Recent Progress and Perspective in Electrode Materials for K-Ion Batteries

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Recent Progress and Perspective in Electrode Materials for K-ion Batteries

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The development of rechargeable batteries using K ions as charge carriers has recently attracted considerable attention in the search for cost-effective and large-scale energy storage systems. In light of this trend, various materials for positive and negative electrodes are proposed and evaluated for application in K-ion batteries. Here, a comprehensive review of ongoing materials research on nonaqueous K-ion batteries is offered. Information on the status of new materials discovery and insights to help understand the K-storage mechanisms are provided. In addition, strategies to enhance the electrochemical properties of K-ion batteries and computational approaches to better understand their thermodynamic properties are included. Finally, K-ion batteries are compared to competing Li and Na systems and pragmatic opportunities and future research directions are discussed.

1. Introduction

Energy consumption in modern society has been continuously increasing. The International Energy Outlook 2016 (IEO 2016) prepared by the U.S. Energy Information Administration estimates that the world energy consumption will grow by 48% between 2012 and 2040.[1] With concerns over depleting fossil fuels as well as global warming, it is critical to utilize renewable energy resources. Indeed, wind, solar, and geothermal resources are becoming the world’s fastest-growing sources for power generation. IEO 2016 also reports that renewable-energy-generated power will increase by an average of 2.6% annually through 2040.[1] However, renewable energy is inherently intermittent, creating a discrepancy between energy harvesting and demand in terms of time and space. Thus, grid-level stationary energy storage systems (ESSs) play a key role in making renewable energies both effective and efficient and thereby shaping a more sustainable and environmental friendly society.

Although different energy storage technologies including mechanical, electrical, chemical, and electrochemical systems have been proposed,[2-4] mechanical energy storage through pumped hydroelectricity currently dominates the market (~95% of the installed capacity, ~183 GW).[4] Electrochemical energy storage is also being considered as a promising option for ESSs based on its flexibility of deployment with little restriction on size and geographical location, low maintenance costs, large energy density, high round-trip efficiency, and long cycle life.[5,6]

The market for Li-ion batteries (LIBs), originally commercialized for portable electronic devices (i.e., cell phones and laptops), is now expanding to electric vehicles (EVs) and grid-level ESSs. However, it remains debatable whether the global Li reserves, ~14 million tons, can meet the increasing demand for such large-scale applications.[7-9] The price of lithium carbonate, which is a primary precursor for LIBs, has been continuously increasing since 2000,[10] and this trend is likely to accelerate once the EV and ESS markets take off. Moreover, Li is geographically limited to specific regions: ~86% of the Li reserves are located in Bolivia, Chile, China, Argentina, and Australia;[9] therefore, geopolitical issues may arise. A more pressing issue for Li-ion markets is the use of Co in all high-energy-density systems. With more than 50% of all mined Co destined for use in Li-ion technology, and a substantial fraction of that coming from the Democratic Republic of the Congo, Li-ion growth may be hampered by the availability of Co.[11] As a less expensive alternative to LIBs, Na-ion batteries (NIBs) have been extensively studied.[6,12-14] The relatively high standard redox potential of Na/Na+ leads to a lower working voltage and thereby lower energy density than Li-ion. In addition, hard carbon, which is associated with a high production cost and low material’s density, must be used as an anode in NIBs, as graphite, which is the standard anode for LIBs, cannot store Na ions.[15-17]

Recently, K-ion batteries (KIBs) have emerged as another possible energy storage system.[18-20] It is notable that the abundance of K resources in the Earth’s crust and oceans is similar to that of Na (Figure 1a).[21,22] The cost of potassium carbonate...
trode materials for KIBs in a broader context.

- Prussian blue analogues, layered compounds, poly-
- Metal-alloying-reaction compounds, organic compounds.
- K metal-alloying-reaction compounds, K
- graphite and its electrochemical properties; briefly discuss the negative and positive electrodes and their underlying K storage mechanisms. For anodes, we concentrate on K-intercalation in graphite and its electrochemical properties; briefly discuss the alternative anode materials including hard carbon, K intercalation compounds, K metal-alloying-reaction compounds, K conversion-reaction compounds, organic compounds. We also emphasize the development of promising cathode materials, including Prussian blue analogues, layered compounds, polyanions, and organic materials, and provide perspectives on electrode materials for KIBs in a broader context.

2. Anode Materials

The development of post-Li-ion technologies has largely been motivated by the necessity to overcome the limits of LIBs in terms of performance and cost. The latter, in particular, has raised increasing concern as the price of Li precursors has steeply increased in the last few years. The lower price of sodium carbonate has therefore driven a large body of research on NIBs. Recently, interest in KIBs has been sparked by a development on the anode side, i.e., the fact that K, unlike Na, can intercalate into graphite. This section will include research on negative electrode materials for KIBs, including graphite, various forms of carbon, metal alloys, intercalation compounds, organics, and conversion anodes.

2.1. Graphite Anodes

K-graphite intercalated compounds (K-GICs) have been reported in the literature since the 1950s. These compounds were prepared using non-electrochemical methods, through a two-zone vapor transport method, which applies K vapor onto graphite in a custom-made double furnace. Several compounds were isolated in these studies from stage 1 to stage 5 of potassiation, with stage 1 corresponding to the most K-rich compound, K<sub>G</sub>. Analogous to the case of Li-GICs, one refers to an nth stage compound to indicate insertion of an intercalate layer into every nth graphite interlayer space.

A recent density functional theory (DFT) study compared the intercalation of Li, Na, and K into graphite. The authors found that the intercalation of Na is indeed energetically unfavorable,
unlike that of Li. More interestingly, K intercalation is even more favorable than that of Li (with formation enthalpies for KC8 and LiC6 of $-27.5$ and $-16.5$ kJ mol$^{-1}$, respectively).

Consistent with these computations, Komaba et al.\cite{26} and Jian et al.\cite{35} demonstrated that electrochemical intercalation of K into graphite in a KIB cell is possible. Figure 2 illustrates the main features of this process. A large 1st discharge capacity was reported, with a 1st cycle reversibility strongly dependent on the electrode’s formulation (consistent with the role of the solid-electrolyte interphase (SEI) as discussed in the following). After the 1st cycle, graphite consistently delivered a capacity as high as 273 mA h g$^{-1}$ (vs the theoretical capacity of 279 mA h g$^{-1}$, calculated using the molecular weight of KC8 as the most potassiated phase). Plateaus are observed close to 0.1–0.17 and 0.27–0.32 V during potassiation and depotassiation, respectively, with a typical polarization of 0.1–0.2 V. Figure 2a–d also compares Li and K cells. Overall, K intercalates at higher voltage than Li, consistent with its more negative formation energy.\cite{10} In addition, for K intercalation a large peak is centered at 0.32 V with two shoulders at 0.41 and 0.52 V instead of the three definite processes at 0.23, 0.16, and 0.12 V for Li intercalation, leading to a smooth voltage curve at high voltage. The higher average voltage for K insertion into graphite as compared to Li can lower the energy density of a full cell. However, a higher anode voltage is also beneficial as it reduces the risk of metal plating under high rate or low-T conditions, when Li plating is highly problematic.

Jian et al.\cite{35} confirmed the known K-graphite intercalation compounds (K-GICs) using ex situ X-ray diffraction (XRD) on electrochemically discharged samples. They observed the reversible sequence C–KC36–KC24–KC8 (Figure 2e,f), indicating that the stage 3, 2, and 1 compounds crystallized in a sequence analogous to the crystallization of the phases prepared by the two-zone vapor method.\cite{31,32} except that the stage 4 and 5 compounds were not detected electrochemically. This discrepancy could originate from the fact that ex situ diffraction was only performed on a limited number of samples (i.e., nonoperando conditions) and it is easy to miss phases that exist in a narrow composition range. Note that for the stage 1 compound, K is regularly arranged in the center of carbon hexagons in every layer, forming an arrangement with a nominal composition of KC8. For stage 2, K ions occupy every other layer, and the K content in each K-filled layer is found to be two thirds of that of the stage 1 phase; the composition of stage 2 compound then becomes K2/3C16 (i.e., KC24), rather than KC16.\cite{32} The ex situ experiments also revealed a large volume expansion upon potassiation, corresponding to an increase in the unit cell parameter c of $\approx 60\%$ (3.35–5.35 Å). Nonetheless, reversibility of the graphite peak during cycling was observed, indicating that exfoliation of the material does not occur.

A large volume expansion is often blamed for poor capacity retention upon cycling. Komaba et al.\cite{26} showed that the cell configuration and, in particular, the selection of binder and electrolyte are crucial to obtain good 1st cycle efficiency and capacity retention. Their work thoroughly compares the use of different binders coupled with graphite. As observed in Figure 3, the use of different binders results in significant differences in the electrochemical performance. Replacing polyvinylidene difluoride (PVDF) with sodium polyacrylate (PANa) drastically improves the 1st cycle coulombic efficiency, cycle stability, and rate capability. In particular, its use results in impressive rate performance (230 mA h g$^{-1}$ retained at 15 C–4.2 A g$^{-1}$), as shown in Figure 3d. However, a large amount of the literature published after this work still uses PVDF as the functional binder, which results in many reports claiming improved performance achieved by various forms of carbon, but only over this poorly chosen baseline.
In addition, Zhao et al. [36] showed that the electrolyte can critically influence whether stable SEI layers form. Evaluating 1 M KPF₆ in ethylene carbonate:dimethyl carbonate (EC:DMC), EC:diethyl carbonate (EC:DEC), and EC:propylene carbonate (EC:PC) electrolytes in K metal | graphite + Na alginate (binder) cells they found that EC:DMC results in poor performance. They attribute this to the lack of stable SEI formation as in DMC-containing electrolytes severe and continuous decomposition occurred. By contrast, EC:DEC (which is used in most of KIB literature) and EC:PC worked well with the graphite anode, resulting in more than 200 reversible cycles. The use of EC:PC resulted in slightly better capacity retention and higher 1st cycle coulombic efficiency.

Xu et al. [37] computed the intrinsic mobility of K in graphite using a dispersion-corrected density functional (DFT-D2). The authors analyzed the kinetics in various real and artificial K-GICs (KC₈ₓ (n = 1, 2, 3) and KC₁₂ₓ (n = 1, 2)) by estimating the defect energies and activation energies for K migration. In the K-GICs, the activation energies for K migration by the vacancy mechanism is low (E_a = 0.16–0.27 eV) while the activation energies for K migration by a Frenkel mechanism is very high (2.42 eV). Although these activation energies for K migration were calculated on very few data points along the K displacement path, the values reported by the authors are undoubtedly low and indicate good K kinetics. In fact, the authors claimed that all the activation energies for K migration via the vacancy mechanism are lower than those of Li in Li-GICs based on comparison of their values with those of Thinius et al. [38] Thus, migration through the vacancy mechanism likely indicates good K mobility in graphite, at least comparable to Li (the values reported by Xu et al. are indeed quite similar to those reported by Persson et al.). [39]

Figure 2. a,b) Cyclic voltammetry curves and c,d) charge/discharge voltage profiles of graphite in (a,c) KIBs and (b,d) LIBs cycled versus metal in EC:PC electrolytes. Reproduced with permission.[36] Copyright 2016, WILEY-VCH. e) 1st cycle voltage–capacity profile of a K-graphite cell cycled at C/10. f) XRD patterns of electrodes corresponding to the marked state of charges in (e). Reproduced with permission.[35] Copyright 2015, American Chemical Society.
Although the above theoretical study suggests comparable kinetics of K and Li ions in graphite and the measured mobility of K in the electrolyte is higher than that of Li,[26] Li-graphite cells perform “better” in experiments, namely they have lower polarization and resistance.[36] This may imply that the interface and SEI resistances are larger in the K-graphite cell. Thus, engineering of the electrode and electrolyte compositions is a key to obtaining high rate capabilities in graphite-based negative electrodes in KIBs.

2.2. Other Carbon Anodes

Similarly to the findings reported for Na,[40] several forms of carbon other than graphite have been reported to successfully intercalate K, including soft carbon,[15] hard carbon microspheres,[41] hard–soft composites,[42] N-doped hard carbon and carbon nanofibers,[43] pencil-trace carbon,[44] tire-derived carbon,[45] polyananocrystalline graphite,[46] reduced graphene oxide,[47] and F-, N-, P-, and O-doped, and undoped graphene.[48–51] Most of these materials exhibit remarkable capacities, even in excess of the theoretical capacity of graphite. N-doped and F-doped graphenes are demonstrated to deliver close to 350 mA h g\(^{-1}\).[48,50] Their rate capability and capacity retention are fair (Table 1) but not as good as those obtained with graphite and PANa by Komaba et al. (230 mA h g\(^{-1}\) at a 15 C rate), as shown in Figure 3d.[26] Chen et al.[43] reported a N-doped carbon material with high rate capability using non-graphitic carbon: 154 mA h g\(^{-1}\) at a 72 C rate. In this case the authors argue from their CV curves that instead of true intercalation, a mainly surface-driven adsorption reaction is responsible for the electrochemical activity. In addition, Jian et al.[45] demonstrated that the limited rate capability of hard carbon and the capacity fading of soft carbon can be overcome by forming hard–soft composites, merging the best aspects of both materials. Tai et al. and Adams et al. prepared self-standing films of carbon nanofibers or graphene[44,52] to avoid the use of binders, which simplifies the SEI chemistry and results in remarkable long-term cycling stability (1900 cycles at 1 C rate).

Carbon anodes can also be synthesized using waste or scrap materials derived from waste tires,[45] seafood waste (chitin),[53] or pencils.[44] The idea of recycling waste materials to produce anodes for KIBs is interesting and may help to reduce battery fabrication costs. Finally, co-intercalation using glyme-based solvents has also been demonstrated for KIBs,[53,54] analogous to the work performed for NIBs.[16]

In conclusion, several authors proved the storage of K ions into nongraphitic carbonaceous anodes, and showed they can deliver satisfactory performances in terms of specific capacity and rate capability. However, practically the nongraphitic carbonaceous anodes are unlikely to rival graphite, especially from a volumetric energy density standpoint. Nonetheless, some of these nongraphitic carbonaceous anodes can be produced from waste materials and presumably at very low cost, so it is possible that they will find application in low-cost KIB full cells.

2.3. Alloying Anodes

Alloying of alkali metals with other elements has been regarded as a potential route to prepare high-capacity anodes for Li[55,56]...
Table 1. Electrochemical performance of graphite- and carbon-based negative electrodes for KIBs.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Anode type</th>
<th>Binder and carbon additive</th>
<th>Electrolyte</th>
<th>1st K insertion [mA h g(^{-1})]</th>
<th>1st K extraction [mA h g(^{-1})]</th>
<th>Initial coulombic efficiency</th>
<th>Capacity retention</th>
<th>Best rate capability [mA h g(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jian et al.\cite{35}</td>
<td>Graphite</td>
<td>PVDF</td>
<td>0.8 m KPF(_6) in EC:DEC</td>
<td>475</td>
<td>273</td>
<td>57.4%</td>
<td>51% (50 cycles)</td>
<td>80 at 1 C</td>
</tr>
<tr>
<td>Komaba et al.\cite{26}</td>
<td>Graphite</td>
<td>PVDF</td>
<td>1 m KFSI in EC:DEC</td>
<td>≈540</td>
<td>273</td>
<td>≥50%</td>
<td>81.4% (50 cycles)</td>
<td>140 at 5 C (1.4 A g(^{-1}))</td>
</tr>
<tr>
<td>Share et al.\cite{50}</td>
<td>N-doped graphene</td>
<td>None</td>
<td>0.5 m KPF(_6) in EC:DEC</td>
<td>280</td>
<td>207</td>
<td>74.3%</td>
<td>–</td>
<td>141 at 200 mA g(^{-1})</td>
</tr>
<tr>
<td>Cohn et al.\cite{53}</td>
<td>F-doped graphene</td>
<td>Super P + PVDF</td>
<td>0.8 m KPF(_6) in EC:DEC</td>
<td>480</td>
<td>225</td>
<td>47%</td>
<td>200 mA h g(^{-1}) (200 cycles)</td>
<td>–</td>
</tr>
<tr>
<td>Luo et al.\cite{47}</td>
<td>Reduced graphene oxide</td>
<td>None</td>
<td>0.8 m KPF(_6) in EC:DEC</td>
<td>≈500</td>
<td>220</td>
<td>59%</td>
<td>Negligible fade (20 cycles)</td>
<td>–</td>
</tr>
<tr>
<td>Jian and co-workers\cite{37}</td>
<td>Hard carbon microspheres</td>
<td>Carbon additive + PVDF</td>
<td>0.8 m KPF(_6) in EC:DEC</td>
<td>≈300</td>
<td>262</td>
<td>≈87.3%</td>
<td>83% (100 cycles)</td>
<td>136 at 5 C</td>
</tr>
<tr>
<td>Zhao et al.\cite{36}</td>
<td>Graphite</td>
<td>Na alginate</td>
<td>0.8 m KPF(_6) in EC:DEC</td>
<td>≈480</td>
<td>225</td>
<td>47%</td>
<td>200 mA h g(^{-1}) (200 cycles)</td>
<td>–</td>
</tr>
<tr>
<td>Li et al.\cite{45}</td>
<td>N-doped graphene</td>
<td>None</td>
<td>0.8 m KPF(_6) in EC:DEC</td>
<td>≈640</td>
<td>350</td>
<td>55%</td>
<td>210 mA h g(^{-1}) (100 cycles)</td>
<td>50 at 200 mA g(^{-1})</td>
</tr>
<tr>
<td>Zuo et al.\cite{49}</td>
<td>Few-layer graphene</td>
<td>None</td>
<td>0.8 m KPF(_6) in EC:DEC</td>
<td>≈450</td>
<td>215</td>
<td>≈47%</td>
<td>140 mA h g(^{-1}) (100 cycles)</td>
<td>60 at 100 mA g(^{-1})</td>
</tr>
<tr>
<td>Xing et al.\cite{46}</td>
<td>Poly nanocrystalline graphite</td>
<td>C black + CMC</td>
<td>0.8 m KPF(_6) in EC:DEC</td>
<td>414</td>
<td>224</td>
<td>54.1%</td>
<td>50% (240 cycles)</td>
<td>43.2 at 1000 mA g(^{-1})</td>
</tr>
<tr>
<td>Share et al.\cite{40}</td>
<td>N-doped graphene</td>
<td>None</td>
<td>0.8 m KPF(_6) in EC:DEC</td>
<td>≈640</td>
<td>350</td>
<td>55%</td>
<td>210 mA h g(^{-1}) (100 cycles)</td>
<td>50 at 200 mA g(^{-1})</td>
</tr>
<tr>
<td>Tai et al.\cite{31}</td>
<td>P- and O-doped graphene</td>
<td>None (also no current collector)</td>
<td>0.8 m KPF(_6) in EC:DEC</td>
<td>≈510</td>
<td>220</td>
<td>42.7%</td>
<td>Failure after 140 cycles</td>
<td>–</td>
</tr>
<tr>
<td>Chen et al.\cite{43}</td>
<td>N-rich hard carbon</td>
<td>None</td>
<td>0.8 m KPF(_6) in EC:DEC</td>
<td>≈500</td>
<td>220</td>
<td>42.7%</td>
<td>Failure after 140 cycles</td>
<td>–</td>
</tr>
<tr>
<td>Jian et al.\cite{44}</td>
<td>Hard–soft carbon composite</td>
<td>None</td>
<td>0.8 m KPF(_6) in EC:DEC</td>
<td>389</td>
<td>261</td>
<td>67%</td>
<td>200 mA h g(^{-1}) (200 cycles)</td>
<td>81 at 10 C</td>
</tr>
<tr>
<td>Lin et al.\cite{39}</td>
<td>N- and O-rich carbon nanofibers</td>
<td>None</td>
<td>0.8 m KPF(_6) in EC:DEC</td>
<td>600</td>
<td>245</td>
<td>41%</td>
<td>170 mA h g(^{-1}) (1900 cycles at 1 C)</td>
<td>–</td>
</tr>
</tbody>
</table>
and Na batteries. These anodes exploit the ability of certain elements to alloy with Li, Na, and K, leading to substantially higher achievable specific capacity compared with those of carbon-based anodes. Figure 4a shows which elements alloy with Li, Na, or K. Similar to Li and Na, K alloys with several elements, including Si, P, Ge, Sn, Sb, and Pb. Among those more heavily investigated in the past, Sb is attractive because of its reasonably low cost and its ability to alloy up to composition Li$_3$Sb (or Na$_3$Sb), resulting in a capacity of 660 mA h g$^{-1}$. Similar alloys are known to form with K, leading to the natural choice of the K–Sb system as a potential anode material. In addition, Sn is well known for its ability to alloy with Li and Na, forming Li$_4.4$Sn and Na$_15$Sn$_4$ compounds with theoretical capacities of 991 and 845 mA h g$^{-1}$, respectively. Finally, red phosphorous is one of the most promising anode materials for NIBs. Similar to Na and unlike Li, K does not alloy with Al, potentially enabling its use as a less expensive current collector on the anode than Cu.

Using first-principles DFT calculations, we computed and compared the energetics of alloying K and Na (A) with different anode materials (M) known to alloy with Na, such as Si, P, Ge, Sn, Sb, and Pb. The average voltage was calculated from the ground-state DFT energies as:

$$\langle V \rangle = \frac{-E(A_xM_y) - E(A) - (x_2 - x_1)E(A)}{(x_1 - x_2)F}$$

where $E(A_xM_y)$ are the DFT energies of the most stable $A_xM_y$ configurations at each composition and $E(A)$ is the energy of the metal A. Figure 4b compares the alloying voltages of A with M to form $A_xM_y$. Two general trends are observed: first, the amount of K that can be alloyed is less than or equal to that of Na, indicating that the capacities of the K alloying anodes are generally expected to be smaller than those of their Na counterparts. Second, for almost all of the alloying reactions, the average voltage for K is higher than that for Na, except for partial states of reaction in P and Sb. This higher voltage leads to a loss of energy density for K systems. Note that the higher average voltage but lower capacity for K may at first seem at odds with each other, since the maximum capacity is set by the composition where the voltage reaches zero. Hence, one might expect a higher alloying capacity for K. But the higher average
Voltage of K is accompanied by an average larger voltage slope for alloying K with metals. This leads the voltage curve to reach 0 V at smaller capacity than for Na. A similarly high slope for K was observed in layered cathode materials.\cite{57,58}

In Figure 4c, we also compare the volume expansions computed for the K and Na alloying anodes. The volume expansion for the K system is substantially larger than that for the Na system because of the larger size of K. To make the K alloying anodes competitive, morphology optimization (the introduction of high porosity or nanostructuring) should be considered to prevent particle pulverization upon cycling.

K alloying reactions have been experimentally observed for Sb, Sn, and P, and the results agree well with our computations. McCulloch et al. demonstrated that a Sb–C composite anode, in which C acts as a buffer layer to accommodate the large volume change, reversibly alloys with K for up to 10 cycles, forming cubic K2Sn with a capacity of \( \approx 650 \) mA h g\(^{-1}\).\cite{59,60} Unlike Li–Sn and Na–Sn alloys, which can alloy up to Li4Sn and Na11Sn, our DFT calculation predicts that K can alloy with Sn only up to a one-to-one ratio to produce the end-member KSn with a capacity of 226 mA h g\(^{-1}\). Sultana et al. reported that a ball-milled Sn–graphite nanocomposite anode for KIBs\cite{61} sustained a capacity of 150–170 mA h g\(^{-1}\) for \( \approx 10–15 \) cycles, whereas bulk Sn is electrochemically inactive. The potassiated phases were determined to likely be K2Sn3 and K6Sn23 based on ex situ XRD characterization. Phosphorus has a high theoretical capacity of 2594 mA h g\(^{-1}\) assuming that K3P can be formed. Zhang et al.\cite{62} investigated the electrochemical performance of P–C and Sn4P3–C composite anodes for KIBs. The P–C anode exhibited a high initial capacity (more than 2000 and 1000 mA h g\(^{-1}\) for the first two charge cycles), followed by an abrupt capacity fade, with retention of 9% of the capacity after 20 cycles. The results obtained for the Sn4P3–C composite anode are more promising, as shown in Figure 5. A reversible capacity of \( \approx 380 \) mA h g\(^{-1}\) was achieved with an average voltage of \( \approx 0.5 \) V over 50 cycles. In addition, Sn4P3–C exhibited good rate capability: \( \approx 385 \) mA h g\(^{-1}\) at 50 mA g\(^{-1}\) and \( \approx 222 \) mA h g\(^{-1}\) at 1 A g\(^{-1}\). Importantly, this alloy retained a capacity of more than 300 mA h g\(^{-1}\) after 50 cycles.

Clearly, some metal alloying systems have shown promising enough initial performance for storing K at low voltage to warrant further investigation. However, from a cell energy density perspective, the large volume expansion of K-alloying reactions will pose challenges, and as has been argued for Na\cite{13}, it remains to be seen whether alloying can be competitive with intercalation anodes.

2.4. Intercalation Anodes

Titanate-based compounds, including Li4Ti5O12\cite{63} and Na3Ti2O7,\cite{64} have been widely investigated as nongraphitic intercalation anodes for Li and Na systems. For KIBs, Kishore et al. proposed the use of K2TiO7, which has a layered structure with a interlayer spacing suitable to host K\(^{+}\).\cite{65} Its theoretical capacity is 129 mA h g\(^{-1}\) based on the reaction

\[
\text{K}_2\text{Ti}_4\text{O}_9 + 2\text{K}^+ + 2\text{e}^- \leftrightarrow 2\text{K}_3\text{Ti}_4\text{O}_9
\]

\[\text{K}_2\text{Ti}_4\text{O}_9 + 2\text{K}^+ + 2\text{e}^- \leftrightarrow 2\text{K}_3\text{Ti}_4\text{O}_9\] (2)

The structure of K2Ti4O9 consists of layers of zig-zag ribbons of TiO2 octahedra joined together at the corners (Figure 6a). Even though the capacity of 97 mA h g\(^{-1}\) obtained at 0.2 C (Figure 6b) is rather poor compared with that of other anode materials, the large interlayer distance (8 Å) induces a negligible volume change upon cycling, as observed from ex situ XRD characterization. Another titanate compound, K3Ti8O17, was reported by Han et al.,\cite{66} with a similar but not identical framework to K2Ti4O9 (Figure 6d). In K2Ti4O17, the stepped layered structure is formed by edge- and corner-sharing TiO2 octahedra, providing large interstitial spaces and open channels for K\(^+\) transport. The material was synthesized by a hydrothermal method combined with a subsequent annealing treatment, inducing a peculiar high-surface-area morphology. A discharge capacity of 181.5 mA h g\(^{-1}\) at 20 mA g\(^{-1}\) was reported between 0.01 and 3.0 V versus K/K\(^+\), corresponding to approximately two-thirds of the theoretical capacity (300 mA h g\(^{-1}\) assuming \( \text{K}_2\text{Ti}_4\text{O}_9\)), as shown in Figure 6e,f.

The structure of K2Ti4O9 was synthesized using the NASICON (Na superionic conductors) family, KTi4(PO4)3, which has also been studied as an anode for KIBs. Its structure is analogous to NaTi4(PO4)3 as proven by Rietveld refinement.\cite{67} In general, the NASICON structure consists of basic “lantern units” composed of two TiO2 octahedra that corner-share with three PO4 tetrahedra. K ions can occupy the interstitial sites, which are sufficiently large to allow for further

Figure 5. a) First three discharge/charge profiles of Sn4P3–C in KIB at a current density of 50 mA g\(^{-1}\). b) Cycling performance of the Sn4P3–C, Sn/C, and P/C electrodes in KIBs at a current density of 50 mA g\(^{-1}\). c) Rate performance of Sn4P3–C electrode in KIBs at current densities ranging from 50 to 1000 mA g\(^{-1}\). Reproduced with permission.\cite{62} Copyright 2017, American Chemical Society.
K intercalation. Pure KTi$_2$(PO$_4$)$_3$ with nanocubic morphology can be synthesized hydrothermally and coated with carbon to improve the electrical conductivity.[68] The theoretical capacity of one K insertion is 127.7 mA h g$^{-1}$, which is achieved by reducing Ti$^{4+}$ to Ti$^{3.5+}$. The carbon-coated material delivers 75.6 mA h g$^{-1}$ at 0.5 C and 42 mA h g$^{-1}$ at 11 C between 1.2 and 2.8 V (Figure 6h). The discharge and charge plateaus are located at $\approx$1.60 and 2.14 V, respectively, in the first discharge/charge curve. The good capacity retention observed over 100 cycles in Figure 6i has been attributed to the highly stable NASICON framework. While these results are promising, and it is reasonable to assume that the very high cycle life of some titanates as Li-anodes can be paralleled for K insertion, the relatively high voltage of these titanates is a significant limitation for their use in KIBs.

The only sulfur-based material reported as an anode for KIBs to date is MoS$_2$, which is a layered material, for which the intercalation properties have been extensively studied for select alkali and alkali-earth metals.[69] Ren et al. demonstrated K intercalation within the layers of MoS$_2$[70] as observed for other alkali metals.[71] After a first discharge of 98 mA h g$^{-1}$ (theoretical capacity = 167 mA h g$^{-1}$), the capacity stabilized at $\approx$65 mA h g$^{-1}$ for 200 cycles. Using ex situ XRD, the authors showed that intercalation on an initial plateau at $\approx$1.08 V corresponds to the formation of a K$_{0.4}$MoS$_2$ phase, before reaching another small plateau at $\approx$0.80 V. While more capacity could be obtained for K$_x$MoS$_2$ ($0.4 < x < 0.5$) in the sloped region at 0.8 V, no change was observed in the XRD pattern except for a stronger intensity of the main (002) peak, which suggests the presence of a K$_x$MoS$_2$ phase ($0.4 < x < 0.5$) that remains layered. Discharge to a lower cut-off voltage leads to the formation of metallic Mo and K$_x$S. Note that the Li and Na counterparts are able to intercalate more than 0.4 per formula unit, resulting in a hexagonal-to-tetragonal phase transition at $x = 0.5$ in Li$_x$MoS$_2$ and Na$_x$MoS$_2$.

2.5. Organic Anodes

The use of organic molecules as anodes for KIBs was recently reported by Deng et al.[72] and Lei et al.[73] Dipotassium terephthalate (K$_2$TP) and potassium 2,5-pyridinedicarboxylate (K$_2$PC)
are organic crystals built on a layered structure with K⁺ transport channels. Terephthalates, in particular, are well-known as anodes for LIBs and NIBs. Although these small molecules crystallize in different space groups depending on the alkali species (A), they all react following a reaction $A_2TP \rightarrow A_3TP$ upon discharge. Hence, their use as anodes for KIBs is based on the insertion of 2 K per molecule, resulting in a promising theoretical capacity of 220 mA h g⁻¹; however, their low density is a drawback for practical applications. The oxidation/reduction capacity of these molecules is provided by gaining/losing electrons of the para-aromatic dicarboxylates while the K⁺ ions shuttle back and forth within the battery to maintain charge neutralization. They have been used in K-ion cells, delivering initial capacities of 270 and 245 mA h g⁻¹ stabilizing at 181 and 190 mA h g⁻¹ after 100 cycles, respectively. K insertion occurs through a plateau at 0.5 V for K₂TP, whereas a more sloped feature is observed for K₃PC between 0.7 and 0.5 V. Interestingly, the charge voltage of Na₂TP (0.3 V) and Li₂TP (0.8 V). In situ XRD revealed that upon depassivation, the crystal structure completely lost, resulting in the formation of an amorphous structure. Upon potassiation, however, the crystal structure was almost entirely recovered. This is in part analogous to the behavior observed for Li₁TP: the material is crystalline at the end of the first discharge. However, after 10 cycles to low voltage though, the material was shown to undergo amorphization. Fourier-transform infrared spectroscopy and X-ray photoelectron spectroscopy studies also confirmed that the carboxylate group in K₂TP is responsible for the redox activity through the reduction of CO₂ to CO.

In the past, organic electrode materials have been plagued by the issue of solubility in the organic electrolyte, and by unanswered question of whether the reaction is proceeding in some cases through a dissolution/reprecipitation mechanism. However, in the case of TP there is no evidence for such detrimental mechanism, and the storage of alkali is carried out through a dissolution/reprecipitation mechanism. How- ever, in the early stage of development, and should be further evaluated.

3. Cathode Materials

Potassium can be stored in a wide variety of structures: hexacyanometallates, oxides, polyanionic compounds, and organic materials. Although efforts to discover and develop new cathode materials for KIBs are in their infancy compared with those for anodes, several results reported to date demonstrate promising K-storage capability, and a rapid advancement of research in this area is expected. In this section, we review the ongoing research activity on cathode materials for KIBs, providing our key findings in four subsections on different material systems.

3.1. Hexacyanometallate Groups (Prussian Blue Analogues)

Hexacyanometallates, also known as Prussian blue analogues, have been the subject of intense research activity on cathode materials for KIBs, providing our key findings in four subsections on different material systems.

Negative electrodes that exploit the reduction of oxides to their metallic state—known as conversion anodes—are well-known for LIBs. Recently, the use of a composite Co₃O₄–Fe₂O₃ as a conversion anode for KIBs was demonstrated. The Co₃O₄–Fe₂O₃ nanoparticles dispersed in a Super P carbon matrix were prepared by magnetor-ball-milling of molten-salt-syntheized nanoparticles of Co₂O₃ and Fe₂O₃ with Super P carbon black under a controlled atmosphere. This composite anode exhibited a reversible capacity of 220 mA h g⁻¹ at 50 mA g⁻¹ for 50 cycles, which is lower than that achieved for a similar material within Na cells (440 mA h g⁻¹). The average working potential of the Co₃O₄–Fe₂O₃/C electrode in K cells is lower than those in Na and Li cells.

To summarize, the most meaningful finding in this early stage of research on anodes for KIBs has undoubtedly been K intercalation into graphite. Provided that appropriate binders and electrolytes are used, graphite demonstrates reasonable capacity, rate capability, and capacity retention. Although several other forms of carbon have been shown to store K ions, they are unlikely to rival graphite in terms of specific energy. Allowing anodes are likely to be a poor choice for KIBs, because the same issues that plague them in LIBs and NIBs are only exacerbated in KIBs (i.e., higher voltage, lower capacity, even higher volume increase upon alloying, all resulting in drastically reduced energy density, especially volumetric). On the other hand, intercalation anodes have been shown to be stable for long term cycling, but suitable candidates with higher capacity and low voltage still need to be found. Finally, conversion anodes and organic anode materials are still in the very early stage of development, and should be further evaluated.
Figure 7. a,b) Schematic crystal structures of hexacyanometallate groups. Reproduced with permission.© 2011, Royal Society of Chemistry.

difficult because of the fast kinetics of the precipitation reaction. Water incorporation lowers the amount of redox metal present in the structure and reduces the number of available sites for K ions, limiting the overall performance of the material.

Since the first demonstration of K-ion activity in KFe[Fe(CN)6] with a nonaqueous electrolyte by Erfekhahani in 2004,[85] for which ≈1 K reactivity was shown, several attempts have been made to explore the electrochemical properties of Prussian blue analogues.[82,83,88,89] Whereas the MB site is generally occupied by Fe, the use of different transition metals for the MA site leads to different K intercalation capacities and rate capability.[86] Figure 8 presents voltage profiles of K1.75Mn[Fe(CN)6]0.93–0.16H2O as a function of specific capacity, as reported by Bie et al.[88] A reversible discharge capacity of 137 mA h g−1, which reflects near theoretical K intercalation (1.88 K), is achieved at a cycling rate of 30 mA g−1. Note that in the first few charge cycles, more than the theoretical capacity (≈155 mA h g−1) was achieved, possibly due to parasitic reactions with the electrolyte and/or electrochemical dehydration, as often observed in Prussian blue analogues.[88] Two distinct plateaus were observed during charge (4.05 and 4.1 V) and discharge (3.85 and 4 V) with a small voltage step. Xue et al. suggested that the low-voltage plateau originates from a low-spin Fe2+3+ redox reaction, whereas the high-voltage plateau reflects a high-spin Mn2+3+ reaction.[83] These authors found voltage hysteresis between charge and discharge cycles and attributed it to electrolyte resistance due to the limited solubility of K salts in carbonate solvents. However, the authors did not provide specific evidence for these arguments, and the statement is at odds with the density functional theory prediction of faster mobility of K ion over Li and Na ions in nonaqueous electrolytes by Okoshi et al., and the experimental demonstration of this by Zhao et al. using electrochemical impedance spectroscopy.[27,90]

Overall, the specific energy achievable in K0.5Mn[Fe(CN)6]0.5−nH2O with the two-electron redox reaction rivals that of LiFePO4, though its volumetric energy density is unsatisfactory.[83,88] The full cell performance against the graphite anode shown in Figure 8b reveals excellent discharge rate capability, with delivery of 62 mA h g−1 at a 2 A g−1 rate.[88]

Figure 9 shows voltage–capacity profiles of K0.5Mn[Fe(CN)6]0.5−nH2O (MA = Fe, Co, Ni, Cu) in 2–4.5 V (vs K+/K) at room temperature. The reversible capacity achieved for the MA = Fe composition is 105 mA h g−1, whereas the other compositions deliver discharge capacities equal to or less than 65 mA h g−1.[91]

From Figures 8 and 9, one can conclude that promising performance can be achieved in compositions with Mn and Fe in the MA site. This difference in performance may be due to indirect effects rather than to the specific properties of the redox center. Wu et al. observed that the overall water content increases as the atomic number of MA increases, thereby affecting the electrochemical performance.[91]

The K intercalation mechanism can be studied using XRD. Bie et al. demonstrated how the structure of K1.75+3,Mn[Fe(CN)6]0.93–0.16H2O evolves during electrochemical cycling.[88] Upon K extraction, the material undergoes a two-phase reaction from a structure with monoclinic (space group P21/n) to a cubic (space group Fm3m) structure in the range 0.4 < x < 0.9, which corresponds to the voltage plateau at 4.08 V in Figure 8a. Further potassium extraction transforms the cubic phase to a tetragonal (space group I-4m2) phase through a two-phase reaction from x = 1.4 to the end of charge. This reactions appears as a plateau at 4.11 V in Figure 8a. These authors suggested that the monoclinic-cubic transition is due to a transition from cooperatively rotated MnN6 and FeC6 polyhedra (K = 2) to an unrotated alignment (K = 1) as illustrated in Figure 10.[88] The cubic-to-tetragonal transition, on the other hand, can be explained by the Jahn–Teller distortion caused by the high-spin Mn3+.[88] Note that when the MA site is occupied by Jahn–Teller inactive elements such as high-spin Fe3+, the cubic-to-tetragonal phase transformation is unobservable,[82,83] and instead a solid-solution type intercalation reaction occurs.

High specific energy and excellent cycling stability make Prussian blue analogues attractive cathode materials for K storage. In addition, the material uses earth-abundant Fe and Mn redox centers and is synthesizable by a scalable precipitation method, satisfying the low-cost requirement for development of large-scale ESSs. Still, there is room for improvement to achieve higher energy storage capacity. Given that the water
content directly affects the electrochemical performance, synthesizing dehydrated composition will further enhance the specific energy effectively.

3.2. Layered Oxides

Layered transition metal oxides, used in LIBs and NIBs, are considered potential candidates for K storage materials. These materials generally have high theoretical energy density resulting from their close-packed structure.\textsuperscript{[92,93]} As a result, the most studied K-layered compounds have structures and transition metal content similar to those used in LIBs and NIBs.

Layered compounds can be conveniently categorized using an alphanumeric expression developed by Delmas et al.\textsuperscript{[94]} In this notation, a letter describes the alkali metal sites as edge-sharing octahedral (O) or face-sharing prismatic (P) sites. The transition metals occupy the octahedral site in the next layer, framing alternating alkali and transition metal slabs. The number in the notation refers to the periodicity of the slab stacking. For instance, octahedral alkali metal and octahedral transition metal slabs repeat in a period of three

Figure 8. a) Typical charge/discharge profiles of K\textsubscript{1.75}Mn[Fe(CN)\textsubscript{6}]\textsubscript{0.93–0.16}H\textsubscript{2}O at 30 mA g\textsubscript{cathode}\textsuperscript{−1}. b) Rate capability of KIB using K\textsubscript{1.75}Mn[Fe(CN)\textsubscript{6}]\textsubscript{0.93–0.16}H\textsubscript{2}O cathode and graphite anode. Reproduced with permission.\textsuperscript{[88]} Copyright 2017, Royal Society of Chemistry.

Figure 9. Charge/discharge profiles of a) FeFe-PW, b) CoFe-PW, c) NiFe-PW, and d) CuFe-PW where PW stands for Prussian white, one of the Prussian blue analogues with a nominal K\textsubscript{2}M\textsubscript{2}[Fe(CN)\textsubscript{6}]. Reproduced with permission.\textsuperscript{[91]} Copyright 2017, Elsevier.
(ABCABC stacking) in an O3-type layered structure, whereas prismatic alkali metal and octahedral transition metal slabs repeat in a period of two (ABBA stacking) in a P2-type layered structure or three (ABBCCA stacking) in a P3-type layered structure.\cite{94}

Vaalma et al. demonstrated that a layered compound can be a host for K storage.\cite{24} They evaluated K0.3MnO2, which forms in an orthorhombic distortion of the P2-type structure, (Cmcm space group) as a cathode for KIBs. The K0.3MnO2 cathode delivered reversible capacities of \( \approx 70 \text{ mA h g}^{-1} \) in the voltage range of 1.5–3.5 V, as shown in Figure 11a, but exhibited poor cyclability in a more extended voltage range (1.5–4 V). These authors claimed that the large volume change and layer gliding upon K extraction are likely responsible for the capacity degradation but no direct evidence to substantiate that mechanism is available. The authors also demonstrated the practical feasibility of a rocking-chair KIB with a K0.3MnO2 cathode and hard carbon anode (after prepotassiation). This full cell delivered a reversible discharge capacity of 82 mA h g\(^{-1}\) (based on the cathode).

Later, Wang et al. proposed K0.7Mn0.5Fe0.5O2 nanowires as a cathode material for KIBs.\cite{95} Although the XRD pattern of these nanowires is similar to that of a typical layered compound, the detailed structure could not be defined. The nanowire was composed of 10–20 nm nanocrystallites with a 4.8 wt% carbon coating. The K0.7Mn0.5Fe0.5O2 nanowire cathode provided a high specific capacity of \( \approx 180 \text{ mA h g}^{-1} \) with an average voltage of \( \approx 2.25 \text{ V at 20 mA g}^{-1} \) in the voltage range of 1.5–4.0 V (Figure 11b) and maintained \( \approx 70\% \) of its initial capacity after 45 cycles. The nanowire morphology resulted in superior specific capacity and rate capability compared to a nanoparticle morphology, a result the authors attribute to the interconnected nanostructure providing fast K kinetics. In situ XRD characterization revealed that depotassiation occurs via a two-phase reaction at a low state of charge and proceeds upon further charge with a solid-solution reaction. The discharge process follows the opposite reaction, indicating reversible K de/intercalation. The authors also demonstrated the practical feasibility of a K0.7Mn0.5Fe0.5O2 cathode by constructing a full cell with a soft carbon anode, which delivered a reversible capacity of \( \approx 82 \text{ mA h g}^{-1} \) at 40 mA g\(^{-1}\) based on the cathode weight.

Recently, Hironaka et al.\cite{58} and Kim et al.\cite{57} reported P2-type K\(_x\)CoO\(_2\) (\( x \approx 0.4 \) and 0.6, respectively) cathodes for KIBs. According to Hironaka et al., P2-type K0.4CoO2 exhibits a reversible capacity of \( \approx 60 \text{ mA h g}^{-1} \) between 2.0 and 3.9 V.\cite{58} However, Kim et al. demonstrated that P2-K0.6CoO2 delivers a reversible capacity of \( \approx 80 \text{ mA h g}^{-1} \) between 1.7 and 4.0 V.\cite{57} The different K activities can likely be attributed to different cut-off

Figure 10. Crystal structures and phase transitions observed upon electrochemical potassium extraction (charging) and insertion (discharging). Reproduced with permission.\cite{88} Copyright 2017, Royal Society of Chemistry.

Figure 11. a) Galvanostatic measurements of K0.3MnO2. Reproduced with permission.\cite{24} Copyright 2016, The Electrochemical Society. b) Galvanostatic measurements of K0.7Fe0.5Mn0.5O2. Reproduced with permission.\cite{95} Copyright 2016 American Chemical Society. c) Galvanostatic measurements of K0.6CoO2 cathode materials in K half-cell configurations. Reproduced with permission.\cite{57} Copyright 2017, WILEY-VCH.
voltages. Figure 11c presents capacity–voltage curves of P2-type K_{0.6}CoO_2, which exhibit stair-like charge/discharge profiles, indicating multiple phase transitions upon K de/intercalation. In situ XRD (Figure 12) shows that upon charge, the (008) peak shifts to lower angles, indicative of c-axis expansion due to the increasing coulombic repulsion between the oxygen layers when K is extracted. In addition, asymmetric peak evolutions observed for the (008) peak suggest multiple phase transitions in K_xCoO_2 even though the P2 framework is maintained. Hence, the phase transitions observed are likely due to K^+ vacancy ordering. Upon discharge, the (008) peak shifts back to its original position, confirming the reversibility of K extraction and insertion. Kim et al. also demonstrated the practical feasibility of a P2-type K_{0.6}CoO_2 by pairing with a graphite anode in a full cell, delivering a reversible capacity of \( \approx 53 \) mA h per g of cathode.\cite{57}

In general, the voltage curves of K layered compounds have steeper slopes than those of Li and Na systems. This feature is likely attributable to the size of K^+: The K^+ creates a much larger slab spacing in K_xMO_2 compounds compared to the Na_xMO_2 and Li_xMO_2 analogues. The larger oxygen–oxygen distance leads to less effective screening of the K^+–K^+ repulsion, creating large effective ordering interactions. As a result, a remarkable amount of stable intermediate phases is stabilized showing up as a multitude of features in the voltage curve upon K de/intercalation. The larger average slope in the voltage curves, in turn, results in a reduced capacity for a given voltage window. In practice, this behavior leads to a low specific capacity of K layered compounds, and is a considerable drawback for layered K_xMO_2 compounds as compared to their Na and Li analogues.

### 3.3. Polyanionic Compounds

Polyanionic compounds are promising cathode materials because of their high stability against oxygen loss and the ability to tune the redox voltage through the inductive effect.\cite{96–98} In addition, polyanionic frameworks are expected to better screen the K–K repulsion in the structure, unlike the layered structure where the strong K–K repulsion limits the K storage capability.\cite{57} In this respect, polyanion materials may be particularly relevant for KIBs.

Recham et al. demonstrated that fluorosulfates can reversibly intercalate Li, Na, and K.\cite{99} They prepared FeSO_4F, consisting of chains of FeO_4F_2 octahedra linked through F atoms, by electrochemically extracting K from KFeSO_4F using Li/KFeSO_4F cells, and evaluated the electrochemical properties for each alkali metal. As observed in Figure 13a–c, FeSO_4F can accommodate \( \approx 0.9 \) Li, \( \approx 0.85 \) Na, and \( \approx 0.8 \) K. Interestingly, the voltage steps in the K cells are the most pronounced, implying the presence of multiple stable intermediate phases. In addition, Fedotov et al. developed KVPO_4F, which has a similar structure as KFeSO_4F, and extracted \( \approx 0.85 \) K from KVPO_4F in order to use the material as a charged cathode for LIBs.\cite{100} Very recently, Chihara et al. reported that KVPO_4F can also be used for KIBs,\cite{101} delivering \( \approx 90 \) mA h g\(^{-1}\) with an average voltage of \( \approx 4.13 \) V, which is significantly higher than the voltages observed for K layered compounds.

Amorphous FePO_4 was reported as a host material for various cations, including Li, Na, K, Mg, and Zn, by Mathew et al.\cite{102} These researchers argued that the amorphous structure with short-range ordering can facilitate guest-ion insertions regardless of their sizes. Amorphous FePO_4 was shown to reversibly insert K up to \( \approx 150 \) mA h g\(^{-1}\) with an average voltage of \( \approx 2.5 \) V (Figure 13d). Interestingly, their ex situ XRD results reveal an electrochemically induced amorphous-to-crystalline transition, as shown in Figure 13e. Upon K insertion, a new XRD pattern evolved, which corresponds to KFe_2(PO_4)_3; upon subsequent K extraction, all the XRD peaks disappear, indicating the formation of an amorphous phase. Recently, the use of K_3V_2(PO_4)_3 as a cathode for KIBs was proposed by Han et al.\cite{103} Although the stoichiometry might suggest...
a NASICON-type compound, the detailed crystal structure of K₃V₂(PO₄)₃ has not been identified. The K₃V₂(PO₄)₃ cathode delivered a reversible capacity of ≈54 mA h g⁻¹ with an average voltage of ≈3.7 V and retained ≈80% of the initial capacity after 100 cycles.

Polyanionic compounds can be good candidates because of their high working voltage. KVPO₄F especially provides the highest working voltage (≈4.13 V versus K/K⁺) among cathode materials developed to date. In addition, the wide pool of polyanion species, including (PO₄)³⁻, (SO₄)²⁻, and (P₂O₇)⁴⁻ can provide many opportunities to find new crystal structures for K storage.

3.4. Organic Cathodes

Xing et al. observed electrochemical activity for K storage in organic compounds, in which the charge transfer occurs in C=O bonds, and an aromatic ring hosts the K ions.[104,105] Using 3,4,9,10-perylene-tetracarboxylic acid-dianhydride as a K storage host, they reported a capacity of 129 mA h g⁻¹ for the first discharge at 20 mA g⁻¹ in the voltage range of 1.2–3.2 V with 0.8 mM KPF₆ in EC:DEC with a 1:1 ratio by volume.[104] However, ex situ XRD and infrared spectroscopy indicate that the structural evolution upon K insertion and extraction is irreversible, suggesting possible parasitic contributions to the capacity. K storage in poly(anthraquinonyl) sulfide (PAQS) was also demonstrated by Jian et al.[105] One PAQS molecule was observed to uptake two K ions upon discharge (211 mA h g⁻¹ at 20 mA g⁻¹ in 1.5–3.4 V) when using 0.5 M KTFSI in mixed dimethoxyethane and dioxolane solution (1:1 ratio by volume). Zhao et al. showed that oxocarbon (C₆O₆) can cycle two K ions in the voltage range of 1–3.2 V, delivering a capacity of 212 mA h g⁻¹ at 0.2 C.[106] These authors also compared the kinetics of K storage in the oxocarbon with that for Li and Na and found that the K diffusivity estimated by cyclic voltammetry is higher than those of Li and Na for the same system. Overall, the energy densities of organic cathode compounds are low because of the large molecular volume combined with a low operating voltage. In addition, the underlying mechanisms for K storage in organic materials are not yet clear: further investigation is needed to ensure whether reversible redox reaction occurs in the solid phase or by dissolution reprecipitation in the electrolyte, as discussed in other alkali metal systems.[106] Nevertheless, some materials exhibit higher rate capability than their Li or Na counterparts and reasonable reversibility, suggesting opportunities for low-cost, high-power applications for these materials.

4. Discussion and Outlook

Several types of anode materials have already been proposed for KIBs, closely resembling those reported for LIBs and NIBs. The majority of these candidates are carbonaceous materials. Graphite, in particular, has been demonstrated to be viable and to exhibit remarkable rate capabilities by Komaba et al.[26] Subsequent studies confirmed that graphite has low migration barriers for K diffusion, high capacity, and sufficiently low intercalation potential, making it truly promising for KIBs;
however, a stable SEI is key to obtaining good performance upon repeated cycling. Therefore, suitable binders (such as PANa) and electrolytes (such as EC:PC or EC:DEC with KPF6 or KTFSI salts) must be used. When these measures are taken, the performance of graphite anodes in KIBs can reach levels comparable to those in LIBs with the additional potential benefit of a superior charge-rate capability because of the higher potassiation voltage. Although several other carbons such as soft and hard carbon, composites, or graphene-related (possibly doped) materials have been demonstrated to perform well in KIBs, they nevertheless lead to low volumetric densities and often have higher voltage than graphite, which will negatively affect the overall energy density of the cell. These drawbacks have been well documented for NIBs, for which graphite anodes cannot be used.

Among noncarbonaceous anodes, few possibilities among those reported to date are truly promising. Anodes based on alloying reactions are unlikely to be good candidates: the capacities and voltages are calculated to be lower and higher, respectively, than those of LIBs and NIBs, resulting in lower energy densities. Moreover, the problem of avoiding large volume expansion upon alloying, which already plagues Li and Na, is exacerbated for K, making long-term cycling difficult to achieve.

Intercalation anodes are potential alternatives to carbon-based ones: titanium-containing materials such as K$_2$Ti$_3$O$_7$ can reach rather high capacities of 181.5 mA h g$^{-1}$ at 20 mA g$^{-1}$. Unfortunately, their voltages are quite high; therefore, if better candidates with lower voltages (and possibly higher density) can be found, these materials could be used in full KIB cells. However, it should be stressed that more than 20 years of research to find titanates with voltages lower than that of Li$_4$Ti$_5$O$_12$ delivered no significant results.

Finally, organic anodes using K$_2$TP and K$_2$PC with remarkable capacities that are stable for more than 100 cycles have also been reported. Their drawback is the low volumetric energy density of organic molecules; however, because organic cathodes have also been reported, a full-organic KIB is a practical possibility. As with all small molecular organic species, solubility of the charged and/or discharged state in the organic electrolyte solvent upon prolonged cycling should be carefully investigated.

In KIBs, the development of cathode materials that can deliver high gravimetric and volumetric energy density comparable to those of LIBs and NIBs is crucial. Even though applications such as grid do not fundamentally require high energy density, a lower energy density of cells often leads to higher cost. Focused research on cathode materials should be conducted for such a nascent chemistry to become practical.

To provide further guidelines for the investigation of cathode materials for KIBs, we predicted the K-intercalation voltages of various cathode materials using DFT/generalized gradient approximation (GGA) with Hubbard U correction (GGA+U$^{[106]}$) and Equation (1). The U values of 3.5 eV, 3.9 eV, 4.0 eV, and 3.4 V were used for Cr, Mn, Fe, and Co, respectively.$^{[109]}$

Figure 15a presents the calculated average voltages of layered P2- and P3-K$_x$MO$_2$ (0 ≤ x ≤ 0.66, M = Cr, Mn, Co) for Na and K insertion. In all cases, the average K and Na-insertion voltages are similar. Nevertheless, the larger voltage slope that has been observed for K-insertion leads to a lower specific capacity and presents a fundamental limitation for K-layered cathodes. In addition, the K layered compounds developed to date all have K-deficient compositions (x < 0.7 in K$_x$MO$_2$). Because the alkali ions in a full cell tend to originate from the cathode materials, it is critical to develop fully potassiated K layered compounds (KMO$_2$).

We also calculated the average voltages of A$_x$FePO$_4$ (A = Li, Na, K) and A$_x$FeSO$_4$F (A = Li, Na, K) at 0 ≤ x ≤ 1, as shown in Figure 15b. For each compound, voltages were first calculated in the preferred structure for the composition, namely, LiFePO$_4$ (Pnma), maricite NaFePO$_4$ (Pnma), KFePO$_4$ (P2$_1$/n),avorite LiFeSO$_4$F (P-1), NaFeSO$_4$F (C2/z), and KFeSO$_4$F (C2/z). In this comparison, the K-compounds exhibit slightly higher average voltages than their Na analogues and comparable voltages to their Li analogues. To study the relation between the voltage and structural preferences for Li, Na, and K compounds, we also compared the K, Na, and Li average voltages across a fixed structure namely the olivine structure of LiFePO$_4$ and the KFeSO$_4$F structure. We fully relaxed each structure with Li, Na, and K ions using DFT and calculated their average voltages. Because the K$^+$ ionic radius (138 pm) is much larger than that of Li$^+$ (76 pm) and Na$^+$ (102 pm), the K insertion into olivine Li$_x$FePO$_4$ (x = 0) structure is less favorable than either Na or Li insertion, resulting in lower K insertion voltage as observed in Figure 15b. By

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Figure 14. Demonstrated, gravimetric versus volumetric energy of cathode materials for KIBs and comparison with Li and Na cathode materials. The mass and volume of the active electrode materials were considered to calculate the gravimetric and volumetric energies. The data were obtained from the literature.$^{[24,57,88,95,99,101,104,107]}$
contrast, the voltage of AFeSO4F (A = Li, Na, K) within the KFeSO4F framework increases with increasing ionic size due to the large cavities for alkali ions in the KFeSO4F framework. These results imply that K compounds exhibit stronger structural preferences than Na compounds because of their larger ionic radii.

The comparable voltages of K compounds and their Na analogues can be explained in terms of the cathodic and anodic contributions to the redox potential. The anodic contribution is determined by the energy cost for extracting an alkali atom from the metal anode. The smaller cohesive energy of K metal (0.934 eV per atom) compared with those of Na metal (1.113 eV per atom) and Li metal (1.63 eV per atom) implies a smaller energy cost for K extraction than for Li and Na extraction, increasing the voltages of K compounds. The cathodic contribution is determined by the energy gain for alkali-ion insertion into a host structure. The formation energy of K2O (−363 kJ mol−1) is lower than those of Na2O (−417.98 kJ mol−1) and Li2O (−598.73 kJ mol−1), implying that K–O bonding is generally weaker than Na–O and Li–O bonding. Thus, the energy gain for K insertion is lower than that for Na or Li insertion, decreasing the voltages of K compounds. However, the difference in the formation energy between K2O and Na2O is much less than that between K2O and Li2O. The negative cathodic contribution can be compensated by a positive anodic contribution; thus, K cathode compounds have redox potentials that are comparable to those of Na cathode compounds.

5. Summary

In this review, we summarized the most up-to-date progress in materials development for K-ion batteries and discussed some of the challenges and opportunities. One of the greatest advantages motivating KIBs and differentiating them from NIBs is the K intercalation into graphite anodes, though its reversibility requires careful tuning of binders and electrolytes. Among other possible anode chemistries, alloying anodes are hardly good candidates: they exhibit substantial capacity but have high voltages and suffer from large volume expansion. These issues could be moderated by particle nanosizing or morphology optimization. By contrast, intercalation anodes exhibit small volume change and good capacity retention, but so far have shown limited capacity. We also reviewed a wide variety of cathode chemistries. The K layered oxides may not be as attractive as in the Li and Na systems as the large K size only allows a limited amount of K into the structure, thereby reducing the achievable capacity. We suggest that there may be more opportunities in polyanionic materials or Prussian blue analogues that have multielectron redox reactions.

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Conflict of Interest

The authors declare no conflict of interest.

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