, determined by resistance measurement of symmetric stainless-steel cells. The 1M NaPF₆ G4 electrolyte consistently exhibited higher ionic conductivity than the 1M NaPF₆ DEGDBE counterpart across all temperatures tested, with increasing disparity as the temperature increases. At -20 °C, the ionic conductivities were 0.37 mS cm⁻¹ for 1M NaPF₆ G4 and 0.10 mS cm⁻¹ for 1M NaPF₆ DEGDBE. This difference is enlarged to 5.49 mS cm⁻¹ for NaPF₆ G4 and 0.87 mS cm⁻¹ for 1 M NaPF₆ DEGDBE at 60 °C.



Figure 6.7 Temperature-dependent ionic conductivity of 1 M NaPF₆ DEGDBE and 1 M NaBF₄ G4 electrolytes.

Subsequently, the t_{Na+} values of the two electrolytes were further estimated based on the Nyquist plots of symmetric Na//Na cells and the corresponding polarization curves (Figure 6.8). According to Equation 2.10, the t_{Na+} values of 1 M NaPF₆ DEGDBE and 1 M NaPF₆ G4 electrolytes were determined to be 0.519 and 0.396, respectively. Correspondingly, the room temperature (RT = 25 °C) Na⁺ ion conductivity of 1 M NaBF₄ G4 electrolyte was calculated to be 1.13 mS cm⁻¹, which is about five times that of 0.22 mS cm⁻¹ of 1 M NaPF₆ DEGDBE electrolyte. The viscosity of G4 is higher than DEGDBE (see Table 6.1), meaning that the intermolecular attraction retarding Na⁺ mobility is stronger. Therefore, the much higher Na⁺ ion conductivity of 1 M NaPF₆ G4 electrolyte should be ascribed to its higher solvation level (55% SSIP).

Colvert	Melting	Boiling	Viscosity	Donor number	Dielectric
Solvent	point (°C)	point (°C)	(mPa·s)	$(kJ mol^{-1})$	constant (ε)
Diethylene glycol dibutyl ether (DEGDBE)	-60	256	2.3	-	-
Tetraglyme (TEGDME, G4)	-30	275	3.4	-	7.5

Table 6.1 Physicochemical properties of DEGDBE and G4 solvents.^[151]



Figure 6.8 Nyquist plots and the variation in current during the voltage bias process for the (a) 1 M NaPF₆ DEGDBE and (b) 1 M NaBF₄ G4 electrolytes.

Figure 6.9 shows the charge distributions within the DEGDBE and G4 solvent molecules revealed by electrostatic potential (ESP) maps. In both molecules, the ether oxygen atoms exhibit the lowest electrostatic potential because of lone pairs of electrons. DEGDBE and G4 molecules possess the same ether oxygen groups and identical molecular chain lengths. The primary structural distinction between DEGDBE and G4 lies in the number of these ether oxygen atoms present in each molecule.



Figure 6.9 Electrostatic potential maps of DEGDBE and G4 molecules.

Despite the high structural similarity between DEGDBE and G4 solvents, as-formulated two electrolytes exhibit remarkably different oxidative stabilities when evaluated against high-voltage $Na_3V_2O_2(PO_4)_2F$ cathodes. The $Na_3V_2O_2(PO_4)_2F$ //Na cells were cycled at 1 C with a charge cutoff voltage of 4.4 V *vs*. Na⁺/Na after three formation cycles at 0.5 C. As shown in Figure 6.10a, a decomposition plateau at 4.2 V *vs*. Na⁺/Na was observed for the cells using 1 M NaPF₆ DEGDBE electrolyte, indicating the oxidative decomposition of the DEGDBE solvent. In contrast, no obvious decomposition plateau was observed until 4.4V *vs*. Na⁺/Na for 1 M NaPF₆ G4 system. There is also a big difference in the long-term galvanostatic cycling performance (Figure 6.10b).

A CE lower than 90% and fast capacity decay were exhibited in the 1 M NaPF₆ DEGDBE system. In contrast, the 1 M NaPF₆ G4 system achieved a significantly higher average long-cycling CE of 99.7% and a capacity retention rate of 93.1% over 500 cycles.



Figure 6.10 (a) The charge-discharge curves and (b) long-term galvanostatic cycling performance of the $Na_3V_2O_2(PO_4)_2F/Na$ cells with the 1 M NaPF₆ DEGDBE and the 1 M NaPF₆ G4 electrolytes.

The formation of crown-like complexes facilitated by multivalent binding with ether oxygens is thermodynamically favored because of the strong enthalpic association. This configuration results in a lower free energy for the bound state than the unbound state.^[275] To gain deeper insights into this phenomenon, density functional theory (DFT) calculations were performed to analyze the HOMO energy levels of the solvation structures. Figure 6.11 illustrates the HOMO and LUMO energy levels of solvent molecules, anion, and solvated complexes. In the 1 M NaPF₆ DEGDBE electrolyte, the predominant solvation structure is the AGG (Na⁺–2PF₆⁻–DEGDBE) complex. Notably, the HOMO energy level of this complex is higher than that of the free DEGDBE solvent, indicating that the solvation process increases the susceptibility to oxidative decomposition. Conversely, in the 1 M NaPF₆ G4 electrolyte, AGGs are scarce, and the prevalent solvation structures are SSIP (Na⁺-2G2) and the CIP (Na⁺-PF₆⁻-1G4). These structures exhibit coordination between Na⁺ ions and 4-5 ether oxygen atoms of each G2 solvent, forming crown-like configurations. Importantly, the HOMO energy levels of the SSIP (Na⁺-2G4) and the CIP (Na⁺- PF_6 –1G4) solvate complexes are -6.18 eV and -6.13 eV, respectively, which are lower than that of the free G4 solvent of -6.00 eV. This observation suggests that the formation of crown-like structures enhances the oxidative stability of the G4 solvent.



Figure 6.11 HOMO and LUMO energy levels of solvent molecules, Na^+ ion, PF_6^- anion, and solvated complexes in 1 M NaPF₆ DEGDBE and 1 M NaPF₆ G4 electrolytes.

Furthermore, the Fukui functions of the solvated complexes in both electrolytes were calculated by DFT with some results shown in Figure 6.12. Fukui functions provide insights into the reactivity of a complex by quantifying the sensitivity of its electron density to changes in the total number of electrons. This analysis effectively maps the propensity for electron addition or removal at specific sites within the complex. Higher Fukui function values for electrophilic attack correlate with a greater susceptibility to electron loss and oxidation reaction. The results demonstrate that the ether oxygen and hydrogen atoms exhibit relatively high Fukui function values in all solvation structures, indicating their vulnerability as the primary sites for oxidation. Therefore, while the DEGDBE solvent in the dominated solvation structures of the NaPF₆ DEGDBE electrolyte exhibits increased susceptibility to oxidative decomposition compared to the pure solvent, the G4 solvent in the NaPF₆ G4 electrolyte demonstrates enhanced oxidative stability because of the formed crown-like solvation structures.



Figure 6.12 Oxidation reaction site prediction of solvation structures in 1 M NaPF₆ DEGDBE (a) and 1 M NaPF₆ G4 electrolytes (b) via Fukui function analysis.

6.4 Further improvement of high-voltage reversibility and mechanistic study

The crown-like structures of the G4 solvent enhance the oxidative stability of the 1 M NaPF₆ G4 electrolyte. An initial Coulombic efficiency (ICE) of 86.5%, a high average long-cycling CE of 99.7%, and a capacity retention rate of 93.1% over 500 cycles in the Na₃V₂O₂(PO₄)₂F//Na cells have been realized. However, long-life AFSMBs necessitate a high ICE and rapid CE stabilization at a high value to minimize sodium loss during the initial charge-discharge cycles.

6.4.1 Improvement of high-voltage reversibility by electrolyte optimization

To address this challenge, NaBF₄ was employed to replace NaPF₆, which may produce favorable boron-containing CEIs.^[182] Moreover, further concentrating the electrolyte to 2.5 M NaBF₄ in G4 results in more crown-like solvates and boosts the charge/discharge CE. The impact of this modification on oxidative stability was evaluated in the Na₃V₂O₂(PO₄)₂F//Na half-cells. After three formation cycles at 0.5 C, the cells were cycled at 1 C with a charge cutoff voltage of 4.4 V *vs*. Na⁺/Na. Notably, the cell utilizing 2.5 M NaBF₄ G4 electrolyte exhibited a higher ICE of 89.4% compared to 86.5% for the cell with 1 M NaPF₆ G4 electrolyte. Moreover, the 2.5 M NaBF₄ G4 electrolyte only reached 98.8%. This rapid CE stabilization in the 2.5 M NaBF₄ G4 electrolyte, as

depicted in Figure 6.13, highlights its potential for enhancing the long-term cycling performance of AFSMBs.



Figure 6.13 The Coulombic efficiency of SMBs within the first 50 cycles using 1 M NaPF₆ G4 and 2.5 M NaBF₄ G4 electrolytes.

6.4.2 Solvation structures and ion-conducting properties of electrolytes

To gain insight into the improved high-voltage reversibility, electrolyte solvation structures were investigated first. Figure 6.14a presents the Raman spectra of the 1 M NaBF₄ G4 and 2.5 M NaBF₄ G4 electrolytes and their individual components. Figure 6.14b provides an enlarged view of the characteristic peaks for the G4 solvents. Similar to PF_6^- anion, the B–F symmetric stretching (v₁) of BF₄⁻ anion exhibits a red shift from 785 cm⁻¹ in pure NaBF₄ salts to approximately 766 cm⁻¹ in NaBF₄-G4 electrolyte. Notably, in the Raman spectra of the 2.5 M NaBF₄ G4 electrolyte, the broad peaks between 780-870 cm⁻¹, attributed to the G4 solvent, are less pronounced compared to the 1 M NaBF₄ G4 electrolyte. Conversely, the intensity of the new peak at ~867.9 cm⁻¹, corresponding to the crown-like structure, is significantly higher. This suggests a lower content of free G4 solvent and a higher content of the crown-like structure in the 2.5 M NaBF₄ G4 electrolyte compared to the 1 M NaPF₆ G4 electrolyte. Given the enhanced HOMO energy level within these crown-like structures relative to the free G4 solvent, it can be inferred that the 2.5 M NaBF₄ G4 electrolyte possesses superior oxidative stability than the 1 M NaBF₄ G4 electrolyte.



Figure 6.14 (a) Raman spectra of the studied electrolytes and corresponding components. (b) Enlarged view of the characteristic peaks of G4 solvent.

Ionic conductivities and Na⁺ ion transference numbers were first examined for 1 M NaPF₆ G4 and 2.5 M NaBF₄ G4 electrolytes to compare the Na⁺ ion conductivity difference. As depicted in Figure 6.15, the 2.5 M NaBF₄-G4 electrolyte exhibited lower ionic conductivity compared to its 1 M NaPF₆-G4 counterpart across the entire temperature range -20 °C to 60 °C. Specifically, at 20 °C, the ionic conductivity of 2.5 M NaBF₄-G4 was 1.57 mS cm⁻¹, approximately two-thirds that of 1 M NaPF₆ G4.



Figure 6.15 Temperature-dependent ionic conductivity of 1 M NaBF₄ G4 and 2.5 M NaBF₄ G4 electrolytes.

Subsequently, the Na⁺ ion transference numbers were further compared. Figure 6.16 displays the Nyquist plots obtained before and after applying a voltage bias, along with the corresponding current variations. According to Equation 2.10, the Na⁺ ion transference number for the 2.5 M

NaBF₄ G4 electrolyte was determined to be 0.721. Consequently, the RT (RT = 25 °C) Na⁺ ion conductivity was calculated to be 1.13 mS cm⁻¹, surpassing that of the 1 M NaBF₄ G4 electrolyte.



Figure 6.16 Nyquist plots and the variation in current during the voltage bias process for the 1 M NaBF₄ G4 (a) and 2.5 M NaBF₄ G4 (b) electrolytes.

6.4.3 Characterization of electrode-electrolyte interphases

The surface chemistry and compositional depth profile of the cathode-electrolyte interphase (CEI) formed on $Na_3V_2O_2(PO_4)_2F$ cathode after 1000 cycles were investigated using X-ray photoelectron spectroscopy (XPS) with Ar⁺ sputtering. Half-cell configurations using either 1 M NaPF₆ G4 or 2.5 M NaBF₄ G4 electrolytes were utilized. Figures 6.17-19 present the normalized high-resolution F 1s, C 1s, and B 1s XPS spectra obtained at various sputtering depths.

In the F 1s spectra, the peak at 684.3 eV corresponds to NaF, while the peak at 688 eV can be attributed to either $Na_xBO_yF_z$ or $Na_xPO_yF_z$ species. These components originate from the decomposition of the respective sodium salts.^[276] Notably, the intensity of $Na_xBO_yF_z$ in the 2.5 M NaBF₄-G4 electrolyte is significantly higher than that of $Na_xPO_yF_z$ in the 1 M NaPF₆ G4 electrolyte, both at the surface and after 5s and 10s of sputtering. This observation suggests a larger extent of anion decomposition during CEI formation in the 2.5 M NaBF₄ G4 electrolyte. Furthermore, the B 1s spectra of the 2.5 M NaBF₄ G4 electrolyte exhibit a B-O peak at 191 eV, assigned to $Na_xBO_yF_z$, which maintains a consistent intensity from the surface to a sputtering depth of 10s. This indicates a uniform distribution of inorganic $Na_xBO_yF_z$ components within the CEI formed in the 2.5 M NaBF₄ G4 electrolyte.



Figure 6.17 The in-depth XPS F 1s spectra of CEI formed in two electrolytes.



Figure 6.18 The in-depth XPS B 1s spectra of CEI formed in 2.5 M NaBF₄ G4 electrolyte.

For both electrolytes, the C 1s spectra display similar features, with deconvoluted peaks corresponding to C–C (284.8 eV), C–H (285.7 eV), C–O–C (286.7 eV), –COOR (288.5 eV), and C–F (291 eV). The C–F signal originates from the polyvinylidene fluoride (PVDF) binder, while the other components arise from the decomposition of the G4 solvent.^[265] In both electrolytes, the

intensity of C–C increases with increasing sputtering depth (from the surface to 10s), while the intensity of C–O–C decreases.



Figure 6.19 The in-depth XPS C 1s spectra of CEI formed in two electrolytes.

6.5 High-performance AFSMBs

The long-term galvanostatic cycling performances of Na//Na₃V₂O₂(PO₄)₂F half-cells using 2.5 M NaBF₄-G4 electrolyte and 1 M NaPF₆-G4 electrolyte were further investigated. Cells were cycled at 1 C after three formation cycles at 0.5 C with an upper voltage limit of 4.4 V *vs.* Na⁺/Na. As depicted in Figure 6.20, the cells with 2.5 M NaBF₄-G4 electrolyte exhibited superior performance, achieving an average CE of 99.9% over 1000 cycles, compared to 99.7% for the 1 M NaPF₆-G4 electrolyte. Moreover, the 2.5 M NaBF₄-G4 electrolyte enabled a capacity of 95.5% after 1000 cycles, significantly higher than the 85.5% retention observed for 1 M NaPF₆-G4 electrolyte. This excellent performance represents a significant advancement compared to the reported results to date, as summarized in Table 6.2. For instance, Chen and co-workers realized an average CE of 99.4% in a carbonate-based electrolyte with the addition of LiDFBOP additive.^[270] Liu and co-workers further improved the obtained average CE to 99.6% using a 1 M NaClO₄ DEC/SN with 5% FEC electrolyte.^[186] For ether-based electrolytes, the conventional 1 M NaPF₆ G2 electrolyte has been reported to achieve a high average CE of 99.6%.^[108] The ether-based electrolytes proposed in this work demonstrate even greater stability, achieving average CEs of 99.7% and 99.9% with an upper voltage limit of 4.4 V *vs.* Na⁺/Na.



Figure 6.20 Long-term galvanostatic cycling performance of SMBs with (a) 1 M NaPF₆ G4 and (b) 2.5 M NaBF₄ G4 electrolytes.

Table 6.2 Comparison of average long-cycling CE values of the SMBs using 1 M NaPF₆ G4 and 2.5 M NaBF₄ G4 electrolytes with those using reported electrolytes.

Cathode	Electrolyte	Voltage range	Rate	Coulombic efficiency
NVPF	3.36 m-NaPF ₆ G2/DOL	1.5-4.3 V	1 C	99.4% ^[240]
NVPF	3A zeolite modified 1 M NaPF ₆ G2	2-4.25 V	1 C	99.55% ^[89]
NVPF	1 M NaPF ₆ FEC/DEC +0.5 wt% LiDFBOP	2-4.5 V	1 C	99.4% ^[179]
NVOPF	1 M NaClO4 DEC/SN +5% FEC	2-4.3 V	1C	99.6% ^[163]
NVOPF	1 M NaPF ₆ G2	3-4.3 V	1C	99.6% ^[167]
NVOPF	1 M NaPF ₆ G4	2.5-4.4 V	1C	99.7% (This work)
NVOPF	2.5 M NaBF ₄ G4	2.5-4.4 V	1 C	99.9% (This work)

High Na plating/stripping reversibility at high current rates is a prerequisite for practical applications of AFSMBs. To investigate the Na reversibility in 1 M NaPF₆ G4 and 2.5 M NaBF₄ G4 electrolytes, Na//Al cells were assembled and tested. As depicted in Figure 6.21, while both electrolytes achieve an average CE of 99.7% over 200 cycles at 0.5 mA cm⁻², 2 mAh cm⁻², the 1 M NaPF₆ G4 system exhibits more pronounced fluctuations. This suggests that the Na plating/stripping process in the 2.5 M NaBF₄ G4 system is more stable.

To evaluate the feasibility of the 2.5 M NaBF₄ G4 electrolyte for practical applications, AFSMB full cells were fabricated comprising Al/C anodes and Na₃V₂O₂(PO₄)₂F cathodes. A presodiation strategy was employed for the Na₃V₂O₂(PO₄)₂F cathodes before full cell assembly to enhance the cycling stability of AFSMBs. This involved discharging Na₃V₂O₂(PO₄)₂F//Na half cells to 0.5 V, thereby inserting more Na⁺ ions into the cathodes and converting Na₃V₂O₂(PO₄)₂F to Na₄V₂O₂(PO₄)₂F. Following this pre-sodiation treatment, the cathodes were disassembled and used in the AFSMBs. During the initial charge of the AFSMBs, the pre-sodiated Na⁺ ions plate onto the Al/C current collector, residing on the anode side and serving as a supplemental sodium reservoir to compensate for irreversible sodium loss during subsequent cycling.



Figure 6.21 Cycling stability of Na//Al cells 1 M NaPF₆ G4 and 2.5 M NaBF₄ G4 electrolytes.

Figure 6.22 presents the long-term cycling performances of AFSMBs using the two electrolytes. Note that the initial charge capacity includes that from the pre-sodiated Na⁺ ions. Thus, the ICEs were determined to be only 51.1% and 52.9% for 1 M NaPF₆ G4 and 2.5 M NaBF₄ G4 systems, respectively. The 1 M NaPF₆ G4 system exhibited an initial reversible capacity of 88.9

mAh g^{-1} at 1C, followed by a short capacity activation and subsequent rapid capacity decay, resulting in a low capacity retention of 35%. In contrast, the 2.5 M NaBF₄ G4 system demonstrated a higher initial reversible capacity of 98.6 mAh g^{-1} at 1C and a remarkable capacity retention of 94% over 200 cycles. The consistent electrochemical performance was observed across multiple cells tested under each condition. The substantial improvement in cycling performance with the 2.5 M NaBF₄ G4 electrolyte is attributed to the formation of a stable CEI layer, effectively inhibiting persistent parasitic reactions at the interface and avoiding the consumption of limited Na sources.



Figure 6.22 Long-term galvanostatic cycling performance of AFSMBs with 1 M NaPF₆ G4 and 2.5 M NaBF₄ G4 electrolytes.

6.6 Summary

This part of the research has demonstrated highly reversible high-voltage AFSMBs enabled by a unique crown-like electrolyte solvation structure. It effectively decreases the oxidative decomposition of free ether solvents at high-voltage battery operation and, more importantly, enables decreased HOMO energy levels toward boosted high-voltage stability of as-formulated electrolytes. Intriguingly, unlike conventional solvent engineering approaches that often compromise salt dissociation and ionic conductivity of electrolytes, this strategy ensures a SSIP-dominated electrolyte solvation structure with high Na⁺ mobility. After further optimizing the salt selection and electrolyte concentration, a record-high average CE of 99.9% is realized at a high operation voltage of 4.4 V over 1000 cycles. A remarkable capacity retention of 94% was achieved over 200 cycles in the as-fabricated AFSMB. It thus paves the way for practically viable high-voltage AFSMBs.

Chapter 7 Conclusions

7.1 Contributions to knowledge

To improve the reversibility of SMBs at low-temperature and high-voltage operations, this research has proposed and tested three electrolyte formulation strategies. The contributions to knowledge are as follows:

 The G2-based electrolyte solvation has been restructured with a versatile diluent of DOL, to address the challenges of limited Na⁺ ion conductivity and unstable SEI for reversible operation of SMBs at LT.

DOL dilution enables an impressive Na⁺ ion conductivity of 5.46 mS cm⁻¹ at 25 °C and a decreased desolvation energy of 245.1 kJ mol⁻¹. The distribution of the lowest unoccupied molecular orbital energy level in the electrolyte solvates has been regulated toward a concentrated electron cloud around PF_6^- and thus their preferential decomposition. An inorganic-rich SEI with compositional uniformity and a high Young's modulus of 1.1 GPa is generated. High interfacial charge transfer kinetics with an exchange current densities of 0.83 mA cm⁻² have been realized at -25 °C, enabling homogeneous sodium deposition and high Na plating/stripping CE beyond 99.9%. A practical 1-Ah level pouch cell with an anode-free configuration, featuring a high-mass-loading (~30 mg cm⁻²) Na₃V₂(PO₄)₃ cathode, achieved an initial discharge capacity of 78.3 mAh g⁻¹ and a capacity retention of 95% over 100 cycles at a discharge current of 0.2C at -25 °C.

 A solubilizing DOL solvent has been introduced to the NaPF₆-G2 electrolyte to enhance its oxidative stability and achieve a higher charging cut-off voltage, thereby boosting energy density.

DOL promotes the coordination of G2 solvent with Na⁺, increasing the solubility of NaPF₆ salt in G2 solvent from approximately 2.4 M to 3.3 M and decreasing the free G2 solvent ratio from 35% to 24%. It also induces more anion participation in the solvation sheath, with the ratio of CIP and AGG solvates increasing from 23% to 32%, promoting the formation of a stable NaF-rich CEI. Both factors benefit the improved high-voltage stability of the electrolyte. Furthermore, the introduction of DOL in the solvation sheath helps shield the intermolecular attractions of G2, leading to a moderate electrolyte viscosity of 10.83 mPa·s at 25 °C even at a high concentration of 2.5 M. Rapid Na⁺ ion mobility with a Na⁺ ion conductivity of 3.68 mS

cm⁻¹ at 25 °C has thus been realized to ensure smooth charge transfer kinetics during charge/discharge cycles. Consequently, as-fabricated Na//Na₃V₂O₂(PO₄)₂F cell using the 2.5 M NaPF₆ G2/DOL electrolyte achieved an initial capacity of 111.2 mAh g⁻¹ and retained 89.9% capacity over 2000 cycles at 1C with a high charging cut-off voltage of 4.4 V.

3) The high voltage stability of 1M NaPF₆ in tetraethylene glycol dimethyl ether (G4) electrolyte has been boosted through forming a crown-like solvation structure.

The as-formed crown-like solvation structure effectively suppresses the oxidative decomposition of free ether solvents at high-voltage battery operation. More importantly, it decreases the HOMO energy levels of the SSIP (Na⁺–2G4) and the CIP (Na⁺–PF₆⁻–1G4) solvate complexes to -6.18 eV and -6.13 eV, thereby enhancing the high-voltage stability of the formulated electrolytes. Intriguingly, unlike conventional solvent engineering approaches that often compromise salt dissociation and ionic conductivity of electrolytes, this strategy ensures a SSIP-dominated electrolyte solvation structure with high Na⁺ ion conductivity of 1.13 mS cm⁻¹ at 25 °C. As a result, the fabricated Na₃V₂O₂(PO₄)₂F cathode achieved a high average charge/discharge CE of 99.7%, an initial capacity of 104.2 mAh g⁻¹ and a capacity retention of 93.1% over 500 cycles at 1C with a high charging cut-off voltage of 4.4 V.

 Highly reversible high-voltage AFSMBs with a record-high charge/discharge CE of 99.9% have been constructed using a 2.5M NaBF₄ G4 electrolyte.

Achieving near 99.9% CE at both positive and negative electrodes is crucial for sustainable operation of AFSMBs but still challenging, especially at high operation voltage. Based on the findings in 3), NaPF₆ was replaced with NaBF₄ resulting in the formation of more favorable boron-containing CEIs. Additionally, concentrating the electrolyte to 2.5 M leads to the formation of more crown-like solvates, further boosting the charge/discharge CE of the Na₃V₂O₂(PO₄)₂F cathode to a record-high 99.9% with a charging cut-off voltage of 4.4 V. The Na plating/stripping CE in the as-formulated electrolyte is also as high as 99.7%. Consequently, the fabricated high-voltage AFSMB exhibits superior cycling performance, maintaining a remarkable capacity retention of 94% over 200 cycles at 1 C.

7.2 Suggestions for future research

The engineering of battery electrolytes and electrolyte-electrolyte interphases has gained significant research attention in recent years. However, the currently available experimental/simulation tools remain limited because of the high disorder of liquid solutions as
well as complex components and dynamic evolution of interphases. To further advance the understanding along this research direction and improve the electrochemical performance of SMBs, the challenges and prospects are summarized below:

- Raman spectroscopy and nuclear magnetic resonance have been utilized to characterize electrolyte solvation structures in this research. While valuable, these techniques primarily provide insights into local molecular bonds and orientations within a short range below 1 nm. However, in high-concentration electrolytes, large solvation structures are formed and significantly influence the Na⁺ ions transport. As such, novel techniques for long-range characterization like small-angle X-ray scattering (SAXS) could offer valuable insights into the formation of clusters or networks in the electrolyte.
- 2) This research employed X-ray photoelectron spectroscopy (XPS) to analyze the surface properties of electrolyte-electrolyte interphase, which are ex-situ characterizations. Likewise, molecular dynamics (MD) calculations were utilized to simulate static solvation structures. Intuitive real-time techniques, such as in situ differential electrochemical mass spectrometry (DEMS), can be used to monitor gas evolution and electrolyte decomposition during battery cycling. And ab initio molecular dynamics (AIMD) can be utilized to simulate the dynamic evolution process of interphases.
- 3) The electrochemical performances of SMBs need to be further optimized. While a 99.9% CE value at the cathode side has been realized, it necessitates many charge-discharge cycles to stabilize. Moreover, it is still quite challenging to achieve 99.9% CE at positive and negative electrodes simultaneously, thereby achieving the ideal high reversibility required for high-voltage AFSMBs. Novel electrolyte formulations should be explored to further boost the electrochemical performance toward practically viable SMBs.

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Appendix: List of publications

- [1] Liang Hu, Jiaojiao Deng, Yuxiao Lin, Qinghua Liang, Bingcheng Ge, Qingsong Weng, Yu Bai, Yunsong Li, Yonghong Deng*, Guohua Chen*, Xiaoliang Yu*. Restructuring electrolyte solvation by a versatile diluent toward beyond 99.9% Coulombic efficiency of sodium plating/stripping at ultralow temperatures. Advanced Materials, 2024, 36(17), 2312161.
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- [10] Hui Wang, Genyuan Wang, Liang Hu, Bingcheng Ge, Xiaoliang Yu*, Jiaojiao Deng*. Porous polymer materials for CO₂ capture and electrocatalytic reduction. Materials, 2023, 16(4), 1630.
- [11] **Liang Hu**, Guohua Chen*, Xiaoliang Yu*. High voltage sodium metal batteries induced by cyclic ether solubilization. (manuscript under preparation).
- [12] Liang Hu, Guohua Chen*, Xiaoliang Yu*. Highly reversible high voltage anode-free sodium metal batteries enabled by crown-like electrolyte solvation. (manuscript under preparation).