Strategies for High Energy Density Dual-Ion Batteries Using Carbon-Based Cathodes

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The rapid-growing demands for lithium-ion batteries (LIBs) have raised concerns over lithium’s scarcity as well as the scarcity of other materials and components used in LIBs. Tremendous efforts have been dedicated to investigating alternative technologies. Dual-ion batteries (DIBs) represent an emerging battery technology with an attractive future such as high working voltage and a high-power density enabled by a “nonrocking chair” operation. Research in DIBs is still at an early stage. The energy density of DIBs remains a challenge to solve, especially in comparison with LIBs. This review highlights current challenges in the research on DIBs from different aspects, including undesirable graphite exfoliation during ions intercalation, limited choices of cathode materials, unstable electrolytes, battery safety, and discusses potential strategies for addressing these challenges. Perspectives for exploring the next-generation DIBs with high energy density are also provided.

1. Introduction

The rapid-growing demand for lithium-ion batteries (LIBs), which are dominating the market in portable electronic devices and electric vehicles, has some disadvantages relating to the sustainability of lithium itself and the components required in a LIB. Compared with 229 GWh in 2020, global battery demand (Figure 1) is expected to grow 9.3 times to reach 2623 GWh in 2030 according to a report (A Vision for a Sustainable Battery Value Chain in 2030) from the World Economic Forum.[11]

LIBs have a high energy density of up to 270 Wh kg⁻¹ or 750 Wh L⁻¹ at the cell level in comparison with 80 Wh kg⁻¹ and 250 Wh L⁻¹ for nickel–metal hydride (NiMH) batteries, while LIBs have a higher energy efficiency over NiMH (=65%) or lead–acid batteries (≈70%).[2] It is expected that LIBs will continue to dominate the market owing to their high energy density, safety, and long life cycle. The limited lithium reserves (0.002 wt% in the earth’s crust representing 20 mg kg⁻¹ earth’s crust; 0.18 mg L⁻¹ in seawater) cumulated with the geographically uneven distribution are raising concerns regarding the future availability of lithium and the unethical processes used for its mining. Furthermore, LIBs are currently based on expensive elements (nickel, cobalt) in the cathodes that further need to be processed by toxic organic solvents such as N-methyl-2-pyrrolidone.[3,4] The cost of these transition metals used in LIBs has increased substantially over recent years, and at the current consumption rate, the current reserves of these materials will not meet future demand.[5] CO₂ emissions will increase from 24 Mt CO₂e in 2018 to 182 Mt CO₂e in 2030 according to the same report from World Economic Forum; raw materials mining, raw materials refining, active materials, and other components take account for 6%, 12%, and 35%, respectively.[11] A greener CO₂ footprint for batteries will inevitably be a prerequisite in the near future to reach truly net-zero target commitments.[8,9] Here, new emerging battery technologies, including sodium-ion batteries,[10–14] potassium-ion batteries,[15,16] multivalent ion batteries,[17] and dual-ion batteries (DIBs), are regarded as more sustainable alternatives to LIBs.

Among these alternatives, the advantages of DIBs (some common to the other battery chemistries) are: 1) eliminating lithium and critical elements such as nickel and cobalt thus removing the elements scarcity; 2) high working voltage and fast-charging (e.g., dual-graphite DIBs can reach a high power density of 8.66 kW kg⁻¹ and a high energy density of 227 Wh kg⁻¹);[18] and 3) sodium/potassium-based DIBs offer considerable opportunities due to the abundance of sodium reserves (2.7 wt %/28 400 mg kg⁻¹ earth’s crust; 11 000 mg L⁻¹ seawater) and potassium reserves (2.4 wt% /26 000 mg kg⁻¹ earth’s crust; 380 mg L⁻¹ seawater).[19] These merits allow DIBs to power small electric vehicles and large-scale stationary (“grid”) energy storage.

Cation–anion DIBs consist of Li+,[20] K⁺,[15,21–23] Na⁺,[24] Mg⁺,[15] Ca⁺,[26] Al⁺,[27,28] and Zn⁺[29,30] DIBs. Anion intercalants include PF₆⁻, BF₄⁻, FSI⁻, TFSI⁻, TFSI⁻, AlC₄⁻, and so on which can be inserted into graphitized cathodes.[31,32] In “rocking
“Chair” operation mode, electrolyte is used to establish an ionic connection to shuttle active alkali metal ions between two electrodes while the active ions mainly come from the cathode material; in DIB systems, the active ions in DIBs are only derived from the electrolyte usually containing alkali metal cations and various anions, which will be described in following sections. Therefore, DIBs work on a principle where upon charging, the electrolyte is depleted of ions as cations incorporate into an anode and anions intercalate into a graphite cathode, while, during discharge, cations and anions return to the electrolyte. Although supercapacitors and hybrid capacitors also promise high power density and apply both cations and anions to store energy, such devices have at least one electrode operating on capacitive behavior. Thus, the inherent low energy density hinders their application.[33–35]

DIBs research has become popular over recent years, while most research efforts have been dedicating to improving their energy density. This review highlights a series of strategies for electrodes and electrolytes development to achieve a higher energy density of DIBs.

2. Ion Intercalations

Graphite is widely studied both as cathode and anode due to its redox-amphoteric nature under different operating voltages. It can act both as acceptor and donor forming graphite intercalation compounds (GICs) to cations (e.g., LiC₆) and anions (e.g., C₂₄PF₆[97]C₀[97]).[18,36] Cation–anion DIBs feature high working voltage owing to anion intercalation, and Figure 2 shows the process of anion intercalation via the conventional Rüdorff staging model with a representative charging curve in a Na-based DIBs. At the beginning of intercalation, solvated anions in bulk electrolyte mitigate to graphite cathode via under applied current. Solvated anions have to desolvate to get rid of the solvation sheath before entering graphite layers as naked anions forming binary GICs (without electrolyte molecules). Occasionally, cointercalation of charge carrier with solvents molecules with a larger overall size than naked anions may happen to form trinary GICs (with electrolyte molecules) likely to cause graphite exfoliation. Then GICs are gradually formed by cation layer between graphite layers (Figure 2), starting from stage-5 GICs and ideally ending with stage-1 GICs. The stage number means the number of graphene layers between layers of intercalated anions. For example, PF₆⁻ interaction into graphite is a reversible redox process which can be expressed as

\[
C_n + nPF_6^- \leftrightarrow C_nPF_6 + e^-
\]  

(1)

Owing to anion intercalation, DIBs can achieve high rate performance and fast charging ability. Taking dual graphite batteries with LiPF₆ salt in ethyl carbonate (EC)–dimethyl carbonate (DMC) electrolyte as an example, Li⁺ ions are solvated in the electrolyte, whereas PF₆⁻ is less solvated in the organic electrolyte because of its large size. A small solvation sheath means faster solvation/desolvation processes so that the diffusivity of PF₆⁻ is fast. Furthermore, from the energetics viewpoint, desolvation has the highest energy barrier among several processes (solid diffusion, liquid diffusion, crossing solid electrolyte interphase [SEI], and desolvation).[37] The value of activation energies for interfacial anion transfer is smaller than that of interfacial Li⁺-ion transfer;[38] consequently, the superior power density of DIBs possibly be attributed to the rapid diffusion of PF₆⁻ into graphitic carbon.[39]

To reveal a detailed intercalation mechanism, the intercalation process has been studied by in situ techniques. The staging mechanism has been studied by in situ X-ray diffraction.
(XRD) together with in situ dilatometry, which further confirmed the GICs of stage-1 (C26PF6) and solvent cointercalation behavior of a ratio of $\approx 0.7 \pm 0.2$ solvent molecules per anion during anion intercalation.[40] The volume expansion induced by anion has been also probed by in situ XRD.[41] It was found that TFSI$^-$, PF6$^-$ intercalation expands the interlayer distance of graphite to 0.799 nm (139%) forming C26TFSI and to 0.789 nm (136%) forming GIC stoichiometry of C24PF6, respectively. Fang et al.[42] reported the thickness changes during cycling using operando optical microscopy to observe the cross section of the graphite cathode. A 60% volume expansion in the first cycle and irreversible <20% expansion in the following cycles are found. In situ Raman spectroscopy elucidates the behavior of intercalating species such as Li$^+$, K$^+$, PF6$^-$ into graphite.[42] Atomic force microscope (AFM) is an efficient probe to detect roughness and height changes at interfacial morphology during electrochemical processes in LIBs and beyond. Pan and Yang used in situ AFM technique to characterize the PF6$^-$ intercalation and its influence on highly oriented pyrolytic graphite (HOPG)[43] revealing that the intercalation speed of 2 μm min$^{-1}$, intercalation position of edge sites at one of every three graphene layers and intercalation voltage around 4.8 V versus Li$^+$/Li$^-$. 

3. Challenges of DIBs

DIBs feature a high-power density, yet more research is needed to develop high energy density electrodes. This session discusses current challenges associated with DIBs, including graphite exfoliation, limited choices of cathode materials, unstable electrolyte, and battery safety concerns. These challenges from the atomic level to the cell level require in-depth understanding both from an academic and industrial perspective to gain realistic commercial perspectives. Figure 3 schematically illustrates the working principle and summarizes the current challenges of DIBs. The anodes can be of three types: insertion, alloying, and conversion, while the cathode can be graphite and other carbon materials. Figure 3 also depicts different electrolytes from a liquid state to a solid state with possible anions (e.g., AlCl4$^-$, PF6$^-$, TFSI$^-$, and so on) and cations (e.g., Li$^+$, Na$^+$, K$^+$, Mg$^{2+}$, and so on).

3.1. Graphite Exfoliation

Weak van der Waals forces (16.7 kJ mol$^{-1}$) hold the laminated structure of graphite layers with a spacing of 0.335 nm.[37,44] When such forces are not strong enough to hold repeated intercalation, exfoliation occurs. Although graphite exfoliation is a common issue for both LIBs (as an anode) and DIBs, graphite is more susceptible to exfoliate when used as a cathode intercalating anions because anions (e.g., ClO4$^-$, TFSI$^-$, PF6$^-$, FSI$^-$, and so on) are much bigger than the graphite interlayer space. LiC6 GICs bring a volume expansion of 10% (0.37 nm), while PF6$^-$ intercalation leads to a volume change in 136% (0.789 nm), forming GIC stoichiometry of C24PF6. Conventional liquid electrolytes would cointercalate into the graphite cathode and form trinary GICs, accelerating graphite exfoliation.[45] In addition to anion intercalation, uneven internal stress, particle cracking, electrolyte reduction, and gas evolution will eventually lead to structural exfoliation, thus triggering rapid degradation of the electrode, irreversible capacity loss, and low Coulombic efficiency.[46,47] The change in volume during cycling causes internal stress and rupture of the SEI, which exposes a fresh graphite surface, and therefore more electrolyte is needed to form a thicker SEI.[47] Such thick SEI increases the diffusion resistance and causes electrolyte loss, thus reducing the graphite capacity upon cycling.

3.2. Limited Choices of Cathode Materials

As in any battery, the energy density of a DIB depends on the voltage and capacity, both parameters being determined by anion hosting materials. A graphite cathode can deliver a discharge capacity of around 100 mAh g$^{-1}$ and a high working voltage beyond 4.5 V with LiPF6 in EMC as an electrolyte. Other materials capable of electrochemically accommodating anions are carbonaceous materials,[48–50] metal–organic frameworks,[51] organic-based materials,[52,53] diamino-rubicene,[54] hydrocarbons,[55] and coronene (a polycyclic aromatic hydrocarbon).[54] Most of them have either a lower gravimetric capacity or lower working voltage than graphite cathode. Therefore, graphite to date is still the most promising cathode for DIBs.

DIBs using at least one graphitic electrode will have limited volumetric energy density because of the low packing density of carbon materials.[56] Unlike LIBs where the amount of electrolyte can be minimized to reach high energy density, DIBs must have enough or excess electrolyte to provide the ions needed during charge–discharge. Thicker glassy fiber separators able to uptake more solvents are normally used in DIBs instead of commercially available polyethylene (PE) membranes due to more electrolyte consumption than in LIBs. The excess electrolyte, thicker fiber separators, and low-density carbon will further limit the volumetric energy density of DIBs. Thus, new cathode materials for DIBs are also required to be developed.

3.3. Unstable Electrolytes

Electrolytes play one of the most crucial roles in DIBs. A high charging voltage (usually >4.5 V) is essential to open up the interlayer spacing of graphite to intercalate larger anions. Both higher intercalation energy and desolvation energy can lead to an increase in the intercalation voltage. Nevertheless, the poor oxidative stability of conventional organic electrolytes under high voltage results in unsatisfactory electrochemical performance such as a low initial Coulombic efficiency and a poor cycle life.[32]

To ensure the thermodynamic stability, $eV_{oc}$ ($e$ is the magnitude of the electron charge, $V_{oc}$ is open-circuit potential) needs to be less than the window of the electrolyte $E_f$ (Figure 4).[44] For ideal electrolyte, to minimize side reactions between electrodes and electrolyte, the highest occupied molecular orbital (HOMO) should be lower than the chemical potential of the cathode ($\mu_{C1}$), and the lowest unoccupied molecular orbital (LUMO) energy higher than the chemical potential of the anode ($\mu_{A1}$). In practical cases, $\mu_{A2} > LUMO$ and/or $\mu_{C2} < HOMO$ can trigger the formation of an SEI layer and/or a cathode electrolyte interphase (CEI) layer. Strong oxidant cathodes with $\mu_{C2}$ can effectively oxidize the salts and solvents to create a CEI layer between electrolyte and cathode.
Figure 3. Challenges of DIBs with a working principle diagram.

Figure 4. Schematic illustration of open-circuit energy diagram, open circuit potential ($V_{oc}$) and energy states of electrodes and electrolytes in an ideal electrolyte and practical cases. $E_r$ is the thermodynamic stability window of the electrolyte. $\Phi_{A1}$ and $\Phi_{A2}$ are the anode work functions. $V_{oc}$ is the voltage window of open-circuit voltage. $\Phi_{C1}$ and $\Phi_{C2}$ are the cathode work functions. LUMO, lowest unoccupied molecular orbital; HOMO, highest occupied molecular orbital; CEI, cathode electrolyte interphase; and SEI, solid electrolyte interphase.
to block electron transfer from the electrolyte HOMO to the cathode; anode with a $\mu_{A2}$ higher than LUMO will reduce the electrolyte to form a passivation SEI layer which acts as a barrier to electron transfer from the anode to the electrolyte LUMO. The resulting SEI layer and CEI layer can enhance kinetic stability to a larger $V_{\text{OC}}$.

The reasons for poor electrochemical performance are: 1) due to high operation voltage above 4.5 V, ensuring a thermodynamically stable window for the electrolyte is difficult; Therefore, the formation of SEI and thick CEI on the surface of anode and cathode, respectively, is challenging to control; 2) anions irreversibly react with defects, surface functional groups leading often to irreversible intercalation; 3) the decomposition of electrolyte occurs especially under high operating voltage; and 4) the electrolyte can corrode the current collector, causing low Coulombic efficiency during cycling. Consequently, further development of SEI-forming additives for electrolytes is vital to improve the Coulombic efficiency of the DIBs at low discharge rates. More research attention should also be paid to the electrolytes and additives development to prevent a short lifetime by continuous consumptions of active ions in the electrolyte.

3.4. Safety

Battery safety becomes particularly important for EVs and portable electronics. The downsides of LIBs are flammability, overheating, poor heat dissipation, and thermal runaway. Lu et al. conducted safety tests on industrial grade Li-based DIBs. Nail penetration test did not cause explosion, fire or even smoke, while still could power a LED light without obvious hazardous. Theoretically, DIBs with a graphite cathode have negligible oxygen content coming mainly from the few available functional surface groups in graphite compared with layered oxide cathodes in LIBs. Furthermore, DIBs eliminate thermally unstable Ni and Co cathodes using thermally stable graphite instead, ensuring a high level of safety. The high working voltage easily causes side reactions between electrodes and electrolytes such as gas formation, pressurized batteries. Few studies have been currently performed on the safety of DIBs to date, and we believe this aspect should be given the necessary attention in future DIBs research.

4. Strategies to Higher Energy Density

Identifying and solving the challenges of DIBs can facilitate designing DIBs with a higher energy density. This section discusses strategies that can be used to improve the energy density of DIBs.

4.1. Optimizing Carbon-Based Cathodes

4.1.1. Morphology of Carbon Materials

Paired with a carbon anode, DIBs with graphite cathode make up an all-carbon configuration with advantages of sustainable sourcing (in the case of synthetic graphite from biomass [i.e., lignin] or pitch) and electrochemical stability. A comprehensive understanding of the mechanism of intercalation chemistry and strategies for functionalization/modification can increase the specific capacity of carbon-based cathodes (graphite and nongraphitized carbons). For graphite cathodes, great research efforts have been devoted to investigating the relationships between the structural properties and performance of DIBs. Placke et al. analyzed the effect of the particle size of graphite on discharge capacity and found an increased surface area or smaller particle size can increase the first discharge capacity. This finding can be linked to modification strategies for LIBs that decreasing the particle size of the active material increases the rate performance of LIBs. Some mechanical techniques can help to reduce particle sizes, such as wet-milling, dry-milling, and high-pressure homogenization. Therefore, particle size and specific surface area analysis play important roles, thus gas adsorption analysis via the Brunauer–Emmett–Teller and density functional theory. From the perspective of ion intercalation, the channels to enter graphite are located at the edge of graphite instead of its basal plane, which twists the ion pathway and inhibits ion diffusion kinetics. This principle can also be applied to anion intercalation: the nanostructural design of graphite cathodes can shorten the pathway for ion diffusion to improve the rate performance of DIBs (Figure 5). Graphite with a higher ratio of nonbasal plane/basal plane has more intrinsic channels and pathways for migration of anion, resulting in better rate performance. This strategy can be correlated to graphite with small particle size with better rate performance because the small-sized particle has a higher ratio of edge plane to the basal plane. Peng et al. compared the rate performance between porous graphite cathode (high ratio of edge plane to basal plane) and nonporous graphite cathode in DIBs. Porous graphite cathode delivers a specific capacity of $\approx65$ mAh g$^{-1}$ higher than $\approx31$ mAh g$^{-1}$ of commercial graphite nanosheet and $\approx21$ mAh g$^{-1}$ of graphite powder at 1.8 A g$^{-1}$, and a specific capacity of $\approx61$ mAh g$^{-1}$ at 10 A g$^{-1}$.

Taking advantage of the redox-amphoteric nature of graphite, Feng et al. designed a polarity-switchable DIB with a symmetric graphite configuration enabling reversible switching between anode and cathode. Figure 6a shows the working principle and the ability to switch intercalation. This polarity-switchable DIB shows long at least 500 cycles with 96% capacity retention, a power density of 8660 W kg$^{-1}$ and a high energy density of 227 Wh kg$^{-1}$.

Different degrees of graphitization would influence its capacity. Placke et al. revealed that the increase in degrees of graphitization directly leads to an enhanced specific discharge capacity, while the crystallite height shows a negligible contribution to the capacity. Figure 6b shows the relationship between the degree of graphitization and anion intercalation capacity. It is worth noting that for carbons with a low degree of graphitization, the main anion storage mechanism is still the staging mechanism.

4.1.2. Defect Tuning

It has been reported that defects play the role of storage sites for cations in LIBs and SIBs (Figure 7). However, in DIBs, a defect-free strategy is desired at the carbon cathode for anions storage, the defects in the graphitic carbon obstruct fast anion insertion/intercalation, reduces the number of active sites, and lowers the electrical conductivity. Chen et al. reported...
a defect-free graphene-based cathode for accommodating \( \text{AlCl}_4^- \), as shown in Figure 6c, inhibiting the defect sites (oxygen-containing groups and \( sp^3 \) sites) of reduced graphene oxide can significantly increase the capacity of cathode. This defect-free cathode has a long-range crystalline arrangement of \( sp^2 \)-bonded carbon hexagons and large-sized \( sp^2 \) domains without detectable defect sites, removing inactive defects and facilitating the fast intercalation of large-sized anions while simultaneously providing more active sites for energy storage. The defect-free cathode (GA-3000: reduced graphene oxide treated at 3000 °C) affords a high reversible capacity of 100 mAh g\(^{-1}\) from 0.2 A g\(^{-1}\) to 5 mA g\(^{-1}\) and excellent cycle stability (97% capacity retention after 25 000 cycles). This defect-free strategy is consistent with the finding that for \( \text{AlCl}_4^- \) intercalation, N-doped
graphene can lead to chlorine gas formation once the AlCl4− anions intercalation takes place.[60,72] The downside of producing defect-free carbon cathodes is that high energy input is required to reach annealing temperatures above 2500 °C, which hinders the sustainability of DIBs. Potentially fast heating sources such as spark plasma sintering or laser ablation could bring a benefit, in particular, if coupled with electricity from renewable sources. Dryfe et al.[60] also proposed defect-free graphene as a positive electrode via electrochemical exfoliation of graphite with the aid of Co2+ as an antioxidant. The resulting defect-free graphene cathode shows an excellent rate capacity of 150 mAh g−1 at a current density from 0.1 to 3 A g−1 in a DIB with 2 m LiPF6 in EMC as the electrolyte. The specific capacity of such electrode is the highest value among reported cathodes for DIBs to date, although the relatively low Coulombic efficiency at low current densities.

To sum up, the reversible capacities of DIBs based on different electrochemistry are summarized for comparison in Figure 8.

4.1.3. Interface Stabilization on Carbon Materials

The mismatch between the size of the intercalated anion and interlayer spacing in graphite layers results in significant volume changes. Therefore, the mechanical stability of the electrode should be improved by suitable measures such as elastic and conductive binders and/or an artificial protective layer.

A CEI layer containing Florine on a graphite cathode has shown to reduce the graphite volume expansion.[59,73] Wang et al.[59] has studied the protection of F-containing CEI by the degree of graphitization of the graphite cathode via XRD and by the intensity ratio of the D band and G band (I_D/I_G) via Raman spectroscopy over cycling. XRD results and Raman spectra of electrodes (pristine, after 10th and after 200th cycle) showed that graphite electrodes cycled in 5% fluoroethylene carbonate (FEC) electrolyte have narrower XRD patterns and slightly higher I_D/I_G than results of graphite cycled in FEC-free electrolyte; even after 200th cycle, the graphite cycled in 5% FEC electrolyte shows 65.1% of the degree of graphitization in comparison with 77.9% of the pristine electrode and 32.5% of the electrode after 200th cycle in FEC-free electrolyte. These results suggest that FEC-derived CEI can maintain the structural integration of graphite during repeatedly anion de/intercalation. Wu et al.[11] engineered an artificial SEI layer on the graphite electrode by precycling at 100 mA g−1 for five cycles in a potential window of 0.3−2.0 V versus Li+/Li (electrolyte: 1 m LiPF6 in ethyl methyl carbonate[EMC]) before assembling into a DIB. X-ray photoelectron spectroscopy (XPS) revealed that the LiF content of the SEI-modified graphite is higher than that of the unmodified graphite, suggesting that LiF is from five precycles in a LIB rather than the electrolyte decomposition in a DIB. Moreover, it is reported that the increased ratio of LiF in the SEI layer is beneficial to prevent electron exchange between the electrode and electrolyte, thus suppressing electrolyte decomposition and side reactions.[74,75] Transmission electron microscopy (TEM) revealed that after 200 cycles, the unmodified graphite shows a more deteriorated surface structure than that of SEI-modified graphite which means the artificial SEI helps protect the structural stability from volume expansion. The corresponding interlayer distance of the unmodified graphite is 0.356 nm wider than 0.346 nm of the SEI-modified graphite which indicates that the artificial SEI layer helps mitigate the solvation effect induced by anions intercalation. The SEI-modified graphite delivers a specific capacity of 84.5 mAh g−1 (higher than 75.2 mAh g−1 of unmodified graphite) at the upper cutoff voltage of 5.0 V under a current density of 200 mA g−1 with 96% capacity retention after 500 cycles. Such an artificial layer can prevent further electrolyte decomposition on the surface of the graphite cathode suppressing the solvation effect of anions.

4.2. Rational Development of Novel Anode Materials

Except for graphite cathodes in DIBs, anode materials also play an important role in enhancing the energy density of DIBs. Not only reversible capacity but also other parameters such as rate, cycling performance, and initial Coulombic efficiency all contribute to the energy density of DIBs. However, the intercalation of ions into active materials is not the only reaction mechanism for the anode part. Therefore, a rational selection of anode materials to couple with cathode materials described earlier is needed. Independent of the cation choice, the reaction mechanisms of anode materials can be generally categorized into three main types: 1) insertion/intercalation, 2) alloying, and 3) conversion.

Some carbonaceous materials and transition metal oxides can serve as host materials that allow the insertion/intercalation of guest cations (e.g., Li+, Na+, K+, and so on). In contrast, intermetallic materials can react with cations to form alloys. Some metal oxides/sulfides and organic compounds are driven via the conversion mechanism to store cations. The following sections mainly focus on discussing the anode materials for lithium- and sodium-based dual-ion batteries, which have been widely developed and systemically studied. Strategies for overcoming the disadvantages of anode materials by rationally tuning their structures are summarized to guide the further improvement in the energy density of dual-ion batteries based on various battery chemistries in the future.
4.2.1. Insertion/Intercalation Materials

As mentioned earlier, one of the advantages of DIBs is the fast-charging ability. The graphite cathode side, due to the intercalation mechanism, possesses fast kinetics of the intercalation reaction, while the lack of anode materials with appropriate kinetics severely obstructs the further boost in the energy and power densities of DIBs. Anode materials based on insertion/intercalation mechanism are considered to be the most promising anode materials for DIBs because they allow fast kinetics and thus match the fast-charging graphite cathode. However, the electrochemical performance of insertion/intercalation anode materials still awaits further progress.

Among various insertion/intercalation anode materials, carbonaceous materials are promising candidates for DIBs because of their mechanical and chemical stability, high conductivity, and tunable microstructure. In particular, tailor-made carbonaceous materials derived from biomass, previously applied for other battery chemistries such as Na ions, are attractive candidates because of their low cost, sustainable nature, and tunability, enabling more active sites to store cations. Wang et al. prepared a hard carbon anode derived from pine needles. After carefully washing the precursors using 3 M HCl (aq) and 2 M NaOH (aq), the precursor was calcined at 1000 °C for 3 h to produce hard carbon materials. The obtained hard carbon materials inherited the hierarchical structure of pine needles, demonstrating a plate-like shape to facilitate ion diffusion. In addition, heteroatoms doping such as nitrogen and phosphorus derived from the natural pine needles can offer more active ion storage sites. The hard carbon delivered a reversible capacity of 175 mAh g⁻¹ at the current density of 50 mA g⁻¹ (Figure 9a).

When coupled with a graphite cathode, the all-carbon-based DIB configuration based on sodium salts can be achieved with a superior energy density of 200 Wh kg⁻¹ at the power density of 131 W kg⁻¹ (Figure 9b). After 1000 cycles, the retention of the DIBs can reach 87.2%, exhibiting excellent cycling stability. As the cost-effective precursors, the hierarchical structures and rich functional group of biomass resources optimized by nature for thousands of years can be translated into hard carbon materials, thus greatly enhancing the electrochemical performance of insertion anode materials.

Except for biomass-derived carbonaceous materials, some inorganic materials such as metal oxides can also be used as the insertion/intercalation anodes for DIBs. Compared with carbonaceous materials, these insertion/intercalation anode materials with specific opened frameworks and channels can deliver a better rate and cycling performance owing to the faster kinetics of insertion/intercalation of ions. Ti-based oxides such as TiO₂ have been regarded as a classic intercalation metal oxide anode material for DIBs. Wang et al. built sodium-based DIBs using anatase TiO₂ as the intercalation anode material, where the energy density can reach 113 Wh kg⁻¹ at the power density of 74 W kg⁻¹.
However, most metal oxides are prepared based on expensive/critical elements such as nickel and cobalt, which decreases the sustainability of intercalation metal oxide anodes due to their limited abundance especially when considering that the development of recycling technologies for batteries is still at the initial stage. Therefore, the fabrication of high-performance insertion/intercalation anodes based on earth-abundant elements gradually becomes a rising research area in DIBs. Li et al. developed a FePO4 anode for sodium-based DIBs without utilizing rare transition metals. As a cation host material, FePO4 can be sodiated by the insertion of sodium ions, thus delivering a specific capacity of 116.6 mAh g\(^{-1}\) (Figure 9a). Figure 9c shows a DIB charge–discharge process using layered graphite cathode and FePO4 anode. When pairing with the graphite cathode, the sodium-based DIBs can exhibit a specific capacity of 120 mAh g\(^{-1}\) at the current density of 0.2 A g\(^{-1}\). After 250 cycles, the retention of the specific capacity can maintain at 92.2%. Although the insertion/intercalation anode materials mechanism undergoes a negligible volume change during cycling, the limited active sites for cation insertion/intercalation in the nanostructures can contribute to rather low theoretical capacities. Furthermore, some insertion/intercalation anode materials such as metal oxides are essentially nonconductive, which also hinder the energy/power density of DIBs. Therefore, the application of carbon materials during the fabrication of novel insertion/intercalation anodes is of great necessity to facilitate ion and electron transportation.

Doping strategy (prelithiation/presodiation) also applies to DIBs. A diluted carbonate electrolyte means a lack of active ions and low Coulombic efficiency due to SEI and CEI formation during the first few cycles. The loss of active ions can be compensated via prelithiation/presodiation technologies, which further guarantees an enhanced energy density. Liu et al. used a presodiation method that can form an SEI on the anode to compensate for the irreversible capacity loss, exhibiting a high Coulombic efficiency of over 90%. The further target of developing novel insertion/intercalation anodes should focus on using earth-abundant elements combined with biomass-derived uniform carbon coating on the surface of particles, paving the way for the research on high-performance DIBs in terms of sustainability.

4.2.2. Alloy-Based Anodes

Different from insertion/intercalation anode materials, alloying anode materials can exhibit a promising capacity when storing...
cations as each atom of alloying anode material can usually combine with significantly more cations. For example, compared with the LiC₆ formed by the intercalation of Li⁺ ions into graphite anodes, each tin atom can combine with 4.4 lithium atoms, resulting in a much higher theoretical capacity of 991 mAh g⁻¹.[82] However, alloying anode materials suffer from excessive degradation because of the huge volume changes during cycling, which hinders their practical applications. Importantly, as mentioned earlier, the intercalation of anions into graphite enables outstanding stability of the cathode, so the stability of the anode side based on the alloying mechanism is mismatched with the cathode sides based on the insertion/intercalation mechanism.

To improve the electrochemical performance of anode materials, several strategies have been applied to improve the stability of alloying anodes. One of the useful strategies is the structural design of alloy anodes to confine/control the volume changes. Qin et al. designed a carbon-coated hollow aluminum anode for DIBs where the carbon coating layer can induce the aluminum–lithium alloying reaction within the hollow nanosphere structure.[83] Figure 9d shows the electrode fabrication process where aluminum was deposited onto polystyrene nanospheres by magnetron sputtering, followed by carbonization of the resulting composite nanospheres under a nitrogen atmosphere. This obtained specific structural configuration can confine the volume change of alloying reaction with excellent cycling stability. Coupling with graphite cathodes, the obtained Li-based DIBs can deliver an energy density of 142 Wh kg⁻¹ with a power density of 1780 W kg⁻¹ (Figure 9b). Furthermore, the retention of the full cell can reach around 99% even after 1500 cycles at 2 C.

Apart from nanospherical morphology coated with carbon, 3D porous structures of alloying anodes with a carbon coating are also effective for improving electrochemical performance via preventing the volumetric change. Tong et al. first etched the aluminum foil into a porous morphology with ordered tunnels by a direct current electrochemical etching method.[84] The porous aluminum foil was further infiltrated with polyacrylonitrile (PAN), followed by carbonization to form a carbon coating layer on the porous surface. The obtained porous aluminum foil with carbon coating was tested as alloying anode for the Li-based DIBs. An energy density of 204 Wh kg⁻¹ at a power density of 3084 W kg⁻¹ could be achieved (Figure 9b). The structural design of alloying anodes based on nanotechnologies can obviously shorten the ion diffusion pathways and stabilize the interface of electrode/electrolyte, thus greatly improving the electrochemical performance of DIBs.

Although the structural design strategy based on nanotechnologies can improve the electrochemical performance of alloying anodes, the synthesis process is too complex to be applied in industrial applications. Therefore, the structural design of alloying anodes steps further to combine the alloying anodes with the separator together to confine the volume change directly by taking advantage of the 3D structure of separators. Zhang et al. directly coated a poly(vinylidene fluoride-cohexafluoropropylene) (PVDF-HFP) layer onto the Al foil to prepare a multifunctional electrode which can be used as the separator and the electrode at the same time.[85] The coated PVDF-HFP layer with a porous and 3D structure exhibited a good ionic conductivity ((4.4 ± 0.4) × 10⁻⁴ S cm⁻¹). It showed enough flexibility to allocate the volume changes in the aluminum alloying anode mechanically. When integrating with the graphite cathode, Li-based DIBs achieved a high energy density of 158 Wh kg⁻¹ at 1738 W kg⁻¹ (Figure 9b). After 1000 cycles at a current density of 2 C, DIB retention reached up to 92.4%. Compared with the structural design of alloying anodes based on nanotechnologies, the mechanical integration of alloying anodes and separators can still deliver a similar electrochemical performance based on a more convenient technological process, which is favorable for further industrial practices. In conclusion, the structural design strategies of alloying anodes mentioned earlier both belong to the physical restriction of the volume changes.

Chemical modification of alloying anodes can also show great potential for improving the electrochemical performance of DIBs. Zhang et al. constructed DIBs based on the Li-based ionic liquid electrolytes.[86] The ionic liquid electrolyte with FEC additives can form a stable solid electrolyte interface (SEI) on the surface of aluminum alloying anodes because the fluorine components in FEC are less chemically active, preventing material damage by maintaining the interface stability of the alloying anodes. Therefore, the energy density of DIBs using aluminum alloying anodes can reach 185 Wh kg⁻¹ at the power density of 1141 W kg⁻¹ (Figure 9b).

As discussed before, alloying anodes can provide a higher energy density, but the slow kinetics of alloying anodes will affect the battery performance at higher rates because mechanical degradation via volumetric changes is more serious at a high current density. Therefore, new technologies to restrict the uncontrolled volume expansion of alloying anodes are of great importance to improve the energy density and power density of DIBs. Through the structural design of alloying anodes, the volumetric changes can be adjusted, while using suitable additives in the electrolytes, the interface chemistry of alloying anodes can be further tuned, thus chemically stabilizing the cycling and rate performance of DIBs. Great progress in alloying anodes for DIBs has been achieved, especially for aluminum alloying anodes in Li-based DIBs.

Utilizing alloy-type anodes could induce some negative impacts. The SEI layer on the electrode suffers continuous damage due to the volume expansion behaviors during cycling and depleting the active ions from electrolyte; also the damage and pulverization of anodes result in dead metal and capacity fade (Si: 300%; Sn: 260% Al: 97%). In the future, more attention is required to make those technologies more cost-effective and sustainable, for example, by using bio-based binders and separators as well as by avoiding fluorinated compounds in both binders and electrolytes.

4.2.3. Conversion Materials

Conversion anode materials such as transition metal oxides (e.g., MnO₂, Co₃O₄, and so on) are another type of anode material for DIBs, which can store cations with high specific capacities by reversible redox reactions between cations of choice and metals in transition metal oxides. Depending on the ionic bond strength between metals and anionic species, the reaction potential of conversion anodes can be higher than insertion/intercalation anodes, which avoids the dendrite formation and ensures the safety of DIBs during fast charge/discharge processes. However, conversion
anodes suffer from slow kinetics of redox reactions, low intrinsic conductivity, and, similar to alloying anodes, poor mechanical stability upon cycling. The literature reports on the utilization of conversion anodes for DIBs are scarce. The development of nanostructured conversion anode materials is still in its fancy to achieve high-performance DIBs. Lu et al.\textsuperscript{[74]} have summarized the design strategies for novel conversion anodes, including structural engineering and carbon hybridization. More efforts are needed to make conversion materials practical alternative anodes for DIBs and move toward oxides based on abundant elements.

4.3. Optimization of Electrolyte

The electrolytes directly inherited from the state-of-art LIBs have some limitations in delivering satisfactory electrochemical performance in DIBs. Different solvents, salts, additives, concentrated electrolytes, and ionic liquids offered more opportunities for DIBs research.

4.3.1. Standard Electrolytes

Electrolytes of high purity and extremely high oxidation resistance are needed to minimize the side reactions, especially at high voltages DIB cathodes operate. Some solvents have a high oxidation voltage beyond 5.0 V, such as 5.3 V versus Li\textsuperscript{+}/Li for 99.985% DMC and 5.5 V versus Li\textsuperscript{+}/Li for 99.979% EC. However, their oxidative stability is noticeably reduced in the presence of anions.\textsuperscript{[87-89]} For example, Clo\textsubscript{4}\textsuperscript{-} in carbonate electrolytes is oxidized over 4.6 V, leading to a lower charge cutoff potential and therefore lower reversible capacity.\textsuperscript{[89]}

For pure carbonate solvents, DMC features low viscosity and higher ionic conductivity than other linear carbonates (e.g., diethyl carbonate [DEC]). For example, the Ionic conductivity of 3 M LiPF\textsubscript{6} in DMC is higher than 3 M LiPF\textsubscript{6} in EMC.\textsuperscript{[73, 90]} DMC is an appropriate solvent for achieving a discharge capacity of over 100 mAh g\textsuperscript{-1} due to the low viscosity.\textsuperscript{[58]} EC, a key electrolyte ingredient in LIBs, protects graphite from exfoliation via forming inorganic SEI during the first cycles to inhibit electrolyte decomposition and intercalation.\textsuperscript{[90-94]} On the contrary, EC has a large dielectric constant of 89.78,\textsuperscript{[95]} and stronger solvation ability. Thus, EC-solvated anions have less ability to intercalate into graphite.\textsuperscript{[42]} Specifically, the intercalation-retardant ability of EC binding tightly with PF\textsubscript{6}\textsuperscript{-} prevents PF\textsubscript{6}\textsuperscript{-} intercalation into graphite and also shows sluggish transport inside the graphite electrode.\textsuperscript{[76]} The increase in EC content in the electrolyte reduces the capacity of a graphite cathode.\textsuperscript{[58]} Therefore, different from LIBs, the strong interaction between PF\textsubscript{6}\textsuperscript{-} and EC molecule has an adverse influence on the electrochemical performance of a DIB. EMC is a strong competitor to EC in the formation of hydrogen bonding with PF\textsubscript{6}\textsuperscript{-} anion. The solvated PF\textsubscript{6}\textsuperscript{-} with linear EMC molecules is more favorable for intercalation into graphite than cyclic EC molecules.\textsuperscript{[97]} EMC also forms a thinner and more stable CEI layer than DMC and DEC, while fewer Li-F and ROCO\textsubscript{2}-Li are detected after cycling revealed by XPS and TEM.\textsuperscript{[51]} Higher EMC content resulted in lower onset potential, indicating that PF\textsubscript{6}\textsuperscript{-} is easier to intercalate in EMC and thus increase the capacity.\textsuperscript{[42]} Thus, substituting EC with EMC has become a popular trend in DIBs. Dou et al.\textsuperscript{[98]} utilized propylene carbonate (PC) as a sole electrolyte in a Na-based DIB and obtained a reversible capacity was only 62 mAh g\textsuperscript{-1} at the current density of 0.04 A g\textsuperscript{-1}. In situ XRD and in situ Raman spectroscopy were used to probe the stage mechanism, identifying stage-4 GICs and stage-5 GICs at 5.0 V rather than stage-1 GICs, which means PF\textsubscript{6}\textsuperscript{-} fails to fully intercalate among PC environment. Thus, PC is not an ideal electrolyte to be used alone due to the high dielectric constant of 64.92,\textsuperscript{[95]} potentially preventing PF\textsubscript{6}\textsuperscript{-} intercalation. Strategies to stabilize electrolytes under a high oxidative voltage, such as additives, higher concentration, and so on, will provide more insights to optimize the energy density and lifetime of DIBs.

4.3.2. Concentrated Electrolytes

The concentration of 1 M has been optimized due to the accumulated LIBs’s industrial experience over decades. The “rocking-chair” batteries used in combination with concentrated electrolytes, in most cases, could reduce the energy density.\textsuperscript{[87]} Whether concentrated electrolytes benefit in emerging DIBs is still under debate. DIBs using a concentrated electrolyte can have high energy density and good power density, making them a viable alternative to LIBs.\textsuperscript{[159]} Concentrated electrolytes are drawing increasing research attention owing to some advantages over diluted ones: 1) a high concentration ensures plenty of active ions available to intercalate as the depletion of electrolyte over the charging process lead to a the decrease in the concentration of the electrolyte; therefore, concentrated electrolytes provide enough ions for intercalation; 2) significantly increased power density of a DIB because concentrated electrolyte shorten the ion pathway; 3) increased energy density because the less solvated anions have a smaller size in concentrated electrolyte than bigger solvation sheath in diluted electrolytes leading to a lower onset voltage for anion intercalation, indicating that more anions can be incorporated into graphite with a specific cutoff potential;\textsuperscript{[87]} 4) reduce the free solvent molecules with a smaller solvation sheath surrounding anions suppressing cointercalation of solvent molecules into an electrode, which ensure a longer lifetime of DIBs by preventing electrode damage;\textsuperscript{[40,44,94,99]} and 5) the oxidation potential of concentrated electrolyte is higher than diluted ones.\textsuperscript{[74]} Figure 10a shows solvation and interfacial structures of superhigh and ultralow concentrated electrolytes. Wang et al.\textsuperscript{[11]} reported DIBs using 3 M LiPF\textsubscript{6} in different electrolytes (EMC, DMC, and DEC), showing an enhanced Coulombic efficiency and excellent rate performance of a 3 M salt in EMC. The 90% efficiency of the available capacity can be maintained even at 1200 mA g\textsuperscript{-1}, as shown in Figure 10b, c. Kovalenko and Pathak et al.\textsuperscript{[100]} fabricated potassium-based DIBs using 5.0 M potassium bis(fluorosulfonyl)imide in alkyl carbonates, offering an energy density of 207 Wh kg\textsuperscript{-1} with a high energy efficiency of 89% and an average discharge voltage of 4.7 V. The high cathodic capacity of up to 100 mAh g\textsuperscript{-1} is higher than other reported capacity of diluted electrolytes. Tang’s group\textsuperscript{[24]} reported a DIB using 7.5 M lithium bis(fluorosulfonyl)imide (LiFSI) in EC:DMC (1:1, v/v) mixed electrolyte exhibits a discharge capacity of 94.0 mAh g\textsuperscript{-1} at 200 mA g\textsuperscript{-1} and 96.8% capacity retention after 500 cycles. By counting both the electrode materials and electrolyte, the energy density of this DIB reaches...
up to \(\approx 180\) Wh kg\(^{-1}\), which is among the best performance of reported DIBs. Figure 10d shows the electrochemical performance of the DIBs using 0.8, 4.0, and 7.5 M LiFSI. Reproduced with permission.\(^{74}\) Copyright 2020, Wiley-VCH GmbH. e) Charge–discharge curves of a Na|GPE|graphite DIB at different current densities. Reproduced with permission.\(^{112}\) Copyright 2020, Elsevier B.V.

Adding less amount of a concentrated electrolyte can also increase DIBs energy density. However, such electrolytes would lead to high viscosity and high cost, and the current collectors/battery cases suffer corrosion. Based on the DIBs’ principle that the active ions only originate from the electrolyte, concentrated electrolytes are promising in further practical applications. Ideally, a better design for appropriate additives for concentrated electrolytes would be needed to improve the energy density of DIBs.

### 4.3.3. Salt in Electrolyte

The size of anions and the different solubility of various salts in the aforementioned organic solvents bring about different intercalation chemistry. In carbonate solvents, LiPF\(_6\) usually can reach up to 4 M, while LiTFSI/LiFSI salts can go up to 8 M. The reason for low solubility in carbonate electrolytes of LiPF\(_6\) is the strong interaction and high dissociation energy between cation–anion, while TFSI\(^-\)/FSI\(^-\) have weaker interaction.\(^{74}\) Different size of anions leads to different intercalation voltage and discharge capacity: the intercalation voltage of FSI\(^-\) is often found to be higher than that of PF\(_6^+\) intercalation because larger anion size of FSI\(^-\) (95 Å\(^3\)) than that of PF\(_6^+\) (69 Å\(^3\)).\(^{100,101}\) A smaller sized anions TFSI\(^-\)-based DIB has a higher theoretical discharge capacity. This means each TFSI\(^-\) anion can electrochemically react with more carbon atoms forming a C\(_{27}\)TFSI to C\(_{26}\)TFSI stoichiometry with a capacity of 99.3 mAh g\(^{-1}\) than FTFSI\(^-\) (C\(_{23}\)FTFSI to C\(_{22}\)FTFSI, 84.7 mAh g\(^{-1}\)).\(^{41}\) PF\(_6^-\) salt appears a better candidate for emerging DIBs because their reasonable price compared with much higher TFSI\(^-\)/FSI\(^-\) salts. In addition, FSI\(^-\) may corrode the AI current collector leading to loss of active ions and low Coulombic efficiency. Thus, some strategies may...
enhance the current collector stability and better select electrolyte additives (e.g., LiPF$_6$, NaPF$_6$) (Table 1).

Ionic liquids (ILs, or molten salts) bring fantastic opportunities to overcome the poor stability of carbonate electrolytes under high voltage owing to their low flammability, high thermal stability, low safety hazards, negligible vapor pressure and low volatility at ambient pressure, and overall good compatibility in the battery system.[115,116,117] However, at a low temperature, ionic liquids-based electrolytes usually lead to poor electrochemical performance due to the increase in viscosity and a decrease in conductivity. Research into ionic liquids-based electrolytes (e.g., Pyr$_{14}$, Pyr$_{14}$ as cations) would further eliminate the use of metal ions in the electrolyte without metallic dendrite formation upon cycling. Dendrites formation is the main factor triggering the safety problems.[114] Thus, ionic liquids largely ensure the safety and reliability of DIBs. Placke developed a DIB based on dual KS6L graphite as electrodes with a mixed electrolyte of 1 M LiTFSI and ionic liquid Pyr$_{14}$TFSI, delivering 98 mAh g$^{-1}$ at 0.03 A g$^{-1}$.[112] Wang et al.[113] reported a dual-graphite battery in a configuration and discharge capacity.

### Table 1. Different anions in DIBs with corresponding voltage range, configuration and discharge capacity.

| Anion | Anion structure | Voltage [V] | Anode | Electrolyte | Cathode | Discharge capacity | References |
|-------|-----------------|-------------|-------|-------------|---------|-------------------|------------|
| PF$_6^-$ | ![Structure](image) | 3.0–5.0 | Al | 4 M LiPF$_6$ in EM/VC | natural graphite | 104 mAh g$^{-1}$ at 0.2 A g$^{-1}$ | Zhang et al.[97] |
| TFSI$^-$ | ![Structure](image) | 3.0–4.8 | Al | 1 M LiTFSI in Pyr$_{14}$TFSI/FEC | mesocarbon microbead | 98 mAh g$^{-1}$ at 0.05 A g$^{-1}$ | Zhang et al.[98] |
| FTSI$^-$ | ![Structure](image) | 3.4–5.0 | Li | 3.4 M LiTFSI in DMC | synthetic graphite | 75 mAh g$^{-1}$ at 0.05 A g$^{-1}$ | Heckmann et al.[126] |
| FTFSI$^-$ | ![Structure](image) | 3.4–5.0 | Li | 1.0 M LiTFSI in Pyr$_{14}$TFSI | synthetic graphite | 82 mAh g$^{-1}$ at 0.03 A g$^{-1}$ | Fan et al.[106] |
| BF$_4^-$ | ![Structure](image) | 0–3.5 | Activated carbon | 1.5 M SBPBF$_4$ in PC | natural graphite | 32 mAh g$^{-1}$ at 0.1 A g$^{-1}$ | Gao et al.[128] |
| FSI$^-$ | ![Structure](image) | 3.0–5.2 | Li | 7.5 M LiFSI in EC/DMC | expanded graphite | 94.0 mAh g$^{-1}$ at 0.2 A g$^{-1}$ | Xiang et al.[74] |
| 3.2–5.25 | K | 5.0 M KFSI in EC/DMC | natural graphite | 98 mAh g$^{-1}$ at 0.05 A g$^{-1}$ | Kravchyk et al.[100] |
| 3.0–5.1 | Li | 1.0 M LiFSI in EC/DEC | highly oriented pyrolytic graphite | 60 mAh g$^{-1}$ at 0.01 A g$^{-1}$ | Fukutsuka et al.[38] |
| AlCl$_4^-$ | ![Structure](image) | 0–2.45 | Al | AlCl$_4$ in [EMIm][Cl (r = 1.3)] | natural graphite | 150 mAh g$^{-1}$ at 0.01 A g$^{-1}$ | Kravchyk et al.[73] |

in the earth’s crust which promise a sustainable trend toward future energy devices.[106] As organic solvent molecules are not present in the electrolyte, solvent intercalation at high potentials is precluded so that highly stable cycling is achieved that stability of $\approx 1000$% capacity retention for 600 cycles. Although ionic liquids show a promising future, if the high costs of most ionic liquid electrolytes cannot be solved out,[33] it is too early to say ILs can easily replace existing commercial electrolytes.

### 4.3.4. The Additive

A high operating voltage usually causes degradation and decomposition to electrolyte with less oxidative ability. A small amount of additive help improves the electrochemical performance in battery research. Ethylene sulfite (ES) allows stable and highly reversible Li$^+$ and TFSI$^-$ intercalation/deintercalation into/from the graphite anode and cathode, respectively. By adding ethylene sulfite, the discharge capacity for the anion intercalation can be remarkably increased from 50 to 97 mAh g$^{-1}$.[104] This enhancement may be related to the reduced coordination of Li$^+$ ions with TFSI$^-$ anions in the presence of ES. Placke and Winter et al. showed ES reduced the onset potential for anion intercalation and decreased the overpotentials of cation plating, thus enhancing the reversible capacity of Li$^+$- and Na$^+$-based DIBs.[105] FEC has been widely proved to be an efficient additive FEC characteristic higher reduction potential, especially at high charging voltage and at elevated temperature.[108] In DIBs, FEC additive protects metallic anode by forming a compact and stable SEI layer.

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**Adapted from:***Advanced Energy Sustainability Research*** (2021) 2100074 (19 of 19) © 2021 The Authors. Advanced Energy and Sustainability Research published by Wiley-VCH GmbH
beneficial for evenly depositing, and forms an F-containing CEI layer on a graphite cathode. This CEI layer helps increase the cycle number and discharge capacity of graphite and protect it against volume expansion. The FEC additive exhibits low self-discharge in DIBs with a graphite-based cathode and ben-eficial to DIBs by forming a stable SEI film on the Al foil. Due to side reactions taking place during cycling, gas formation is not a negligible factor that reduces cell capacity and decreases Coulombic efficiency. Tetraethylammonium tetrafluoroborate (TEABF₄) is an additive capable of suppressing gas formation in DIBs. TEA⁺ cations from the additive can weaken the hard-ness of the Lewis acidity to decrease irreversible capacity and suppress gas formation preventing the degradation of storage capacity during cycling of a DIB. Lithium-titanite anode coupled with a graphitic carbon cathode can deliver a long lifecycle over 1000 cycles releasing negligible gas.

4.3.5. Quasi-Solid-State Electrolyte

The development of quasi-solid-state electrolytes for DIBs could be another effective strategy to optimize cycling stability due to some advantages over carbonate solvents such as more stable at high voltage and their 3D polymer skeleton beneficial for attenuating the stress caused by the volume expansion of electrode materials, especially alloying-type anodes. DIBs based on gel polymer electrolyte (GPE) was also developed by Tang’s group, delivering cycling stability with a capacity retention of 92% after 2000 cycles at a current rate of 500 mA g⁻¹. The electrolyte was a PVDF-HFP GPE codoped with poly(ethylene oxide) (PEO) and graphene oxide by soaking 4M LiPF₆ in EMC with 2 vol% VC. Wang et al. developed a multifunctional quasi-solid-state GPE prepared by in situ polymerizing an ethoxylated pentaerythritol tetraacrylatemonomer for DIBs using a diluted electrolyte of 0.5 M electrolyte and achieve. The GPE has high ionic conductivity (5.33 × 10⁻³ S cm⁻¹ at 25°C), high electrochemical stability up to 5.5 V versus Na⁺/Na, and low flammability. Such electrolyte can significantly improve the reversible capacity and cyclability of DIBs, delivering a high energy density of 484 Wh kg⁻¹ with an operating voltage of 4.4 V and excellent long-term cycling performance. The electrochemical performance is shown in Figure 10e.

4.4. Multi-ion Strategies

Apart from DIBs which involve two active ions from electrolyte, similar cases have been extended to multi-ion batteries. For example, Tang’s group added LiPF₆ (30 at%) salt into Na-based DIBs (Sn anode, graphite cathode, and NaPF₆ salt in mixed carbonate electrolyte) to form a triple-ion battery (Li⁺, Na⁺, PF₆⁻) (Figure 11a). Such configurations proved to deliver a good rate performance up to 3 A g⁻¹. The addition of Li⁺ ion can help in three ways: 1) a high mechanical stability can be achieved via a reduction in volume expansion during cycling because the ≈22% volume expansion of Li₂Sn₅ phase was much smaller than ≈120% of the NaSn; 2) improving the ion transfer efficiency by which rate capability can be enhanced due to Li faster mobility than the Na atom in the Sn crystal; 3) Sn was chosen as anode due to the reversible coalloying of both Na⁺ and Li⁺ ions with high capacity. The simulation work on the density of states of both Li₂Sn₅ and NaSn suggests NaSn shows a semiconductor characteristic, but Li₂Sn₅ shows a typical metal characteristic, resulting in that the formation of conductive Li₂Sn₅ would facilitate the electron transport during the alloying process and therefore improve the rate performance.

Figure 11. a) Schematic illustration of the operation mode of sodium-ion-based multi-ion full battery (SMIB). Reproduced with permission. Copyright 2018, Wiley-VCH GmbH. b) Schematic illustration of the multi-ions battery during the charging and discharging process. Reproduced with permission. Copyright 2017, Wiley-VCH GmbH. c) Rate performance of a calcium-based tri-ion battery at varied current rates (0.2–1.5 A g⁻¹). d) Cycling performance of a calcium-based tri-ion battery at 0.5 A g⁻¹. Reproduced with permission. Copyright 2019, Wiley-VCH GmbH.
expansion of the Li2Sn5 phase (the addition of the Li element introduces a much smaller volume reduces the charge transfer resistance of calcium ions while

tal understanding is needed to accelerate the development of
strategies are closely linked together and a synergetic fundamen-
tal development of novel anode materials, optimization of
electrolyte, and multi-ion strategies. It worth noting that these
be adapted to achieve a higher energy density, especially for those
capacity than DIBs. It is expected that the multi-ion strategy can
enhance diffusion kinetics of charge carriers, and deliver more

To sum up, multi-ion strategies can reduce volume expansion,
encourage diffusion kinetics of charge carriers, and deliver more capacity than DIBs. It is expected that the multi-ion strategy can be adapted to achieve a higher energy density, especially for those low-cost metallic anodes of high-volume change issue.

This section discussed strategies applied to complex DIBs sys-
tems, including the optimization of carbon-based cathodes, ratio-
nal development of novel anode materials, optimization of
electrolyte, and multi-ion strategies. It worth noting that these strategies are closely linked together and a synergetic fundamental understanding is needed to accelerate the development of DIBs.

5. Summary and Perspectives

DIBs are promising energy storage devices and have attracted considerable attention over recent years. As DIBs technologies are not well established yet to be commercialized, huge research efforts are needed to further improve the electrochemical performance before they could be massed produced. We hope that the perspectives below could provide some inspiration for DIBs relevant future research. Figure 12 shows an overall perspective on the development of DIBs.

5.1. Novel Electrode Materials

Among the reported cathode materials in DIBs, the critical role of graphite (or expanded graphite) is expected to be maintained as the most stable and accessible material, while natural graphite is considered a critical material. As sustainability and cost-effective-
ness will be a prerequisite, in the long run, recycling and reusing graphite from spent LIBs or producing synthetic graphite from oil residues used in the chemical industries would be desired. Unfortunately, most of the “ordered” precursors needed to make high-quality synthetic graphite are based on fossil fuel, and ide-
ally, graphite could be produced from a sustainable bioprecursor.

Synthetic graphite also requires a high temperature to be pro-
duced, and being able to increase the substantiality and efficiency of its manufacturing step is vital.

Alkali metals are now the most used anode in DIB research owing to the stable potential of electrochemical reactions (plating/stripping). For practical use, metallic anodes have dendritic formation issues, but solid-state electrolytes promise in protect-
ing metallic anodes and restraining the issue of dendrite growth.[116] For practical anode design, insertion/intercalation materials (graphite or hard carbon) appear as a safe option for mass production. The design of all carbon cell is attractive for designing safe batteries. Their drawbacks are that relatively low gravimetric and volumetric capacity making DIBs are to com-
pete with current LIBs. Alloying and conversion materials are promising due to high theoretical capacities but have low stability and suffer volume expansion. More research is also needed to further develop conversion materials to be a practical alternative for DIBs.

5.2. Electrolyte Stable under High Voltage

Conventional carbonate electrolytes are degradable under the voltage window that DIBs must operate. Quasi-solid-state electrolytes, additives, and concentrated electrolytes can serve as potential more stable alternatives compared with unstable organic electrolyte. A high concentrated solution that increases the weight of salt in the DIBs system will compromise the energy density, which most likely not be favored by battery industries.

Decreasing the size of the anion in ionic liquid or carbonate electrolytes could further maximize the reversible discharge capacity and rate capability. Thus, finding suitable ionic liquid electrolytes or organic solvent-based electrolytes with appropriate salts while electrolytes display high electrochemical stability
versus oxidation become sensible to improve the specific discharge capacity.

5.3. Battery Safety

The electrification of transport and switch to renewable energy stimulates the growing market for energy storage. The promising high power density qualifies DIBs a place in battery research. Pushing this battery technology toward a higher energy density is vital. In recent decades, as portable batteries are extended to many areas, safety concerns are drawing attention from society, especially after cell explosion in smartphone and electric vehicles. Subsequently, research into flame-retardant electrolyte becomes valuable.[117] It is no doubt that battery safety is another ultimate focus in which involves cell design and integrity design. A series of safety tests will be necessary to guarantee the reliability of products and user experience.

5.4. Advanced Characterization

Operando characterization techniques have been applied in energy storage research such as neutron scattering, cryogenic TEM, operando XPS, in situ AFM, synchrotron X-ray sources, and in situ nuclear magnetic resonance (NMR). To further enhance the energy density of DIBs, more atomic understanding of working principles, cation and anion behaviors will contribute to more rationally designed electrode, electrolyte, and interphase.

Owing to the crystal and expandable nature of graphite cathode, XRD is one of the most efficient techniques to characterize the intercalation phenomena, the change in layer spacing, and the staging mechanism.[19,40,118] Raman spectroscopy is also an advantageous technique to detect defects and graphite ordering.

While there has been significant research on revealing and analyzing the changes in anodes and cathodes, the most severe part of the system, electrolyte, has been less investigated. For example, how the electrolyte degrades, is there any gas formation under high voltage? The excellent rate performance of cointercalation is well studied and linked with the energy barrier of solvent/desolvation dominated during electrochemical reactions. The research topic upon whether anions undergo solvation and desolvation remains unclear. The fast kinetics of anion could stem from cointercalation with electrolyte molecules from Na–ether molecular cointercalation into graphite. It could also stem from a not-solvated anion, as mentioned earlier. As a result, more efforts are worth investigating the fundamental mechanism of DIBs.

5.5. Full-Cell Design toward Practical Use

For battery research, gravimetric and volumetric energy densities are among the most important parameters as they are directly related to performance. Three ways, in brief, can increase it: 1) increase the electrode capacity of both electrodes; 2) expand the operation voltage window; and 3) increase the ratio of active materials to inert materials. From theoretical value to practical energy density, the volumetric energy density of a manufactured cell only retains less than 30% of its theoretical volumetric energy density. Reduction in the mass of current collector[119] or using ultralightweight 3D carbon current collectors[120] and redesign module, or even elimination of current collector (free-standing design) can increase gravimetric energy density. The capacity ratio of negative to positive electrodes (N/P ratio) is one of the most vital factors to design DIBs. Feng et al.[118] discussed the N/P ratio and calculation steps which would be beneficial for pairing a full cell. Ishihara et al.[110] reported that unbalanced capacity between negative and positive electrode results from electrolyte decomposition as a side reaction during cycling is one reason for decreased cycle stability of a DIB.

When it comes to commercial application, DIBs are clearly in its infancy. Their merits are low cost and sustainability (i.e., by eliminating Co and Ni). DIBs possess high-power density, particularly promising for grid storage applications and short distance electrical transportation. Although DIBs have still not been yet used in practical applications, recent fundamental developments cumulated with a demonstrator for their commercial viability of DIBs by a Japanese company (PJP Eye Ltd.) are encouraging toward potential commercialization of this low-cost technology in the near future.[121] In summary, DIBs are an emerging technology promising in electric vehicles and large-scale energy storage. There are still many fundamental scientific and engineering problems that need to be addressed before they reach commercialization. This review discusses some potential strategies to improve the energy density of DIBs with the hope that DIBs would become a practical reality in the near future.

Acknowledgements

Z.G. and Z.X. contributed equally to this work. Z.G., Z.X., and J.F. acknowledge China Scholarship Council and Science and Technology Facilities Council (STFC) Batteries Network (ST/R006873/1) for the funding support. M.-M.T. acknowledges EPSRC grants EP/S018204/2 and EP/R021554/2 as well as Royal Academy of Engineering for the award of a Chair in Emerging Technologies.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

dual-ion batteries, energy density, energy storage, graphite cathodes

Received: March 15, 2021
Revised: April 1, 2021
Published online:

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