

## Graphite electrode as a versatile ion intercalation host for energy storage

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### Abstract

Graphite is actively investigated as an electrode material for rechargeable batteries because of its capability of intercalating versatile ion species combined with its low production cost and non-toxicity. This mini review will provide an overview of recent achievements as well as an outlook for graphite electrode of rechargeable batteries (*i.e.* Li-, Na-, K-, and Al-ion batteries), focusing on the energy storage properties of graphite electrode in various battery systems and its underlying intercalation mechanism. This mini review will provide insights into designing low-cost graphite-based energy storage systems.

### 1. Introduction

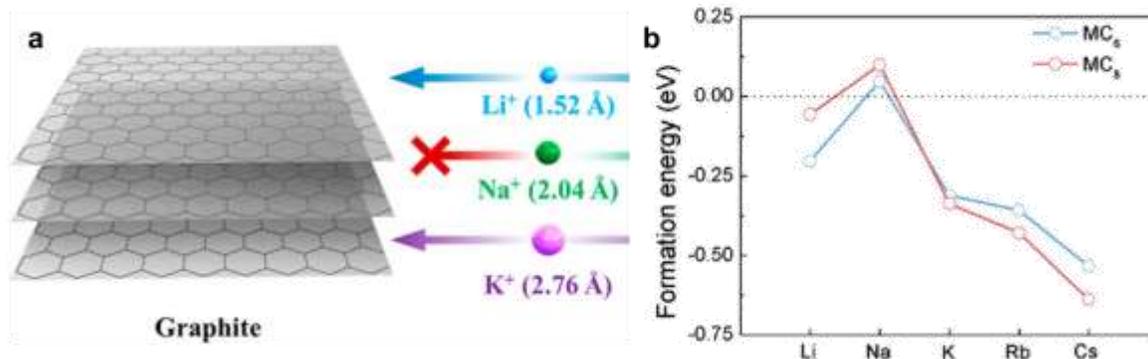
Energy storage is one of the most important technologies in modern society because global energy consumption continuously increases. The U.S. Energy Information Administration estimates that starting from 2012, world energy consumption will grow by 48% within 30 years.<sup>[1]</sup> In consideration of global climate change and depletion of fossil fuels, we need to focus on renewable energy resources, such as solar, wind, and geothermal energies. However, energy harvesting from renewable resources is intermittent in time and space, meaning that there is a discrepancy between energy demand and harvesting. Thus, it is highly important to develop efficient energy storage systems. Rechargeable batteries that electrochemically store energy have been widely studied because of their high gravimetric and volumetric energy density, low maintenance costs, long cycle life, and high round-trip efficiency.<sup>[2-5]</sup>

Graphite can intercalate a wide range of guest species, including alkali, alkaline-earth, rare-earth elements, halogens, protons, and Lewis acids between graphene layers.<sup>[6]</sup> In particular, graphite intercalation compounds (GICs) provide distinctive physical and chemical properties compared with pristine graphite, depending on the intercalation species and intercalation concentration.<sup>[7-10]</sup> For example, the electrical conductivity of GICs increases

along the *c*-axis (~10,000 times) and *a/b*-axes (~10 times) when highly concentrated ionized species are intercalated.<sup>[7-10]</sup> Because of this unique structure–property relationship of GICs, graphite and GICs have a variety of applications in energy storage and conversion and as electrical/thermal conductors.<sup>[11-15]</sup>

Graphite has been actively investigated for a long time as electrode materials for the rechargeable battery technology because of its capability of intercalating versatile ion species.<sup>[16-22]</sup> Graphite is a promising electrode candidate considering its low production cost, non-toxicity, and good electrochemical properties. In fact, graphite has been used as a standard anode for Li-ion batteries (LIBs) because of its low working voltage, high specific capacity, and high material's density compared to other types of anode materials. Graphite was also investigated as an electrode material for many types of rechargeable batteries, including Na-, K-, and Al-ion batteries which are considered alternative rechargeable battery system for large-scale applications.<sup>[16-17, 23]</sup> This mini review will provide an overview of recent achievements as well as an outlook for graphite electrode of rechargeable batteries. Here, we will focus on the energy storage properties of graphite in various battery systems and its underlying intercalation mechanism.

## 2. Alkali ion intercalation



**Figure 1.** a. Schematic of alkali ion intercalation into graphite. Reproduced with permission. Copyright 2015 American Chemical Society. [18] b. Stability of alkali ion intercalated graphite compounds. Reproduced with permission. [28] Copyright 2016 WILEY-VCH.

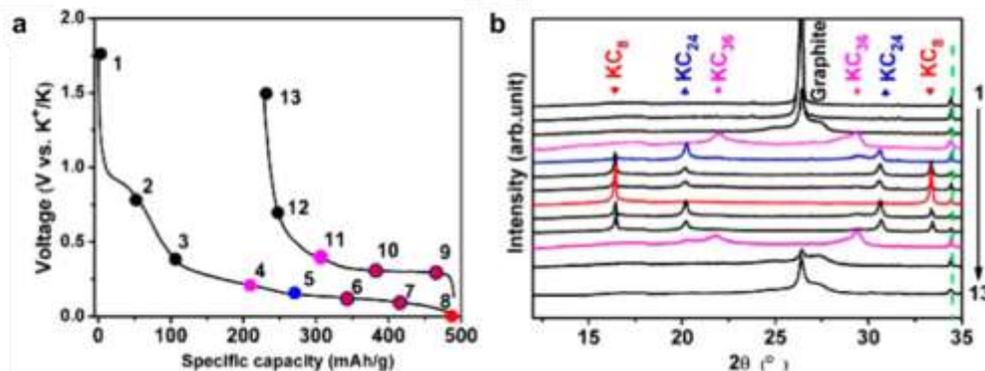
Graphite has been used as the standard anode material for LIBs. Graphite intercalates Li ions reversibly up to LiC<sub>6</sub>, providing a theoretical capacity of ~370 mAh/g with a very low working voltage (~0.15 V vs. Li/Li<sup>+</sup>).<sup>[24]</sup> The low production cost (\$7,000-\$12,000 per metric ton) also plays a key role in making graphite practical for LIBs.<sup>[25]</sup> In contrast, Na ions cannot intercalate into graphite.<sup>[26]</sup> Graphite delivers only ~20 mAh/g in the Na-ion battery (NIB) system. For a long time, it has been believed that Na ions cannot intercalate into graphite because of its larger ionic size than Li. However, it has been demonstrated that K ions, which have larger ionic size than Na, can intercalate into graphite galleries with high reversibility (Figure 1a).<sup>[17-18, 27]</sup> Graphite can store K ions up to KC<sub>8</sub> composition, delivering a high reversible capacity > 250 mAh/g. It clearly demonstrates that the ionic size does not have considerable role in determining the alkali ion intercalation into graphite. Recent work by Yoon *et al.* studied the alkali ion intercalation behaviors by density functional theory (DFT) calculations.<sup>[28]</sup> They investigated the thermodynamic stability of stage 1 alkali ion-GICs in compositions of MC<sub>6</sub> and MC<sub>8</sub> (M= Li, Na, K, Rb, and Cs) as shown in Figure 1b. The formation energy is calculated as:

$$E_f (\text{Formation energy}) = E_{MC_x} - x \times E_g - E_M$$

where  $E_{MC_x}$  ( $x = 6$  or  $8$ ) denotes the energy of the MC<sub>x</sub> formula unit,  $E_g$  is the energy of graphite per carbon atom, and  $E_M$  is the energy of the stable metallic phase of M per metal atom. Their calculations confirmed that Na-GIC is thermodynamically unstable, but other alkali ions can form stable M-GICs in either MC<sub>6</sub> or MC<sub>8</sub> compositions. They also found that K, Rb, and Cs prefer to form MC<sub>8</sub> compositions, while Li forms LiC<sub>6</sub> more favorably than LiC<sub>8</sub>. They argued that larger alkali ions prefer to form MC<sub>8</sub> to reduce metal-metal repulsion. To better understand the instability in the formation of Na-GICs, they categorized the parameters that can affect the formation energy of M-GICs. In the stage 1 Na-GICs, Na ions are rearranged in the graphite galleries. Thus, one should consider the structural deviation of Na and graphite in GICs from their pristine structure (Na metal and pristine graphite). Thus, they extract the energy penalty of metal decohesion and graphite deformation. However, no abnormal behavior is observed in Na-GICs compared to Li-GICs, K-GICs, Rb-GICs, and Cs-GICs. Finally, they consider the local interaction between Na and graphene layers. In the

calculations, they found that the Na ion binding to a graphene layer is unstable by  $\sim 0.5$  eV while the binding of other alkali to graphene were in fact stable. While further study is required, their

results indicate that the intrinsically poor Na ion adsorption on a graphene layer is the origin of instability of Na-GICs.



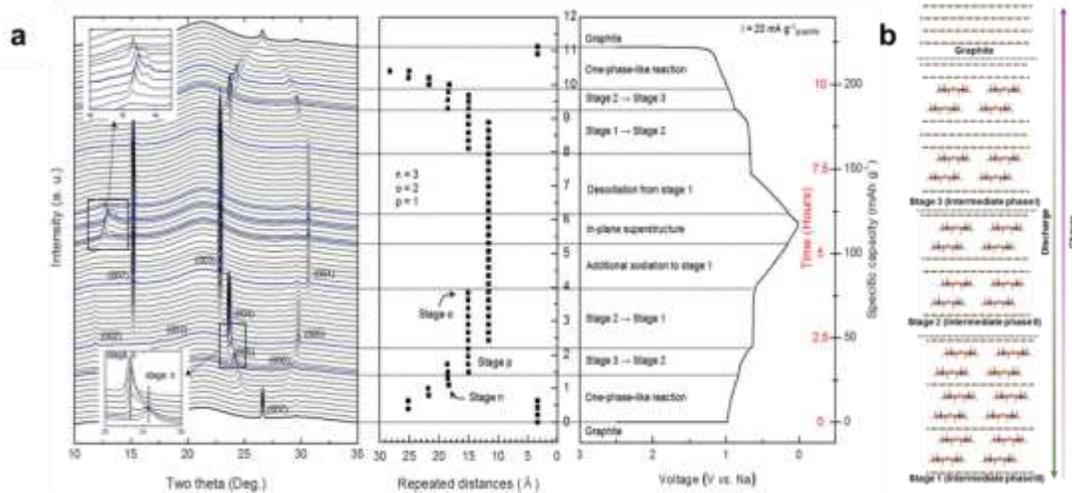
**Figure 2.** a. Capacity-voltage curves of graphite electrode in K cells. b. *Ex-situ* XRD patterns of graphite cycled in K cells. Reproduced with permission. [27] Copyright 2015 American Chemical Society.

In 2015, Komaba *et al.*<sup>[17]</sup> and Zelang *et al.*<sup>[27]</sup> demonstrated that K ions can intercalate into graphite reversibly in the electrochemical cells. In contrast to the Na system, the K-ion battery (KIB) can use graphite as an anode because of the good reversibility of K intercalation into graphite, delivering a high specific capacity of  $>250$  mAh/g. Figure 2a shows the typical charge/discharge curves of graphite anode in K-ion system. Zelang *et al.* investigated the structure evolution of graphite during K intercalation and deintercalation using *ex-situ* X-ray diffraction (XRD) analysis as observed in Figure 2b.<sup>[27]</sup> As K intercalation proceeds, the XRD peak of graphite disappears and a new series of peaks evolves. During K intercalation, a new set of XRD peaks at  $22.0^\circ$  and  $29.4^\circ$  appears, indicating the formation of  $KC_{36}$ . Then, new XRD patterns at  $20.2^\circ$  and  $30.6^\circ$  evolve, forming  $KC_{24}$  by further K insertion. At the end of discharge, new XRD peaks appear at  $16.4^\circ$  and  $33.4^\circ$ , indicating structure transformation from  $KC_{24}$  to  $KC_8$ . Reversible phase

transformations are observed during charge. Komaba *et al.* also confirmed the formation of  $KC_8$  at the fully discharge state and recovery of graphite after charge by *ex-situ* XRD characterization.<sup>[17]</sup> The *ex-situ* XRD characterization shows large volume expansion by  $\sim 60\%$  upon K intercalation into graphite, but it is notable that graphite still provides good reversibility and cycle life despite such large volume expansion.

It has been known for a long time that Na ions cannot intercalate into graphite unlike other alkali ions, including Li and K ions. While Yoon *et al.* show that the intrinsically poor Na ion adsorption on a graphene layer is the origin of instability of Na-GICs,<sup>[28]</sup> its physical interpretation and meaning is yet unclear. Therefore, careful investigation of why Na ions have poor adsorption energy on a graphene layer is needed in order to finally provide an insight how to make Na ion intercalation into graphite possible.

### 3. Alkali ion-solvent co-intercalation



**Figure 3. a.** In operando XRD patterns of graphite electrode combined with charge/discharge profiles in Na cells with diglyme-based electrolytes. Reproduced with permission. Copyright 2015 Royal Society of Chemistry. **b.** Schematics of Na-solvent co-intercalation into graphite. Reproduced with permission. [30] Copyright 2016 American Chemical Society.

For a long time, it is known that graphite cannot intercalate Na ions, unlike Li and K ions, preventing the practical feasibility of NIBs. Recently, Jache *et al.*<sup>[29]</sup> and Kim *et al.*<sup>[23]</sup> demonstrated that co-intercalation chemistry enables the Na intercalation into graphite. According to their reports, graphite can store Na ions with high reversibility when specific ether-based electrolytes are used. In conventional carbonate-based electrolyte systems, graphite delivers a negligible specific capacity of < 30 mAh/g; however, graphite provides a high reversible capacity of ~120 mAh/g when ether-based electrolytes are utilized. Kim *et al.* investigated the Na storage mechanism in graphite using various diagnostic characterizations, including XRD, Raman, Fourier transform infrared, mass analyzer, transmission electron microscopy, and computational analysis, and found that Na ions are co-intercalated into graphite with solvent molecules.<sup>[23, 30]</sup> Figure 3a shows the *in operando* synchrotron XRD analysis of graphite upon Na intercalation and deintercalation. For this experiment, Kim *et al.* used a coin-type Na

half-cell with a pin-hole. 1M NaPF<sub>6</sub> in diethylene glycol dimethyl ether electrolyte was used. When Na ions intercalate into graphite, the typical (002) peak of graphite disappears and new XRD peaks at ~25° and ~28° evolves, which belong to (005) and (006) of stage 3 Na-ether-graphite compound. Further discharge generates new peaks at ~24° (004) and ~29° (005), indicating the formation of stage 2 Na-ether-graphite compound. The fully discharged state shows XRD peaks at 15°, 22.5° and 31°, which are (002), (003), and (004) of stage 1 Na-ether-graphite compound. The Na extraction process follows the opposite reaction of Na intercalation, indicating the reversible reaction of Na intercalation in graphite. Figure 3b shows the schematics of stage 3, 2, 1 Na-ether-graphite compounds. Based on their XRD characterization, they confirmed the large volume expansion of ~300% by Na-solvent co-intercalation. Nevertheless, graphite could provide exceptionally high cycling stability: graphite maintains >85% of initial charge capacity after 2,500 cycles. Similarly, Zhu *et al.* proved that graphite can retain ~90% of the

capacity even after 6,000 cycles.<sup>[31]</sup> Kim *et al.* further demonstrated that the Na storage voltage can be tuned by the selection of electrolyte solvents.<sup>[30]</sup> The average Na storage voltage changes by 23% from 0.77 V to 0.59 V when the chain length of solvent molecules decreases because it is likely that longer solvent molecules have the stronger screening effects on the repulsion between Na ions in the discharged products. Another interesting phenomenon of Na-solvent co-intercalation chemistry is the exceptionally high rate capability. For example, Zhu *et al.* shows that graphite can deliver ~103 mAh/g at a very high current rate of 10 A/g, which indicates that graphite can be fully charged within 1 min.<sup>[31]</sup> Later, Kim *et al.* demonstrated that Li and K ions can also co-intercalate into graphite with ether-based solvent molecules, and that these Li and K intercalation reactions are reversible and have high-rate capability similar to the Na system.<sup>[20]</sup> The high rate capability of the co-intercalation system is attributable to (i) absence of solid-electrolyte-interphase, which usually slows down alkali ion diffusion at the surface of the electrode materials, (ii) low desolvation energy, and (iii) pseudocapacitive reaction process.<sup>[32-33]</sup> They also found that the operating voltage changes as the size of intercalating ion increases, which is likely due to the large inter-slab distance, reducing repulsion between negatively charged graphene layers in the discharged states.

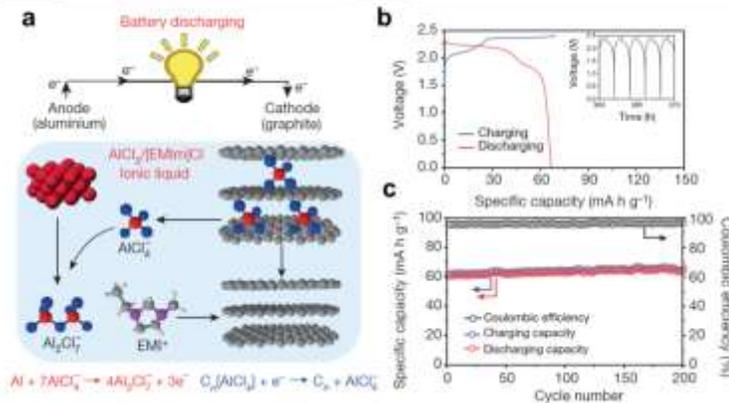
The Na-solvent co-intercalation leads to large volume expansion (~300%). Nevertheless, it delivers a very stable cycle life as demonstrated by Kim *et al.*<sup>[23]</sup> and Zhu *et al.*<sup>[31]</sup> The good cycle stability of graphite in co-intercalation system is very impressive when we compare its cycle stability to the Si anode in LIBs. The Si anode, in fact, suffers from high volume change (~340%) upon charge and discharge, and thereby leads to rapid capacity degradation.<sup>[34-35]</sup> In the Si anode, the large volume change leads to pulverization of active particles and therefore the making of dead zones. The stable cycle life

of graphite is likely attributable to anisotropic volume expansion, whose effect can be reduced in cell configurations with pressure (*i.e.* coin-cells) unlike in the case of the Si anode. However, further study is required.

The co-intercalation chemistry provides a good cycle stability and rate capability in electrochemical cells. However, this new co-intercalation reaction requires an excessive amount of electrolytes because solvent molecules itself participate into electrochemical reactions. In addition, most of the previous studies were conducted in a lab-scale setting (*i.e.* coin cells). In contrast, practical feasibility of the co-intercalation chemistry needs to be verified at the large-scale.

#### 4. Anion intercalation

Graphite cathode has been demonstrated to cycle with reversible anion intercalation and deintercalation. Seel *et al.* investigated the electrochemical intercalation of  $\text{PF}_6^-$  into graphite in the Li battery system.<sup>[19]</sup> They used the mixture electrolyte of EC and DEC or EMS with  $\text{LiPF}_6$  salt. In the voltage range of 5.6-1.0 V, graphite delivers a reversible capacity of ~100 mAh/g. They argued that the EMS solvent can provide good oxidation stability up to 5.6 V. They confirmed reversible structural changes upon  $\text{PF}_6^-$  intercalation and deintercalation by *in-situ* XRD characterization. Based on their electrochemical and XRD analysis, they argued that the fully charged product is stage 2 phase with a  $(\text{PF}_6)_{0.5}\text{C}_8$  composition. Later, Placke *et al.* showed that TFSI<sup>-</sup> can also intercalate into graphite at high voltage >4.0 V.<sup>[36]</sup> In the voltage between 5.3 V and 3.5 V, graphite delivers a reversible capacity of ~95 mAh/g at room temperature. In their system, graphite exhibits a very good stability, maintaining almost 100% of capacity up to 500 cycles. Aladinli *et al.* proved that graphite cathode can also function in Na battery system, where graphite provides a reversible capacity of ~90 mAh/g at high voltage above 4.0 V.<sup>[37]</sup>



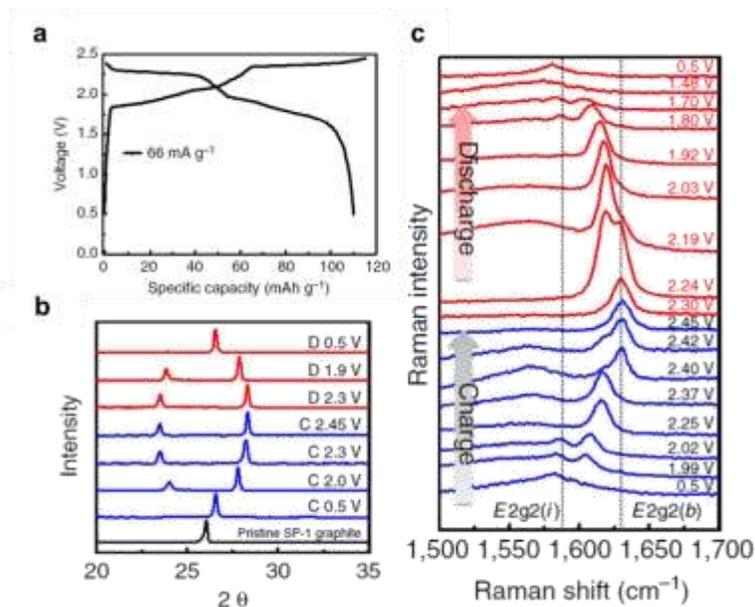
**Figure 4.** a. Schematic of discharge process of graphite cathode in Al-ion batteries. b. Capacity-voltage curve of graphite cathodes. c. Cycle stability of graphite cathodes. Reproduced with permission. [16] Copyright 2015 Springer Nature.

In 2015, Lin *et al.* found that the Al-containing anion,  $(AlCl_4)^-$ , can reversibly intercalate into graphite, delivering a specific capacity of  $\sim 70$  mAh/g, which makes graphite as a cathode for Al-ion batteries.<sup>[16]</sup> They constructed Al/graphite cells in Swagelok or pouch cells, using an aluminum foil (thickness, 15–250  $\mu m$ ) anode, a pyrolytic graphite cathode, and an  $AlCl_3/1$ -ethyl-3-methylimidazolium chloride ( $[EMIm]Cl$ ) ionic liquid electrolyte. Figure 4a shows the schematic of the Al/graphite cell during discharge. Metallic Al and  $(AlCl_4)^-$  are transformed into  $(Al_2Cl_7)^-$  during discharging on the anode side.  $(AlCl_4)^-$  is extracted from graphite galleries during discharging on the cathode side. Figure 4b presents galvanostatic charge and discharge curves of an Al/graphite cell at 66 mA/g. In this system, graphite delivers a reversible capacity of  $\sim 70$  mAh/g with an average voltage of  $\sim 2.3$  V, which is remarkably higher than other cathode compounds. In addition, graphite provides a good cycle stability up to 200 cycles with a coulombic efficiency of 95–98% as shown in Figure 4c. Later, Wang *et al.* improved the electrochemical performance by using natural graphite electrode mixed with PVDF binder (10 wt.%).<sup>[38]</sup> In their battery configuration, graphite exhibits a high specific capacity of  $\sim 110$  mAh/g with two distinct plateaus at  $\sim 1.8$  V and  $\sim 2.2$  V as

observed in Figure 5a. In their study, natural graphite can be operated over 5,000 cycles without noticeable capacity decay. They also investigated the  $(AlCl_4)^-$  intercalation process into natural graphite. Figure 5b shows *ex-situ* XRD patterns of natural graphite upon charging and discharging. The electrode shows typical (002) peak of graphite at  $26.6^\circ$ . At 2.0 V during charge, the (002) peak disappears and new XRD peaks at  $24^\circ$  and  $27.5^\circ$  evolve, indicating a new phase formation. Further charge  $>2.3$  V forms a new XRD pattern at  $23.4^\circ$  and  $28.4^\circ$ , which demonstrates a new compound formation. Opposite reactions occur during the discharge process. It clearly confirms that the intercalation and deintercalation of  $(AlCl_4)^-$  is processed in reversible manners. Figure 5c shows the *in-situ* Raman spectra of natural graphite during charge and discharge. As the charge proceeds to 1.99 V, Raman peaks of the E2g2(i) mode ( $1,586\text{ cm}^{-1}$ ) and the E2g2(b) mode ( $1,607\text{ cm}^{-1}$ ) appear. The doublet peaks result from the graphite G band splitting into (i) a lower-frequency component (E2g2(i)), attributed to vibrations of carbon atoms in the interior of graphite layer planes and (ii) a higher-frequency component (E2g2(b)), resulting from vibrations of carbon atoms in bounding graphite layers. During charge to 2.45 V, the E2g2(b) peak is blue shifted, generating a

peak at  $1,630\text{ cm}^{-1}$ . During discharge, the opposite trends are observed, and the original graphite spectrum is recovered in the fully

discharged state. It demonstrates the reversible intercalation and deintercalation process of  $(\text{AlCl}_4)^-$  in natural graphite.



**Figure 5.** a. Charge/discharge profiles of natural graphite cathodes. b. *Ex-situ* XRD analysis of graphite upon charging and discharging. c. *In-situ* Raman of graphite cathode during battery operation. Reproduced with permission. [38] Copyright 2017 Springer Nature.

Graphite provides good cycle stability and rate capability using anion intercalation reactions in various battery systems. However, the anion intercalation makes un-rocking chair type batteries. During charge, cations are stored at an anode side and anions intercalate into graphite, making electrolytes dilute. In the dilute electrolytes, the ionic conductivity decreases significantly and thereby deteriorates electrochemical performance. To mitigate this issue, an excessive amount of salts needs to be used, which will increase the overall cost of rechargeable batteries.

## 5. Summary and discussion

This mini review summarizes the recent advances on graphite electrode materials for rechargeable batteries, including Li-, Na-, K-,

and Al-ion batteries. Graphite has been widely used as the anode and cathode for versatile rechargeable batteries through cation, anion, and solvent-co-intercalation reactions. While the electrochemical Li intercalation into graphite is well-established, the mechanisms for other chemistries are yet unclear. Unlike in the case of Li intercalation, the K ion, anion, and solvent-co-intercalation reactions lead to large volume change (50-300%) upon charge and discharge in the electrochemical cells. Graphite was demonstrated to be stably cycled in those battery systems despite the large volume change upon charge and discharge, but most of the experiments were conducted at small lab-scale settings (*i.e.* coin cells). Therefore, investigation of the practical feasibility of graphite electrodes in K ion, anion, and solvent-co-intercalation reactions is needed. In addition, we need to design and develop nano/micro-

structure of graphite and functional binders that can mitigate large volume change of graphite electrodes upon charge and discharge in the electrochemical cells. The solvent-co-intercalation and anion intercalation can change the concentration of electrolytes during battery operations, and thereby affect their conductivities and deteriorate corresponding electrochemical performance. Thus, researchers need to investigate the feasibility of those battery systems in practical, large-scale settings. These studies will finally provide a new avenue for efficient and low-cost energy storage systems.

The solid-electrolyte-interphase (SEI) buildup on the surface of graphite electrode during charge/discharge deteriorates its cycling stability and rate capability. In particular, Li and anion intercalation into graphite occurs at too high ( $\sim 5.0$  V) and low ( $\sim 0.1$  V) a voltage, which leads to oxidative and reductive decomposition of electrolytes and builds up thick SEI layers. The formation of SEI layers mitigate effective alkali ion diffusion, which deteriorate cycling stability and rate capability. Therefore, investigation of new electrolytes that can prevent SEI buildup on the surface of graphite electrode is needed.

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