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ANION HOSTING GRAPHITIC CARBON CATHODES FOR DUAL ION BATTERY

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Anion Hosting Graphitic Carbon Cathodes for Dual Ion Battery

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

Apr 2021

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Dedicated to my parents and my friends for their unwavering support

Abstract

As an alternative energy storage system, dual ion battery (DIB) with graphite cathode is attractive due to its high operating voltage > 4.0 V versus Li/Li⁺, environmental benignity, and abundant raw materials. Graphite is capable of different anions (de)intercalation in various systems. However, graphite seldom delivers a reversible capacity higher than 100 mAh g⁻¹ even when voltage reaches 5.0 V (vs. Li/Li⁺), impeding its further development and commercialization. Other found cathodes, like hard carbon, metal-organic frameworks, polycyclic aromatic hydrocarbon, and aromatic molecules inclusion organic crystalline solids, are capable of anion hosting but deliver even lower capacity compared to graphite. Therefore, exploration of potential high-capacity anion hosting cathodes and capacity optimization of the graphite cathode are performed, contributing to develop and diversify green and sustainable energy storage systems.

Acknowledging reduced graphene oxide anode's high capacity gifted by increased active exposed edges and surface area, we reckon this law should also be applicable for it as cathode. Because reduced graphene oxide still preserves graphite's bipolarity, the ability to host polarity distinct cation and anion. Hence, hydrothermally reduced graphene oxide (HrGO) is chosen to investigate its hexafluorophosphate (PF_6^-) storage capability as a high-performance cathode. Particularly, 3D porous structure of HrGO offers a reversible capacity of 186 mAh g⁻¹ and self-induced electrochemical activation drives the capacity grows to 320 mAh g⁻¹ after 300 cycles, which is the highest DIB cathode capacity ever reported. The electrochemical activation comes from surface area increment, originated from multilayer reduced graphene oxide rolls formation,

accumulation and structural order increase in cycling. The formation of rolls is plausibly a result of strain release of reduced graphene layers after electrochemical interaction with PF_6^- . Additionally, charge storage mechanism of HrGO is unveiled. At active surface sites of HrGO, PF_6^- is consistently stored in a pseudocapacitive manner. In contrast, at well-crystallized domains, pseudocapacitive PF_6^- uptake occurs at low voltage region while PF_6^- intercalation dominates at higher potentials. Supportive lithium storage also contributes to total capacity. This work offers valuable insights of electrochemical interaction between PF_6^- and reduced graphene oxide and provides guidance for high-capacity cathode construction.

The disclosure of the HrGO's remarkable reversible capacity and long-term cyclability encourages us further an in-depth drilling of it. To verify whether the used concentrated electrolyte contributes to the observed current density independent electrochemical activation of the HrGO in previous study, characterization of the HrGO in three electrolytes with different concentrations is conducted. Since concentration variation is known to affect capacity and working potential of anion hosting cathode. And the operable voltage range for the HrGO is another important parameter. The upper cut-off voltage variation tests are carried out. Additionally, the HrGO can also serve as additive for lithium ion battery (LIB) cathode, for example lithium iron phosphate (LiFePO₄, LFP), improving overall capacity. Such hybrid cathode, HrLFP, is a parallel cathode with PF_6^- storage at the HrGO and Li⁺ delithiation from the LFP simultaneously during cell charging. The prepared parallel hybrid cathode exhibits capacity higher than the theoretical capacity of the LFP. The study confirms that the HrGO is active in the hybrid cathode and demonstrates that the concept is practical.

In this thesis, another hybrid cathode functions in serial manner is also proposed and studied. The cathode incorporates a physical mixture of high working potential graphite matrix interacting with anion and nontoxic LFP as cation host. Since toxic transition-metal free cathode alternatives are highly desirable for sustainable energy storage system advancement. And this hybrid cathode presents a simple and effective approach. Then the proposed hybrid cathode, capable of both cation and anion storage, is examined. Characterization results reveal that the hybrid cathode, during charging, starts with the LFP delithiation in lower voltage region and finishes with graphite intercalation with anion in high voltage region. During discharging, processes are reversed with stepwise anion deintercalation and cation insertion, without interfering individual constituent's proper functioning. The transfer of two polarity distinct ions inside the hybrid cathode is independent, without any added kinetic difficulties. Such hybrid cathode can work stably with the LFP and the graphite in varied proportions. The addition of 40 wt% LFP to graphite cathode shows doubled capacity and excellent long-term cyclability. And the hybrid cathode is also demonstrated cyclable in a full cell configuration.

Publications arising from the thesis

- <u>L. Lyu¹</u>, J. Hu¹, K. Cheng, D. Lin, K. Li, Z. Lu, H. Yao, L. Zhou (2022). Insights into self-induced electrochemical activation of carbon cathode, *Carbon.*, 188, 177-186. (<u>Co-first author</u>)
- L. Lyu, J. Hu, D. Lin, H. Yao, L. Zhou (2021). A sustainable LiFePO₄/graphite hybrid cathode capable of stepwise cation and anion storage, *Electrochimica Acta.*, 391, 138936.

Other publications during the PhD period

- D. Lin, <u>L. Lyu</u>, K. Li, G. Chen, H. Yao, F. Kang, B. Li, L. Zhou (2021). Ultrahigh capacity and cyclability of dual-phase TiO₂ nanowires with low working potential at room and subzero temperatures, *Journal of Materials Chemistry A*, 2021, 9, 9256-9265.
- J. Hu, Z. Xu, X. Li, S. Liang, Y. Chen, <u>L. Lyu</u>, H. Yao, Z. Lu, L. Zhou (2020). Partially graphitic hierarchical porous carbon nanofiber for high performance supercapacitors and lithium ion batteries, *Journal of Power Sources*, 2020, 462, 228098.
- J. Hu, Z. Wang, Y. Fu, <u>L. Lyu</u>, Z. Lu, L. Zhou (2020). In situ assembly of MnO₂ nanosheets on sulfur-embedded multichannel carbon nanofiber composites as cathodes for lithium-sulfur batteries, *Science China Materials*, 2020, 63, 728-738.
- K. Li, D. Lin, <u>L. Lyu</u>, T. Zhang, L. Zhou (2019). Real-time and direct observation of lithiation of ultra-small tin oxide nanoparticles, *Journal of Power Sources*, 2019, 448, 227461.
- D. Lin, K. Li, Q. Wang, <u>L. Lyu</u>, B. Li, L. Zhou (2019), Rate-independent and ultra-stable low-temperature sodium storage in pseudocapacitive TiO₂ nanowires, *Journal of Materials Chemistry A*, 2019, 7, 19297-19304.
- X. Li, K. Li, S, Zhu, K. Fan, <u>L. Lyu</u>, H. Yao, Y. Li, J. Hu, H. Huang, Y. Mai, John B. Goodenough (2019), Fiber-in-tube design of Co₉S₈-carbon/Co₉S₈: enabling efficient sodium storage, *Angewandte Chemie International Edition*, 2019, 58, 6239-6243.

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Chapter 1. Introduction

The commercialization of lithium ion battery (LIB) by Sony company in 1990s [1] lays a firm foundation for prosperity of portable electronic devices [2] and remarkable advancement of electric vehicles [3]. Nowadays, the LIB is still one of the most dominant electrochemical energy storage systems, crediting to its the state-of-art high energy density, long shelf life, and stable cyclic performance. However, the dominance of LIB and growing demand of it in various applications, make the foreseeable problem—raw material shortage acute. Because the precursors of commercialized LIB cathodes mainly contain poisonous, expensive, and resource limited transition metals, like cobalt, manganese, and nickel [4]. Therefore, exploration of LIB alternatives draws considerable attention.

1.1 Working mechanism of dual ion battery

Among these potential candidates, dual ion battery (DIB) stands for a highly sustainable electrochemical energy storage system. When the DIB is mentioned, it usually means that the representative dual graphite battery (DGB) [5], with graphite as both cathode and anode. To have a better understanding of DIB, DGB is used for further rationale. It is rational to consider DGB as the fascinating eco-friendly technique as graphite is the only active electrode material. In addition, there are other widely studied electrochemical energy storage devices, like LIB, sodium ion battery, potassium ion battery, and aluminum ion battery. DGB also can function in these systems. Because, in these systems, graphite cathode and graphite anode are capable of the storage of common anions and cations, respectively. It also means that the available choices for DIB are further extended. Furthermore, DGB is known for its high working potential compared to other energy storage techniques [6], which positively contributes to energy density. Therefore, DGB is appealing.

The working mechanism of DIB is different from LIB. In the well-known LIB, only lithium ion (Li^+) shuttles between cathode (a lithium metal oxide) and anode (graphite) while both cation and anion, composing the salt in electrolyte, participate in electrochemical redox reactions at both electrodes in the DGB. A schematic showing the classic charging process of rocking-chair LIB with LiCoO₂ as cathode, graphite as



Figure 1.1 Schematic of charging state rocking-chair LIB in a LiPF₆-based liquid electrolyte.



Figure 1.2 Schematic of charging state DGB in a LiPF₆-based liquid electrolyte.

anode and LiPF₆ as the lithium salt, is illustrated in Figure 1.1. Specifically, lithium deintercalates from layered LiCoO₂, travels to anode, and intercalates into interlayers of graphite. And Li⁺ follows the same path back to delithiated LiCoO₂ from intercalated graphite during discharging. Although, DGB functions in distinct mechanism, similarity is shared with respect to electrochemical reactions occurred at anode. As displayed in Figure 1.2, solvated Li⁺ in the electrolyte, originated from LiPF₆ instead of LiCoO₂, intercalates into interlayers of graphite anode during charging. Concurrently, solvated PF₆⁻ in electrolyte intercalates into graphite cathode. Generally, high resemblance of anode redox reaction mechanism for both DGB and LIB makes LIB's anodes suitable anode candidates for DGB (or DIB). And the deintercalation of cation from LIB cathode does not conflict with anion intercalation into DGB cathode during charging. Because the flow of charge carriers agrees with the electric field direction inside a cell and is the same for both cells. These facts offer theoretical fundaments for the building a cell where LIB and DIB coexist and operate orderly together.

1.2 Operating potential of dual ion battery

In addition to DIB's high flexibility in various energy storage systems, it also possesses high operating potential. The anion intercalation into graphite cathode occurs at a voltage higher than that of delithiation in LIB cathode. Consequently, the operating voltage of DIB is also higher than that of LIB. Specifically, there are mainly three factors, solvent type, used salt, and electrolyte concentration, affecting the operating potential of DIB [7]. In other word, for a DIB, it is all about the electrolyte. The overall DIB reactions in a lithium-salt-based electrolyte can be expressed as

$$xLi^+ + C + xA^- + C \leftrightarrow Li_xC + A_xC \tag{1.1}$$

for DGB, where *x* indicates the amount of ion participating in reactions, A^- represents anion, C means graphite, Li_xC and A_xC are graphite intercalation compounds (GIC, Li-GIC for Li_xC and A-GIC for A_xC) after intercalation of Li^+ and A^- , respectively. Then, the potential (*V*) of DGB can be calculated according to

$$-neV = n(\mu_{Li} - \mu_{Li^+}) + n(\mu_A - \mu_{A^-})$$
(1.2)

where *n* is the number of electrons exchanged, *e* is the charge of an electron, μ_{Li} and μ_{Li^+} are chemical potential of Li-GIC and solvated Li⁺ in electrolyte, respectively, μ_A and μ_A^- are chemical potential of A-GIC and solvated A⁻ in electrolyte, respectively. The chemical potential of GICs varies with the changing of the intercalated number of ions, *x*. And μ_{Li^+} and μ_A^- are functions of corresponding ions' concentration ([Li⁺] and [A⁻], respectively). Within the dilute electrolyte limit, they can be expressed by the Nernst equation

$$\mu_{Li^+} = \mu_{Li^+}^o + kTln[Li^+] \tag{1.3}$$

$$\mu_{A^{-}} = \mu_{A^{-}}^{o} + kT ln[A^{-}] \tag{1.4}$$

where $\mu_{Li^+}^o$ and μ_A^o are chemical potentials of corresponding ions in 1 mol L⁻¹ (M) solution, *k* is Boltzmann factor, *T* is temperature. $\mu_{Li^+}^o$ and μ_A^o are highly related to the solvent used in the electrolyte. Substituting Equation 1.3 and 1.4 into Equation 1.2, it becomes

$$-eV = \mu_{Li} + \mu_A - \mu_{Li^+}^o - \mu_{A^-}^o - 2kTln[Li^+]$$
(1.5)

in a neutral electrolyte [6-7]. The variables at left side of Equation 1.5 determines the potential of DGB. Therefore, electrolyte concentration ([Li⁺] or [A⁻]), solvent, and salt

 $(\mu_{Li}^o, \mu_A^o, \mu_A, \text{ and } \mu_{Li})$, influence DGB's potential. Thus, proper electrolyte is vital for DGB. The general rules, with appropriate amendments, also are applicable for DIB.

1.3 Electrolyte of dual ion battery

As electrolyte is the only source of charge carriers and it is crucial to the working potential of DIB, its compatibility with electrodes and stability against electrochemical oxidation/reduction at respective electrode's interface need to be assessed. The window of liquid electrolyte (E_g) is constrained by the energy gap between the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) [8]. For a cell to work normally, the electrochemical potential of both anode (μ_A) and cathode (μ_C) should be located within the electrolyte window as illustrated in Figure 1.3. To avoid confusion with symbols appeared previously, the two symbols are not used. The electrochemical potential (the Fermi level) of anode located higher than LUMO would lead to reduction of electrolyte. And the Fermi level of cathode positioning lower than HOMO would result in oxidation of electrolyte.



Figure 1.3 Schematic of relative energy location of electrolyte window (E_g), anode and cathode electrochemical potentials (μ_A and μ_C , respectively) for compatible liquid electrolyte and solid electrodes (adapted from ref. [8]).

Moreover, DIB operates at high voltage. Therefore, research on electrolyte with high stability and compatibility is extensively performed.

1.3.1 Ionic liquid

Studied candidates are mainly ionic liquid (IL) electrolytes and carbonate-based organic electrolytes. Combinations of room temperature ILs among 1-ethyl-3methylimidazolum (EMI⁺) and dimethyl-3-propylimidazolium (DMPI⁺) as cation and tetrachloroaluminate (AlCl₄⁻), tetrafluoroborate (BF₄⁻) or PF₆⁻ as anion were confirmed to be applicable as electrolyte for DGB [9-10]. ILs have wide stability window, especially against anodic oxidation, and are safer than carbonate-based electrolytes owing to their low vapor pressure and high thermal stability [11]. As they can't form stable solid electrolyte interphase (SEI) at graphite anode, with graphite cathode, lithium titanate (Li₄Ti₅O₁₂) anode and an IL electrolyte, N-butyl-Nmethylpyrrolidinium bis(trifluoromethanesulfonyl)imide (Pyr₁₄TFSI), a DIB was built. And it could deliver a capacity over 100 mAh g⁻¹ and retain 99% capacity over 500 cycles [12]. However, the introduction of Li₄Ti₅O₁₂ anode decreases the working potential of DIB due to its much higher operating potential of than that of graphite anode. Ethylene sulfite (ES), facilitating SEI formation, was used as additive in Pyr₁₄TFSI-LiTFSI electrolyte for DGB [13]. Doubling of discharge capacity (half-cell configuration) and stable cyclic performance (full-cell configuration) after the addition of ES proved the effectiveness of such SEI formation additive. A fancy DGB design with high oxidative stability IL electrolyte for cathode and high reversibility etherbased organic electrolyte (capable of stable SEI formation) for anode was raised as illustrated in Figure 1.4 [14]. The independent functioning of IL and ether electrolytes at cathodic and anodic sides was achieved with the pretreated Nafion-based separator. 6

Thus, high stability and high coulombic efficiency (CE) are available for DGB, evident from over 3,000 cycles at 0.1 A g^{-1} and 99.7% CE achieved by such DGB. Nevertheless, the large-scale utilization of IL electrolyte in DIB is still hindered by their high price.



Figure 1.4 Schematic illustration of hybrid electrolytes design involving IL electrolyte for cathode, ether-based organic electrolyte for anode and Nafion-based separator for DGB (adapted from ref. [14]).

1.3.2 Carbonate solvent

In organic carbonate-based electrolytes of DIB, the inclusion of ethylene carbonate (EC), which prompts stable SEI formation on graphite anode surface in LIB, is avoided. Because, in electrolyte, EC strongly solvates and coordinates anions and it impedes anion intercalation into graphite cathode [15-17]. Fortunately, ethyl methyl carbonate (EMC), another frequently used solvent in LIB, shows high affinity towards PF_6^- and eases anion intercalation into graphite [18]. The low viscosity EMC is occupied to pair with different high viscosity and oxidatively stable solvents, propylene carbonate (PC) [17], EC [18], and sulfolane (SL) [19]. The introduction of appropriate amount of EMC provides long-term cyclic stability, high CE, and higher level of anion intercalation (up to stage 1 at 5.2 V), specifically capacity higher than 100 mAh g⁻¹ [17-19].
However, it is found that EMC would co-intercalate with anion into graphite cathode when the voltage is up to 5.2 V at full charge [20]. It is reported that the formation of stage 1 GIC, $C_{20}PF_6$, is accompanied with approximately 0.7 ± 0.2 solvent co-intercalation for every intercalated anion. But the contact between graphene sheets and anions remains close, indicating anion is dominant and solvent is ancillary in the finalization of GIC structure. It is worth to mention that the increase of EMC's weighting (compared to EC in mixture electrolyte) would shift anion intercalation voltage to a lower value [18]. This indicates the possibility of bridging DIB electrolytes with commercialized LIB electrolytes, making DIB capable of operating in LIB electrolytes.

1.3.3 Salt

Usually, the salt needs to be dissolved in solvent to form an electrolyte. Then, solvated cation and anion can commute between electrodes and liquid electrolyte in cell during cycling. It emphasizes the good match between salt and solvent, reflected by solubility of salt and solvation energy of ions in a solvent (or solvents). The solubility is evaluated by lattice energy, which is the energy needed for the separation of polarity opposite ions from the crystalline salt's lattice, and is semi-quantitatively indicated by salt's melting temperature [21]. On the other hand, when separated ions are solvated in solvent, they obtain extra energy, called solvation energy, which has a positive correlation with ions' charge density [22]. After meticulous assessment of constituents for electrolyte, 5 M potassium bis(fluorosulfonyl)imide (KFSI) in EC/dimethyl carbonate electrolyte (DMC) based DGB was built, delivering an energy density as high as 207 Wh kg⁻¹, stable cycling over 300 cycles, a high average discharge voltage

about 4.7 V [23]. The harmony between PF_6^- and EMC has been demonstrated multiple times [17-19], in governing smooth intercalation/deintercalation.

The compatibility between ions generated by dissolved salt and two electrodes is also crucial for DIB. Recall the two terms in Equation 1.5, μ_A and μ_{Li} , which are functions of intercalated anion and ion in graphite cathode and anode of DGB, respectively. Different ions have differing ionic size. Then, the energy needed for intercalation/deintercalation and the fillable number of differing ions in both cathode and anode are distinct. The same applies to DIB. The ideal graphite usually has an interlayer distance of 3.35 Å between two adjacent graphene sheets [24]. Despite it varies with graphitization degrees, the interlayer space ($d_{(002)}$) is smaller in comparison to the sizes of most anions in DIB. Four common anions' structural models and their estimated sizes are displayed in Figure 1.5 [25]. Except BF₄⁻ has a smaller ionic size than graphite's $d_{(002)}$ -spacing , the rest three anions have larger sizes. It does not mean that the intercalation of BF₄⁻ into graphite is effortless. Instead, it even needs more energy to supply its intercalation, indicated by its higher intercalation starting potential than that of PF₆⁻ (4.83 and 4.67 V for BF₄⁻ and PF₆⁻, respectively. Solvent is ethyl



Figure 1.5 Anion structure model of PF_6^- , $TFSI^-$, BF_4^- , and fluorosulfonyl-(trifluoromethanesulfonyl) imide (FTFSI⁻) (adapted from ref. [25]).

methyl sulfone (EMS) for both anions.). Moreover, being fully charged (up to 5.4 V), their discharge capacities are similar (94.7 and 97.6 mAh g⁻¹ for PF₆⁻ and BF₄⁻, respectively) when stage-1 compounds are formed (approximately, $C_{23}PF_6$ and $C_{23}BF_4$, respectively) [25]. Additionally, the half-cell with FTFSI⁻ ion showed the highest discharge capacity over the four anions. Therefore, it implies that anion size has a minor effect on anion intercalation and capacity. It is reported that ion-ion interaction (formation of ion pair, for example Li⁺ with two coordinate TFSI⁻ in a Pyr₁₄TFSI electrolyte) and self-aggregation dominate the starting potential of anion intercalation instead of anion size (before a certain point) [26]. The formation of ion pair is related to the charge density of ions. High charge density could result in overpotential, an increased anion uptake potential. Therefore, further emphasis on electrolyte constituents' compatibility is put forward.

1.3.4 Concentration

It has been shown in Equation 1.5 that the potential of DGB (or DIB) is also a function of solvated ions concentration. The increase of electrolyte concentration should decrease the potential of the cell. This seems to be adverse for DIB, known for its high operating voltage. As a matter of fact, high concentration electrolyte is favorable for DIB. Its operating voltage (graphite-based cathode) is still superior (> 4 V). In terms of anion intercalation voltage, a concentration increment from 1 M to 4 M for a LiPF₆ based organic electrolyte only showed a decrease from 4.45 to 4.34 V [27]. More importantly, considerable capacity enhancement was observed from 54 to 84 mAh g⁻¹. Such capacity increase was also observed in the KFSI based DIB [23]. Furthermore, the increase of a NaPF₆-based electrolyte concentration did result in the decrease of anion intercalation voltage but was rewarded with simultaneous increase of 10 deintercalation voltage potential [28]. And this is an indicator of the reduction of electrochemical polarization after the increase of electrolyte concentration. Unlike LIB, the only source of intercalate is in electrolyte for the classic DIB. It is known that local ion concentration varies during charging and discharging in DIB, high concentration electrolyte would offer enough intercalates [29]. Although increase of concentration has limited contribution to electrolyte stability, high concentration electrolyte is preferred in DIBs. It is pointed out that to make DGB comparable with LIB based on energy density, concentration has to be higher than 4 M [30].

However, electrolyte concentration increase will cause high viscosity, giving rise to possible difficulty in electrode wetting, ionic conductivity decrease, and development of concentration gradient, which resulting in possible increase of diffusion resistance. It is indicated that electrolyte concentration increases to higher than 2 M would trigger rapid viscosity increment and followed serious ionic conductivity decay in LIB organic electrolytes [31-32]. It was shown that during cycling of DIB half-cell (graphite cathode and lithium anode), local electrolyte resistance increases for lithium anode and decreases for graphite cathode in charging [33], while the trends are reversed during discharging. It is interesting that the ionic conductivity change is much more significant for lithium anode, instead of graphite cathode. It is ascribed to that Li⁺ has the lowest mobility, compared to other two species (TFSI⁻ and Pry⁺) in their mixture electrolyte. It has to be mentioned that the observed electrolyte resistance variation is below 20 Ω . Hence, it suggests that cycling developed local electrolyte resistance is not dominant. Additionally, it was also shown that electrolyte ionic conductivity has minor influence on anion uptake starting voltage and reversible capacity [26]. Furthermore, chemical diffusion coefficients calculated based on galvanostatic

intermittent titration technique (GITT) and electrochemical impedance spectroscopy (EIS) measurements were independent of electrolyte concentration (LiPF₆-based electrolytes, 1.0, 3.1, and 3.7 M) [34]. Despite that there are some issues need to be resolved, high concentration electrolyte for DIB is preferred.

1.4 Objectives and scope of thesis

Although DIB's high working voltage is attractive, the carbonate-based electrolyte's oxidative stability is a crucial safety problem and is yet fully addressed. For graphite cathode, relatively high reversible capacity is accessible only when upper cut-off voltage is up to 5.4 V or even higher. Even though the increase of electrolyte concentration contributes considerably to capacity enhancement. The obtainable value is still limited to the expected theoretical capacity of 124 mAh g^{-1} (C₁₈PF₆) for graphite capacity worth further study. Besides, there are probable junctions for bridging DIB and LIB (or other metallic ion batteries) together to increase capacity and lower charging potential. Thence, hybrid cathodes with traditional LIB cathode and graphite cathode are proposed and studied to verify their potential as green and sustainable energy storage systems.

In Chapter 1, the DIB as sustainable energy storage system is introduced for mitigating heavy reliance on the LIB. Comparison of fundamental working mechanisms is made between the LIB and DIB. And origins of the well-known high operating potential of the DIB are introduced and clarified, showing high relevance with electrolyte's constituents. Although the electrolyte's oxidative instability is emphasized and electrolyte modification has been performed, the limited improvement of capacity by electrolyte modification urges other perspectives. In Chapter 2, the typical graphite cathode for the DIB is emphasized. The detailed working principles and factors resulting in deviations between theoretical predictions and experimental observations are introduced and discussed. Other DIB cathode candidates are also introduced briefly. With deep understanding of the fundaments of the DIB and LIB cathodes, the possibility of conjunction two different energy storage systems' cathodes in one hybrid cathode is seen. Therefore, the concept of hybrid cathode consisting of the DIB cathode and the LIB cathode is proposed. In Chapter 3, the original work exploiting alternative high-capacity cathode is elucidated in detail. With guidance for highcapacity DIB carbon cathode design, the HrGO is studied. Fundamental understanding of its energy conversion mechanism and its dynamic evolution in morphology, structure, and electrochemical performance are presented. Further study of the HrGO is performed in Chapter 4. The suitable voltage window focusing on the upper cut-off voltage and influences of electrolyte concentration change on the HrGO are focused. And the proof-of-concept regarding with the parallel hybrid cathode is demonstrated. Another conceptual hybrid cathode working in serial manner is designed and investigated with the graphite and the LFP in Chapter 5. Influences of compositional ratio change and kinetic properties of such hybrid cathode are inspected. In Chapter 6, conclusions of the thesis are drawn, and future work is introduced.

Chapter 2. Challenges and opportunities of dual ion battery cathode

Alternative cathodes for DIB are extensively investigated, aiming to diversify potential cathode candidates and realize their commercialization. Besides, the relatively inferior available capacity of typical graphite cathode, low organic electrolyte oxidative stability, and low compatibility of IL electrolyte compatibility and its high cost collectively drive further drilling of other DIB cathodes. Nonetheless, in a full cell configuration, cathode and anode has to be well matched. With respect to anode, high similarity is shared by DIB and LIB, making it possible to build a hybrid cell, governed by working principles of both DIB and LIB. Therefore, a brief introduction of potential anodes of DIB is included before detailed introduction of cathode.

2.1 Briefing of anode

The high flexibility of DIB is that DIB can function normally with different metal ion batteries' configuration, granting numerous anode candidates. Anodes studied in energy storage systems with Li+ as charge carrier have been studied as DIB anode, like molybdenum trioxide (MoO3) [35], titanium dioxide (TiO2) [36], silicon (Si) [37], and aluminum (Al) [27, 38-39] with either high working potential in avoiding lithium dendrite growth or high capacity. When the Na+ carriers charge, sodium storable molybdenum disulfide (MoS2) [40-41], sodium trititanate (Na2Ti3O7) [42], tin (Sn) [28], iron phosphate (FePO4) [43], and soft carbon [44] are also widely investigated. Graphite anode for sodium ion-based DIB is relatively retarded. Since graphite, without any amelioration, is a poor sodium host [45]. In potassium ion-based DIB,

graphite [46], Sn [47], and mesocarbon microbead(MCMB) [48] are utilized as anode. Besides, for non-alkali metal ion based DIB, Al-based DIBs with graphite [49] and Al [50] anodes are also investigated, as three charges are transferred per Al atom. It's obvious that DIB is capable of adopting different energy storage systems. And studied high-capacity anodes of DIBs showed considerable cyclic stability and high rate capability. However, low-capacity values after long-term cycling (< 100 mAh g-1) are presented when they are paired with graphite cathode, summarized in Table 2.1.

Table 2.1 DIB cyclic performance comparison of different anodes paired with graphitic carbon cathode.

Anode	Cathode	Electrolyte	Voltage Window [V]	Capacity [mAh g ⁻¹]	Current Density [A g ⁻¹]	Reference
MoO ₃	Graphite (KS-6)	1 M LiPF ₆ EC:DMC (1:2 vol)	1.5-3.3	88 (1st)	0.1	[35]
TiO ₂	Graphite (KS-6)	1 M LiPF ₆ EC:DMC (1:2 vol)	1.5-3.7	91 (1st) 86 (30th)	0.1	[36]
Si (Lithiated)	Graphite (Natural)	1 M LiPF ₆ SL:EMC (3:7), 10 wt% FEC ^a	3.0-5.1	95.5 (1st) 82.5 (250th)	_	[37]
Al Foil	Graphite (Natural)	4 M LiPF ₆ EMC, 2 wt% VC ^b	3.0-5.0	92 (200th)	0.2	[27]
Core-Shell Al and Carbon Nanosphere	Graphite (Natural)	4 M LiPF ₆ EMC, 5 wt% VC	3.0-5.0	104 (reversible ^c) 91 (1000th)	0.2	[38]
3D Porous Al with Carbon Coating	Graphite	4 M LiPF ₆ EMC, 5 wt% VC	3.0-4.95	93 (1000th)	0.2	[39]
MoS ₂ / Carbon Nanotube	Expanded Graphite	1 M NaPF ₆ EC:EMC:DMC (1:1:1)	1.0-4.0	65 (reversible) 55 (200th)	0.2	[40]
MoS ₂ /3D Carbon Framework	Graphite	1 M NaPF ₆ EC:DMC (6:4)	1.0-4.5	110.3 (1st) 90.5 (500th)	0.2 0.5	[41]
Sn Foil	Expanded Graphite	$\begin{array}{c} 1 \text{ M NaPF}_6\\ \text{EC:EMC:DMC}\\ (1:1:1 \text{ vol}\%) \end{array}$	2.0-4.8	70 (400th)	0.2	[28]
FePO ₄	Graphite	1 M NaPF ₆ PC:EMC (3:7)	1.2-4.2	121.2 ^d (1st) 111.8 ^d (250th)	0.2	[42]
Soft Carbon Nanosheets	Expanded Graphite	1 M NaPF ₆ EC:EMC:DMC (1:1:1 wt%)	3.5-4.75	56.6 (350th)	0.1	[44]

Anode	Cathode	Electrolyte	Voltage Window [V]	Capacity [mAh g ⁻¹]	Current Density [A g ⁻¹]	Reference
Nano-Graphite	Nano- Graphite	0.8 M KPF6 EC:DMC (1:1 vol%)	3.0-5.0	53 (60th)	0.1	[46]
Sn Foil	Expanded Graphite	0.8 M KPF ₆ EC:EMC:DMC (4:2:3 vol%)	3.0-5.0	66 (300th)	0.05	[47]
МСМВ	Expanded Graphite	0.8 M KPF ₆ EC:EMC:DMC (4:2:3 vol%)	3.0-5.2	82 (1st) 61 (100th)	0.1	[48]
Carbon Paper	Graphite Paper	AlCl3/[EMIm]Cl (1.3:1 molar ratio)	0.5-2.4	70 (600th)	0.02	[49]
Al Nanowire/Al Foil	3DGF	1 M Al(ClO ₄) ₃ /PC, 5.5 wt% FEC	0.6-2.2	101 (400th) 150 (150th)	2 0.2	[50]

a) fluoroethylene carbonate; b) vinylene carbonate; c) exhibited maximum discharge capacity during cycling; d) the full-cell capacity based on anode weight.

There are two observed exceptions, FePO₄ [43] and three-dimensional (3D) graphene foam (GF) [50]. For FePO₄-based DIB, the larger capacity is a result of well-match between graphite and FePO₄. Graphite is claimed to be able to operate stably to form $C_8(PF_6)_{0.5}$ in half-cell, offering a capacity of 124 mAh g⁻¹ [43]. In half-cell, the FePO₄ anode only delivers a capacity of 116.6 mAh g⁻¹. Thus, this high full-cell capacity is believed to come from high compatibility of two electrode materials instead of being facilitated by anode's high capacity. Since no half-cell data were given, the calculation of the anode's contribution is unavailable. Therefore, anode modification does contribute to capacity increment of DIB in a decent manner. However, it is still restrained by cathode capacity based on the given data.

2.2 Graphite cathode

Anion hosting graphite cathode is the very first prototype of DIB. Thus, fundamental

knowledge of its working principle as cathode is indispensable. Thence, basics of how graphite interacts with anions are elucidated before the introduction of other graphitic cathodes.

2.2.1 Staging mechanism

Amphotericity of graphite enables it the capability of both cation and anion storage. Anion storage in graphite obeys a staging mechanism, sharing high similarity with its Li^+ storage as anode. A schematic elucidating intercalant staging into graphite is shown in Figure 2.1 [51]. The ion intercalation of graphite starts from high index stage-4 and ends at low index stage-1. Generally, the stage index (*n*, an integer) refers to the



Figure 2.1 Schematic illustration of Rüdorff and Daumas–Hérold modeled intercalant staging mechanism in graphite. I_c is the periodic repeat distance; n is the stage index; d_i is the intercalant gallery height (adapted from ref. [51]).

number of vacant graphene layers between two adjacent occupied layers which are in equivalent environment. The intercalation continues and subsequently the unoccupied graphene layers decrease, leading to stage index value decline. The Daumas–Hérold model takes the electron donation/acceptance between intercalant and graphene layers into consideration and assumes consequent in-plane lattice strain and resultant graphene layers distortion [52]. In contrast, the Rüdorff model presumes no structural distortion. Deviations from both models are observed in experimental results, which will be discussed later.

The observable interlayer distance (d_{obs}) of two adjacent graphene layers is calculated by

$$I_c = d_i + 3.35 \text{\AA} \cdot (n-1) = \Delta d + 3.35 \text{\AA} \cdot n = l \cdot d_{obs}$$
(2.1)

where I_c is the periodically repeating distance, d_i is the gallery height of intercalant, Δd is the gallery expansion, and l is index of the (001) planes vertically aligned along c-axis [53]. When a graphite is at stage n, the pristine characteristic (002) peak (the same for (004) and (006) peaks) would split into two peaks, (00n) and (00n+1), located at two sides of (002) peak in an X-ray diffraction pattern [7, 20, 54]. Therefore, X-ray diffractometer (XRD) is utilized to verify the stage index of intercalation based on the characteristic peaks and their locations. Then, the n value is calculated by

$$d_{00n} = I_c/n = \lambda/(2sin\theta_{00n})$$
(2.2)

$$n = 1/[(\sin\theta_{00n+1}/\sin\theta_{00n}) - 1]$$
(2.3)

where d_{00n} is the plane spacing of (00n), Θ_{00n} is the corresponding Bragg angle of (00n) planes, and λ is the wavelength of applied X-ray [7, 20, 54]. Thus, the measured XRD spectra help resolve introduced parameters in Equation 2.1, providing insights for graphite intercalation with different intercalates.

2.2.2 Capacity and voltage

With continued anion intercalation into graphite, stage index deceases and the concentration of intercalates in graphite increases, reflected by capacity increase. Theoretical capacity is calculated based on the corresponding stage-*n* GIC. Theoretically, potential GICs may adopt different stoichiometries, providing varying capacity values. The proposed common GICs in literature are listed in Table 2.2 [7, 25, 55-56]. Stage-1 GIC should not be assigned based on XRD data alone. It can be seen from Table 2.2 that stage-3 of C_8A has the same theoretical capacity with stage-1 of $C_{24}A$. The stage index *n* is different, but the calculated capacity value is the same. Therefore, the assignment of stage index to GIC during cycling usually requires the combination of measured XRD data and practical capacity-voltage plot (voltage profile).

GICs with stage-1 stoichiometries of C_6A and C_8A are frequently utilized to model cation-based GICs, like LiC₆ and KC₈ [57-58]. In contrast, the two stoichiometries are scarcely used for anion based GICs modeling due to large deviation from obtainable experimental capacity of graphite cathode. The $C_{18}A$ is a frequently occupied for modeling various anion based GICs owing to well-match with experimental capacity

Table 2.2 Common GICs with different stoichiometry and their corresponding calculated capacity at different stages, based on ref. [7, 25, 55-56].

	Calculated Theoretical Capacity [mAh g ⁻¹]			
Stage-1 GIC	Stage-1	Stage-2	Stage-3	Stage-4
C ₆ A ^a	372	186	124	93
C_8A	279	140	93	70
$C_{14}A$	160	80	53	40
$C_{18}A$	124	62	41	31
$C_{24}A$	93	47	31	23

a) A indicates intercalate.

of graphite. For instance, for a PF₆⁻⁻-based GIC, stage-4, stage-3, stage-2, and stage-1 GICs are theoretically expressed by $C_{72}PF_6$, $C_{54}PF_6$, $C_{36}PF_6$, and $C_{18}PF_6$, respectively [55-56]. And, theoretically, this is applicable to other anions, like BF₄⁻⁻, ClO₄⁻⁻ and AlCl₄⁻⁻. In contrast, TFSI⁻⁻ is assigned to $C_{24}A$ [56]. Deviations do exist between theoretical models and experimental results. Stage-1 GICs, $C_{19}TFSI$ (117 mAh g⁻¹, charged to 5.2 V) and $C_{23}PF_6$ - $C_{24}PF_6$ (95 mAh g⁻¹, charged to 5.4 V), were determined based on experimental data [25]. The stage-1 $C_{19}TFSI$ and $C_{23}PF_6$ could be viewed as a slight deviation from stage-1 $C_{18}TFSI$ and $C_{24}PF_6$, respectively, due to insufficient anion intercalation. This is reasonable as extra anion intercalation deviates GICs from common stage-1 stoichiometry is also uncovered. With charging potential growing from 5.0 to 5.2 V, probable extra anion intercalation results in formed stage-1 GIC, $C_{24}PF_6$, increases anion concentration in graphite, and changes its stoichiometry to $C_{20}PF_6$ through a possible one-phase solid solution reaction [20]. Overall, it is rational to set a ceiling (124 mAh g⁻¹) for graphite cathode's practical capacity, supported by numerous experimentally exhibited capacity values of graphite cathode.

The staging mechanism of anion intercalation in graphite follows the first principle two phase transformation with well-defined flat plateaus presented in voltage profiles, as shown in Figure 2.2. Notably, high potential is required for the initiation of $PF_6^$ intercalation. Because the size of the anion is larger than ideal $d_{(002)}$ -spacing of graphite. Then, its intercalation into graphite cathode requires considerable energy to expand the interlayer distance of graphene sheets. It is reflected by high charging potential in voltage profiles. Slight potential increase could facilitate reduction of staging index and capacity increment. However, the actual applicable voltage is usually constrained by the oxidative instability of common organic electrolytes. Then, the accessible stage-1 GIC is limited by low applicable upper cut-off voltage.



Figure 2.2 Schematic illustration of staging voltage profiles of calculated and experimental data of PF_6^- -based GIC with stage-1 stoichiometry of $C_{18}PF_6$ from left to right (adapted from ref. [55]).

2.2.3 Stability of anion intercalated graphite

The stability of a specific anion based GICs is a critical criterion for the compatibility evaluation between the anion and graphite and it is an indicator of the anion's reversibility in cycling. Firstly, the large size anion intercalation will directly lead to considerable graphite interlayer expansion along *c*-axis. The calculated gallery height expansion of three common anion-based stage-1 GICs are approximately, 133% (TFSI⁻), 114% (PF⁻), and 151% (AlCl^{4⁻}) [55-56, 59]. Such expansion is adverse for cyclability. Secondly, the in-plane arrangement of intercalated anions determines how many anions could be packed within graphene layers. A minimum inter-anion distance of 7.38 Å is calculated and the minimum distance has to be maintained to avoid strong electrostatic repulsion of anions, fitting well with C₁₈A stage-1 stoichiometry [56]. An in-plane arrangement of C₂₄PF₆ with an inter-anion distance of 9.8 Å is illustrated in

Figure 2.3 [25]. Unlike Li⁺ GIC, in which Li⁺ prefers the center of hexagonal carbon ring [57, 60], studied anions, BF_4^- , CIO_4^- , $AICI_4^-$ TFSI⁻ and PF⁻, show little site preference [56]. This agrees with the description of observed deviation from stage-1 $C_{24}PF_6$ to $C_{20}PF_6$. Because the little site preference exhibits little hindrance to the packing and ordering of intercalated anions within graphene layers [7, 20, 61]. And these anions-based GICs all exhibited negative formation energy with an increasing stability in an order of $CIO_4^- < AICI_4^- < TFSI^- < BF_4^- < PF_6^-$ [56]. It indicates that PF_6^- is least favorable for deintercalation, which partially explains the lower discharge capacity than charge capacity.



Figure 2.3 Schematic illustration of PF₆⁻ arrangement in plane (adapted from ref. [25]).

2.2.4 Kinetic properties of anion intercalated graphite

Mobility of electrons and anions of formed GICs is important kinetic criterion in evaluating reversibility and rate capability of an electrode. Calculation suggests that the graphite's high electronic conductivity is retained in PF_6^- -based GICs owing to orbital overlapping between F 2p and C 2p [55]. The intercalation leads to electron

transfer from carbon atom to neighboring fluorine atom, approximately one electron charge, indicating the bonding between F and C atom is graphene layers is of ionic character [55-56]. This implies possible difficulty of anion extraction. However, theoretical calculation and experimental data reveal a fast diffusivity of PF_6^- in graphite. The minimum energy path is found to be <100> family directions, shown in Figure 2.4 [34]. There are other calculated possible preferred diffusion paths, shown in Figure 2.5 [55]. The result implies that path 3 is preferred. It is known that ionic size of anion is larger than that of Li⁺ [51, 62]. Then, it is interesting that both the calculated diffusion energy barriers are lower than that of Li⁺ in graphite, > 0.3 eV [63-64].



Figure 2.4 Estimated energy barrier of PF_6^- diffusion in graphite lattice. (a) <100> direction and (b) <110> direction (adapted from ref. [34]).



Figure 2.5 (a) Optimized minimum energy paths for PF diffusion in graphite lattice, (b) calculated energy barriers of corresponding paths (adapted from ref. [55]).

2.3 Other carbon cathodes

A preliminary survey on various carbonaceous materials' storage capability of $PF_6^$ was made and summarized in Table 2.3 [24]. Based on the high initial charge capacity exhibited by high-surface-area graphite and C_{60} , it seems that surface area tends to offer "extra" capacity. Even though poor reversibility is shown, their 1st discharge capacity values are still higher than other carbon materials. For graphitic carbon, a positive correlation between crystallinity and capacity is claimed. Higher degree of crystallinity of graphitic carbon is demonstrated to facilitate anion uptake [65]. In contrast, "non-graphitic carbon" might encounter difficulty in anion accommodation in amorphous structure [66-68]. As anion uptake must go through carbon surface, surface properties, like defects and surface area, are vital for anion storage capability of carbon [66, 69].

Acknowledging the importance of surface properties, numerous studies were carried out with respect to the enhancement of anion storage capability by active surface area enlargement. A plain approach is interlayer expansion of pristine graphite, forming

Sample	1st Charge Capacity	1st Discharge Capacity		
	$[mAh g^{-1}]$	$[mAh g^{-1}]$		
Graphite Particle (6 µm)	66.3	38.4		
Graphite Particle (4 µm)	54.8	29.1		
High-Surface-Area Graphite	130.8	35.3		
Vapor-Phase Growth Carbon	52.1	17.5		
Filament				
C_{60}	134.0	47.0		
MCMB	44.9	19.5		
Amorphous Carbon	28.7	6.6		
Sintered Graphite	64.7	33.8		
MWCNTs	49.1	12.6		
Pick Cokes	13.7	12.9		

Table 2.3 Measured specific capacities of different PF_6^- hosting carbons (adapted from ref. [24]).

Electrolyte used: 1 M LiPF₆ in EC:DMC (1:2 vol%). Voltage window: 4.9-3.5 V.

expanded graphite, which has been frequently utilized, listed at Table 2.1. However, capacity increment seems to be limited using expanded graphite. Attempt to further increase surface area was made using alkaline activated expanded graphite [70]. Measured Brunauer-Emmett-Teller (BET) surface area increased from 478 to 1890 m² g⁻¹ after the alkaline activation. Decreased redox peaks' location separation and increased redox current response in cyclic voltammetry (CV) curves indicate that the activated expanded graphite possesses better reversibility and higher electrochemical activity compared to pristine expanded graphite. This is further reflected by capacitance increase from 27 to 70 F g⁻¹ at a current density of 0.5 A g⁻¹. Concurrent oxidation of expanded graphite introduces surface functional groups impeding anion diffusion on surface. But promoted anion (de)intercalation kinetics are revealed owing to such surface area increment.

Alternatively, exfoliation of expanded graphite also grants higher surface area. Electrochemically exfoliated graphene nanosheets can deliver an initial discharge capacity of 90 mAh g⁻¹, which gradually increases to a maximum of 120 mAh g⁻¹ at 0.1 A g⁻¹ after 30 cycles and retains a capacity higher than 90 mAh g⁻¹ after 250 cycles [71]. The capacity growth is ascribed to possible continued electrolyte wetting of cathode in the first 30 cycles. Meanwhile, a 4 V (vs. Na/Na⁺) operating voltage is viable, indicating the feasibility of such approach.

Structure engineering of high crystallinity or/and defect-free graphene lattice in 3D form will confer extra surface area, high electron conductivity, and increased ion mobility at graphene surface. The 3D structure prevents restacking of exfoliated graphene layers and provides connected network for charge transfer. Besides, consequent high macro- or meso-porosity of the 3D structure can give better wetting of electrolyte and consequential shorter ion transfer distance. This idea has been

extensively applied for graphene-based cathode design in aluminum-ion battery or aluminum dual ion battery [50, 72-76]. These 3D graphene-based cathodes not only offer enhanced reversible capacity but also guarantee excellent rate capability. A defect-free few-layer graphene aerogel shows a reversible capacity of 100 mAh g⁻¹ at a high current density, 5 A g⁻¹ [76]. Trihigh tricontinuous graphene film can operate at 6 A g⁻¹ and retain high capacity of 120 mAh g⁻¹ after 16,000 cycles [75]. Such capacity enhancement is achieved at only stage-3 when the cathode is fully charged, demonstrating the effectiveness of this design. Moreover, under 400 A g⁻¹, high reversible capacity of 111 mAh g⁻¹ is maintained.

Introduction of nanovoids within the highly crystallized graphene structure is unveiled to contribute additional capacity [74]. The nanoholes are attractive for $AlCl_4^-$ through short range interaction between Cl and C atoms (no bonding formation) at edges of the holes, leading to uniform distribution of anions near the edges. Highly porous 3D graphene with graphene nanoribbons can retain a high capacity of 123 mAh g⁻¹ at a current density of 5 A g⁻¹ after 10,000 cycles.

There are also carbon cathodes that do not stress the high crystallinity but highlight porosity of structure. It is believed that highly porous carbon structure is able to store anion through adsorption/desorption and pledge faster kinetics, extra capacity and higher structure stability in comparison to intercalation dominant carbon cathodes. Accordingly, 3D porous microcrystalline carbon cathode coupled with tin anode as a DIB manifests the success of such design, delivering a high capacity of 168 mAh g⁻¹ at 0.3 A g⁻¹ [77]. Decent cyclability is demonstrated by approximately 70% capacity retention over 2,000 cycles at 1 A g⁻¹. On top of porous structure design, heteroatom doping is said to accelerate electron mobility in carbonaceous material, motivating the construction of nitrogen-doped microporous hard carbon cathode [78]. The cathode

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shows high reversible capacities of 68, 141, and 197 mAh g⁻¹ at current densities of 5, 2, and 1 A g⁻¹, respectively. Longevity is exhibited by maintaining a capacity of 100 mAh g⁻¹ at 0.1 A g⁻¹ within 4.7-1.0 V (vs. Na/Na⁺) after 1,000 cycles. The cathode pairing with soft carbon anode, after 12 h aging under approximately -25 °C, can deliver a capacity of 121 mAh g⁻¹ at 1 A g⁻¹ over 380 cycles.

Comprehensively, these designs provide vital principles for high-capacity carbonaceous cathode design for DIB. High surface area is of high importance for additional capacity supply; high crystallinity promises high rate performance; porous interconnected structure accelerates liquid electrolyte wetting and decreases travel distance of solvated ions. Targeting differing applications, effective design strategies should be applied accordingly.

2.4 Organic cathodes

Substantial studies employing organic materials as active electrode materials have been implemented, credited to their low cost, environmental benignity, low weight, controllable structural functionalization, and consequent structural diversity [79-81]. Usually, p-type organic materials are used for DIB cathodes. During charging, oxidation of organic material leaves it in positively charged state, which is neutralized by anion [82-84]. Processes reverse during discharging. Schematic illustration of an organic cathode's working principle is presented in Figure 2.6. During charging, poly triphenylamine (PTPAn) losses one electron to external circuit, leading to the formation of anion interactable N⁺ [85]. Concurrently, anion absorbs to N⁺ and forms a stable neutral compound. In a half-cell, the PTPAn cathode can deliver a capacity of 71 mAh g⁻¹ after 60 cycles at 0.1 A g⁻¹ in 4.0-2.0 V (vs. K/K⁺). In a full-cell configuration, with the PTPAn as cathode and graphite as anode, a reversible capacity of 49 mAh g⁻¹ is obtained at 0.1 A g⁻¹, giving a median discharge voltage of 3.2 V. For the full-cell, a reversible capacity of 37 mAh g⁻¹, corresponding to 75.5% capacity retention, is maintained after 500 cycles. A crystallized aromatic amine cathode, dilithium 2,5-(dianilino)terephthalate (Li₂DAnT), is demonstrated to deliver an initial charge capacity of 73 mAh g⁻¹ while it operates with an average potential of 3.22 V (vs. Li/Li⁺) [83]. The Li₂DAnT is calculated to possess a theoretical capacity of 148 mAh g⁻¹ with two electron exchange. But probable dissolution/exfoliation of it



Figure 2.6 Working mechanism of poly triphenylamine (PTPAn) cathode. (a) the PTPAn molecule's electrochemical behavior during cycling; Working mechanism of a DIB full-cell, configured with PTPAn cathode and graphite anode, during (b) charging and (c) discharging, respectively (adapted from ref. [85]).

at higher state of charge undermines its reversibility and limits its capacity. Except liquid organic-electrolyte-based DIB, organic cathode can also operate in aqueous electrolyte. Poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate) (PTMA) cathode, with a theoretical capacity of 111 mAh g⁻¹, shows a reversible capacity of 80 mAh g⁻¹ at 0.5 A g⁻¹ when it interacts with SO_4^{2-} in an aqueous electrolyte [82]. A PTMA cathode included full-cell is capable of delivering a high reversible capacity of 136.5 mAh g⁻¹ at 0.5 A g⁻¹, shows 86.4% capacity retention after 10,000 cycles at a high current density of 5 A g⁻¹, and presents a maximum operating potential of 1.9 V. Another high theoretical capacity (150 mAh g⁻¹, two-electron exchange) organic proprietor is 5,12-diaminorubicene (DARb), showing high initial capacity of 115 mAh g⁻¹ [86].

Unlike abovementioned organic cathodes whose positive charge is centered around N atom, polycyclic aromatic hydrocarbon is also competent for anion storage as cathode. The polycyclic aromatic hydrocarbons' competence as anion host stems from its HOMO's capability to accommodate additional delocalized electron holes [5, 87]. Two representatives, coronene [87] and polypyrene [88], are illustrated in Figure 2.7. Coronene cathode has a theoretical capacity of 89.2 mAh g⁻¹ and it can charge up to



Figure 2.7 Molecular structures of two polycyclic aromatic hydrocarbons. (a) Coronene; (b) Polypyrene in positively charged state (adapted from ref. [87] and [88], respectively).

4.2 V (vs. Li/Li⁺), displaying an initial charge capacity of 60.6 mAh g⁻¹ [87]. At a current density of 0.02 A g⁻¹, it can cycle up to 960 cycles with 92% capacity retention. As for polypyrene cathode, theoretical capacity is 133 mAh g⁻¹ based on one anion uptake per pyrene (four condensed aromatic rings) [88]. Because pyrene is vulnerable of dissolution in electrolyte and conjugated π -system deficiency. Pyrene shows poor cyclability. In contrast, amorphous polypyrene circumvents these issues, maintaining a capacity of 70 mAh g⁻¹ after 300 cycles at 0.2 A g⁻¹.

In addition, a metal-organic framework (MOF) is demonstrated to store anion with oxidation of center metal (Fe (II/III)) possessing multivalence states, accompanied with intriguing unit cell contraction during charging [89]. The controllable microporous structure gives enough space for large size anion accommodation and the charge neutrality requires anion insertion to the positively charged MOF. A capacity about 90 mAh g⁻¹ is obtained at 1 C (theoretical capacity 140 mAh g⁻¹) in half-cell configuration. For MOFs, metal centers are well-dispersed within organic entities, granting decent structure flexibility but suffering low electronic conductivity [90]. In this regard, a Cu (I)-based MOF with electronic conductivity of 2.5×10^{-1} S cm⁻¹ is studied as a DIB cathode [90]. In its preliminary study, wide voltage range gives an initial reversible capacity of 157 mAh g⁻¹ while narrower voltage range shows a lower capacity of roughly 70 mAh g⁻¹ at 0.02 A g⁻¹. The wider voltage window enables additional redox couple. Thus, higher capacity is delivered for this voltage window. A MOF cathode with two redox couples (Fe (II/III) and Co (II/III)) exhibits high reversible capacity of 175 mAh g⁻¹ at 0.05 A g⁻¹ and displays a high operating potential of 3.63 V (vs. Li/Li⁺) in a half-cell [91]. Cyclic stability is represented by capacity of nearly 140.7 mAh g⁻¹ over 500 cycles at 0.05 A g⁻¹ and an average capacity of 74.9 mAh g⁻¹ over 8,000 cycles at 2 A g⁻¹. Organic ligand-cobalt-based complex nanosheets are also build for DIB cathode and function through interaction between Co (II/III) and anion [92].

Overall, organic cathodes as anion host have lower working potential than graphite, avoiding electrolyte decomposition. But prevention of organic cathode dissolution in electrolyte has to be prioritized in DIB design, putting rigid requirements on the compatibility between electrode and electrolyte. Besides, stable electrochemical performance in long-term cycling needs to be improved.

2.5 Conjunction of carbon cathodes and conventional LIB cathodes

Scrutinizing the working mechanisms of DIB and LIB, one can find that DIB not only effortlessly utilizes accessible anodes but also readily adopts conventional cathodes to form novel hybrid cathodes. These hybrid cathodes are qualified for anion and cation storage in parallel or serial manner. Specifically, during charging, whatever cell is used, static electric field forms under applied voltage, which drives the movements of anions and cations in opposite directions in liquid electrolyte due to their distinct polarity. That is, cations move from cathode to anode and anions travel from anode to cathode. Delithiation of cathodes in LIB agrees with the former cations' movement and the later anions' motion is in line with anion storage of DIB cathodes. Therefore, hybridization of LIB and DIB cathodes together within one cathode, interacting with both cation and anion, is straightforwardly ready.

When a hybrid cathode incorporates a typical DIB graphite cathode and a conventional LIB cathode into one electrode. The hybrid cathode would be benefited from high working voltage of graphite cathode and high capacity from the LIB cathode. The LIB cathode governs cation storage in low voltage range while graphite cathode is in charge

of anion uptake in high voltage range. That is, a serial or stepwise manner is adopted. Such hybrid cathode is expected to show higher capacity than graphite cathode and higher working potential than ordinary LIB cathode. This represents an alternative approach to increase DIB's cathode capacity while circumventing high charging potential causing degradation of common organic electrolytes. The first demonstration and study of this kind of cell is presented by our original work in Chapter 5 (serial manner) of this thesis.

If a hybrid cathode interacts with anion and cation simultaneously within the same potential range, it adopts a parallel manner. This cell working in parallel manner has been studied in Chapter 4. Similar conceptual cells have been extensively studied with respect to hybridization of capacitor and LIB [93-97], called metal-ion capacitors (MICs). In the MICs, these hybrid cathodes mostly utilize a mixture of activated carbon (AC) and a common LIB cathode, and they work below 4.5 V (vs. Li/Li⁺). AC is frequently occupied in cathode [98] for its large surface area qualified for anion adsorption and it works through rapid response non-Faradic electric double layer [99]. Thus, with the occupation of AC in hybrid cathode, these MICs usually target for high rate performance. However, the capacity of AC cathode is relatively low [94, 96], constraining MICs' energy density. Therefore, this puts an emphasis on high-capacity anion storable cathode capable of working below 4.5 V (vs. Li/Li⁺). High-capacity DIB carbonaceous cathode design can be guided by critical factors given in Section 2.3.

Except hybrid cathode, sole cathode material is also active towards polarity-distinctions. A Mn (II)-based MOF is synthesized and revealed to follow a "bipolar charging" principle, as shown in Figure 2.8 [100]. Explicitly, during the first charging, centered Mn^{2+} , in the neutral state of the MOF, is oxidized to Mn^{3+} and is neutralized by anion uptake. During the first discharging, this process reverses, and further reduction leads to accommodation of cations by coordinated ligands. Actually, the "bipolar charging" is realized starting from the second charging. Initiated with delithiation from ligands and followed by anion storage near oxidized metal, the "bipolar charging" is achieved. With 1.3 nm-wide one-dimensional (1D) channels and about 40% interior voids, the MOF cathode delivers a high capacity of 205 mAh g⁻¹ and losses 7% of its initial capacity over 50 cycles at a current of 1 mA. Another example is presented by Mn₃O₄. The Mn₃O₄ cathode is found to be able to reversibly store PF₆⁻ in a pseudocapacitive manner at high voltage range (2.75-4.8 V vs. Li/Li⁺) and it is active for lithium insertion at low voltage range (1.5-2.75 V vs. Li/Li⁺) [101]. A reversible capacity of 250 mAh g⁻¹ is obtained at a current density of 0.6 A g⁻¹.



Figure 2.8 Schematic illustration of working mechanism of a MOF cathode in a half-cell (adapted from ref. [100]).

To summarize, by bridging DIB and LIB cathodes, the active hybrid cathode active to bipolar ions offers a new angle for cathode design and full-cell construction. Single cathode, capable of polarity-distinct-ions' storage, is also highly desired. Although the two mentioned cases show considerably high reversibly capacity, their long-term cyclability is yet to be improved.

Chapter 3. An anion hosting 3D graphitic carbon cathode

3.1 Introduction

The possible exhaustion of fossil fuels and the concurrent energy storage market expansion require the diversity of renewable energy storage devices [102]. Lithium ion batteries (LIBs), the market's dominant and state-of-the-art sustainable energy storage system, offer specific energy density ranging only from 90 to 250 Wh kg⁻¹ [103]. Additionally, the majority of LIB cathode materials comprise mainly transition metal oxides. To circumvent the shortage of raw materials containing transition metals and the subsequent price increase, and ameliorate their inferior electrochemical performance, it is necessary to increase the diversity of electrochemical energy storage techniques [104].

As an alternative sustainable energy storage system, dual ion batteries (DIBs) usually use graphite as cathode [105]. Graphite can charge to a voltage of 5.0 V vs. Li/Li⁺ (in a lithium-ion-based DIB, L-DIB), directly contributing to energy density enhancement [106-109]. However, the obtainable capacity of graphite cathode is limited to the theoretical capacity of 124 mAh g⁻¹, corresponding to the formation of stage 1 compound C₁₈PF₆ [7, 25, 55-56]. Practically, the reported graphite cathodes deliver reversible capacities scarcely higher than 100 mAh g⁻¹ [24, 105-106, 110]. Carbonaceous material with higher graphitization degree can promote higher reversible capacity [65]. And high-quality natural graphite is reported to deliver a reversible capacity of 110 mAh g⁻¹ and maintain a capacity of approximately 100 mAh g⁻¹ after 1,100 cycles [111]. But the capacity is still limited to the low theoretical capacity of graphite. Another more serious issue is that the most of available capacity of graphite is obtained above 5.0 V, where oxidation of common carbonate electrolytes occurs [5, 12-13]. Therefore, it critical to find suitable high-capacity cathode, working within a stable voltage window of carbonate electrolyte.

High-crystallinity and defect-free graphene exhibits high rate capability and improved capacity in anion hosting aluminum ion battery [75-76]. A capacity of 111 mAh g⁻¹ is retained after 250,000 cycles [75]. Besides, a composite cathode of three-dimensional (3D) graphene foam and nano-graphite can deliver a capacity of 150 mAh g⁻¹ after 150 cycles in aluminum DIB [50]. It indicates superior anion storage capability of graphene-based cathodes in comparison to graphite. However, demanding of high graphitization level increases the complexity of synthesis. It is known that changing of electrolyte will vary anion storage behavior thermodynamically and kinetically [55-56, 112-113]. So far, their application in L-DIB is rarely studied. Bridging with mature technique (LIB) saves efforts for future commercialization.

In this regard, we demonstrate that a 3D hydrothermally reduced graphene oxide (HrGO) can work with concentrated LiPF₆-based carbonate electrolyte within a stable voltage window, 4.5-1.5 V, and provide ultra-high reversible capacity. A concentrated electrolyte is chosen as higher concentration provides sufficient charge carriers and lower anion uptake potential [23, 27-28]. The 3D HrGO could deliver a reversible capacity of 186 mAh g⁻¹. In elongated cycling, in situ structural order increment and reduced graphene oxide rolls formation and growth collectively contribute to electrochemical activation, 308 mAh g⁻¹ after 400 cycles. Such electrochemical activation is current density independent. Using in situ Raman spectroscopy, we confirmed that the capacity of HrGO cathode mainly comes from combined surface pseudo-capacitance and intercalation/deintercalation anion storage. It is found that supportive lithium storage/extraction exists approximately below 2.0 V, whose

contribution decreases in continued cycling. As a result, at wider voltage window of 4.95-1.5 V, the activated HrGO is able to deliver reversible capacities of over 500 mAh g⁻¹.

3.2 Experimental details

3.2.1 Material synthesis

Typically, graphene oxide (GO) was prepared using a modified Hummers method [114]. GO (50 mg) was dispersed in deionized water (70 ml) and sonicated for 1 h. Then, the uniform solution was transferred to a 100 ml Teflon-lined stainless-steel autoclave, heated in an electric oven at 453.15 K for 24 h, and allowed to cool down naturally. After vacuum filtration and a 24-hour freeze-drying, the HrGO was obtained.

3.2.2 Material characterization

Phase characterization was carried out using X-ray diffractometer (XRD) (Rigaku SmartLab 9 kW, Cu K α radiation, $\lambda = 1.54$ Å). X-ray photoelectron spectroscopy (XPS) (PHI 5000 Versa Probe II, monochromatic Al K α radiation) was used for surface chemical composition identification. The morphology and structure were investigated using transmission electron microscope (TEM) (Joel JEM-2100F) and scanning electron microscope (SEM) (TESCAN VEGA3). The surface area and pore size distribution were estimated using N₂ adsorption/desorption at 77 K (Micromeritics ASAP 2020). In situ Raman spectra were obtained using confocal Raman spectrometer (Renishaw) with a 633 nm laser, and cyclic voltammetry (CV) was performed simultaneously with a scan rate of 0.2 mV s⁻¹ over 4.5–1.5 V.

3.2.3 Electrochemical measurements

Typically, electrode preparation started with the abrasion of HrGO with acetylene black carbon and polyvinylidene fluoride (PVDF) at a mass ratio of 8:1:1, followed by the addition of *N*-methyl pyrrolidinone (NMP) to form a uniform slurry. Then, the slurry was coated onto Al foil and vacuum dried at 393.15 K for 12 h. Finally, the electrodes were cut into circular shape (diameter: 1 cm, areal density: $1.0-1.2 \text{ mg cm}^{-2}$) for further use. For performance comparison, GO and graphite were prepared using the same procedures. Coin cells (CR2032) were assembled with the HrGO electrode as the working electrode, lithium foil as the counter and reference electrode, Celgard 2400 as the membrane, and 2 M LiPF₆ in ethyl methyl carbonate (EMC) with 3 wt% of vinylene carbonate (VC) as the electrolyte. Galvanostatic charge-discharge tests were performed using a LAND CT-2001A (5 V) system, within a voltage window 4.5–1.5 V. CV and electrochemical impedance spectroscopy (EIS) measurements were obtained using an AutoLab PGSTAT302N electrochemical workstation.

3.2.4 In situ Raman measurements

The cell used for in situ Raman is shown in Figure 3.1. To exclude any possible influence from binder and electrically conductive agent in Raman inspection, only active material is used for electrode preparation. Electrodes were prepared by vacuum infiltration of HrGO onto separator without addition of conductive carbon and binder. Aluminum mesh was used for cathode current collector and a circular hole was opened on cathode shell and covered by a mica plate as the laser window. The rest parts were the same as the cells used for electrochemical measurements. The Raman spectra were collected using confocal Raman spectrometer (Renishaw, 633 nm laser) while the CV

was sweeping on an electrochemical workstation (Autolab) within given voltage window. A 20 min stabilization of cell at predefined potential was performed prior to the Raman spectrum collection. The data collection was performed every 100 mV and the acquisition time was set to be 10 s per spectrum.



Figure 3.1 Illustration of cell configuration used for in situ Raman measurements.

3.3 Results and discussion

3.3.1 Characterization of pristine materials

Characterization results (Figure 3.2-3.4) indicate the success synthesis of 3D HrGO. Figure 3.2a shows two peaks of GO at 10.56° and 42.32°, representing the expanded graphite (0002) and (10 $\overline{10}$) planes, respectively. The (0002) peak shifted to 24.71° after hydrothermal reduction of GO, implying the success of partial deoxygenation and an increase in the electrical conductance [115]. The (10 $\overline{10}$) peak shifted a little to 43.1°, indicating possible compression of corresponding planes. The N₂ adsorption–desorption isotherms of GO and HrGO are shown in Figure 3.2b. The measured



Figure 3.2 XRD, surface area, and pore size distribution of pristine HrGO and GO. (a) XRD of HrGO and GO; (b) N₂ adsorption/desorption isotherms of GO and HrGO; (c)-(d) Barrett–Joyner– Halenda (BJH) and Horvath–Kawazoe (HK) plots in correspondence to (b), respectively.

Brunauer–Emmett–Teller (BET) surface areas of the GO and HrGO were 105 and 166 $m^2 g^{-1}$, respectively. According to IUPAC (1985), the isotherms of GO and HrGO both belong to type IV. An H4 hysteresis loop (p/p₀ > 0.4) developed for GO and HrGO, indicating the existence of mesopores in them. And the nearly vertical N₂ adsorption line (at p/p₀ < 0.01) represents the micropore filling process. It means that both GO 42

and HrGO possess micropores. In Figure 3.2 c, Barrett–Joyner–Halenda (BJH) plots, based on a modified Kelvin equation, show mesopore distribution of GO and HrGO. The HrGO exhibits a relatively large number of mesopores over a wide range, but only small number of mesopores (< 6 nm) exist for GO. Micropore distribution comparison of GO and HrGO are illustrated in the Horvath–Kawazoe (HK) plots in Figure 3.2d. The mean pore diameters of HrGO and GO are 8.7 and 2.9 nm, respectively. Overall, the HrGO exhibits more mesopores in comparison to GO.

Figure 3.3a and 3.3b show that the pristine GO has lateral dimension of over 200 microns with puckered basal planes. In contrast, as illustrated in Figure 3.3d and 3.3e, the HrGO has a macropore-rich 3D framework supported by hydrothermally reduced graphene oxide layers, whose lateral dimension decreased to below 10 microns.



Figure 3.3 SEM and TEM characterization of GO and HrGO. (a) and (d) SEM images, (b) and (e) TEM images, (c) and (f) high resolution TEM (HRTEM) images of GO and HrGO, respectively. The insets in (c) and (f) are selected Inverse Fast Fourier Transformation (IFFT) images. Scale bar: (a) and (d) 200 μ m; inset in (d) 5 μ m; (b) and (e) 100 nm; (c) and (f) 10 nm; SAED inset in (b) and (e) 10 nm⁻¹.
Electron diffraction spectroscopy (EDS) surveys were carried out, revealing the decrease of atomic ratio of O (from 27.43% to 16.66%) and the increase of atomic ratio of C (from 72.57% to 83.34%) after the reduction of GO.

Selected area electron diffraction (SAED) images in the insets of Figure 3.3b and 3.3e show two blurred diffraction rings for both GO and HrGO, implying such reduction doesn't endow long range order. The exposed edges of GO and HrGO are shown in Figure 3.3c and 3.3f, respectively. Six layers of oxidized graphene are exposed at the GO edge with an interlayer distance of about 0.452 nm. The HrGO exhibits reduced $d_{(0002)}$ -spacing varying from 0.385 nm to 0.452 nm, revealing the existence of differences in the reduction level. Mesopores can be observed clearly between the yellow and red rectangles in Figure 3.3f.

Figure 3.4 shows full XPS spectra comparison between GO and HrGO. The surface oxygen ratio decreases from 34% to 15%, indicating the reduction of GO. Therefore, GO was hydrothermally reduced to form HrGO, but this reduction was dominated by deoxygenation instead of crystalline structure ordering. Even so, the hydrothermal



Figure 3.4 XPS full surveys of GO and HrGO.

reduction gave the HrGO a rich macro- and meso-porous structure, enlarged surface area, and 3D structure.

3.3.2 Electrochemical performance and electrochemical activation

A simple cyclic performance comparison of typical graphite cathode, precursor GO, and HrGO, in the range of 4.5–1.5 V at 0.05 A g⁻¹ is shown in Figure 3.5a. The HrGO greatly outperforms other samples, demonstrating its competence as anion hosting cathode. Specifically, the 100th discharge capacities are 21, 78, and 214 mAh g⁻¹ for graphite, GO, and HrGO, respectively. Particularly, the HrGO shows continuous capacity increase from the first (186 mAh g⁻¹) to 300th cycle (320 mAh g⁻¹), and the capacity is maintained until the 400th cycle (308 mAh g⁻¹). Although the initial coulombic efficiency (CE) is only 72.2%, the CE increases to 94.2% at the second cycle and the average CE of the 400 cycles is 94.3%. Two possibilities exist for such low initial CE. One possibility is originated from unextractable anions stored in HrGO during initial charging process, which is noticeable for other reported graphite cathodes. Another possibility is the irreversible oxidation of HrGO, supported by later oxygen-containing functional groups' weighting increase after initial charge. The initial CE is decent and the rapid recovery of CE making it a trivial issue in this study. Comprehensively, the barely studied electrochemical activation of carbon cathode encourages further investigation.

The CV curves of the HrGO (Figure 3.5b) resemble rectangles within the range of approximately 2.0–4.0 V, and redox peaks are located close to the cut-off voltages. This suggests a collective capacity contribution from adsorption and intercalation. The peaks at lower potentials should be Li^+ insertion into the HrGO [116]. It is verified by

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the measurement of the HrGO's electrochemical behaviors initiated with discharging to 1.5 V (Figure 3.6). Thus, Li⁺ storage supportively contributes to overall capacity within about 2.0–1.5 V while anion storage dominates above 2.0 V. At first glance, the voltammograms appear to superimpose well. However, careful examination discloses



Figure 3.5 Electrochemical characterization of HrGO in 4.5–1.5 V. (a) Cyclic performance comparison of GO, graphite, and HrGO, 0.05 A g⁻¹; (b) Cyclic voltammetry profiles of HrGO at scan rate 0.1 mV s⁻¹; (c) Voltage profiles of HrGO at different cycles, 0.05 A g⁻¹; (d) Cyclic performance of HrGO, 1 A g⁻¹; (e) Rate performance of HrGO; (f) Absolute and proportional capacity contribution of selected cycles in divided voltage regions.

that there is a gradual current increase during cycling within a range of ~ 2.0–4.0 V, indicating the activation process during cycling. Voltage profiles of HrGO (Figure 3.5c) further support the collective capacity contribution and electrochemical activation. The profiles resemble the linear lines for supercapacitors, but deviations are perceptible. Progressive capacity increase can also be observed, which is consistent with the current increase during cycling in the CV curves. Existence of cation storage is indiscernible through the voltage profiles owing to higher charge capacities. The longevity of HrGO is demonstrated by cycling at 1 A g⁻¹ for 10,000 cycles, as shown Figure 3.5d. A capacity of 93 mAh g⁻¹ is maintained, with an average CE of 99.4%. Fig. 1e shows that HrGO could deliver capacities of 148, 130, 109, and 72 mAh g⁻¹ at current densities of 0.1, 0.2, 0.5, and 2 A g⁻¹, respectively. The continued cycling of HrGO at 0.1 A g⁻¹ gives a capacity of 182 mAh g⁻¹ at the 450th cycle.



Figure 3.6 Electrochemical performance of two HrGO samples started with discharging to 1.5 V in the voltage window of 4.5–1.5 V. Current density: 0.05 A g^{-1} .

Figure 3.5a–3.5e all show increasing capacity for HrGO, no matter what current density was used. Such activation is worth further study.

The test voltage window was divided into three regions, 4.5–3.0 (anion extraction), 3.0–2.0 (anion extraction), and 2.0–1.5 V (lithiation). An extra region, 1.7–1.5 V was intentionally chosen to represent the major lithiation region during discharge. As shown in Figure 3.5f, the absolute regional contribution values of selected cycles mainly show an upward trend, except for the 400th cycle. The decrease of the 400th discharge capacity is due to the capacity decrease below 3.0 V. There is even an increase in the capacity value in the 4.5–3.0 V region. The capacity contribution percentages (Figure 3.5f) indicate a small amount of growth before the 150th cycle but considerable increase in the 300th and the 400th cycles in 4.5–3.0 V. Rapid growth was achieved within 50 cycles and the increased percentage was maintained until the 400th cycle in 3.0–2.0 V region. In contrast, the 2.0–1.5 and 1.7–1.5 V regions all show continuous decline. The contribution from the 1.7–1.5 V even falls below 50%



Figure 3.7 HrGO middle discharge voltage versus cycle number plot at 0.05 A g⁻¹.

of that from the 2.0–1.5 V region after the 150th cycle. Therefore, firstly, an overall capacity increase (activation process) was present. All voltage ranges contributed to this increase, suggesting collectively capacity growth from both anion extraction and cation storage. Secondly, the regional contribution ratio changes show a continuous decrease of the low discharge voltage region weighting, even in the assumed "dominant lithiation region" (1.7–1.5 V). This implies that anion contribution grows while cation contribution decreases in continued cycling. The weighting reduction of the low voltage region (lithiation) facilitates the middle discharge voltage (MDV) increase, as shown in Figure 3.7. Comprehensively, the HrGO exhibits a remarkable electrochemical performance.

3.3.3 In situ Raman revealing anion storage mechanisms

To obtain insights of the charge storage mechanisms of HrGO, in situ Raman measurements were carried out while the HrGO cycled in 4.5–1.5 V. Two-dimensional (2D) contour Raman spectra, Figure 3.8a, clearly show the evolution of two characteristic HrGO peaks, the D-band peak (1322 cm⁻¹) and an "apparent G-band peak" (1590 cm⁻¹), during the second electrochemical cycle. During charging from 1.5 to 2.3 V, bare shift for both D- and G-band peaks (Figure 3.8a), I_d/I_g decrease, and slight growth of G-band peak intensity (Figure 3.8b) suggest the occurrence of delithiation from HrGO [52]. Continued charging from 2.3 to 3.2 V, both D- and G-band peak shift is a result of concentration increase of PF₆⁻, occupying HrGO active surface sites (edges or defects in reduced graphene oxide sheets). Because continuing faradic pseudocapacitive anion storage at HrGO would increase positive electronic charge concentration of HrGO [117] and



Figure 3.8 In situ Raman spectra of HrGO cycled in the range of 4.5–1.5 V. (a) All columns share the same Y-axis (voltage variation in one cycle). From left to right, the first column shows the Raman contour plot of HrGO; the second and third columns are the D-peak and G-peak shift; the fourth column shows the D-peak and G-peak intensity ratio change; and the last column is an unfolded CV curve, during second cycle. (b) Selected Raman spectra at different potentials as indicated by colored circles in (a).

enhance bond force constants between atoms at edges/defects and neighboring PF_6^- [52, 118-119]. Similarly, the blueshift of apparent G-band peak is due to density increment of positive electronic charge, causing in-plane lattice contraction, and inplane carbon bonds force constants increase as PF_6^- occupation of regional welldefined basal planes [52, 118-119]. Charging potential increases from 3.2 to 4.5 V, the D-band peak continues to shift linearly with almost the same slope as earlier charging region.

However, the blueshift of G-band peak slows down compared to that of D-band peak. This could be explained by the different anion storage mechanisms in the two voltage regions, region 1 and region 2 marked in apparent G-band Raman shift plot. Within voltage range of 2.3–3.2 V, pseudocapacitive anion storage at edges/defects of HrGO dominates. In 3.2-4.5 V, PF_6^- intercalation into interlayers of highly graphitized domains dominates. Because the mobility of anions at surfaces is larger than at interlayers, resulting in slowing down of the positive charge density increase and delaying in-plane carbon bonds force constants increase. Another probable origin is the starting of anion packing and rearrangement within interlayers during intercalation [119]. It correlates to the "apparent G-band peak".

The G-band peak splitting is well-known for graphite when the stage index of guest ion intercalation is larger than or equals to 2. Such peak splitting reflects the differences in the environment of the graphene (or graphene oxide) layers and the adjacent layers due to different degrees of (de)intercalation of guest ion [52, 118, 120-122]. However, such splitting is absent. Similar phenomena have been observed in both anion- and cation-hosting graphene (or graphene oxide) [71-72, 121]. In our case, the fitting of the G-band peak requires two peaks (Figure 3.9). Two possible situations are given. At earlier lithiation stage of graphite, G-band peak shifts upward without splitting as a result of random Li⁺ distribution in dilute stage 1 [52, 118-119]. The other situation is that stage 2 or 1 graphite intercalation compounds' formation leads to the absence of splitting and the G-band peak due to low Raman scattering intensity, resulted from optical skin depth reduction of the formed highly electrically conductive compounds [52, 119]. Obviously, present case does not fit with the two situations. We



Figure 3.9 Comparison of selected Raman spectra's peak fitting with one and two peaks for Gband peak. (a) 1.6 V in charge; (b) 4.5 V in shaded region. Fitting envelopes are indicated by black lines. Deviations of fitting and original data are marked by yellow circles.

believe the possible root is the intercalation environment in HrGO is not distinct enough to separate the two peaks, corresponding to anion- rich and poor regions. Therefore, the "apparent G-band peak" was used in the analysis. The anion packing and rearrangement postulations are supported by gradual apparent G-band peak narrowing, suggesting reduced difference between anion-poor and anion-rich regions during continuous anion intercalation.

During discharging, processes reverse for D-band peak. Meanwhile, the G-band peak almost remains without noticeable shift in region 2*, 4.5–2.9 V. The gradual broadening of apparent G-band peak indicates the growing differences of anion-rich and anion-poor region, implying the anion deintercalation does take place. In addition to the relative slow process of deintercalation, no notable anion deintercalation seems to occur. Voltage decreases from 2.9 to 2.0 V (region 1*), obvious anion detach occurs in the pseudocapacitive manner. This is consistent with indication obtained from CV curves, mixed anion storage of HrGO. Further discharging leads to sallow lithiation of HrGO.

The measure of the structural order, the intensity ratio between the D-band peak and the apparent G-band peak, I_d/I_g , varies quite irregularly. Roughly, the ratio value is shown to decrease during charging and increase during discharging, Figure 3.8a. Selected Raman spectra, Figure 3.8b, show the evolution of spectrum from the start to the end of the cycle. It indicates that there was an increase in the structural order of HrGO during cycling, especially during delithiation and anion storage, which is supported by the results of subsequent ex situ characterization.

3.3.4 Consolidation of charge storage mechanisms

CV measurements with different scan rates were made to confirm the charge storage mechanisms of HrGO. Deviation from a rectangular capacitive CV shape is observed in Figure 3.10a. Representative potentials in the charge and discharge were selected and their current contributions were deconvoluted based on equations [123]

$$i = av^b \tag{3.1}$$

$$\log i = \log a + b \log v \tag{3.2}$$

where *i* is the measured current, *v* is the scan rate, and *a* and *b* are adjustable parameters. The *b* value tells the capacitive and diffusive contributions to the measured current. *b* = 0.5 implies diffusion contribution, while b = 1 implies capacitive contribution. Linear profiles of *log i* vs. *log v* are shown in Figure 3.10b. Three potentials were chosen, 1.55, 3.0, and 4.45 V. Additional potentials, 1.52 and 4.48 V, were further assigned to the lithiation and anion uptake, respectively. During cycling, all calculated *b* values are between 0.5 and 1.0, suggesting a collective capacitive and diffusive contribution for both PF_6^- and Li⁺ storage.



Figure 3.10 CV characterization of HrGO with varied scan rates. (a) CV curves. (b) Plots of log i versus log v at selected potentials in (a).

3.3.5 Ex situ XRD suggesting HrGO structure rearrangement

To gain a better understanding of the influence of polarity distinct ions' storage on HrGO and how the observed electrochemical activation of HrGO started and evolved, ex situ characterizations were carried out. No notable peak shift is observed in ex situ spectra obtained from XRD, Figure 3.11a. Progressive sharpening of the $(10\overline{1}0)$ and the (0002) peaks reveals possible rearrangement and ordering of the HrGO planes in the first cycle. The (0002) peak intensity increase for pristine HrGO after the first charge is accompanied by a slight broadening of the (0002) peak while almost only peak intensity increase is observed from first charge (1C) to first discharge (1D).



Figure 3.11 Ex situ XRD and XPS characterization of HrGO at different stages of cycling. (a) Ex situ XRD; (b) Ex situ XPS. Before cycling (Pristine), after the first charge (1C) and after the first discharge (1D). In (a), C-P is the resulted spectrum through 1C spectrum subtraction of Pristine spectrum to indicate spectrum difference. Similarly, D-P and D-C applies to 1D subtraction of Pristine and 1D subtraction of 1C, respectively. Inset of (a) shows the enlarged view of selected area.

3.3.6 Ex situ XPS indicating structural order increase

The evolution of deconvoluted HrGO high resolution XPS C 1s envelopes during the first cycle is shown in Figure 3.11b. The existence of C=C (sp², 284.6 eV), C-C (sp³, 284.8 eV), C-O (hydroxyl/epoxide, 286.2 eV), C=O (carbonyl, 288.0 eV), and O-C=O 55

(carboxyl, 290.0 eV) [115] is confirmed for the pristine HrGO. The weightings of these functional groups are listed in Table 3.1. There is noticeable doubling of the C-O and C=O weightings and a decrease of the C=C and C-C weightings, indicating the occurrence of probable oxidation of HrGO during the first charge. The slight O-C=O reduction might contribute to the C-O increase during oxidation [124]. After the first discharge, there are negligible decrease in the C=O weighting and a small decrease in the C=O and O-C=O weightings, revealing that the electrochemical reduction has limited influence on these functional groups.

	8	8	BB-
Bonds	Pristine	1C	1D
C=C	38.68%	32.72%	43.47%
C-C	28.65%	10.97%	4.15%
C-0	13.51%	28.39%	28.25%
C=O	7.26%	17.97%	14.86%
O-C=O	11.90%	7.31%	5.58%

Table 3.1 HrGO's functional groups' weighting of C 1s at different stages of cycling.

However, it is intriguing that the C=C weighting increases considerably to a value even higher than that for the pristine HrGO while the C-C weighting decreases continuously. In general, the ex situ XPS results are consistent with the ex situ XRD results. During the charge process, the (0002) peak width widening should be a result of oxidation of the HrGO while the peak intensity increase might be resulted from a large amount of C-C loss. On the other hand, in the discharge process, except for C=C bonding showing a considerable increase, other functional groups' weightings all show a different degree of reduction, which is consistent with the increased intensity of the (0002) peak.

Therefore, the rearrangement and ordering together with the increase in sp² bonding after cycling could be correlated with the activation observed during the HrGO cycling.

3.3.7 Visualization of electrochemical activation by ex situ TEM

Ex situ TEM of HrGO was also employed for HrGO to further unveil the mechanism of activation. In Figure 3.12a, 3.12c, and 3.12e, HrGO's morphology evolution occurred with the appearance of graphene oxide rolls, gradual cumulation, and structural order increase. Small graphene oxide rolls of approximately < 20 nm appeared. High resolution TEM (HRTEM) image of selected rolls shows expanded interlayer distances of 3.84, 4.16, and 3.84 Å from the bottom to the top (Figure 3.12b). During charging, oxidations occur, together with rearrangement or ordering of HrGO. This is consistent with the broadening and intensity growth of the 1C XRD peak, the increase of the oxygen-containing functional groups, and the breaking of the sp² carbon double bonds shown in the XPS at 1C. It is also consistent with the absence of an observable (0002) ring in the selected area electron diffraction (SAED) data. After 1D, there are rolls (Figure 3.12c) with decreased $d_{(0002)}$ -spacing, as shown in Figure 3.12d. Specifically, blue–blue and red–red distances are 3.53 and 3.85 Å, respectively. This is consistent with the exclusive (0002) peak intensification in the 1D XRD and the weighting increase of sp² carbon double bonds in the 1D XPS. Cycle repetition leads to the formation of considerable number of graphene oxide rolls (Figure 3.12e). Particularly, the interlayer distances decrease to 3.69 and 3.47 Å. Besides, a (0002) SAED ring with sharp spots is clearly present (Figure 3.12e), which is due to structural order increase of the reduced graphene oxide rolls (Figure 3.12f). The structural order



Figure 3.12 Ex situ TEM images of HrGO at different stages of cycling. (a) and (b), after the first charge; (c) and (d) the first discharge; (e) and (f) after 5,000 cycles. All SAED inset scale bars are 5 nm⁻¹. The (b), (d), and (f) are HRTEM images of blue squared part in (a), (c), and (e), respectively. And the upper right parts are the corresponding inversed fast Fourier transform (IFFT) images of red rectangular in (b), (d), and (f), respectively. The interlayer distances between red-red or red-blue lines are same in each image and larger than that of blue-blue lines.



Figure 3.13 HRTEM image HrGO after the 5,000th cycle. (a) HRTEM image, inset SAED scale bar: 5 nm⁻¹; (b) enlarged view of selected area in (a). The upper two squares are FFT and the lower right square is IFFT of selected area. The amorphous and crystalline area are separated by the yellow dotted line. Scale bar: 20 nm.

increment is also supported by observed hexagonal reduced graphene oxide layer *AB* stacking (Figure 3.13) [124], suggesting relatively long-range order is developed. Besides, notable accumulation of mesopores (Figure 3.13a) might also contribute to active surface area enlargement [74]. The possible formation mechanism of the reduced graphene oxide rolls is discussed. In general, the shedding of graphene layers

occur for graphite [78, 125]. Instead, graphene oxide rolls form for HrGO. A plausible hypothesis of the formation mechanism of graphene oxide rolls is illustrated in Figure 3.14. During charging, in-plane reduced graphene oxide lattice contraction and local anion intercalated region expansion lead to strain build up and lift up of surface layers during continuous anion uptake. Releasing of such strain gives driving force for the surface layers rolls up, forming the reduced graphene oxide rolls. When the PF_6^- stored at edges leaves during discharging, a possibly resultant "tensile force" may also facilitate the rolling process. In general, the universal electrochemical activation of HrGO is due to the increased surface area and followed structural order increase of the graphene oxide rolls during repeated cycling.



Figure 3.14 Schematic illustration of plausible formation mechanism of reduced graphene oxide rolls.

3.3.8 Kinetic improvement by electrochemical activation

The intrinsic kinetic properties of HrGO cathode were studied using EIS. Figure 3.15a shows Nyquist plots of HrGO before cycling (pristine), after the first charge (1C), after the first discharge (1D), and after the 5,000th discharge (5000th). Two models were carefully built to fit the experimental



Figure 3.15 EIS results of HrGO at different stages of cycling. (a) Nyquist plots of HrGO at different stages, fitting results are in solid lines; (b) Plots of real part impedance versus inverse square root of angular frequency corresponding to (a). After 5,000 cycles (5000th).

		e		e
	$R_e\left[\Omega ight]$	$R_a \left[\Omega ight]$	R_c [Ω]
Pristine HrGO	2.8	8.4×10^{-6}	206	5.6
			R_{et}	R_{ct}
1C	3.7	3	965.7	1043
1D	3.4	57.2	819.3	1575
5000th	6.2	1.5	74.1	501.2

Table 3.2 Nyquist plot fitting results of HrGO at different stages.

Table 3.3 Calculated HrGO diffusion coefficients at different stages.

	$D [{\rm cm}^2{\rm s}^{-1}]$
Pristine	5.7×10^{-14}
1C	6.9×10^{-13}
1D	6.3×10^{-14}
5000th	7.8×10^{-13}

data. The upper circuit is only applicable to "pristine" HrGO and the one below is applicable to the others. For pristine HrGO, the high-medium frequency region semicircle is originated from the charge transfer processes of the HrGO cathode (R_c) and the Li anode (R_a) [34]. After cycling, R_c is further divided into R_{ct} in the medium frequency range and R_{et} in the high frequency range, representing PF₆⁻ charge transfer resistance between the HrGO and the electrolyte, and electron transfer resistance of the HrGO, respectively [126-127]. R_e is the usual ohmic resistance. The introduction of R_{et} is rational owing to HrGO oxidation resulted decrease of the electrical conductivity and increase of electron transfer difficulty after cycling. Although differences exist with respect to the number and shape of the apparent semicircles for HrGO after cycling, fitting results using the electrical circuit show a high degree of matching. The fitting results of the HrGO are summarized in Table 3.2. The Ret shows continuous reduction from the first charge to the first discharge and further to the 5,000th discharge, and R_{ct} shows the same trend if only the discharged values are considered. Such evolution, especially the R_{et} decrease, indicates probable increase of structural order.

The diffusion coefficient of HrGO at different stages is calculated according to equation [128]

$$D = R^2 T^2 / 2A^2 n^4 F^4 C^2 \sigma^2 \tag{3.3}$$

where the gas constant, *R*, is 8.314 J K⁻¹ mol⁻¹, *T* is the temperature (K), *A* is the electrode surface area (cm²), *n* is the number of electrons exchanged, *F* is the Faraday constant (96,486 C mol⁻¹), *C* is the ion concentration, and σ is the Warburg factor, which could be obtained by calculating the slope of *Z*' versus $\omega^{-1/2}$, as $Z' \propto \sigma \omega^{-1/2}$ (Figure 3.15b). The diffusion coefficients corresponding to the plots in Figure 3.15a are summarized in Table 3.3. Overall, the continuous increase of the *D* value from 62

pristine to the first discharge and finally to the 5,000th discharge, indicates that Li⁺ diffusion in HrGO is accelerated. An increase of the *D* value after the first charge is observed, indicating accelerated PF_6^- diffusion. Such increase may either originate from oxidation resulted a large number of exposed active sites (Figure 3.13) or reduced graphene oxide layer rolling up during charging. The interlayer expansion would not provide such enhancement, as evidenced by a much lower *D* value of highly expanded pristine GO (two orders of magnitude lower than that for 1C HrGO) (Figure 3.16). In conclusion, the earlier ex situ results rationalize the introduction of R_{et} to the electric circuit and corroborate the gradual decrease of R_{et} and R_{ct} , together with the increasing diffusion coefficient in prolonged cycling.



Figure 3.16 Nyquist plot of pristine GO.

3.3.9 Electrochemical performance of activated carbon cathode

The observed electrochemical activation encouraged us to investigate whether the improvement means that HrGO would work for L–DIBs in a wider voltage range of 4.95-1.5 V. Therefore, after 400 cycles in the range 4.5-1.5 V at 0.05 A g⁻¹, the

Results and discussion



Figure 3.17 Cyclic performance of electrochemically activated HrGO at wider voltage range. (a) Voltage profiles and (b) cyclic performance of HrGO at 0.05 A g^{-1} within 4.95–1.5 V. The HrGO cell was cycled within 4.5–1.5 V for 400 cycles and directly used for this electrochemical measurement.



Figure 3.18 Cyclic performance comparison between HrGO and graphite. (a) Voltage profiles and (b) cyclic performance of pristine HrGO in 4.95-1.5 V; (c) voltage profiles and (d) cyclic performance of graphite in 4.95-1.5 V. Current density: 0.05A g⁻¹.

activated HrGO was used to assemble a new half-cell with fresh electrolyte and lithium foil for electrochemical tests in the range of 4.95-1.5 V at the same current density.

The voltage profiles (Figure 3.17a) resemble those in Figure 3.18a. A significant capacity enhancement is observed, with the first discharge capacity increasing to 502 mAh g⁻¹. The capacity values fluctuated a bit in the earlier cycling and started to grow to 640 mAh g⁻¹ at the 100th cycle, shown in Figure 3.17b. However, the initial and average CE are only 71% and 66%, respectively. Although significantly enhanced performance is shown after electrochemical activation in stark comparison to pristine HrGO and graphite (Figure 3.18) working in the same voltage window, the voltage window is still not suitable for HrGO in this system. It would be promising if amendments could be made to improve the inferior CE while maintaining such a high-capacity value.

3.4 Summary

This work focuses on unveiling the observed electrochemical activation and examining whether the HrGO is a suitable anion hosting cathode. The charge storage mechanisms of HrGO are confirmed with the aid of in situ Raman measurements, which implies that HrGO cathode operates through pseudocapacitive PF_6^- storage and intercalative anion uptake at high potentials. Supportive lithium storage/extraction happens at low potentials for HrGO cathode. When HrGO is tested within a voltage window of 4.5–1.5 V, significant electrochemical activation is observed in prolonged cycling, regardless of the applied current density. In-depth investigation reveals that the build-up of graphene oxide rolls and the gradual structural order increase of the graphene oxide rolls during repeated cycling collectively contribute to the activation. In addition, the performance of the activated HrGO was examined in the range of 4.95–1.5 V. Although unprecedented capacity was observed, such high upper cut-off voltage

remains inappropriate for HrGO. The HrGO could stably deliver a reversible capacity of 308 mAh g⁻¹ at 0.05 A g⁻¹ over 400 cycles, with consistent performance over 10,000 cycles. The accompanying activation not only contributed to capacity enhancement, but also promoted working voltage value increase. Comprehensively, the drilling of PF_6^- hosting HrGO cathode sheds light on the graphitic carbon's PF_6^- storage mechanisms and observed electrochemical activation, suggesting HrGO is a potential high-capacity cathode.

Chapter 4. Other factors affecting HrGO cathode and HrGO/LiFePO₄ parallel hybrid cathode

4.1 Introduction

DIB is an emerging renewable and eco-friendly energy storage system, which is promising for stationary applications. However, typical graphite cathode, providing high working potential (> 4.0 V vs. Li/Li⁺), suffers from low theoretical capacity and inferior practical capacity. Limited oxidative stability window of conventional organic electrolytes also hinders its practical application. Thence, finding of alternative highcapacity cathode compatible with the typical electrolytes is of high significance for DIB's development. In Chapter 3, we have unveiled that, with 3D interconnected electronic networks and rich porosity, the HrGO is potentially a high-capacity DIB cathode working within a voltage window of 4.5–1.5 V (vs. Li/Li⁺) in carbonate-based organic electrolyte. To verify operable voltage range of HrGO, upper cut-off voltage variation experiments were conducted. Furthermore, the salt concentration in electrolyte, influencing ions's mobility and anion uptake voltage [5, 7, 105], is yet uncovered. Therefore, concentration variation effects on HrGO are studied.

The intrinsically high porosity and low mass loading of the 3D HrGO are critical problems yet to be addressed. That is, the utilization of the HrGO as the sole active material of cathode is impractical. Graphene (or its derivatives) is frequently used as electronic additive in LIB cathodes owing to its high theoretical surface area and high electronic conductivity [129-131]. However, in the field of DIB, it is proved to be active anion host, contributing appreciable capacity as cathode [73-76]. It is accessible to bridge DIB and LIB cathode materials together as a hybrid cathode. Because

corresponding movement directions of cation and anion in LIB and DIB cathodes are in line with instantaneous ion response under an applied electric field. Mixing different active materials in cathode has been done in LIB for compensating their individual shortcomings and the resultant mixtures exhibit optimized electrochemical performance [132]. Although there is a work mentioning capacity contribution of carbon blacks as anion host when voltage is higher than 4.5 V vs Li/Li⁺, their specific discharge capacity is below 12 mAh g⁻¹ [68]. There also are work studying composite cathodes using anion-adsorption-based AC and LIB cathodes for capacitor and battery hybrid energy storage systems [94, 97, 133]. So far, the concept of building a hybrid cathode, combining high-capacity DIB cathodes with conventional LIB cathode materials, has not been demonstrated.

In this regard, with additive HrGO as active anion host and a typical LIB cathode material as cation host, a hybrid cathode is constructed. The exhibited capacity of the HrGO cathode is higher than reported values of conventional LIB cathodes. It implies the availability of overall electrode capacity enhancement through such hybridization. Besides, the hybrid cathode not only resolves the low-density issue concerning the HrGO but also improves overall electrical conductivity of the LIB only cathode. It is worth noting that the choice of LIB cathode is crucial as the operating voltage of DIB cathode is higher than that of LIB cathode. Increment of upper cut-off voltage will reduce available LIB cathodes owing to inferior thermal stability and side reactions at elevated potentials of certain cathodes [134-135]. Among existing LIB cathodes, LiFePO4 (LFP) has superior thermal stability, lower cost, and lower toxicity to environment [136-139]. Thus, it is optimal to have the LFP as the counterpart of the hybrid cathode with HrGO and LFP (HrLFP) exhibits increased reversible

capacities of 182, 188.8, and 198.6 mAh g^{-1} (the 30th cycle) compared to those of the pristine LFP cathodes 160.3, 163.2, and 145.6 mAh g^{-1} for 1 M, 2 M, and 3 M electrolytes, respectively.

4.2 Electrode preparation and electrochemical measurements

4.2.1 Electrode preparation

The HrGO is synthesized as described in Section 3.2.1. And the LFP is used as received without further purification or extra modification. For the upper cut-off voltage variation measurements and electrolyte concentration effects study, HrGO electrodes are prepared as described in Section 3.2.3. For hybrid cathode preparation, a mass ratio of 7:1:1:1 (LFP: HrGO: carbon black: PVDF) is used. For comparison, a mass ratio of 7:2:1 (LFP: carbon black: PVDF) is employed for pure LFP electrode preparation. Procedures are the same as described in Section 3.2.3.

4.2.2 Electrochemical measurements

For upper cut-off voltage variation tests, the voltage value ranges from 4.4 to 4.7 V (vs. Li/Li⁺) while the lower cut-off voltage remains at 1.5 V. The used electrolyte is 2 M LiPF₆ in EMC with 3 wt% VC. For the electrolyte concentration effect verification, the salt concentration varies from 1 M to 3 M. The rest remains the same as the description in Section 3.2.3.

4.3 Results and discussion

4.3.1 Upper cut-off voltage variation effects

It is known that the increase of upper cut-off voltage value will result in increased anion uptake capability for graphitic carbon cathode in DIB. In return, its incline exacerbates electrochemical stability and cyclic stability. Thus, to identify operable voltage window of HrGO, upper cut-off voltage change experiments were carried out. We have revealed that pristine HrGO performs poorly in the voltage window of 4.95– 1.5 V. Even after electrochemical activation, its CE is still unsatisfactory, indicating high cut-off voltage is not suitable for HrGO and such value should be lowered.



Figure 4.1 Differential capacity (dQ/dV) vs. potential (V) plots of HrGO with different test voltage window. (a) 4.7–1.5 V; (b) 4.6–1.5 V; (c) 4.5–1.5 V; (d) 4.4–1.5 V.

Therefore, the HrGO's performance in four test voltage windows, 4.7–1.5 V, 4.6–1.5 V, 4.5–1.5 V, and 4.4–1.5 V, was evaluated. The voltage window's variation only has a little influence on the shape of differential capacity profiles (Figure 4.1). In Figure 4.1a-4.1c, the differential capacity profiles share high similarity. Except for slight deviation for the 4.4–1.5 V sample in Figure 4.1d, all redox peaks locate about 0.05 V to corresponding applied cut-off voltages and the rest portions of all curves are superimposed capacitor-like linear lines. Although, the reduction of upper cut-off voltage from 4.7 to 4.4 V did not narrow the distances between redox peaks, the open circuit potential (OCP) of HrGO didn't drop significantly with upper voltage's reduction. It indicates that the reversible capacity might be available as expected.

To screen out the operable voltage window, middle discharge voltage (MDV), an indicator of energy density, was also assessed. In Figure 4.2, it could be clearly seen that the HrGO tested in 4.4–1.5 V shows the lowest capacity (57.5 mAh g⁻¹ at the 1,000th cycle) and low MDV (2.41 V for average, 2.40 V at the 1,000th cycle). Meanwhile, sample tested in 4.7–1.5 V shows the lowest MDV (2.31 V for average, 2.34 V at the 1,000th cycle) and inferior capacity (90.6 mAh g⁻¹ at the 1,000th cycle). Nevertheless, the HrGOs exhibit similar discharge capacities in other two voltage windows (4.6–1.5 V, 98.3 mAh g⁻¹ at the 1,000th cycle; 4.5–1.5 V, 98.0 mAh g⁻¹ at the 1,000th cycle). The HrGO tested in 4.5–1.5 V displays higher MDV (4.6–1.5 V, 2.53 V for average, 2.56 V at the 1,000th cycle and 4.5–1.5 V, 2.59 V for average, 2.69 V at the 1,000th cycle). Overall, it seems that 4.5–1.5 V and 4.6–1.5 V are acceptable voltage windows for HrGO in this system. Out of the two suitable voltage ranges, the 4.5–1.5 V is the best and it is used for further studies.



Figure 4.2 The comparison of cyclic performance and middle discharge voltage among the HrGO electrodes tested in the four voltage windows.

4.3.2 Electrolyte concentration variation effects

Cyclic performance of the HrGO in different electrolyte concentrations varying from 1 M to 3 M is studied as shown in Figure 4.3a. Under a current density of 0.05 A g⁻¹ and an applied voltage window of 4.5–1.5 V, the HrGO cathodes exhibit reversible capacities of 154.6, 160.4, and 187.9 mAh g⁻¹ in 1 M, 2 M, and 3 M electrolytes, respectively. The capacity increase with increasing electrolyte concentration can be related to the Equation 1.5 of Chapter 1. It indicates that the operating potential of dual ion battery is related to the dissolved ions' concentration in electrolyte. Theoretically, the increase of ion concentration will decrease the potential of dual ion battery. That is, the anion uptake potential decreases with the increase of electrolyte concentration. On the other hand, cathode capacity depends on upper cutoff voltage. Without interference of side reactions, like electrolyte instability at electrolyte/cathode

interface, higher charging potential should enable higher capacity. Therefore, positive capacity dependency on electrolyte concentration is shown for HrGO.

Additionally, the HrGO cathodes show continuing capacity increment in the three electrolytes. In 1 M electrolyte, the HrGO cathode reaches the maximum of 253.9 mAh g^{-1} at the 244th cycle. Then it declines to 180.6 mAh g^{-1} at the 350th cycle. In contrast, monotonous capacity increase of the HrGO cathodes happens for the 2 M and 3 M electrolytes. At the 385th cycle, high capacities of 318 and 424.6 mAh g^{-1} are delivered by the HrGO cathodes in 2 M and 3 M electrolytes, respectively. The HrGO cathodes show average CE values of 93.85%, 95.60%, 99.02% for 1 M, 2 M, and 3 M electrolytes, respectively. It is noteworthy that CE values of the HrGO in 1 M



Figure 4.3 Electrochemical performance of the HrGO in electrolytes with differing salt concentration. (a) Cyclic performance of the HrGO in 1 M to 3 M LiPF₆ in EMC with 3 wt% VC; (b) MDV change during cycling; Voltage profiles of the HrGO in (c) 1 M, (d) 2 M, (e) 3 M electrolyte, respectively. Applied voltage window: 4.5–1.5 V. Current density: 0.05 A g⁻¹.

electrolyte exhibit distinctive growth after capacity maximum while that of the HrGO in 3 M electrolyte continuously decrease with large fluctuation, especially at elongated cycling. In addition, in 3 M electrolyte, the CE values are frequently observed to be higher than 100% from the starting of electrochemical cycling. This is directly interpreted as: the number of extracted anions is larger than the number of stored anions in the HrGO. Obviously, this is impossible. Two plausible explanations are referred to side reaction during discharging and introduction of lithiation process in the HrGO at low potentials in the 3 M electrolyte. The "side reaction" refers to cathodic electrolyte decomposition at electrode/electrolyte interfaces. Even though the carbonate electrolytes are theoretically stable within employed voltage window, possible reduction of required energy for lithiation might also be present because of high electrolyte concentration. A general speculation was adopted as such possibility was not confirmed in this work. The latter is supported by starting the HrGO test by discharging to 1.5 V instead of charging to 4.5 V, as illustrated in Figure 4.4. It can be seen that with different OCP values, the HrGO electrodes can deliver a capacity ranging from 9.2 to 41.3 mAh g⁻¹ by lithiation. And the extra



Figure 4.4 Voltage profiles of two representative HrGO electrodes started with discharging to 1.5 V.

capacities during discharging of the HrGO cathode making CE values > 100% in the 3 M electrolyte locate well within such presumable capacity range.

In Figure 4.3b, during cycling, the evolution trends of MDV in the three electrolytes resemble each other within the first ten cycles and they all surge to values > 2.3 V. In continued cycling, the HrGO cathode in the 1 M electrolyte exhibits gradual MDV value growth and an extra surging exists for it after the 244th cycle; in the 2 M electrolyte, MDV value increases continuously; in the 3 M electrolyte, MDV value decreases with notable fluctuation. Corresponding voltage profiles of the HrGO cathodes in 1 M, 2 M, and 3 M electrolytes are displayed in Figure 4.3c, 4.3d, and 4.3e, respectively. The profiles' shapes share high similarity, corroborating observed electrochemical activation in Figure 4.3a. Deviations show up at the 350th cycle. In the 1 M electrolyte, the discharging curve of the HrGO becomes convex, which is similar to that of ternary lithium-containing cathodes [140-141] instead concave. This is in line with the highest MDV value of 2.62 V among the three tested electrolytes. In contrast, in the 3 M electrolyte, during discharging, multiple spikes appear and locate at potentials close to 1.5 V, suggesting possible side reactions. Comprehensively, high salt concentration contributes to high capacity and intensified electrochemical activation. But it might also introduce possible lithiation process or unwanted side reactions when discharging to low potentials. The appearance of such phenomena is possibly originated from the eased anion storage and extraction in high concentration electrolyte.

4.3.3 HrGO/LiFePO₄ parallel hybrid cathode

Before the construction of parallel hybrid cathode, pristine LFP cathodes are measured in the three electrolytes with different concentrations within a voltage window of 4.5–

1.5 V at a current density of 0.05 A g⁻¹ (approximately 0.3 C, 1 C = 0.17 A g⁻¹, assuming theoretical capacity of 170 mAh g⁻¹ for LFP), Figure 4.5. As shown in Figure 4.5a, less concentrated electrolytes enable higher reversible capacity. Specifically, at the 30th cycle, LFP cathodes deliver capacities of 160.3, 163.2, and 145.6 mAh g⁻¹ for 1 M, 2 M, and 3 M, correspondingly. Voltage profiles of LFP cathodes in 1 M to 3 M electrolytes are presented in Figure 4.5b to 4.5d. Well-defined long flat charge/discharge plateaus indicate that the concentrated electrolytes do not alter the first principle two-phase reaction mechanism of the LFP [138, 142]. Moreover, it also indicates LFP can cycle stably at the applied voltage window, wider than those commonly employed for LFP [131, 143]. However, in the 1 M electrolyte, the plateaus are shortened and become sloping. The tails of both charge and discharge curves are probably pseudocapacitive due to the existence of Fe^{3+} on the LFP surface [131, 144]. Partial Fe^{3+} presence [145-146] is confirmed by high resolution XPS in Figure 4.6. The polarization observed in the 1 M electrolyte should not be stemmed from poor electrical conductivity of LFP electrode as it is the same batch as those used in the 2 M and 3 M electrolytes. And 20 wt% conductive carbon black is used for all electrodes. Possible explanations are the pristine LFP is nonuniform and occasionally presence of Fe³⁺ defects on the LFP surface. Overall, the LFP cathode can perform normally in the wider voltage window and in concentrated electrolytes.

Thus, with additive HrGO as anion host and capacity facilitator and dominant LFP possessing high thermal stability and working with cation, the designed parallel hybrid cathodes are built. Based on the cyclic performance of the hybrid cathodes shown in Figure 4.7a, the goal of capacity enhancement is definitely achieved, evident from



Figure 4.5 Electrochemical performance of pristine LFP in concentration different electrolytes. (a) Cyclic performance of LFP in 1 M to 3 M electrolyte; Voltage profiles of LFP in (b) 1 M, (c) 2 M, (d) 3 M electrolytes, respectively. Applied voltage window: 4.5–1.5 V. Current density: 0.05 A g⁻¹. Capacity values are calculated based on weight of LFP.



Figure 4.6 High resolution XPS spectra of pristine LFP Fe 2p.

increased reversible capacity at the 30th cycle in all tested electrolytes. Specifically, at current densities of 0.05A g⁻¹, 182, 188.8, and 198.6 mAh g⁻¹ (calculated based on the mass of LFP for comparison with pristine LFP cathodes, 159.3, 165.2, and 173.8 mAh g⁻¹ based on the mass of HrGO and LFP) are maintained in the 1 M, 2 M, 3 M electrolytes, respectively. The measured capacity values are higher than the theoretical value of LFP, indicating the success of such parallel hybrid cathode. The extra capacity comes from the anion storing HrGO. Notably, the HrLFP cathode's capacity increases



Figure 4.7 Electrochemical performance of HrLFP hybrid cathode in concentration different electrolytes. (a) Cyclic performance of the HrLFP in 1 M to 3 M electrolyte; Voltage profiles of the HrLFP in (b) 1 M, (c) 2 M, (d) 3 M electrolytes, respectively. Applied voltage window: 4.5–1.5 V. Current density: 0.05 A g⁻¹. Capacity values are calculated based on weight of LFP.

with inclining salt concentration, implying that the 10 wt% additive HrGO is effective in boosting capacity increment and compensating the suppressed cation storage capability of LFP in the 3 M electrolyte. A comparison among the HrLFP hybrid cathodes' voltage profiles in the three electrolytes is made from Figure 4.7b to 4.7d. Serious polarization and slight pseudocapacitive tails present for the HrLFP in the 1 M electrolyte. In the 2 M electrolyte, polarization is minimized but sloping plateaus show up. In the 3 M electrolyte, voltage file's shapes are highly similar to the pristine LFP without polarization. This comparison reveals poor compatibility between anion-storing HrGO and cation-storing LFP in the dilute electrolyte but good in the concentrated electrolytes.

4.4 Summary

It is confirmed that upper cut-off voltage values set at 4.6 V and 4.5 V are acceptable for the HrGO cathode. Out of the tested voltage windows, the 4.5–1.5 V is the ideal one in our system. In the electrolyte concentration variation tests, the HrGO cathodes displayed divergences when the concentration changes. But they share the same trend, continuing capacity growth over a long cycle life. In the 3 M electrolyte, the HrGO can deliver an ultrahigh capacity of 424.6 mAh g⁻¹ at 0.05 A g⁻¹ at the 385th cycle. After confirming the electrochemical stability of LFP in carbonate-based organic electrolytes with different concentrations, the designed parallel hybrid cathode HrLFP was built and it can work normally without notable polarization in the 3 M electrolyte. Moreover, it can deliver a high capacity surpassing theoretical capacity of the pristine LFP. Thus, the HrLFP not only resolves low-density issue concerning the HrGO but also increases deliverable capacity of the LFP. Furthermore, the success of HrLFP hybrid cathode demonstrates that the idea of simultaneous anion/cation
storage/extraction in one cathode is available. Therefore, extra cautions should be taken when adding graphitic carbons to LIB cathodes as they might be active.

Chapter 5. Graphite/LiFePO4 serial hybrid cathode

5.1 Introduction

To achieve the goal of sustainable energy supply, energy conversion techniques, like wind power and geothermal, are drawing attention. The converted energy that can't be immediately supplied to electric grid would be stored using energy storage systems. LIB is a typical and popular energy storage system. It has been widely employed for high-end portable electronic devices, electrical vehicles, and stationary power banks [147-149]. However, its cathode materials are mainly poisonous and resource-limited transition-metal-oxides, like LiCoO₂, LiNi_{0.8}Co_{0.15}Al_{0.05}O₂, and LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ [150-152]. A balance between the growing demand and finite supply has to be made in a long term.

Alternatively, graphite is reported to be capable of functioning as not only anode but also cathode with a discharge voltage (> 4.0 V vs. Li/Li⁺) higher than commercial LIBs [34, 153]. Such high discharge voltage is offered by simultaneous deintercalation of anion from graphite cathode and cation from anode. Cell governed with this working principle is called DIB. With graphite cathode, the DIB is an optimal solution alleviating the heavy reliance on resource-limited transition-metal-oxide cathodes. However, even being capable of working with different anodes and various anions, graphite cathode exhibits relatively low specific capacity, generally lower than 100 mAh g⁻¹ in extended cycling [6, 24, 106-107, 125, 154]. Using of novel ionic liquid [155], multi-ion electrolyte [156], and micro-engineered aluminum anode showed

decent improvement in capacity [157-158]. But these methods involve complicated nanostructure design and expensive ionic liquids. An approach with better trade-off between capacity enhancement and necessary efforts is desired.

Theoretically, for LIB, during charging, Li⁺ deintercalates from cathode while anode is intercalated with Li⁺. At the same time, anions move from anode side to cathode side. But no anion storage occurs. Because typical LIB cathodes are not anion host. For DIB, during charging, anions intercalate cathode while cations intercalate anode. That is, the two working principles are not contradictive. The difference is that LIB cathode is only cation-storable while DIB cathode is anion-storable. Thus, it implies that LIB and DIB are compatible and capable of functioning in one cell. This idea has been utilized for the building of hybrid lithium ion capacitors [93-95, 97]. The cathodes of these capacitors are commonly composed of physical mixture of lithium metal oxide and activated carbon. This idea can be applied for capacity increment for graphite-based cathode. Thus, a hybrid cathode composing of a physical mixture of graphite and lithium iron phosphate is proposed. The LFP is chosen for its decent theoretical capacity, relatively low price, high abundancy, non-toxicity, and high thermal stability [159-160]. This hybrid cathode is designed to work in a serial manner. To be specific, during charging, deintercalation of Li⁺ from LFP occurs in low voltage region, followed by intercalation of anion into graphite at high voltage region. Additionally, in this hybrid cathode, graphite also acts as electronic conductive matrix for LFP. Even though, the aforementioned hybrid lithium ion capacitor cathode works in a parallel manner is experimentally proved. Whether this graphite and LFP hybrid cathode works in serial manner needs to be confirmed. And the cathode's working mechanism has not been justified yet.

Therefore, in this study, graphite and LFP hybrid cathode is studied as a sustainable cathode alternative. To the best of our knowledge, this serial hybrid cathode has not been studied previously. Thus, in situ XRD and electrochemical measurements were carried out to demonstrate the stepwise cation deintercalation and anion intercalation at the hybrid cathode during charging and verse versa during discharging. Compositional ratio variation between LFP and graphite does not affect high cyclic stability but changes capacity value, varying from 66 to 103 mAh g⁻¹ at the 200th cycle. All studied compositions showed higher capacity than pristine graphite. 40 wt% LFP and 60 wt% graphite hybrid cathode (40LFPG) was chosen as a typical example representing carbon-based hybrid cathode. Further characterizations were mainly performed for the 40LFPG. High compatibility is revealed by distinct voltage plateaus and capacity preservation after long-term cycle, maintained respective apparent diffusion coefficient, and intact micro-morphology. When the 40LFPG was coupled with a graphite anode as full cell, it can deliver a reversible capacity of 77 mAh g⁻¹ at 0.05 A g⁻¹, indicating the potential of such hybrid cathode.

5.2 Experimental details

5.2.1 Electrode preparation and electrochemical measurement

All chemicals were used as received without further purification. All electrodes were prepared with a mass ratio of 8:1:1 among active material, carbon black, and polyvinylidene fluoride. For the hybrid cathode, the active material was composed of LFP and graphite, varying from 30 wt% LFP (70 wt% graphite, 30LFPG) to 70 wt% LFP (30 wt% graphite, 70LFPG). The well-mixed electrode materials were dispersed in *N*-methyl-2-pyrrolidone to form a slurry. Then the slurry was casted onto aluminum

foil and dried in vacuum oven at 393.15 K for 12 h. For half-cell assembly, coin cell 2032 was used, lithium was used as reference and counter electrode, Celgard 2500 was used for separator, and 2 M LiPF₆ dissolved in ethyl methyl carbonate with 3 wt% vinylene carbonate was used as electrolyte. For full cell assembly, electrochemically lithiated graphite was used as counter electrode instead of lithium, glass fiber (Whatman A) was used as separator, the rest remained the same. The prelithiated graphite was prepared by constant current discharging (0.01 A g^{-1}) a half-cell, composed of lithium and graphite electrodes, to 0.01 V and constant voltage discharging at 0.01 V until the current became less than 0.01 A. Then, the half-cell was disassembled in glove box to obtain the lithiated graphite. Galvanostatic cyclic measurements were performed using LAND CT-2001A (5 V) system within a voltage window of 4.8-2.0 V for the half cell and 4.5-1.7 V for the full cell. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests were performed on an AutoLab PGSTAT302N electrochemical workstation. Electrodes for in situ XRD measurements were prepared by casting the same hybrid slurry (40LFPG) onto beryllium window and vacuum dried at 393.15 K for 12 h.

5.2.2 Material characterization

For the in situ XRD measurements, the cell set was used as obtained, illustrated in Figure 5.1. A large hole is opened on the cathode shell and an X-ray permeable beryllium window functions as current collector. After assembly, the sealed cell was positioned inside chamber of the X-ray spectrometer (Rigaku Smartlab 9 kW, Cu K α radiation, $\lambda = 1.54$ Å) and connected to battery test system with concurrent galvanostatic cyclic measurements performed within 4.8–2.0 V. The XRD spectra



Figure 5.1 Illustration of cell configuration used for in situ XRD measurements.

were collected continuously while electrochemical cycling was carried out. Transmission electron microscope (TEM, Joel JEM-2100F) and scanning electron microscope (SEM, TESCAN VEGA3) were utilized for morphology and structure characterization.

5.3 Results and discussion

5.3.1 Working mechanism of the serial hybrid cathode

Figure 5.2 clearly illustrates the working mechanism of a full cell with designed hybrid cathode including LFP and graphite. During charging step 1, at cathode, Li⁺ extracts from LFP, forming FePO₄ (FP) while graphite remains intact. Concurrently, at anode, graphite is intercalated with Li⁺, forming Li_xC. Then in charging step 2, FP formed at step 1 is maintained and PF_6^- intercalates into graphite at cathode, forming C(PF₆)_y. Meanwhile, Li⁺ continues to intercalate into graphite at anode, forming Li_{x+y}C. In discharge, the processes reverse. Such stepwise charge and discharge are beneficial for maintaining integrity of individual components in the hybrid cathode and preventing side reactions.



Figure 5.2 Working mechanism of the proposed hybrid full cell.

5.3.2 Characterization of pristine materials

SEM, TEM, and XRD of the pristine graphite are shown in Figure 5.3, 5.4, and 5.5, respectively. The graphite has irregular particle shape and a particle size of about 10 μ m, in Figure 5.3. Well-defined polycrystalline selected area electron diffraction

(SAED) rings ((002), (100), and (101)) in inset of Figure 5.4a agrees well with the graphite XRD spectra with a card no. 03-065-6212 in Figure 5.5.



Figure 5.3 SEM image of as-received graphite. Scale bar: 5 μ m.



Figure 5.4 TEM image of used pristine graphite at a) low magnification, b) high magnification. Inset: SAED of graphite. Scale bar: 5 nm⁻¹.



Figure 5.5 XRD of pristine graphite.

Judging from Figure 5.6 and 5.7, the pristine LFP particles are coated with carbon. But the carbon coating of purchased LFP particles is nonuniform and relatively poor. The quality of raw LFP would not make a significant difference as this work is focused on concept demonstration. The mapping results reveal atomic ratio of Fe:P is close to 1:1. The TEM characterization results (Figure 5.7) are in line with the XRD results of pristine LFP (Figure 5.8), a well-matched triphylite phase, 01-080-6251. However, partial amorphous phases are observed at the outer layer of the pristine LFP, as illustrated in Figure 5.7b. Since we are focusing on demonstrating the availability of the serial hybrid cathode concept not emphasizing the electrochemical performance, this can be neglected for now.

Graphite/LiFePO4 serial hybrid cathode



Figure 5.6 SEM of as-received LFP and its corresponding mapping images. All scale bars are 2 $\mu m.$



Figure 5.7 TEM images of pristine LFP at a) low magnification, b) high magnification. Inset: SAED of LFP. Scale bar: 5 nm⁻¹.



Figure 5.8 XRD of pristine LFP and corresponding refined spectra.

5.3.3 Electrochemical performance of the hybrid cathode

As shown in Figure 5.9a-5.9c, hybrid cathodes with 5 compositional ratios, ranging from 30LFPG to 70LFPG were prepared and studied (30 wt% LFP-70 wt% graphite for 30LFPG; in all figures abbreviation only uses the LFP percentage number, for example 30). The voltage profiles (Figure 5.9a) of all half cells with different compositional hybrid cathodes exhibit three pairs of charge/discharge plateaus. The flat plateaus at 3.5 V during charging and 3.3 V during discharging belong to the first principle phase transformation reactions of LFP. Besides, the remaining two plateau pairs higher than 4.1 V belong to PF_6^- intercalation/deintercalation in graphite. The voltage profiles agree well with the working mechanism illustrated in Figure 5.2 and suggest the availability of polar distinct ions' interaction at the hybrid cathode. Figure 5.9b shows that capacity increases as LFP weighting increases. In this study, the given capacity values are discharge capacity if not specified. The 70LFPG has the highest



Figure 5.9 Comparison of 30LFPG-70LFPG (a) voltage profiles, (b) galvanostatic cyclic performance, (c) middle discharge voltage profiles. Voltage window: 4.8–2.0 V. Current density: 0.1 A g⁻¹, around 1.1 C for 40LFPG. 1 C means 1 hour is needed to be fully charged/discharged. (d) Galvanostatic cyclic performance comparison of 40LFPG at varied upper cut-off voltages, 4.7–2.0 V, 4.8–2.0 V, and 4.9–2.0 V.

capacity, 103.6 mAh g⁻¹ after 200 cycles. And 30LFPG has the lowest capacity, 66.3 mAh g⁻¹, after 200 cycles. Furthermore, the increase of LFP weighting also results in the increase of coulombic efficiency (CE) from 90% to 95% (from 30LFPG to 70LFPG, average value of 200 cycles). However, such trend is reversed with respect to middle discharge voltage (MDV). The LFP weighting's increment leads to decrease of MDV value (Figure 5.9c). To be specific, MDV decreases from 3.33 V (30LFPG) to 3.07 V (70LFPG) after 200 cycles. So far, a general view of how hybrid cathode weighting ratio variation affects the cathodes' performance is obtained. The well match between such preliminary results and initial electrode design encourages our further exploration. As the study is focusing on graphite-based hybrid, 40LFPG is

chosen for in-depth study. The effect of upper cut-off voltage variation on 40LFPG is studied as shown in Figure 5.9d. In our studied system, 4.8-2.0 V was chosen for further characterization. Since inferior capacity at 4.7-2.0 V and low CE at 4.9-2.0 V are observed.

Galvanostatic CV of 40LFPG, in Figure 5.10a, could roughly be viewed as a CV superimposition of LFP (Figure 5.10b) and graphite (Figure 5.10c). In 40LFPG cathode, below 4.0 V, only LFP redox peaks corresponding to lithium insertion/extraction exist while only graphite redox peaks corresponding to PF_6^- intercalation/deintercalation present between 4.0–4.8 V. Each peak can be found in individual LFP or graphite CV. And unknown redox peaks do not exist in 40LFPG.



Figure 5.10 Galvanostatic CV of (a) 40LFPG, (b) LFP, (c) graphite. Scan rate: 0.2 mV s⁻¹. Voltage window: 4.8–2.0 V. (d) Voltage profiles of 40LFPG. (e) Cyclic performance comparison among 40LFPG, LFP, and graphite. (f) Rate performance of 40LFPG.

Therefore, it indicates stepwise and orderly Li^+ and PF_6^- intercalation/deintercalation in LFP and graphite, correspondingly. Moreover, the large polarization of LFP is mitigated in the 40LFPG. Because LFP has low electronic conductivity [161-162] while graphite has higher electronic conductivity. In spite of that the as-received pristine LFP is coated with carbon, the carbon coating is not conformal over LFP

(Figure 5.7a). Thus, relatively large redox peak separation and broaden of redox peaks of pristine LFP showed up. As designed, the graphite in hybrid cathode not only functions as active material but also serves as electronic conductive matrix for LFP. Voltage profiles of 40LFPG at different cycles (Figure 5.10d) reveal good preservation of characteristic plateaus and almost no noticeable polarization development in extended cycling. Especially, the plateaus belong to electrochemical reactions of graphite are almost intact, indicated by high level of curve overlapping at voltage region approximately 4.0–4.8 V. The deviations of LFP's electrochemical reactions from a two-phase reaction are reflected by shortened flat plateau length and increased sloping plateau length. These sloping plateaus might be intermediate phases frequently observed in LFP [163-164]. It is supported by in situ XRD data presented in latter section. Generally, capacity is well-maintained. This is further consolidated by cyclic performance of 40LFPG shown in Figure 5.10e and 5.10f. Firstly, the capacity of 40LFPG almost doubled compared to pristine graphite (at the 50th cycle, 83.9 and 43.8 mAh g⁻¹ for 40LFPG and graphite, respectively), fulfilling capacity increment goal by such graphite-based hybrid cathode. Secondly, the 40LFPG has high cyclic stability. The capacity of the second cycle is 87.8 mAh g^{-1} and the high retention of capacity was showed, 78.7 mAh g⁻¹, until 500 cycles. The absolute capacity values are not high. But they are very close to theoretical capacity value of the 40LFPG. Assuming 170 mAh g^{-1} for LFP and 45 mAh g^{-1} for graphite (under current density of 0.1 A g^{-1}), the theoretical capacity would be 95 mAh g⁻¹. An 83% retention of theoretical capacity at 0.1 A g⁻¹ after 500 cycles, suggesting that the hybrid cathode works as designed and expected. Furthermore, the 40LFPG preserves a decent MDV despite fast MDV decay in pristine LFP (Figure 5.11). The 40LFPG has average capacities of 102, 89.1, 79.2, 62.9, and 39.4 mAh g^{-1} at current densities of 0.05, 0.1, 0.2, 0.5, and 1 A g^{-1} , respectively. When current density returns to 0.05 A g^{-1} , it has a capacity of 92.9 mAh g^{-1} after 400 cycles.



Figure 5.11 MDV comparison among 40LFPG, pristine LFP, and pristine graphite.

5.3.4 In situ XRD characterization

In situ XRD measurements were carried out to inspect the constituents' phase evolution in 40LFPG hybrid cathode and verify whether LFP and graphite work independently and compatibly. Before electrochemical reactions take place, the selected XRD spectrum of 40LFPG, Figure 5.12, is a superimposition of pristine LFP (triphylite, Card No. 01-080-6251, Figure 5.8) and pristine graphite (hexagonal, Card No. 03-065-6212, Figure 5.5). The peak located around 36° is the signal of lithium at anode. The spectra and voltage variation belong to graphite is marked by red rectangles. The (002) peak (26.4°) of graphite in 40LFPG remains unchanged before charging to 4.7 V. Continued charging to 4.8 V leads to significant intensity drop of (002) peak and concurrent appearance of two new peaks. One locates at 29.7° and the other one continues shift to lower 2 theta value, reaching minimum at 4.8 V. During charging



Figure 5.12 Selected in situ XRD spectra and corresponding voltage versus time plot. 2 theta value of peaks is indicated by location of arrow (beginning end of arrow).

from 4.7 to 4.8 V, the voltage versus time plot exhibits an obvious sloping plateau, corresponding to PF_6^- intercalation into graphite. It has to be mentioned that this does not mean that the anion intercalation starts at 4.7 V. The sloping plateau corresponding to anion intercalation below 4.7 V is hard to point out in the voltage versus time plot. And, at such early stage, the detectable amount of reacted graphite may be insufficient to be detected by XRD. Then discussion was not included in this section. The selected in situ XRD spectra of graphite are well-matched with graphite cathode in DIB with PF_6^- intercalation [7, 25]. Since anion intercalation of graphite at cathode also follows a staging mechanism. Based on stage index calculation method [7], the stage index of tested graphite is calculated to be slightly larger than 5, implying low degree of PF_6^- intercalation. Discharging from 4.8 to 3.0 V, a steeper slope appeared in voltage versus time plot, the 29.7° peak intensity decreases, and the other new peak gradually shifts

back to higher 2 theta value. It also agrees well with reported anion deintercalation from graphite [7, 25]. Although the (002) peak of graphite showed intensity decrease after its reaction with anion, no other noticeable change is observed during further discharging process. This means that graphite is only active in high voltage region as highlighted with red rectangles. With respect to the LFP in the 40LFPG hybrid cathode, no perceptible change of LFP's or FP's (heterosite, Card No. 01-070-6685) characteristic peaks in the graphite active region. At LFP active region, it follows the first order two-phase transformation. During charging, peaks of FP showed up first are (020) and (200) (30.9° and 18.1°, respectively) while peaks of LFP corresponding to (020) and (200) are still present $(29.7^{\circ} \text{ and } 17.2^{\circ}, \text{ respectively})$ with intensity decrease. This indicates that in this hybrid cathode LFP obeys the first order two-phase transformation and [010] is still the preferred Li⁺ diffusion direction as LFP in LIB [160-161, 165-166]. Similarly, FP's peaks continued to appear at higher 2 theta values, like (111), (211), (301), (311), and (121). Only FP's (101) peak locates at slightly lower 2 theta value, bridging with LFP's (101) peak. It suggests that formation of intermediate phase [163], which agrees with the speculation made about the sloping plateaus of 40LFPG at Figure 5.10d. Generally, the unit cell of LFP shrinks during charging, even with a bit extension along [101]. During discharging, processes reverse. At the end of discharge, no obvious FP phase exists but intensity of all LFP peaks decreases. The in situ XRD results further support that our concept-stepwise deintercalation/intercalation of cation and anion in such hybrid cathode is accessible.

5.3.5 Ex situ TEM characterization

Morphological and phase inspections of the 40LFPG after the 1st charge (1C) and discharge (1D) were also conducted. Figure 5.13a is a TEM image showing a selected ⁹⁶



Figure 5.13 TEM images of the 40LFPG after 1C (a-d) and 1D (e-h). (b) and (f) are SAED of (a) and (e); (c) and (g) are enlarged view of solid purple rectangle area of (a) and (e), respectively. (d)

and (h) are FFT reconstructed images of rectangle areas of (c) and (g), respectively. Scale bar of (b) and (f): 5 nm^{-1} . Inset scale bar of (e): 50 nm.

area where both FP and graphite present. SAED image of this area (Figure 5.13b) clearly shows a set of well-defined diffraction spots of FP, marked with solid red circles, and polycrystalline diffraction spots corresponding to slightly expanded graphite, connected with dashed yellow semicircles. It has to be mentioned that the semicircles are used to prevent visual confusion between graphite and FP. The semicircles do not indicate amorphous diffraction rings as no observable amorphous rings present for graphite. High resolution TEM (HRTEM) of purple rectangle region is shown in Figure 5.13c. The fast Fourier transform (FFT) generated diffraction pattern (inset) of orange rectangle marked region is the same as the pattern in Figure 5.13b. By applying FFT and positive mask (Figure 5.14), the marked region is reconstructed to provide close look at LFP's crystalline structure after 1C as shown in Figure 5.13d. The FP (200) planes are well-aligned, except a little distortion of planes. The ordered (002) crystalline planes of graphite are highlighted by two dashed light blue lines (Figure 5.13c). Similarly, after 1D, area containing both LFP and graphite is selected (Figure 5.13e). Figure 5.13f presents polycrystalline diffraction spots of graphite and LFP after 1D. Although the ordered range of LFP decreased, it still presents certain degree of order, indicated by red circles and dashed lines. Figure 5.13g shows enlarged solid purple rectangle area in Figure 5.13e. The ordered crystalline planes of graphite are also marked by light blue lines. FFT generated diffraction pattern of selected area on LFP, highlighted by red parallelogram at inset, agrees well with that obtained by SAED. With positive mask applied (Figure 5.15), reconstructed image (Figure 5.13h) shows regional order of LFP. Comprehensively, the 40LFPG hybrid

cathode after 1C and 1D are still integrated, which is in line with the in situ XRD results.



Figure 5.14 (a) Array mask chosen for Figure 5.13d reconstruction, (b) corresponding applied positive mask.



Figure 5.15 (a) Array mask chosen for Figure 5.13h reconstruction, (b) corresponding applied positive mask.

5.3.6 Kinetic properties

To find out whether there is any degradation in kinetic properties of 40LFPG in comparison to their properties in individual cathode, scan rate varied CV measurements were performed (Figure 5.16a). Three obvious redox pair peaks are



Figure 5.16 (a) Scan rate varied CV of the 40LFPG. (b)-(d) are corresponding redox pair peaks' current versus $v^{1/2}$ plots in (a). (e) Nyquist plots of LFP, graphite, and 40LFPG at different states.



Figure 5.17 (a) Scan rate varied CV of the LFP. (b) corresponding redox pair peaks' current versus $v^{1/2}$ plots.



Figure 5.18 (a) Scan rate varied CV of the graphite. (b) and (c) are corresponding redox pair peaks' current versus $v^{1/2}$ plots.

present with sweep rate varied from 0.1 to 1.0 mV s⁻¹. A-1 and C-1 are anodic and cathodic peaks of LFP, respectively. Similarly, redox peaks of graphite are marked. At high scan rate, the CV shapes of 40LFPG and LFP (Figure 5.17a) indicates that the hybrid cathode significantly reduces polarization observed in LFP cathode. No noticeable difference exists between graphite (Figure 5.18a) and 40LFPG at high sweep rate. Redox reactions of LFP and graphite are controlled by the transfer of Li⁺ and PF₆⁻, correspondingly. Then, peak current and square root of sweep rate ($v^{1/2}$) have a linear relationship, as shown in Figure 5.16b-5.16d (Figure 5.17b and 5.18b-5.18c). Thus, at room temperature, apparent ion diffusion coefficient (*D*) can be calculated using following equation [167],

$$i_n = 2.69 \times 10^5 n^{3/2} A D^{1/2} v^{1/2} \Delta C_0 \tag{5.1}$$

where i_p is the peak current (A), *n* is the number of electrons per ion, *A* is the contact area between electrode and electrolyte (cm²), *D* is the diffusion coefficient (cm² s⁻¹), *v* is scan rate (V s⁻¹), ΔC_o is ion concentration change (Li⁺ or PF₆⁻; mol cm⁻³) before and 101 after specific reaction. The calculated apparent *D* values of corresponding peaks, using the slope of current versus $v^{1/2}$, are summarized in Table 5.1. The apparent *D* values corresponding to LFP lithiation/delithiation indicate that apparent lithium diffusion is slightly slowed down in the hybrid cathode, compared with that of LFP cathode. Since

Graphite [cm² s⁻¹] $40LFPG [cm^{2} s^{-1}]$ LFP $[cm^2 s^{-1}]$ Peak 8.12×10^{-12} 1.57×10^{-11} A-1 1.32×10^{-11} 6.51×10^{-12} C-1 1.52×10^{-9} 3.74×10^{-10} A-2 2.56×10^{-10} 8.78×10^{-10} C-2 1.46×10^{-9} 1.19×10^{-9} A-3 8.88×10^{-10} C-3 1.11×10^{-9}

Table 5.1 Calculated apparent ion diffusion coefficient of redox peaks for 40LFPG (Li⁺ or PF_6^-), LFP (Li⁺ only), and graphite (PF_6^- only).

the LFP cathode showed large polarization, the *D* values were calculated using low polarization data (0.1 mV s⁻¹) for LFP and 40LFPG. Similar results are obtained. Apparent *D* values of A-2 showed slight increase in 40LFPG in comparison to that of graphite cathode, indicating slightly accelerated PF_6^- transfer during its intercalation. Overall, based on the obtained apparent *D* values, the combination of LFP and graphite to form the 40LFPG hybrid cathode makes no big difference with respect to ions' diffusion. Further inspections were conducted using EIS, by which charge transfer resistance of these cathodes was inspected. The Nyquist plots of 40LFPG and LFP show one apparent depressed semicircle at high-medium frequency and a sloping line at low frequency region, while graphite has two depressed semicircles. The first semicircle of graphite cathode is assigned to leakage resistance (*R_a*) relating to reaction on electrode in the bulk [168]. Then, the second semicircle is charge transfer resistance (R_{ct}) . All cathodes were fitted assuming two semicircles as there might also be R_a for other electrodes and one apparent semicircle could be generated by two overlapped semicircles [169]. The 40LFPG has the lowest R_a (7.4 Ω) and R_{ct} (148.2 Ω), compared with LFP (R_a : 74 Ω , R_{ct} : 270.6 Ω) and graphite (R_a : 170.7 Ω , R_{ct} : 187.6 Ω). After 1C, R_{ct} slightly increases to 149 Ω and it further grows up to 241.8 Ω after 1D. It is reasonable to assume that the lowered crystalline degree of LFP in 40LFPG (Figure 5.13f) is reflected by such R_{ct} growth after one cycle. Comprehensively, no undesirable side-effects are observed after combining two polarity distinct ions' hosts into one cathode.

5.3.7 Full cell performance

Full cells were also assembled with graphite as anode to verify whether such hybrid cathode works as well. It can be clearly seen in Figure 5.19a-5.19c that the voltage profiles of 40LFPG full cell resemble that of graphite at voltage higher than 4.0 V and that of LFP below 4.0 V. And 40LFPG full cell inherits the excellent cyclic stability from graphite full cell and high capacity from LFP full cell (Figure 5.19d) and it exhibits a reversible capacity of 76.8 mAh g⁻¹ at the 30th cycle under a current density of 0.05 A g⁻¹.



Figure 5.19 Full cell voltage profiles of (a) 40LFPG, (b) LFP, (c) graphite. (d) Cyclic performance comparison among the 40LFPG, LFP and graphite. Voltage window: 4.5–1.7 V. Current density: 0.05 A g⁻¹.

5.4 Summary

The hybrid cathode, involving a physical mixture of graphite matrix and LFP, is proposed and demonstrated to work with both PF_6^- and Li⁺ compatibly in an orderly manner. The LFP follows the first order two-phase transformation during its lithiation/delithiation at low voltage region. In contrast, the intercalation/deintercalation of PF_6^- in graphite occurs at high voltage region. The hybrid cathode with different weighting ratios can work stably over 200 cycles and shows a capacity of 103.6 mAh g⁻¹ at 0.1 A g⁻¹ for 70LFPG. In a graphite dominant hybrid cathode, 40LFPG also delivers a capacity of 92.9 mAh g⁻¹ under 0.05 A g⁻¹ at the 400th cycle after charge rate variation. The structural integrity of LFP and graphite in the 40LFPG is well preserved. The calculated apparent *D* values of Li⁺ and PF₆⁻ within such hybrid cathode are comparable to that of individual LFP cathode and graphite cathode, respectively. And decreased R_{ct} is observed in the 40LFPG in comparison to LFP and graphite. Furthermore, in a full cell configuration with graphite anode, the 40LFPG still functions normally displaying characteristic plateaus of LFP and graphite and it delivers a reversible capacity of 76.8 mAh g⁻¹ at 0.05 A g⁻¹. Therefore, such hybrid cathode is a potential sustainable cathode alternative, benefited from low-cost, nontoxic, and abundant raw materials, fabrication simplicity, and excellent cyclic performance.

Chapter 6. Conclusions and future work

It takes decades of devoted efforts to realize the commercialization of the LIBs and their prevalence in multiple applications, especially in portable electronic devices and electrical vehicles. In a dilemma of growing needs of the LIBs and limited raw resources limitation, substitutional energy storage systems are urged. Extensive research has been carried out. Targeting high renewability and environmental benignity, the DIBs are emerging promising energy storage systems. The DIBs, governed by distinct electrochemistry compared to the LIBs, make it possible to employ the "inactive" anion as active charge carrier for consequential energy conversion. Among the reported cathodes of the DIBs, graphite is the most studied cathode owing to its low cost, eco-friendliness, and high working voltage. However, limited theoretical capacity of graphite and insufficient oxidative stability of common carbonate-based electrolytes are challenging problem prior to the DIBs' commercialization. This thesis aims to explore and study alternative high-capacity cathodes for the DIBs and tune the candidates to be operable within common organic electrolytes' stability window. Furthermore, making use of the electrochemistry distinctiveness of the LIBs and DIBs and understanding of their compatibility, parallel and serial hybrid cathodes are proposed, designed, and verified, providing new guidelines for high energy density electrode design.

6.1 Conclusions

In this thesis, graphitic carbons are selected as the main cathode materials for the DIBs as they are projected to be potential substitutes for graphite. Recognizing the importance of high porosity of active materials for better electrolyte wetting and extra capacity, the HrGO with 3D interconnected electrical network and rich hierarchical pores is constructed and studied. As expected, within the 4.5–1.5 V (vs. Li/Li⁺) voltage range, using common organic electrolytes, the as-prepared HrGO exhibits much improved reversible capacity which is hardly attainable for graphite even if the upper cut-off voltage is higher than 5.0 V (vs. Li/Li⁺). Unexpectedly, steady capacity growth of the HrGO shows up and the HrGO cathode delivers capacity higher than 300 mAh g⁻¹, a highest value ever reported. In this regard, unveiling of such unexpected electrochemical activation is of high interest and of high significance. Comprehensive characterization and thorough analysis reveal that this phenomenon is a direct result of active surface area increment through numerous reduced graphene rolls' formation, accumulation, and structural order increase. The formation of these rolls is highly relevant to the ways the anions interact electrochemically with the HrGO. Plausible explanations concerning the rolls' formation and structural order increase are raised and elucidated. These insights are vital for the understanding different graphitic carbons' anion storage behaviors, offering a guideline for high-capacity carbon-based DIB cathode design.

To provide a detailed view of the HrGO cathode, further electrochemical characterizations are carried out. Reversibly operable voltage optimization and investigations on the influence of electrolyte concentration variation are conducted due to their high importance regarding with cyclability, deliverable capacity, and operating

potential. In addition to the applied 4.5–1.5 V voltage window, 4.6–1.5 V is found to be another operable voltage window. Higher or lower cut-off will degrade cyclability or accessible reversible capacity, respectively. The increasing of electrolyte concentration results in reversible capacity accretion in long-term cycling. The investigation on the influence of electrolyte concentration, on the other hand, manifests that the electrochemical activation for the HrGO is not only current density but also electrolyte concentration independent. So far, the HrGO is demonstrated as a highly competent cathode for the DIBs. The low mass loading problem of porous materials is troublesome for porous materials and the HrGO is definitely not an exception. Acknowledging the feasibility of conjunction DIB and LIB cathodes together in a hybrid cathode, with both polarity-distinct ions contributing to capacity, the parallel hybrid cathode consisting of the additive HrGO and the dominant LFP is proposed and confirmed. The hybrid cathode represents a solution to low mass loading problem of the HrGO and capacity enhancement for the LFP as well. The parallel hybrid cathode can realize energy conversion through simultaneous anion and cation interactions with the HrGO and the LFP, respectively. Consequently, the parallel hybrid cathode delivers reversible capacity higher than the theoretical capacity of the LFP, confirming the availability of this concept. In return, these results offer a different angle in viewing graphitic carbons' role in common cathodes as these carbons might be possible capacity contributor.

The concept of hybrid cathode can be realized in serial manner by bridging additive LFP and the dominant graphite cathodes together, which diversifies approaches to cathode design and represents itself as a sustainable low-cost cathode. In this way, higher capacity than pristine graphite is achievable and voltage window is lowered below 5.0 V (vs. Li/Li⁺). Ideally, operating potential higher than the LFP will be

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expected in such hybrid cathode because of high operating voltage of the graphite. The serial hybrid cathode differs from the previous parallel one. Stepwise cation and anion interactions with the LFP and the graphite are foreseeable and demonstrated. Over a wide range of mass ratios between the LFP and the graphite, the serial hybrid cathodes are capable of cycling stably and delivering decent reversible capacity values. The results of kinetic analysis demonstrate that no notable increase of charge carrier transfer impedance after such hybridization. Thus, this idea is feasible to resolve low capacity and oxidative instability problems when the graphite cathode is used. And the preparation method of such hybrid cathode is easy for scale up as only physical mixing is required for such hybrid cathode building.

The thesis is dedicated on the exploration of high-capacity cathode for the DIBs. In this process, value insights are offered for high performance cathode construction. What's more, conjunction with the mature energy storage system—LIBs is made with the DIBs. Concepts' demonstrations are extremely meaningful. Because these ideas are applicable for hybridizing other cathodes from different energy storage systems. Through careful and proper designs, high performance cathodes are accessible. Besides, the used hybridization approach in this thesis is simply physical mixing, suggesting the easiness of industrial production.

6.2 Future work

6.2.1 Discharging plateaus restoration of the HrGO

The finding of the HrGO as high-performance cathode for the DIBs is inspiring. In comparison to typical graphite cathode, the well-known high operating voltage is absent for the HrGO, reflected by the loss of discharging plateaus. The electrolyte is ¹¹⁰

not the reason resulting in the vanishment of discharging plateaus. Since multiple different organic electrolytes with differing solvents and salts are employed, still no discharging plateaus present. Whereas the graphite has well-defined redox peaks (equivalent to plateaus) even in the voltage window of 4.5–1.5 V, shown in Figure 6.1. The measurements of voltage window's variation have been conducted to screen out the operable voltage ranges. Yet, the plateaus are absent in these tests. It is of high scientific interest to uncover the origins of the plateaus' disappearance and recover them while maintaining high electrochemical performance. It is noted that noticeable redox peaks appear for highly graphitized carbon materials as illustrated in Figure 6.2 [68]. The low graphitization degree of the prepared HrGO is a probable cause. High temperature treatment might be an optional approach for restoring the plateaus.



Figure 6.1 Differential capacity (dQ/dV) vs. potential (V) plot of the graphite in 4.5–1.5 V. Current density: 0.05 A g⁻¹.



Figure 6.2 CV profiles of three different graphitization degree carbon blacks. (a) and (d) Amorphous; (b) and (e) slightly graphitized; (c) and (f) highly graphitized carbon blacks. Different voltage windows and electrolytes are used for (a)-(c) and (d)-(f), respectively (adapted from ref. [68]).

6.2.2 Study on graphitic carbon structure's influence on electrochemical performance

There are studies suggesting that high graphitization degree contribute to higher capacity for graphitic carbons [65, 76]. Recently, a work utilizing locally ordered graphitized carbon (ketjen black) as cathode for the DIB demonstrates that strong interanion repulsion and concurrent volume expansion are the key factors reducing the attainable capacity of the graphite [170]. It is claimed that the weakening of graphene interlayers' van der Waals force mitigates large volume expansion existing in the graphite and lowers anion uptake voltage. Besides, the interrupted long-range order of graphite in such disordered carbon is reported to offer additional capacity and reduce anion repulsion. It is obviously these are ideas emphasizing two totally different approaches to increase carbon cathodes' capacity, which has been discussed in the Chapter 2 of the thesis. A more detailed study on graphitic carbon structure's variation, from macro- disorder to order and micro- disorder to order, is important and worth for further study.

6.2.3 Other high energy density hybrid cathodes

The inclusion of graphite or other graphitic carbons into common LIB cathodes is a practical way to reduce heavy reliance on limited, expensive, and hazardous transition metal incorporated cathodes. If rationally designed, such hybrid cathodes are expected to offer enhance energy density. In-depth study of these hybrid cathodes will also deepen the understanding of the interfacial dynamics between the anion uptake carbons and the cation storable LIB cathodes. The construction of hybrid cathodes, either in parallel or serial manner, requires high compatibility of the two constituents. This excludes numerous prevailing LIB cathodes as decrease of lower cut-off voltage or increase of upper cut-off voltage will degrade the cathodes' crystalline structure [140, 171-172], leading to the decay of capacity and cyclability. Fortunately, cathodes' structure stability can be maintained through proper modifications. An iron-doped 5 V LIB cathode's performance is shown in Figure 6.3 [173]. The modified LiMn_{1.5}Ni_{0.5}O₄ is expected to be compatible with graphite in one hybrid cathode as their overlapping operable voltage range. There are other high LIB cathodes with high operating potentials similar to that of the graphite cathode, summarized in Table 6.1 [174], suggesting availability of hybridization for them.

Future work



Figure 6.3 Electrochemical performance of Fe-substituted $LiMn_{1.5}Ni_{0.5}O_4$. (a) Discharge voltage profiles; (b) Cyclic performance (adapted from ref. [173]).

Material	Mid-discharge voltage [V] plateau >4.5 V	Redox couple at plateau >4.5 V	Plateau centered at 4.0 V $[mAh g^{-1}]$	Plateau >4.5 V $[mAh g^{-1}]$	V range [V]
Li ₂ CrMn ₃ O ₈	4.8	Cr ^{3+/4+}	70	55	3.4–5.4
LiCrMnO ₄	4.8	Cr ^{3+/4+}		75	3.4–5.4
Li ₂ FeMn ₃ O ₈	4.9	Fe ^{3+/4+}	75	50	3.0–5.3
Li ₂ CoMn ₃ O ₈	5.1	Co ^{3+/4+}	70	60	3.0–5.3
LiCoMnO ₄	5.0	Co ^{3+/4+}	10	95	3.0–5.3
Li ₂ NiMn ₃ O ₈	4.7	Ni ^{2+/4+}	16	95	3.0–4.9
${\rm Li}_{2.02}{\rm Cu}_{0.64}{\rm Mn}_{3.34}{\rm O}_8$	4.9	Cu ^{2+/3+}	48	23	3.3–5.1

Table 6.1 Electrochemical details of high voltage LIB cathodes (adapted from ref. [174]).

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