Dual-Carbon Batteries: Materials and Mechanism

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Abstract: In the last few decades, significant achievements have been made in utilizing various carbon nanomaterials for energy applications (e.g. solar cells, fuel cells, supercapacitors, and batteries). Dual-carbon batteries (DCBs), in which both electrodes are comprised of functionalized carbon materials, can deliver high energy/power density and excellent cyclic stability when they are rationally designed. This short Review focuses on the energy storage properties and electrochemical reaction mechanisms of various carbon electrode materials (graphite, graphene, hard and soft carbon, activated carbon, and their derivatives) in DCB systems. The interfacial chemistry between carbon electrodes and electrolyte is also discussed. Our perspective for further development of DCBs is presented at the end.

1. Introduction

Positive and negative electrodes are the vital components of an electrochemical battery, which are loaded with the host materials to store/release conductive ions and electrons.[1] The dual-carbon battery (DCB), in which the both host materials are carbon materials (graphite, hard carbon, soft carbon, etc.), is free of toxic, heavy and expensive metals, thus being regarded as a green, safe, and low-cost energy storage device.[2] DCBs are considered as one type of most promising rechargeable batteries, since they can satisfy the key requirements for future energy storage devices.[3] Compared to other categories (such as alloy materials [4] and conversion materials[5]), In addition, another advantage of DCBs is high working voltage (> 4.5 V), which can offer the possibility to enable high-density energy storage.[6] Even under extreme condition (nail test), DCBs can still work normally, manifesting their satisfactory safety.[7]

Timeline of DCB An overview of the development of DCB is illustrated in **Figure 1**. The concept of DCBs was first proposed by Rüdorff and Hofmann in 1938, who used graphite as both positive and negative electrode materials, and demonstrated the reversible intercalation of HSO_4^- anions into graphite in concentrated sulfuric acid.[8] In 1989, McCullough *et al.* filed the first DCB patent and foreboded DCBs could be commercialized in the future.[9] In 2000, the Dahn group demonstrated a practical Li dual-graphite battery and investigated the electrochemical intercalation of PF_6^- into graphite via *in situ* X-ray diffraction (XRD) technique for the first time.[10] In recent years, DCBs are being revisited. In 2013, the Winter group introduced a new type of DCBs based on ionic liquid electrolyte ($Pyr_{14}TFSI$), and studied the influence of graphite characteristics (such as particle size distribution, specific surface area, and ratio of basal plane to "non-basal plane" surface areas) on the electrochemical behavior of $TFSI^-$ anion intercalation.[11] To increase the energy density of DCBs, Read *et al.* demonstrated a high-efficiency DCB with a ceiling voltage of 5.2 V through simultaneous accommodation of Li^+ and PF_6^- in two graphitic electrodes, which is enabled by an optimized electrolyte based on a fluorinated solvent and additive ($LiPF_6$ FEC : EMC (4 : 6, w/w) + 5mM HFIP).[12] Besides Li-ion DCB, DCBs based on other alkali-metal (Na^+, K^+) and multivalent cations (Al^{3+}, Ca^{2+}) are of interest to researchers due to the limited lithium resources and potential high capacity. In 2017, Fan *et al.* reported the first Na-ion based DCB using soft carbon as anode and graphite as cathode material, which exhibited excellent rate performance and long-term cycling stability.[13] Tang's group presented the first K-ion based DCB with a high average discharge voltage of 4.5 V, which utilized the expanded graphite (EG) as cathode and mesocarbon microbeads (MCMB) as anode.[14] In 2018, Wang *et al.* introduced the first Al-ion-based DCB

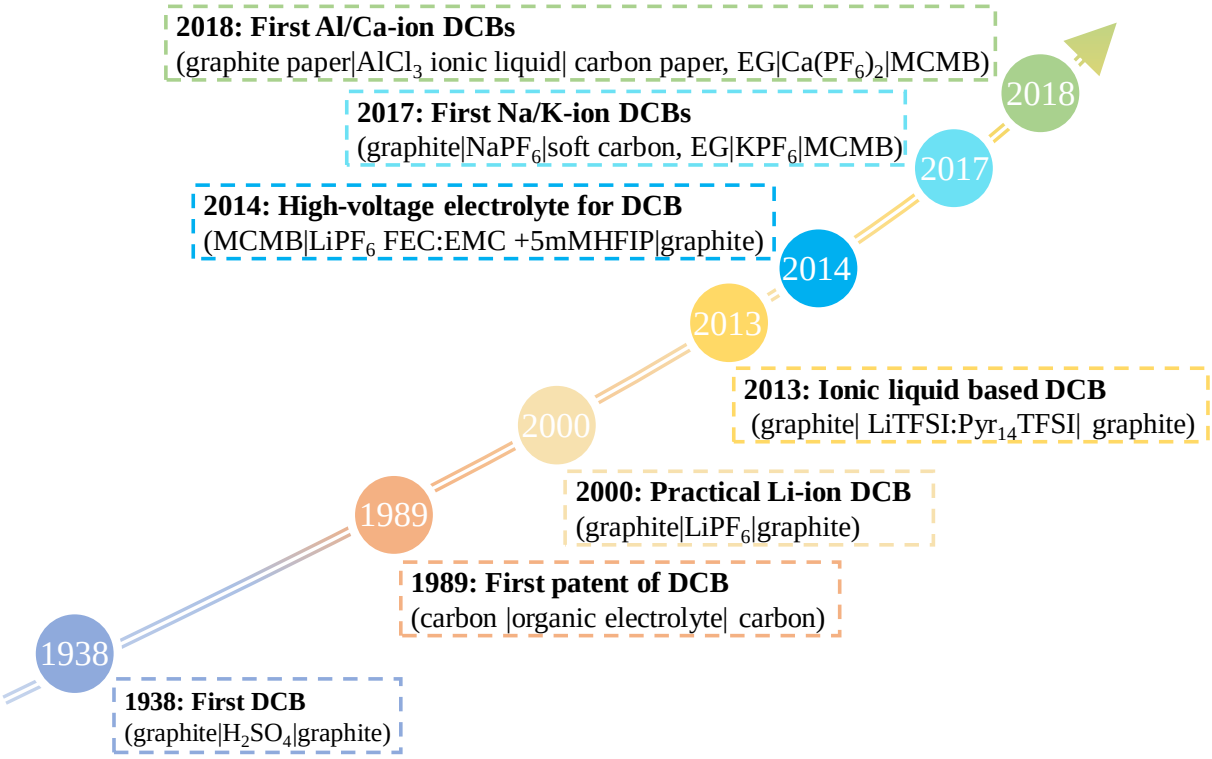

Figure 1. *Timeline of the development of DCB.*

with simultaneous deposition of Al^{3+} and intercalation of $AlCl_4^-$ in graphitic materials using an $[EMIm]Al_xCl_y$ ionic liquid electrolyte. Tang's group reported the first Ca-ion-based DCB revealing a high working voltage of 4.6 V, with MCMB and EG as the anode and cathode, respectively.[15]

2. General Classification of DCB

Different from the conventional rocking-chair batteries, the mechanism of the DCB is determined by the types of carbon materials on the anode and cathode sides.[16] Based on the different microscopic structures of carbon materials and the applied voltage, the charge storage mechanisms of the carbon electrodes can be divided into two major types, which are intercalation/deintercalation reaction and adsorption/desorption reaction.[17] The pure carbon materials, such as graphene and activated carbon (AC), are the common electrode materials used for ion adsorption reaction, because of their high specific surface area, controllable porosity and relatively inert electrochemical properties. For other types of pure carbon materials with layered structure, such as graphite, hard carbon and soft carbon, their charge storage mechanism is ion intercalation/deintercalation reaction.[18] During the charging process, the anions/cations from the electrolyte are simultaneously intercalated/adsorbed into/onto the

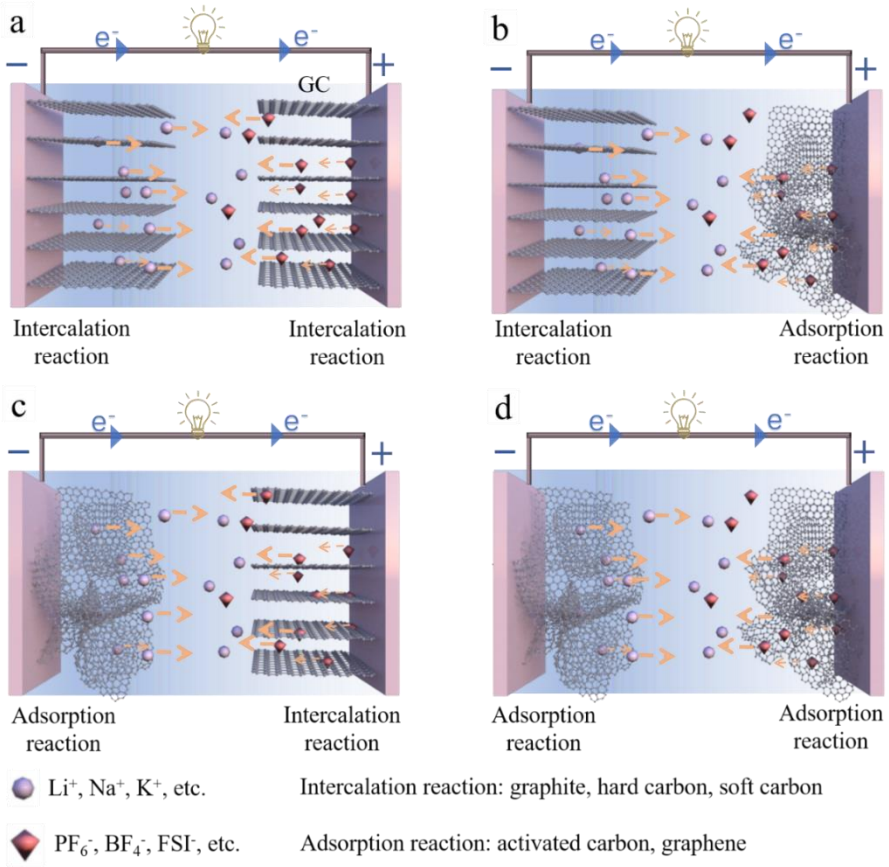

Figure 2. *Schematic of different DCB configurations (discharge process).*

positive/negative carbon electrode. Then most of the ions in the carbon electrodes return to the electrolyte after discharging.[1b, 2a, 19] Based on ion storage mechanisms on anode/cathode electrode, DCBs can be classified into four types: intercalation-intercalation, intercalation-adsorption, adsorption-intercalation and adsorption-adsorption (see schematic in **Figure 2**).

3. Carbon Electrodes in DCB

The energy/power density, long-cycle life, and cost of an energy storage device depend strongly on the electrode materials (in addition to electrolytes). Various carbons with different compositions and microstructures have distinct ion storage abilities and show different discharge capacities. The performance of some recent reported DCB full cells is summarized (**Figure 3a**).[6b, 20] As we can see from the capacity-voltage plot, the two Li-based DCBs (NPG || 1M $LiPF_6$ || AC,[21] MCMB || 1M $LiPF_6$ || Lithiated MCMB[22]) have the highest voltage and high capacities. This suggests that the Li-based DCBs are the most successful and high-performance DCB system at the current stage, as the suitable ionic radius of Li^+ matches well with the interlayer spacing of most carbon materials. The other DCB systems (such as Na, K-based DCBs) can be further improved by modifying the carbon structures and exploring new

carbon materials. Different values of energy density have been reported in various conventional batteries, such as lead-acid (20–35 Wh kg^{-1}), nickel metal hydride (40–100 Wh kg^{-1}), and lithium ion cells (120–170 Wh kg^{-1}).[23] The energy/power density of DCBs based on various electrode materials is shown in Figure 3b. Overall, DCBs show satisfactory energy density mainly resulting from the high operating voltage of the conventional organic electrolytes. For example, the devices (SC||1M $NaPF_6$||NPHC) show the largest energy density (245.7 Wh kg^{-1}).[24] In addition, with rationally designed carbon electrodes to boost the ion transport kinetics, the DCBs can reach a highest power density of up to 16 KW kg^{-1}, which is even higher than most electrochemical capacitors (10 KW kg^{-1}).[25] This high power performance is the consequence of the beneficial features of the carbon electrodes, such as hierarchically porous architecture, sheet-like structure stacking (>15 nm in thickness), and large surface area (up to 2396 m^2 g^{-1}). Nonetheless, there are still lack of research on DCB with both high energy and power densities. For this purpose, we need suitable carbon electrodes that have engineered microstructure and porosity, high electrical conductivity, optimized doping and functionalization, and stable interface with electrolytes.

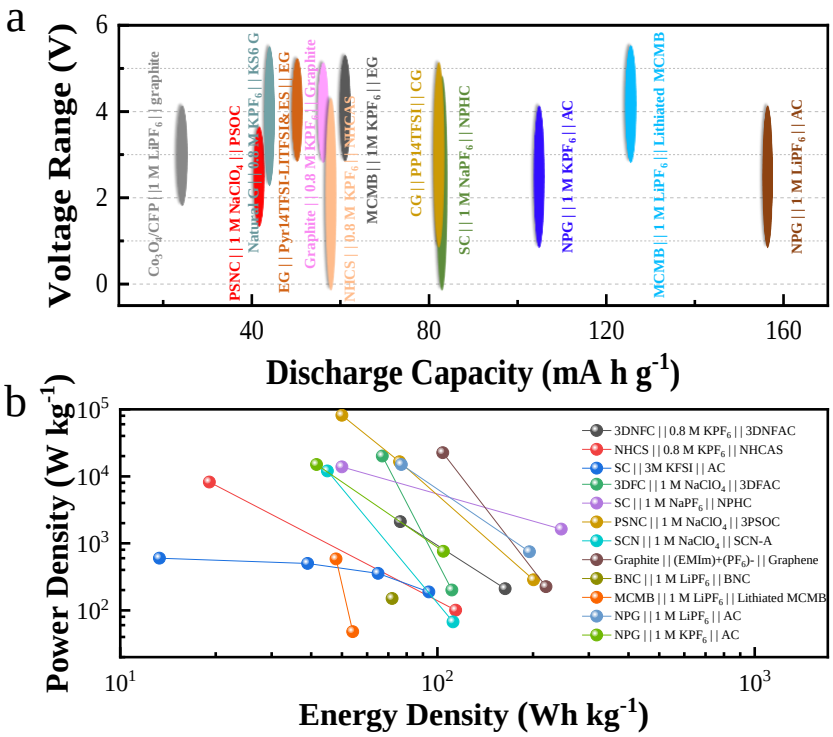

***Figure 3**. A summary of performance in recent reported DCB devices: a) capacity versus voltage plots; b) Ragone Plot.*

Based on the microstructures, carbon materials can be divided into five categories: graphite, graphene, hard carbon (HC), activated carbon (AC) and soft carbon (SC). As shown in **Figure 4**, these carbon materials are compared according to five essential parameters. HC

has the widest interlayer spacing suitable for the insertion of anions; graphene has the largest capacity of Li^+ storage, and AC has a large Brunauer–Emmett–Teller (BET) surface area suitable for adsorption reaction.[25-26] All of them have demonstrated good cation/anion storage performance in literature. In the following section, the fundamental issues, intrinsic drawbacks, and corresponding solutions of all the five types of carbon electrodes are articulated.

3.1 Graphite

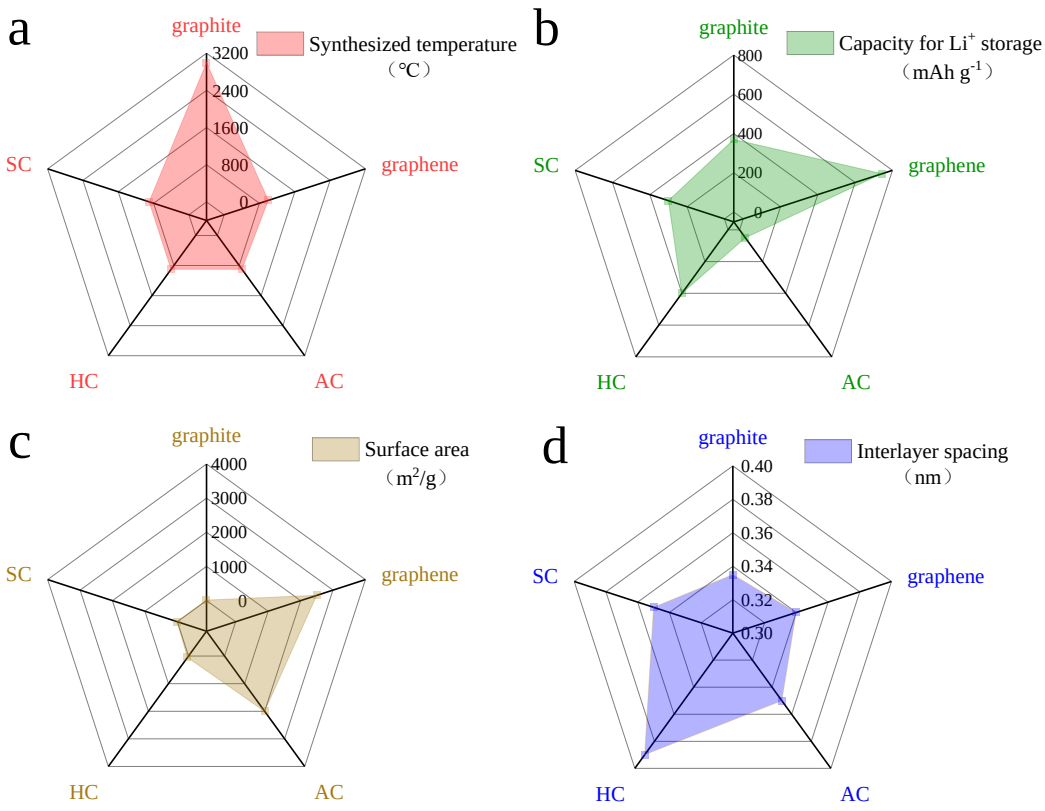

Figure 4. *Key parameters of five types of carbon materials. The surface area and capacity of Li^+ storage correspond to the synthesis temperature in a. The interlayer spacing of graphene in d refers to the interlayer spacing of few-layer graphene.*

Graphite has been extensively studied as the electrode material for the intercalation of various cations and anions. An ideal graphite material consists of regular graphene sheets with a fixed spacing of about 0.335 nm, which are stacked in the ABAB sequence, and linked together through weak Van der Waals forces.[27] In a single graphene sheet, the honeycomb crystal lattice consists of sp^2 hybridized carbon atoms with strong covalent bonds in the plane. The remaining *2p* orbital in the *z*-direction form hybridization with partially filled and delocalized band structure, which allows high electron mobility (~200000 $cm^2\ V^{-1}\ s^{-1}$).[16b] This characteristic can explain its amphoteric redox behavior, such that graphite can act as both electrodes for DCBs. Rechargeable batteries that use graphite as both the anode and cathode

materials are also called dual-graphite batteries. The associated mechanism is based on the intercalation/deintercalation of anions/cations into both graphite electrodes during the charge-discharge process.[28] At a certain potential, charge carriers can overcome the Van der Waals forces and intercalate into graphene sheets. The process of anion/cation intercalation are defined as "stages", that is, the number of graphene sheets between two adjacent intercalated atomic layers. The charge carriers include metal cations (Li^+, Na^+, K^+, and Al^{3+}), cations from molten salts (Pyr_{14}^+, $EMIm^+$), and various anions (PF_6^-, BF_4^-, $AlCl_4^-$, ClO_4^-, and $TFSI^-$) (**Figure 5a**).[16b, 29] For instance, Li^+ intercalation has a maximum stoichiometry of LiC_6 with an in-plane distance of 4.32 Å, and K^+ intercalation has a maximum stoichiometry of KC_8 with an in-plane distance of 4.91 Å. By comparison, PF_6^- intercalation can result in a larger in-plane distance, which causes a volume expansion and lower capacity of anion-intercalated graphite (Figure 5b).[30] To enhance the electrochemical performance, an effective strategy is to modify the structure of graphite, such as introducing disordered region, increasing interlayer distance, and controlling microstructure.

The insertion of alkali metal ions into graphite has been widely studied. Density-functional theory (DFT) calculation indicated that Na-graphite intercalation was only able to form the eighth-stage NaC_{64} compound, while Li-graphite intercalation and K-graphite intercalation could easily form stable LiC_6 and KC_8, respectively.[31] Jian *et al.* first achieved the electrochemical intercalation/deintercalation of K^+ at room temperature. The device was fabricated using commercial graphite as anode and 0.8 M KPF_6 (EC: DEC, v/v=1:1) as electrolyte.[16a] Generally, poor initial coulombic efficiency, fast capacity fading, and mediocre rate performance are the urgent problems of graphite anode. Fan and co-workers reported a K-based DCB by employing graphite as anode and organic as cathode. It demonstrated an ultrahigh initial coulombic efficiency of 94% and an excellent cycling stability of 500 cycles with a good capacity retention of 75.5%, corresponding to a capacity decay of 0.049% per cycle.[32] Beltrop *et al*. also investigated a K-based DCB only using graphite as electrode materials. The uniqueness was the ionic liquid-based electrolyte, which comprised 0.3 M KTFSI in N-butyl-N-methyl bis(trifluoromethanesulfonyl) imide ($Pyr_{14}TFSI$)) and 2 wt.% ethylene sulfites as an electrolyte additive. This K-based DCB exhibited a good capacity retention of 95% after 1500 cycles, and a stable coulombic efficiency (CE) of above 99% within a voltage range of 3.4–5.0 V.[33]

Compared with alkali metal cations, anions with larger ionic diameters (0.436 nm for PF_6^-, 0.39 nm for $TFSI^-$) are more difficult to reversibly insert into graphite with interlayer spacing of 0.335 nm.[16d] Because of this reason, there are limited electrode materials that can maintain

stable structure after undergoing multiple anions insertion/de-insertion process, leading to low capacity and poor rate performance. Taking Li^+ and PF_6^- for example, only 10% volume change occurs for LiC_6 formation with a theoretical capacity of 372 mA h g^{-1}, whereas volume change is up to 136% to form $C_{24}PF_6$ with a theoretical capacity of 93 mA h g^{-1}. The degree of graphitization might be an important factor to the capacity of DCBs. Ishihara *et al*. investigated the electrochemical properties of various carbon materials with PF_6^- insertion as cathodes of DCBs.[34] They discovered that the capacity of graphitic carbon increases as the (200) crystal plane distance decreases.

For further improving the energy density of DCBs, it is necessary to engineer the graphite material with functional groups, and also choose suitable electrolytes. Yan *et al.* assembled K-based DCB using KS6 as cathode, natural graphite as anode, 0.8 M KPF_6 in EC/DEC (1:1, v/v) as electrolyte, and a working voltage range of 2.4–5.4 V. The DCB had good cycling performance (92.5% retention after 400 cycles at 1.0 C), high medium discharge voltage (about ~4.2 V), and high energy density (up to 158.3 Wh kg^{-1}).[28] Ishihara *et al.* showed that the use of functionalized graphitic carbon can effectively improve the electrochemical performance of DCBs. The hybrid capacitor had a capacity of 150 mA h g^{-1} after 100 cycles. The nanobubbles on the graphitic carbon could improve the specific capacity of DCBs due to its large surface area.[35] Ji and co-workers developed a K-based DCB using expanded graphite as cathode material, MCMB as anode material, and 1 M KPF_6 (EC: DMC: EMC, v/v/v=4:3:2) as electrolyte. The DCB had a discharge capacity of 61 mA h g^{-1} at a current density of 100 mA g^{-1} and good cycling stability (no obvious capacity decay after 100 cycles). Furthermore, This DCB had a wide voltage window (3.0–5.2 V) with an discharge voltage of 4.5 V, which could meet the requirements of high-voltage devices.[14]

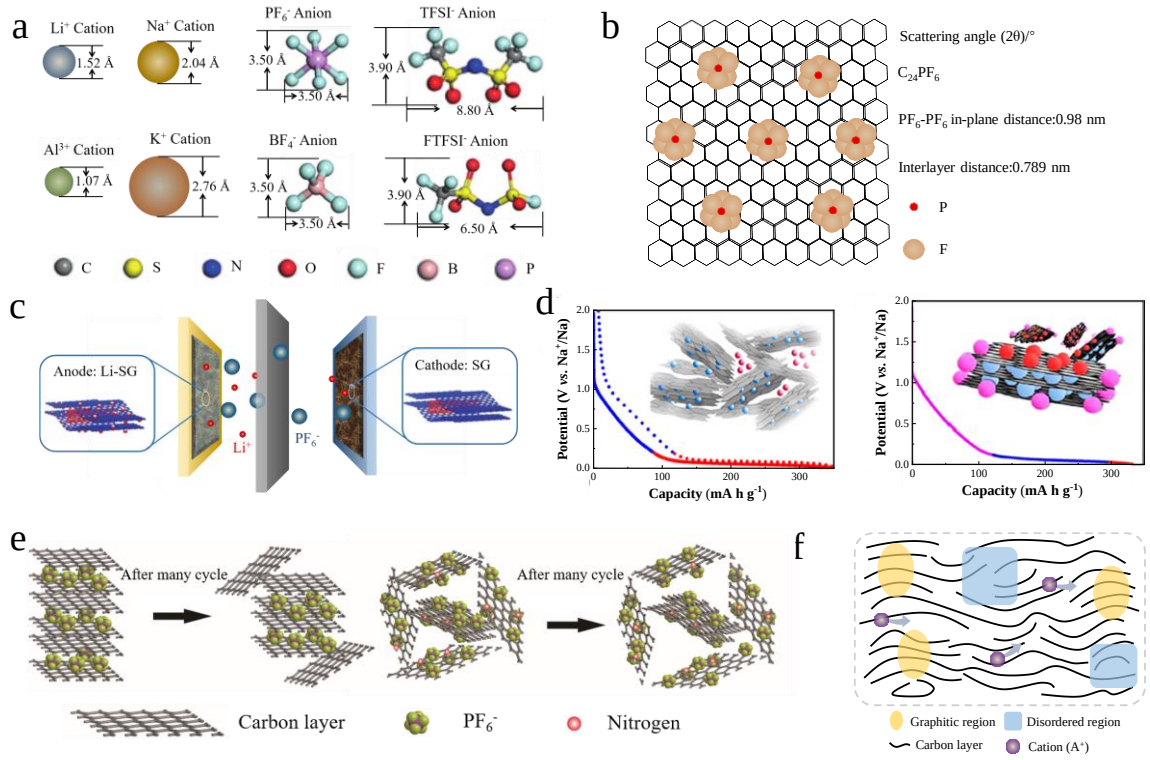

Figure 5. Ion storage in typical carbon materials. *a) Structure and estimated size of typical anions and cations. b) In-plane structures of PF_6 anions intercalated in graphite. Reprinted from Ref* [25]. *c) Schematic of the SG//Li-SG DCB, where SG denotes a physical mixture of SWCNT and Graphene. Reprinted from Ref.* [34] *d) Two typical models proposed for Na ion storage in hard carbons, including both intercalation and adsorption of Na^+ at different potentials. Reprinted from Ref.* [36] *e) Different ways of reaction mode of PF_6^- for graphite and hard carbon. Reprinted from Ref.*[37] *f) Schematic of mesoporous soft carbon. Reconstructed from Ref.*[38]

3.2 Graphene

Graphene, in which the standard hexagonal rings consist of sp^2 hybridized carbon atoms with strong covalent bonds in planar sheets, is a superstar in the carbon family.[36] Based on its special two-dimensional (2D) configuration, graphene presents excellent electronic conductivity, high surface area (2630 m^2 g^{-1}) and good mechanical strength with a remarkable Young's modulus (~1.0 TPa).[27] The approaches to producing single/few-layer graphene can be divided into physical and chemical methods. The physical methods include mechanical exfoliation of graphite and longitudinal 'unzipping' of carbon nanotubes;[39] the chemical ways include epitaxial growth via chemical vapor deposition or organic synthesis and chemical reduction of graphene oxide.[40] Because of the special physicochemical properties, such as high aspect ratio, rich defects and functional groups, and good electrical conductivity, graphene has been a widely popular material in many energy storage devices. For instance, Wang *et al.*

reported a dual-graphene battery using electrochemically exfoliated graphene (EG) nanosheets as both anode and cathode electrodes with an organic electrolyte solution (2 M $NaPF_6$ in DEGDME). With *in situ* Raman spectroscopy and *ex situ* XRD, the research revealed that anions (PF_6^-) intercalated/de-intercalated into EG at charging/discharging voltages of 4.7 and 4.3 V *vs*. Na^+/Na, respectively. At a current density of 50 mA g^{-1}, the full cell showed a capacity of ~68 mA h g^{-1} within an operating voltage range of 3.5–4.0 V, and good cycling stability (> 200 cycles) with a capacity retention of 95%.[37]

A drawback of pristine graphene is that their surfaces are hydrophobic, which will lead to agglomeration in electrolyte solvents. To solve the issue of agglomeration, doping of heteroatoms, introducing of defects and incorporating of functional groups in graphene are effective ways.[37, 41] A typical strategy is using reduced graphene oxides (rGO) with suitable architectures, such as three-dimensional structure, nanobelts and layer films, as the anodes of DCBs.[42] In general, graphene oxide was prepared by the Hummers method using graphene as a precursor, and then transforms to rGO by chemical reduction. A designed DCB adopted the synthesized rGO as the anode material for adsorption/desorption of $EMIm^+$, and graphite as the cathode material for the high potential intercalation reaction of PF_6^-. This battery showed a ultrahigh power density of 1333 W kg^{-1}, with a corresponding energy density of 70 Wh kg^{-1}.[42a] For the special doping, Sun and co-workers prepared a Li-based DCB with asymmetric graphene electrodes, using a composite consisting of single wall carbon nanotubes (SWCNTs) and graphene as both electrodes (Figure 5c). The addition of SWCNTs can improve the conductivity, porosity and structural stability, and more importantly, it can alleviate the agglomeration of graphene sheets. This hybrid device exhibited an energy density of 222 Wh kg^{-1} and a power density of 410 W kg^{-1} with a voltage range of 0.01–4.1 V.[43]

Due to the considerable electrochemical performance in both battery-type anode and capacitive-type cathode, graphene can be also used for asymmetrical DCBs.[37, 43] This has been presented by Dong and co-workers, who synthesized surface oxygen-functionalized crumpled graphene with a dense and porous structure, and used it as both electrodes for a Na-based DCB.[44] The hybrid graphene structure increased the active sites and shortened the diffusion path of ions, and the oxygen-doping improved the energy density without sacrificing power density. The symmetrical device exhibited a high energy density (121.3 Wh kg^{-1}) and power density (8000 W kg^{-1}), with an ultra-long cycle life (capacity retention of 86.7% after 25000 cycles).

Despite the intensive studies on graphene in batteries, graphene-based electrodes in DCBs show relatively low volumetric energy densities, mainly because of the low compact density of

graphene (less amount of active surface for a given volume). The high-density graphene aerogels developed by Yang group [45] could be a useful material for DCB electrodes, which has yet been explored.

3.3 Hard carbon

Hard carbon (HC) is composed of small graphitic micro-crystallites and amorphous regions and is visualized as "house of cards", which is usually synthesized using high-molecular polymer and crosslinking block resin.[38] Existence of non-graphitizable carbon is a characteristic of HC, and even high-temperature treatments cannot transform a HC to a fully graphitic structure.[46] Therefore, the structure of HC inherits the strongly crosslinked microstructure of the precursor. HC has been extensively studied as the anode material, and its ion storage mechanisms include intercalation into graphene sheets in disordered graphitic structures, storage in closed amorphous microspores, and adsorption at surface and defects.[47]

It is known that graphite is not a material for Na ion storage because they do not form binary graphite intercalation compounds (b-GICs). However, HC has bene widely studied for Na ion storage and different mechanisms of Na^+ storage in HC have been proposed over the years.[46b] Figure 5d presents the two commonly accepted scenarios, in which Na^+ may intercalate or physically adsorb at the intersects or edges at different discharge potentials. For instance, Goikolea and co-workers synthesized HC by carbonizing olive nucleus as the anode materials, and further used the high specific surface area AC as the cathode for a Na-based DCB. This DCB showed a maximum energy density of 100 Wh kg^{-1} and a maximum power density of 7000 W kg^{-1}. Moreover, it had a good cycling stability up to 5000 cycles with 70% capacity retention.[48] However, the low potential plateau of HC as anode will cause poor rate capability. To solve this issue, doping or composite method is effective in improving the hydrophilicity and conductivity of HC, leading to performance enhancement in DCBs.[49] For example, Ding and co-workers prepared N-doping HC as anode material for a Na-based DCB with AC as cathode material.[50] The N-doping is proven effective in reducing the ion diffusion rate and increasing the conductivity of the HC electrode. The N-doping HC electrode in a half-cell test HC show improved rate stability, which leads to the high power performance of the DCB (max. about 3 KW kg^{-1}).

Similarly, HC is also suitable for storage of anions with alike mechanisms.[24, 38] Because of the large carbon layer spacing (> 0.36 nm), HC is particularly suitable for storage of large anions. Chen *et al.* prepared nitrogen-doped microporous hard carbons as the cathode in DCBs for storage of PF_6^- (Figure 5e).[24] The long cycle measurement of the HC half-cell showed a reversible capacity of 100 mA h g^{-1} after 1000 cycles at a current density of 2000 mA g^{-1} in a

voltage range of 1.0–4.7 V. When coupled with SC anode in the electrolyte of $NaPF_6$, the assembled DCBs can operate in a wide voltage range (0.01–4.7 V) and run 1000 cycles with a capacity retention of 89%.

3.4 Soft carbon

Soft carbon (SC) is similar to HC in microstructure, except that SC can be graphitized by carbonization at high temperatures (about 2500 °C). [13, 51] The precursors of SC are aromatic hydrocarbons, such as asphalt tar, petroleum, coal and so forth. When used as electrode materials, the unique feature of SC is good compatibility with electrolyte, absence of evident charging/discharging plateau, and high electrical conductivity. A general microstructure of SC has two regions: one is a high strain region with disordered carbon, and the other is a low strain region with graphitic carbon (see Figure 5f). Their percentages of these two regions depend on the process temperature. Existence of the graphitic regions can improve the electrical conductivity, since electrons move faster in these regions than in the disorder regions. The disordered regions, on the other hand, are also beneficial to metal ion insertion/extraction.[52]

SC has been useful as the anode material for Na-based DCBs. At a potential above 0.2 V (versus Na/Na^+), SC presents a good capacity (discharge capacity of 186 mA h g^{-1} at 100 mA g^{-1}) with good stability (no obviously capacity decay after 400 cycles). Fan *et al.* prepared the first Na-based DCB using SC as anode and graphite as cathode. This device can exhibit a high discharge voltage plateau of 3.58 V and high capacity retention (81.8% after 800 cycles).[13] Compared with HC, the disordered region in SC can facilitate the diffusion of ions in the bulk of electrode. Based on this consideration, Han and co-workers employed nitrogen-doped SC for DCB anode, in which the N doping introduces more disorder. As a result, the fabricated DCB device (with AC cathode) delivered a high power performance (2832 W kg^{-1}) and capacity retention at high rates (98.3% after 3000 cycles at 20 C in a voltage range of 1.0–4.0 V). Nevertheless, the initial columbic efficiency of SC is not ideal (e.g., about 85% for Li) and needs to be further improved for their application in DCBs.[53]

3.5 Activated carbon

In previous research for Li-based DCBs, activated carbon (AC) was a universal cathode material. AC has an impressively high surface area (~2000 m^2 g^{-1}), excellent conductivity (~60 S m^{-1}) and good structure stability, which are all favorable to its surface adsorption of ions.[54] AC is usually derived from carbonaceous materials such as charcoal, coal, coke, and biomass carbon. The final microstructure depends strongly on the precursors and synthesis conditions.[55] The activation process for creating micropores can be realized through physical

or chemical methods. Compared with physical activation, chemical activation is superior owing to its lower synthesis temperature, better quality fidelity, and shorter processing time.

However, the ion storage capacity of AC cathode material is only about 50 mA h g^{-1}. To adjust the imbalance of electrochemical capacity between electrodes, the mass loading of an AC electrode is always three times larger than that of the counter electrode. Han and co-works assembled a Na-based DCB using AC cathode and graphitic mesocarbon microbeads anode. Within an optimized voltage range (1–4 V), the capacity retention of the DCB was about 98% after 3000 cycles at a high current density of 20 C.[56] Doping heteroatoms (e.g., nitrogen, boron, sulfur) on the surface of carbon materials can introduce desirable electronic structures for ion transport. For example, the N-rich mesoporous carbon spheres prepared through an aerosol-spraying process possess a high N-doping concentration (14.5 atom %).[57] The Li-based symmetric DCB was constructed using this N-doped AC spheres delivered high energy/power densities (115.4 Wh kg^{-1} at 22.5 kW kg^{-1}). A striking stability was also achieved; only 0.0013% capacitance decay per cycle within 10 000 cycles.

The pore size of AC influences the total specific surface area and subsequently, the charge/discharge capacity. Hence, the capacitive behavior is dependent on the pore size. In general, micropores (1-2 nm) are more efficient than mesopores (2-50 nm) in improving the capacitive, but too small pores are inaccessible for ions. Accordingly, Wang and co-workers prepared peanut skin-derived carbon nanosheets with hierarchical microporous-mesoporous-macroporous disordered structure, and used them as both cathode and anode for symmetric DCB.[58] It is proven that the hierarchical porous structure facilitated the ion transport towards high power performance, and the rich defects due to doping improved the ion storage capacity. As a result, this symmetrical DCB exhibited a maximum energy density of 112 Wh kg^{-1} and a power density of 12 000 W kg^{-1}. On the other hand, it is believed that the rich mesopores may trap the ions and thus reduce the Coulombic efficiency.

4. Carbon-electrolyte Interphases

Solid-electrolyte interphase (SEI) is essential for the successful operation of rechargeable alkali-metal batteries, such as lithium and sodium ion batteries.[59] An robust and stable SEI can benefit the safety, power capability, shelf life, and cycle life of batteries.[60] There are extensive researches focusing on the carbon SEI of the anode side, and many efforts have been devoted to improving the SEI of carbon anodes.[60a, 61] The main problem of carbon anodes is that solvent molecules easily co-intercalate with cations into the host since the solvent-ion intercalation compounds are more stable than the corresponding binary compounds in thermodynamics.[62]

Then, the co-intercalation of solvent molecules can induce the expansion and exfoliation of carbon materials, resulting in the capacity fading. However, Dahn group first proposed that an effective SEI forming during the first cycle can prevent the solvent co-intercalation and guarantee the subsequent cycling stability.[63] Besides the issue of solvent-ion intercalation, cations with large radius (such as K^+) also cause a huge volume expansion of order-structural carbon (such as graphite) anodes.[64] One effective method is constructing a protective layer on the surface of carbon particles. For example, Lu group designed an inorganic-rich passivation layer on graphite anode by virtue of the KFSI-based electrolyte, which allowed 2000 stable cycling with negligible capacity decay.[65] Their results indicate that the inorganic SEI is more conducive to restraining the decomposition of solvent than the organic SEI formed in traditional KPF_6-based electrolyte.

To improve the energy density of DCBs, pre-lithiation on the carbon anode is a useful strategy, and the instability of the pre-lithiated electrode can result in a poorly formed SEI.[66] Hence, an elaborate pre-lithiation process is necessary to optimize the SEI and consequently the cycle life. Furthermore, using high-concentration electrolytes in DCBs can form a more stable anion-derived SEI than that of solvent derived.[67] The high-concentration electrolytes can also lower the anion intercalation potential and reduce the oxidative decomposition of electrolyte on the cathode side.[68]

Apart from anode side, the anion intercalation into cathode and the formation of cathode-electrolyte interphase (CEI) are special and also crucial for the DCB system. A robust and stable CEI can be constructed from carbon electrode to liquid electrolyte (**Figure 6**). By the surface coating of graphite cathode, Han *et al.* proposed $Li_4Ti_5O_{12}$ modified by mesocarbon microbeads as a cathode material (Figure 6a), which exhibited an enhanced cyclability with 85.1% capacity retention after 2000 cycles.[69] The $Li_4Ti_5O_{12}$ layer offered electrocatalytic active sites to form a compatible CEI layer, and the $Li_4Ti_5O_{12}$-CEI interphase could benefit the PF_6^- intercalation and maintain the structural integrity of the graphite cathode (Figure 6b). In another study, an effective artificial SEI layer was constructed on the graphite electrode (Figure 6c), which significantly improved the structural and cycling stability of graphite cathode.[70] Transmission electron microscopy examination (Figure 6d) displayed an evident and intact SEI layer after 200 cycles, which could mitigate the solvation effect accompanied with anion intercalation. Finally, the electrolyte formulation is the most important way to improve the carbon-electrolyte interphase. Recently, ethyl methyl carbonate (EMC) is often chosen as electrolyte solvent, as superior electrochemical performances have been achieved to other solvents.[15b, 21-22, 33, 71] The Yu group clarified that EMC electrolyte formed a thinner layer of carbon-electrolyte interphase

with less Li−F and $ROCO_2Li$ species (Figure 6e), and higher Coulombic efficiency (Figure 6f), polarization, and self-discharge of graphite electrodes.[72]

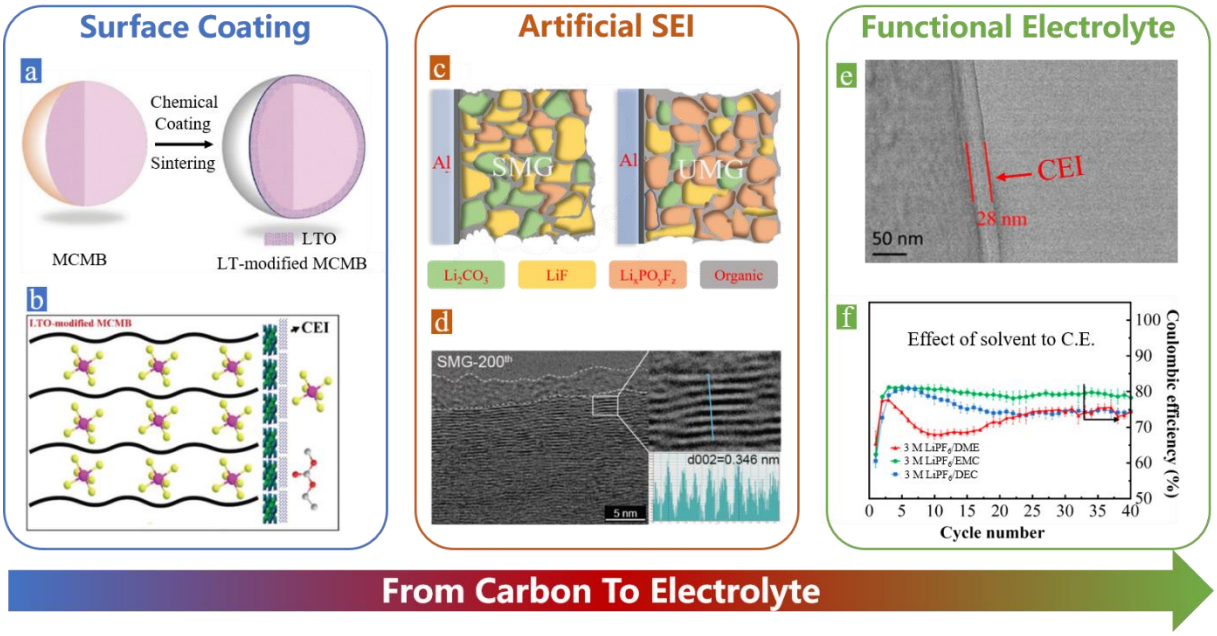

Figure 6. Modifications of carbon-electrolyte interphase. *Surface coating: (a) schematic of the chemical coating of $Li_4Ti_5O_{12}$ on mesocarbon microbeads (MCMB), and (b) proposed mechanisms for PF_6^- intercalation. Reprinted from* [69]. *Artificial SEI: (c) schematics of the interphase composition of SEI-modified graphite (SMG) and ethyl methyl carbonate (EMC), (d) Transmission electron microscopy (TEM) image of SMG after 200 cycles at the upper cutoff voltage of 5.0 V illustrating the graphitic structure. Reprinted from* [70]. *Functional Electrolyte: (e) TEM image of the electrode after cycling with EMC solvent, and (f) Coulombic efficiency of KS6/Li half cells using different electrolytes (3M $LiPF_6$/DMC, $LiPF_6$/EMC, and $LiPF_6$/DEC electrolytes). Reprinted from* [72].

5. Summary and Perspectives

DCBs have been extensively researched as one of important electrochemical systems for next-generation energy storage. Unlike the “rocking-chair” LIBs, the working mechanism of DCBs is based on the reaction of anions and cations in two carbon electrodes (so it belongs to a sub category of dual-ion batteries). This significantly simplifies the battery configuration and electrochemistry. For example, compared with traditional LIBs, the higher operating voltage (>4.5 V) of DCB results in the higher energy density. More importantly, the use of metal-free electrodes reduces the cost and environmental pollution. Despite the promise, the limitation and challenge for DCBs include low capacity, low initial coulombic efficiency, and mediocre cycling performance. Urgent efforts are needed to adopt dense carbon materials, pre-lithiation

and high-loading electrode, and appropriate electrolytes (redox species and their concentrations).

For the most common graphite, insertion of anions with large ionic radii will cause exfoliation of the graphite structure, causing rapid capacity decay. To solve this issue, a viable strategy is to modify the structure of graphite by introducing disordered region or doping ions to increase the interlayer distance. Nonetheless, new carbon materials, such as HC and SC, are better choice than graphite for storing large ions. The "house of cards" structure of hard carbon, with small graphitic micro-crystallites and amorphous regions, allows both intercalation reaction and adsorption reaction of metal ions. Based on adsorption reaction, AC is also a popular electrode material. It has the advantages of good conductivity, large specific surface area, and low cost. However, the low capacity of AC is an issue. In addition to doping heteroatoms on the surface, it is also useful to construct a multiscale porous structure of AC electrode. The nanoporous carbons used for supercapacitor electrode might be also useful for DCBs.[73]

Electrolyte is the "blood" of DCBs. Unlike conventional LIB is, the electrolyte in a in DCB not only acts as a medium for carrier migration, but also provides anions and cations for the intercalation or adsorption to carbon electrodes. Thus, electrolytes are of vital importance to form robust and stable interface with dual-carbon electrodes. So far, most of the electrolytes used for DCBs are conventional organic electrolytes used in metal-ion batteries. In addition, it is noted that aqueous dual-ion batteries have been researched extensively.[16d] Hence, to further increase the safety, aqueous DCB may be also explored by learning from aqueous batteries.[74]

Since DCB electrodes are made from carbon materials, it is natural to compare with and learn from supercapacitors, especially asymmetric supercapacitors[75] or hybrid capacitors.[76] The energy storage via ion adsorption/desorption mechanism makes carbon-based supercapacitors have a higher rate ability and power density than most DCBs. However, low energy density and serious self-discharge are the congenital defects of carbon-based supercapacitors. Improving energy density can be realized by constructing asymmetric devices from electrode materials with different charge storage mechanisms, as summarized recently by Shao and co-worker.[73a] As for the self-discharge, it is probably also a big deal in DCBs since they involve redox-active electrolytes, but there are little data on this. It has been found that, in addition to the electrostatic effects, physical adsorption of ions in carbon surface could play a primary role in self-discharge by preventing the redox-active ions from cross diffusion.[77] Therefore, on one hand, advanced DCB is one of important types of carbon-based devices to achieve high energy-density storage.

On the other hand, there are a lot can be learned from other electrochemical energy storage devices in both electrode and electrolyte.

In a nutshell, although there are scientific and technical challenges for DCBs, including self-discharge, poor safety, and insufficient energy density, the fast development of carbon materials and new electrolytes in the battery community will also benefit the advance in DCBs, making it a competitive or complementary technology to Li-ion batteries.

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