Organic electrolyte design for practical potassium-ion batteries

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Potassium-ion batteries (PIBs) are promising as a low-cost and complementary technology to lithium-ion batteries (LIBs) because of the relative abundance of potassium. Electrolyte is a critical component and governs the electrochemical performance of PIBs. Electrolyte engineering has recently resulted in promising results for both the anode and cathode materials of PIBs. However, the performance of current PIBs is still limited for practical applications. A systematic analysis of recent electrolyte engineering research is required for further improvement. In this review, we first summarize the recent electrolyte research progress and design strategies for PIBs. We then discuss the key features of PIB electrolytes such as the K-ion solvation environment and SEI chemistry, and finally propose several design strategies and considerations for future electrolyte development.

1. Introduction

Energy storage plays a key role in reaching the goal of carbon neutrality by the 2050s by effectively integrating and using renewable energy resources such as hydro, solar and wind. Lithium-ion batteries (LIBs) have dominated the market for consumer electronics due to their high energy density and efficiency. Their applications in electric vehicles and stationary electric energy storage are also increasing due to the strong market demand. However, there is significant concern regarding the supply chain and sustainability, due to the limited and high-cost lithium and cobalt resources. In response to these concerns, low-cost energy storage devices are being developed.

Sodium-ion batteries (SIBs) and potassium-ion batteries (PIBs) have been regarded as promising complementary technologies to LIBs because of their relative abundance. In addition, Na and K do not form alloys with Al electrochemically. It means that low cost Al foil can be used as a current collector for both anode and cathode in SIBs and PIBs, further demonstrating the potential in reducing the cost. Compared to SIBs, graphite, the commercial anode material in LIBs, can be used in PIBs as anodes, providing a critical advantage of PIBs over SIBs (Fig. 1a).

PIBs operate through a similar rocking-chair principle to LIBs, where K ions shuttle between the anode and the cathode through an electrolyte (Fig. 1b). Ideally, the electrochemical potentials of the anode ($m_A$) and the cathode ($m_C$) need to match...
electrolytes that can work for high-voltage cathodes. However, the formation of more stable and uniform SEIs. There are also $K^+/K)$. In the past few years, researchers tried to discover suitable electrolyte formation strategies for PIBs, by optimizing the salts and solvents, tuning the electrolyte additives, enhancing electrolyte concentrations, etc. Some electrolytes could enable the formation of more stable and uniform SEIs. There are also electrolytes that can work for high-voltage cathodes. However, a considerable gap exists in simultaneously achieving good performance for both anodes and high-voltage cathodes to meet the practical requirements.

The electrolyte is critical for PIBs and determining their performance such as cycle stability. Electrolyte engineering has the potential to yield practical PIBs, but innovations are needed to achieve success in this field. To promote electrolyte research development, a systematic investigation of recent electrolyte research is highly needed. In this review, the recent progress in electrolyte research and design strategies for PIBs are first summarized. Then, we discuss the key features of electrolytes such as the K-ion solvation environment and SEI chemistry that are important for battery performance and electrolyte design. Finally, several design strategies and considerations are proposed to further electrolyte development for practical PIBs.

2. Recent progress in electrolyte research for PIBs
2.1. Salt selection
Potassium salt is a key component of electrolytes for PIBs. Several parameters such as high solubility, high ionic window and long cycling lives. She is specialized in frontier technologies of developing low-cost non-flammable electrolytes and stable electrode/electrolyte interfaces.

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conductivity, good electrochemical, chemical, and thermal stability, low-cost, and non-toxic nature should be considered for choosing suitable salts. However, compared to Li and Na salts, K salts normally have lower solubilities in organic solvents due to the larger size and weaker Lewis acidity of K+ ions. Komaba group compared the solubilities of KPF6, KFSI, KTFSI, KClO4, and KBF4 salts in PC.

They found that KFSI, KTFSI, and KPF6 can be dissolved well in 0.5 M PC solutions, while precipitation occurred in the 0.5 M KClO4 and KBF4/PC solutions (Fig. 2A). Although K salts show low solubilities, K salt electrolytes have good ionic conductivity due to the high mobility and large transport number of solvated K+ ions as a result of the weak Lewis acidity of the K+ ions (Fig. 2B). The weak interactions between the K+ ions and solvents/anions also endow the K+ electrolyte with good viscosities. These features make K salts suitable as electrolyte salts.

In 2015, KPF6 and KFSI were successfully used in PIBs to enable the reversible intercalation of graphite, respectively. However, the KPF6 electrolyte was found to decompose during cycling. The initial coulombic efficiency in KPF6 electrolyte is relatively lower than that of KFSI electrolyte. In 2018, our group found that the electrochemical performance of alloy-based anode materials, such as Bi, Sn and Sb, can be significantly improved by replacing KPF6 with KFSI in carbonate electrolytes (Fig. 2C and D). A clear difference of SEIs was observed in these 0.8 M KPF6/EC:DEC and 1 M KFSI/EC:DEC electrolytes. The SEI layer formed in KFSI electrolyte maintained its thickness and integrity from 2 to 10 cycles, while a heterogeneous SEI grew in the KPF6 electrolyte upon cycling (Fig. 2D). The XPS results indicate that the decomposition product of KFSI is a key factor for a stable SEI. Since then, KFSI has been widely used as the salt for anode materials such as phosphorus, phosphides, chalcogenides, and carbon materials. Besides the ability to form a stable SEI, the reduced free solvent molecules in the KFSI electrolyte due to the strong solvation are also helpful to alleviate the parasitic reactions, and thus enable a higher performance. Moreover, KFSI has higher solubility and higher conductivity than KPF6, due to the low ionic association of the K+ and FSI¯/C0 ions. However, the KFSI electrolyte has problems such as electrolyte decomposition and corrosion of Al foil at high voltages (>4 V). By contrast, KPF6 has several advantages such as oxidative stability, passivation of Al foil, and low cost. It was found that the Prussian blue analogue (PBA) cathode presents higher capacity, lower voltage polarization, and more stable cycling in KPF6 electrolyte than in KFSI electrolyte, which can be attributed to the better passivation of KPF6 at high potentials.

The most commonly used salts for PIBs are KPF6 and KFSI, and each salt has its own advantages and disadvantages. KFSI is more appropriate in the anode, while KPF6 is more suitable in high-voltage cathodes. Blending salt solutions is a promising strategy in developing the electrolytes of PIBs as it could retain the advantages while circumventing the disadvantages of both, and can secure its success in full cells. Komaba et al. found that the binary KPF6–KFSI salt electrolyte presents higher ionic conductivity than KPF6 electrolyte. Moreover, KPF6-rich electrolytes with KPF6/KFSA ratios of ≥3 (mol mol⁻¹) provide sufficient oxidation stability and passivation against Al.
corrosion at 4.6 V over 100 h. Due to the stable SEI contributed by the FSI$^-$ anions and the high oxidative stability, the 3.6 V class full cell of graphite$|K_2Mn[Fe(CN)]_6|$ exhibits excellent cycle stability for over 500 cycles in the K(PF$_6$)$_{0.75}$(FSI)$_{0.25}$/EC/PC electrolyte, which is much better than that of the cell with the conventional KPF$_6$/EC/DEC electrolyte (Fig. 2E). This work demonstrated the feasibility of blending salts to improve the performance. Following this strategy, more blending salts can be developed to further improve the performance of PIBs.

2.2. Solvent optimization

Besides the K salts, solvent is another critical component of the electrolyte that can be tuned to enhance the electrochemical performance. Several parameters such as low viscosity for good wettability and transport, high dielectric constants for high dissolution ability, low melting and high boiling point for wide temperature window, low-cost, and non-toxic nature should be considered for choosing suitable solvents. As in the case of LIBs, the organic solvents in PIBs are typically esters and ethers. In the case of carbonate esters, cyclic carbonates (e.g. EC) normally have higher dielectric constants than linear carbonates (e.g. DEC), which could promote salt dissociation and thus increase the solubility. Considering that K salts (e.g. KPF$_6$) normally have a low dissociation degree, cyclic solvents can be one of the solvent components in preparing K$^+$ electrolyte formulations.
In the case of the graphite anode, Zhao et al. compared its electrochemical performance in KPF₆ electrolytes with different solvents (EC:PC, EC:DEC, and EC:DMC). They found that EC:PC had a higher initial CE (66.5%) than EC:DEC (47%) and EC:DMC (43%), which is probably due to the decomposition of DEC and DMC, and the formation of an unstable SEI. In addition, graphite exhibited good cycle performance in the EC:DEC and EC:PC electrolytes (>200 cycles), while significant capacity decay was observed in the EC:DMC electrolyte (Fig. 3A). The same phenomenon occurs in the KVPO₄F cathode. Komaba et al. reported that the KVPO₄F cathode exhibited higher initial coulombic efficiency in EC/PC-based electrolytes than in EC/DEC-based electrolytes, delivering a high discharge capacity of ~92 mA h g⁻¹ at 2.0–5.0 V (Fig. 3B). The results indicate that KPF₆/EC:PC electrolytes are suitable for both low and high voltage materials.

Ether solvents have good solubility and low viscosity for K salts. The electrochemical performance of PIBs in ether-based
electrolytes is different from that in ester-based electrolytes. Ester-based electrolytes enable reversible K⁺ intercalation into graphite, while the co-intercalation of K⁺ and ether into graphite has been confirmed in ether-based electrolytes (Fig. 3C). The co-intercalation behavior avoids the slow desolvation process and facilitates fast kinetics, but increases the working voltage and reduces the capacity. However, ether-based electrolytes have been reported to be suitable electrolytes for other anode or cathode materials (alloyed materials, organic materials, K metal, etc.). Particularly, micrometer-size metal anodes such as Bi, Sn, and Sb (Fig. 3D) could deliver high cycling stability, which is attributed to the stable SEI formation. However, the solvents may need to be optimized for different electrode materials. As shown in Fig. 3E, the red phosphorus/carbon (RP/C) composite exhibits better cycling stability in 1 M KFSI/EC:DEC than in 1 M KFSI/DME. On the other hand, the poor oxidative stability of ether electrolytes limits their applications.

2.3. Novel additives
Additives are widely used in LIBs to improve the electrochemical properties by tuning the electrolyte solvation, manipulating SEI formation, increasing the wettability, reducing the viscosity, preventing overcharging, and improving the thermal stability. Therefore, effective additives will enable more tunabilities and functionalities to realize high performances of PIBs. However, only few additives and their combinations have been explored, such as FEC, vinylene carbonate (VC), DTD, KPO₂F₂ and KNO₃. FEC is one of the most effective electrolyte additives for LIBs which acts by forming a robust SEI. However, the function of FEC is complicated in PIBs. It has been reported that FEC did not play a positive role in some anode materials, such as graphite, GePₓ, Sn,Pₓ [Fig. 4A], and SnS₂-rGO, but the addition of FEC and VC to 1 M KPF₆/PC can increase the coulombic efficiency of Sn anodes from 59 to 76%. Moreover, a small amount of FEC additive (2 and 5%) can significantly improve the CE and cycle life of the Prussian blue cathode at PIBs [Fig. 4B]. These results seem contradictory. Recent investigation indicates that K metal is highly reactive towards the electrolyte, the side products could be transferred and oxidized on the graphite or electrolyte decomposition on the cathode side. Therefore, it is challenging to unravel the function of FEC in half cells, further studies on the origin of FEC should be performed in full cells to avoid the interference of potassium metal.

Ethylene sulfate (DTD) has demonstrated to be an effective additive for graphite, K metal anode, and PBA cathode in a range of electrolytes. Propylene carbonate (PC) is a well-known solvent that is incompatible with graphite due to electrolyte decomposition and/or graphite exfoliation. However, Ming et al. found that 1.0 M KFSI in PC becomes compatible after adding 6 wt% ethylene sulfate (DTD). With this electrolyte, the graphite can deliver a high capacity of 260 mA h g⁻¹ with a good cycle performance (Fig. 4C). Further investigation indicates that DTD can decrease the K⁺-PC interactions by pushing the PC solvent out of the first solvation structure due to its high coordination capability. Based on this finding, they also introduced the DTD additive into a non-flammable TEMP based electrolyte (1 M KFSI in TEMP) to achieve graphite cycling at low concentration. The introduction of DTD not only changed the solvation structure of K⁺, but also the interface behavior of K⁺-solvent (Fig. 4D). Komaba et al. found that 1 wt% of DTD additive in 0.8 M KPF₆/EC:DEC can reduce the plating-stripping polarization of a symmetric K/K cell to ~20 mV (Fig. 4F). The DTD addition could passivate the K-metal surface and inhibit the formation of electrolyte-soluble oligocarbonates. Otherwise, the oligocarbonates will be transferred and oxidized on the positive electrode, causing irreversible capacity. Thus, the K/K Mn₂[Fe(CN)₆]₃ cell with the DTD additive displayed a larger reversible capacity than the DTD-free cells (Fig. 4E).

In 2020, Matsumoto et al. demonstrated that the potassium difluorophosphate (KDFP) additive can increase the cycle stability of graphite (76.8% capacity retention after 400 cycles with KDFP vs. 27.4% after 100 cycles without KDFP) (Fig. 4G). The K/K symmetric cell in the KDFP-containing electrolyte also exhibited higher efficiencies and lower interfacial resistance than the KDFP-free electrolyte. The addition of KDFP enables the formation of a stable and K⁺-conducting SEI (KF, KPF₆ and phosphate (PO₄)). Meanwhile, LiNO₃ has been widely used in lithium metal batteries as an effective additive. KNO₃ was also introduced in an ether-based electrolyte (2.3 M KFSI in DME) to enable dense and uniform K deposition by forming a stable N/F-rich SEI due to the decomposition of NO₃⁻ and FSI anions.

Overall, electrolyte additive engineering is a simple and effective approach to enhance the electrolyte performance. However, the additives may be gradually consumed during cycling due to the repeated SEI repairing, and their function should be evaluated under practical conditions. As in the case of LIBs, the numerous additives and their combinations have great potential for further improving the performance of PIBs.

2.4. High (localized high) concentration electrolytes (HCEs, LHCEs)
Enhancing the electrolyte concentration is an effective strategy to improve the performance of a battery. The idea originates from the research on LIBs. Compared to dilute electrolytes, high concentration electrolytes (HCEs) reduce both the number of free solvent molecules and solvent molecules coordinated with cations, and bring the salt anion into the primary solvation shell, leading to the change of solvation structure and the formation of the salt anion derived SEI (Fig. 5A). In PIBs, different HCEs in esters and ethers were reported. For KPF₆ salt, the concentration was only reported up to 2.5 M in diglyme. However, KFSI and KTFSI can reach the concentration over 5 M due to the weak interaction between anions and K⁺ ions resulting from the low Lewis basicity of FSI⁻ and TFSI⁻ anions. Komaba found that KFSI was highly soluble in various solvents (10 mol kg⁻¹ in PC, 7.5 mol kg⁻¹ in dimethoxyethane (DME), 12 mol kg⁻¹ in γ-butyro lactone (GBL)). Moreover, KFSI exhibits higher solubility than KTFSI and KPF₆ in DME. Therefore, the KFSI salt is mostly used in preparing HCEs.
KFSI-based electrolytes have their advantage for anode materials due to the formation of a stable SEI. The advantage can be further emphasized by HCEs. It is found that the SEI layers in low concentration consist of organic and inorganic components from the decomposition of both salt anions and solvents, while most of the SEI components formed in HCEs are inorganic, largely from the decomposition of the salt anion. The unique solvation and SEI formed in HCEs enable a range of electrode materials with excellent electrochemical performances. For example, the graphite anode with 2.5 M KFSI in EMC can run over 2000 cycles (17 months) with negligible capacity decay. A Sb@CSN composite anode has been reported to deliver a high capacity of 551 mA h g\(^{-1}\) over 100 cycles at 100 mA g\(^{-1}\) in a concentrated 4 M KTFSI/EC + DEC electrolyte. HCEs could also prevent the co-intercalation of ether into graphite. The graphite delivered stable cycling for over 150 cycles at 7 mol kg\(^{-1}\) in KFSI/DME. In addition, HCEs can efficiently suppress the dissolution and shuttle of polysulfide, and enables the highly reversible reaction of sulfur in 5 M KTFSI in DEGDME.
KFSI-based electrolytes have their limitation in high voltage PIBs due to the corrosion of the Al current collector and/or electrolyte decomposition. However, HCEs can stabilize the Al current collector. Komaba found that the 7 mol kg\(^{-1}\) KFSA/DME electrolyte exhibits a wide potential window of 0–4.3 V vs. K\(^+/\)K without Al corrosion (Fig. 5D). The graphite/K\(_2\)Mn[Fe(CN)]\(_6\) full cell also exhibits higher coulombic efficiency and better cyclability than in KPF\(_6\)/carbonate electrolytes.\(^{69-71}\) HCEs could also enable the reversible intercalation of FSI\(^-\) anions into the graphite at high voltage.\(^{69-71}\) Accordingly, potassium-based dual-graphite battery cells were constructed with a high energy density of 207 Wh kg\(^{-1}\) and an average discharge voltage of 4.7 V.\(^{69}\) In addition, Li et al. found that a dual interphase structure consisting of SEI film and inactive spinel interlayer is in situ formed on the KMO cathode in the 6.0 M KFSI/G2 electrolyte.\(^{72}\) The SEI is formed from the decomposition of the FSI\(^-\) anions and G2 molecules, while the spinel interlayer is formed from the Jahn-Teller distortion and disproportionation of Mn\(^{3+}\).
They cooperatively enable the reversible phase transition and mitigate Mn loss, resulting in the stable electrochemical performance of KIBs. Our group also found that a synergy can be created by coupling the binder and electrolyte to maintain the electrode/interface stability of alloy anodes against large volume changes. With the cross-linked carboxymethyl cellulose (CMC), polyacrylic acid (PAA) binder and the 3 M KFSI/DME electrolyte, a micro-sized SnSb/C anode can deliver a high capacity of $\sim$419 mA h g$^{-1}$ with capacity retention of 84.3% for 600 cycles at 50 mA g$^{-1}$, and 340 mA h g$^{-1}$ with 80.7% capacity retention for 800 cycles at 1000 mA g$^{-1}$.75

HCEs brought about an effective electrolyte strategy for PIBs. However, HCEs have several drawbacks such as reduced ionic conductivity, and increased viscosity and cost compared with standard concentration electrolytes. Therefore, localized high concentration electrolytes (LHCEs) have been developed by diluting HCEs to standard concentrations with another solvent. It is believed that the introduced co-solvent does not participate in the solvation process (Fig. 5E).44 1,1,2,2-Tetrafluoroethyl-2,2,2-trifluoroethyl ether (HFE) has been applied as a co-solvent to dilute the concentrated KFSI/DME and KFSI/TMP electrolytes, respectively.44,87 The addition of HFE did not change the solvation structure of the HCEs, but effectively reduced the electrolyte viscosity. As a result, LHCEs facilitate the high performance of graphite (Fig. 5F) and black phosphorus-graphite (BP/G) composite anode, as well as the compatibility with high-voltage cathodes. As in the case of LIBs, the diluents should be stable and miscible with co-solvents, but weakly interacting with K-ions. More LHCEs can be explored to improve the performance of PIBs by following this route.

2.5. Non-flammable electrolytes

Safety is important for the practical applications of PIBs. However, the conventional electrolytes based on carbonates and ethers are highly volatile and flammable, leading to a high risk of ignition and severe safety issues (Fig. 6A). HCEs and LHCEs can enhance the thermal stability of normal electrolytes, but there is still risk especially for large-scale applications. In contrast, developing non-flammable or fire-retardant electrolytes to address battery safety is highly recommended. As in the case of LIBs, fire-retardant phosphate solvents were adopted in PIBs, including triethyl phosphate (TEP), trimethyl phosphate (TMP), and dimethyl methyl phosphonate (DMMP).88-91 In 2019, Feng et al. demonstrated that graphite can perform stable cycling for over 80 cycles with 3.3 M KFSI in TMP.90 Our group systematically investigated the KFSI based electrolytes with different phosphates (TEP, TMP and DMP) and concentrations, and the effects on the K metal and graphite anodes.90,95 We found that the K electrolyte features lower viscosity and higher conductivity than Li and Na electrolytes owing to the relatively weak solvation of K+ cations and phosphates (Fig. 6B and C). With optimization, the moderately concentrated 2 M KFSI/TEP electrolyte enables non-dendritic K-metal plating/stripping with a coulombic efficiency (CE) of 99.6% for over 500 cycles and offers near-theoretical capacity of the graphite anode and stable cycling for over 300 cycles at 0.2C. In contrast, both LiFSI and NaFSI based on phosphate solvents cannot work reversibly below 2 M, whereas high salt concentrations (>3 M) are required to achieve high performance. The success of this non-flammable 2 M-KFSI/TEP electrolyte could be attributed to the solvation structure, which leads to high solvation ratios of TMP (69.4%) and the formation of a robust KFSI salt-derived SEI film with a uniform thickness of about 10 nm. The solvation ratios of phosphate molecules can be further increased to nearly 100% in the KFSI/TMP electrolyte with a salt/solvent molar ratio of 3:8, due to the higher dielectric constant of TMP (Fig. 6D). The nearly 100% solvation of TMP molecules and the formation of FSI- derived F-rich SEI effectively suppress the decomposition of the solvent molecules, enabling unprecedented stability with 74% capacity retention over 24 months of cycling (over 2000 cycles) at the 0.2C current rate (Fig. 6E).

Although the moderate concentration electrolyte exhibits the advantages of low cost, low viscosity, and high conductivity compared to HCEs, the concentration can be further tuned to that of a standard electrolyte (1 M) by developing LHCEs or introducing additives. The BP-graphite (BP/G) anode delivered a capacity of 342 mA h g$^{-1}$ after 300 cycles at 0.3 A g$^{-1}$ in LHCE [KFSI/TMP/HFE = 1:1:7:2 by mol].96 DTD can make the 1 M KFSI/TMP electrolyte (6 wt% DTD) compatible with the graphite anode and enable a high-performance graphite[$k_{0.69}$CrO$_2$] full battery.29

Non-flammable electrolytes based on fire-retardant phosphate solvents not only provide the solution to address battery safety, but also show compatibility with the graphite anode. One issue is that these electrolytes may not tolerate high-voltage. However, it was reported that the K$_{0.3}$MnO$_2$ cathode can work well at 2.0–4.2 V (vs. K+/K) in a TEP-based electrolyte, delivering a large reversible capacity (120 mA h g$^{-1}$) and high capacity retention of 84% after 400 cycles.97 Therefore, by overcoming high-voltage issues, non-flammable electrolytes show huge potential in practical PIBs.

2.6. Ionic-liquid (IL) electrolytes

PIBs are not only a low-cost battery alternative, but also provide a potential high-voltage output. Several types of cathode materials have already been developed, but it is challenging to develop suitable electrolytes for high-voltage operation. Ionic-liquid (IL) electrolytes are promising for high-voltage PIBs due to their wide electrochemical stability window. ILs also have various interesting properties such as good thermal stability, low flammability and low volatility. In 2017, Yamamoto et al. reported that the 0.2 M KFSI-[C$_5$C$_{12}$Pyrr][TFSA] IL has a high ion conductivity (4.8 mS cm$^{-1}$) and wide electrochemical window (5.72 V) (Fig. 6F).92

Some KFSI- and KTFSI-based ILs have been used for both cathodes and anodes with good electrochemical performances. Masese et al. reported that ionic liquids based on KTFSA salt in N-butyl-N-methylpyrrolidinium TFSA (Pyr$_{13}$TFSA) demonstrate a wide electrochemical window (around 6.0 V), and exhibit stable performance when coupled to high-voltage layered oxides such as K$_{0.69}$Ni$_{0.25}$Te$_{1/2}$O$_2$ (Fig. 6G).93,94 Placke et al. demonstrated that ILs based on KTFSA in N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)amide (Pyrr$_{14}$TFSA) can enable...
potassium dual-ion batteries in a potential range from 3.4 V to 5.0 V vs. K⁺/K. In addition, Pasta et al. demonstrated that the KMnFe-PBA cathode can work up to 4.3 V (versus K⁺/K) in a KFSI-based IL electrolyte with high CE and limited Al current collector corrosion (Fig. 6H). More encouragingly, both KFSI- and KTFSI-based ILs show excellent electrochemical performances for the graphite anode. Other anodes such as Sn and Sn₄P₃ were also demonstrated to exhibit good cycling by using KFSI-based ILs.⁹⁷,⁹⁸

While ILs provide good Al passivation, good electrochemical stability and form effective SEIs, their high viscosity, relatively low ionic conductivity, and high cost are likely to prevent their practical applications. Nevertheless, the various combinations of cations and anions in ILs still offer numerous possibilities to PIBs for the desired applications.

2.7 Summary and comparison of different developed electrolytes

In the last several years, different kinds of electrolytes were developed for PIBs. The electrochemical performance of PIBs is closely related to the properties of electrolytes, including the K⁺ ion conductivity, viscosity, chemical/electrochemical/thermal...
stability, the ability to form stable SEI, etc. Ester electrolytes have good ionic conductivity, high thermal stability, and high oxidative stability. EC is an important component of mixed solvents in ester electrolytes as it improves the solubility and ionic conductivity. The binary EC:PC solvent with KPF₆ is a good electrolyte for high-voltage cathode materials. However, ester electrolytes normally have severe side reactions at low potentials due to the formed unstable SEI. Ether electrolytes have good ionic conductivity and low viscosity, and exhibit excellent application for anode materials due to the formation of a stable SEI. However, ether electrolytes have low boiling points and poor oxidative stability, preventing their application for high-voltage cathode materials. Moreover, ether electrolytes are not compatible with graphite anode due to the co-intercalation of K⁺ and ether solvent molecules. The drawbacks of ester and ether electrolytes can be overcome to some extent by increasing the concentration, while HCEs show reduced ionic conductivity, and increased viscosity and cost compared with standard concentration electrolytes. Accordingly, LHCEs are more promising since they retain the advantages of HCEs and standard concentration electrolytes while circumventing the disadvantages of both, but they need to be further exploited. Moreover, ester and ether electrolytes are highly flammable, causing a significant safety issue, particularly with respect to large-scale application of PIBs. The safety can be enhanced in non-flammable electrolytes by using fire-retardant solvents and/or additives, but the battery performance should be optimized. ILs have a broad temperature range and high electrochemical stability, and exhibit good properties for both graphite anode and high-voltage cathode materials. However, their drawbacks of high viscosity, low ion conductivity and high cost need to be addressed toward practical application.

3. Future electrolyte design and considerations for PIBs

Various strategies of electrolyte engineering for PIBs have been summarized in the last section. In this section, we provide several considerations and potential directions for further development of electrolytes for PIBs (Fig. 7 and 8).

3.1. K-ion solvation environment and SEI chemistry

To achieve high performance PIBs, the electrolyte should be compatible with both anodes and cathodes. On the anode side, the SEI formation is critical to achieve high performance. On the cathode side, the oxidative stability of the electrolyte at high-voltages is important. The solvation structure of electrolytes and the derived SEI have a significant impact on the electrolyte stability, ion transport, and battery performance of PIBs.

Compared to Li⁺ and Na⁺, K⁺ is larger in size and has a lower charge density, resulting in much weaker Lewis acidity for K⁺ ions, and thus weaker interaction with Lewis bases such as anions and solvents. This feature provides K⁺ with several advantages such as low ion–solvent interaction, small activation energy for desolvation, small solvation ion radius, and low viscosity, facilitating high rate capability and high ionic conductivity. The solvation structures of MPF₆/EC (M = Li, Na, and K) electrolytes were investigated and compared via first-principles molecular dynamics simulations (MD) (Fig. 7A). It was found that K⁺ has higher average oxygen coordination numbers (7.6) than Li⁺ (4.0) and Na⁺ (5.7) in the first ion solvation shells. The K⁺ ions showed a disordered and flexible solvation structure, which is probably due to the abundant coordinating oxygen atoms, facilitating fast ionic diffusion. In contrast, Li⁺ and Na⁺ ions displayed a tetrahedral solvation arrangement and an intermediate structure between trigonal bipyramidal and square pyramidal geometry, respectively. The MD simulation also indicated that the K⁺ ions in EC have higher diffusion coefficients than Li⁺ ions.

The interaction between the cation and solvent/anion affects both the kinetic properties and stabilities of the electrolytes. Compared to the pure solvents, the coordination of cations and solvents will lower their HOMO and LUMO energy levels, leading to improved oxidation resistance but reduced reduction resistance. First-principles calculations indicated that K⁺–carbonate complexes have lower oxidation stability but higher reduction stability than Li⁺–carbonate complexes (Fig. 7B and C), while the situation is different in K⁺–ether complexes, wherein they exhibit both lower oxidation and reduction stabilities than Li⁺–ether complexes. The results also indicate that the electrolyte properties of PIBs are different from those of LIBs and SIBs, and each electrolyte system needs to be carefully investigated. Lu et al. compared the HOMO and LUMO energies of KPF₆ and KFSI salts and DME, EC, and EMC solvents (Fig. 7D). Both KPF₆ and KFSI have a much lower LUMO energy level than DME, indicating the preferential decomposition of the salt in the DME-based electrolyte. However, the decomposition of KPF₆ and KFSI might compete with the EC and EMC solvents due to their similar LUMOs and HOMOs. The LUMO and HOMO of an electrolyte can be tuned by manipulating its concentration and composition such as the salts, solvents, and additives. The change of LUMO and HOMO energy levels not only affects the oxidation and reduction stabilities, but also the formation of the SEI.

SEI is important for anode materials because most of them work far from the thermodynamic equilibria of the electrolytes. The chemical components of the SEI determine many critical properties such as the K⁺ ion conductivity and mechanical stability, which is related to the K⁺ ion solvation structure of the electrolyte. EC is a critical solvent component in enabling a good SEI for graphite in LIBs. EC is effective in PIBs as well. Ming et al. compared the behaviour of graphite in various ester- and ether-based electrolytes. They found that graphite can run for more than 100 cycles in 1.0 M KPF₆ in EC, while electrolyte decomposition and/or graphite exfoliation was observed in other ester- (e.g. PC, DEC) or ether-based solvents (e.g., DME) (Fig. 3C). It was also reported that graphite exhibits better cycle performance in KPF₆/EC:PC than in KPF₆/EC:DEC electrolyte, due to the decomposition of the DEC solvent. Moreover, the electrolyte can become more compatible with graphite when using KFSI instead of KPF₆. Our group found that a small amount of amorphous SEI was formed on the edge of graphite cycled in 0.8 M-KPF₆/EC:DEC, while the SEI layers are more
clearly observed with a thickness of 5–8 nm in 1 M-KFSI/EC:DEC (Fig. 7E).

The SEI derived from FSI$^-$ anions can be enhanced in high concentration electrolytes. Compared to the SEI formation in 0.9 M-KFSI/TEP, 2 M-KFSI/TEP shows a very uniform thickness (ca. 10 nm) (Fig. 7E). In a highly concentrated environment, the scarcity of solvent molecules allows the salt anions into the first solvation shells, which lowers the LUMO energy level of FSI$^-$ anions, leading to the preferential decomposition of FSI$^-$ anions.

The stabilizing effect of the SEI on the electrode performance has been well recognized, while it has been argued in recent years whether the SEI or solvation structure dominates the role. Ming et al. found that graphite in both LIBs and PIBs can only work well in electrolytes compatible with regulated solvation structures. In contrast, graphite failed in incompatible electrolytes even when it was precoated with an SEI layer formed in a compatible electrolyte. We also designed a series of experiments to investigate the compatibility of graphite in KFSI:TMP electrolytes to understand the role of solvation structure and SEI. As discussed above, graphite exhibited unprecedented stability in a 3:8 (KFSI:TMP) electrolyte due to the nearly 100% solvation of TMP molecules with K$^+$ cations and the formation of FSI$^-$-derived F-rich SEI. In this design, graphite was pre-cycled in the 3:8 (KFSI:TMP) electrolyte to obtain an SEI-coated graphite electrode. Although the SEI-coated graphite exhibits improved cycling performance and CE compared to the graphite in the same 1:8 (KFSI:TMP) electrolyte, the performance is still worse than for the graphite in the 3:8 (KFSI:TMP) electrolyte. The results indicate that the SEI derived from the compatible electrolyte (3:8) has a positive

Fig. 7  (A) Typical solvation structures of (a) Li$^+$, (b) Na$^+$, and (c) K$^+$ ions in EC. Reprinted with permission from ref. 99. Copyright 2017, American Chemical Society. Summary of (B) LUMO and (C) HOMO energy level changes of the ion–solvent complexes compared with those of the pure solvents. Reproduced with permission from ref. 100. Copyright 2018 John Wiley and Sons. (D) HOMO and LUMO energy levels of the potassium salts (KPF$_6$ and KFSI) and solvents (DME, EC, and EMC). Reprinted with permission from ref. 66. Copyright 2018 John Wiley and Sons. (E) STEM images of graphite cycled in 0.8 M-KPF$_6$/EC:DEC (i), 1 M-KFSI/EC:DEC (ii), 0.9 M-KFSI/TEP (iii), and 2 M-KFSI/TEP (iv). Reprinted with permission from ref. 89. Copyright 2020 John Wiley and Sons. (F) Schematic illustrations of the solvation structure and SEI formation on graphite in 1:8 (KFSI:TMP) electrolyte (i) and 3:8 (KFSI:TMP) electrolyte (ii), respectively; iii) the schematic illustration shows a pre-cycled graphite electrode with an F-rich interface cycling in 1:8 (KFSI:TMP) electrolyte. (The orange and red symbols represent the TMP solvent molecule and the FSI$^-$ anion, respectively). Reprinted with permission from ref. 90. Copyright 2021 John Wiley and Sons.
K salts are critical for PIB electrolytes. Compared to KPF$_6$, KFSI is more compatible with the anode materials as the FSI$^-$ anion can induce a more stable SEI. However, KFSI has certain issues at high voltages due to the corrosion of Al. In contrast, KTFSI works better than KFSI at high voltages. The anion of the K salt not only determines the quality of the SEI, but also the oxidative stability. Therefore, design of K salts with novel anions could bring huge opportunities. For example, various fluorosulfonilimides have been reported in LIBs with excellent performance.$^{105-109}$ In addition, fluorine-free anions are also worth exploring. Besides the new anion salts, the combination of different existing and/or new salts can be explored, as a synergy could be probably created to boost the performance of PIBs.

Solvents are also crucial to PIB electrolytes. Nevertheless, the weak interaction of the K$^+$ ion and solvents leads to the low solubility of the K salt. Solvents that have strong interactions with K$^+$ can be explored as they could dissolve more K salts.Ether solvents are more compatible with anodes than carbonate solvents, while the former have weaker oxidation stability. Increasing the fluorination degree of solvents is beneficial for batteries due to their high oxidative stability and F-rich SEI formation.$^{109,110}$ For example, Cui and Bao synthesized a new fluorinated analog of DME, 1,4-dimethoxylbutane (FDMB), and found that 1 M LiFSI/FDMB showed a high oxidative stability of ~6 V.$^{109}$ Therefore, fluorinated solvents can be explored for developing advanced PIB electrolytes. Fluorine-free solvents are also worth exploring due to their eco-friendliness. In addition, non-flammable and low-vapour pressure solvents could be further explored for increasing the battery safety or thermostability. Moreover, the solvents can be mixed to create synergistic effects to further improve the performance of PIBs.

Additives are used in small amounts in the electrolytes, but they can tune the electrolyte properties in several ways, including the solvation structure, the working temperatures, the oxidative stability, and the formation of the SEI. However, only a few additives are reported for PIBs. In contrast, countless additives have been reported for LIBs. Therefore, opportunities exist for additives as in the case of LIBs or SIBs. In addition, other novel additives could be designed through organic and inorganic synthetic methods.

### 3.3. Fundamental understanding and practical considerations for developing PIB electrolytes

Besides the design of components, another direction is highly needed in deeply understanding the structure–property relationships among the electrolyte structure, the electrode–electrolyte interface, and the electrochemical properties. It is challenging to fully understand the highly complex interfacial phenomena between the interacting solvent–solvent, ion–ion, and solvent–ion networks, as well as their physical properties and their influence on SEI formation, composition, structure and function. However, advanced computational and experimental tools, including in situ and operando characterization techniques can be used to quantitatively describe the characteristics and properties of electrolytes and SEI formation and
evolution, and elucidate the structures and properties on both the molecular and the mesoscale. In situ differential electrochemical mass spectrometry (DEMS) can be used to investigate the electrolyte decomposition and the reaction mechanisms of the SEI formation. In situ Raman/Fourier transform infrared spectroscopy can be employed to generate local surface/interface composition images and detailed state-of-charge maps to investigate the electrolyte and the electrode/electrolyte interface evolution during charge–discharge processes. In situ AFM can be employed to show the SEI layer on the surface of the electrodes. In situ TEM can be used to investigate the morphology and chemical composition of the SEI layer. This understanding will facilitate the development of PIBs through rational electrolyte design.

For the design of PIB electrolytes, we also need to consider their practicality for real applications of PIBs. It has been agreed that PIBs are unlikely to compete with LIBs for high-energy applications such as portable electronics and EVs. Pasta et al. calculated that the highest energy density of PIB can only reach 58% of the NMC811 LIB. However, they found that PBA in PIBs is comparable with LFP in terms of both cost (80 vs. 88 USD kW h⁻¹ for LFP) and energy density. It is also noteworthy that the PBA in PIB is cost competitive with the SIB (80 vs. 84 USD kW h⁻¹) and achieves a higher energy density. Therefore, PIBs are likely to find opportunities in low-range EVs and grid-scale storage. In these two kinds of applications, the cost, safety, lifetime, and the wide temperature operation of batteries are important, and thus, these parameters should be considered in designing K salts, solvents, and additives for PIB electrolytes.

3.4. Critical metrics for evaluating PIB electrolytes

The electrolyte is a key to PIBs as it governs their performance and lifetime, while the test parameters can significantly affect the results. These critical parameters include the loading of active materials, the binder, the ratio of active materials, carbon and binder, the electrolyte amount, and the testing conditions such as charge/discharge current density, voltage cut-off range, temperature, etc. For half cells, the thickness and area of K metal should be known. For full cells, the ratio of the positive electrode to the negative electrode should be known. The community has tried to set a standardized criterion to test and evaluate the battery performance. For example, several journals proposed checklists for battery research, which provide excellent guidance for electrolyte research as well.111,113

Besides these key parameters, we need to be careful in evaluating the electrolytes and electrodes in half cells, where K metal is employed as the counter and reference electrode. K metal is highly reactive in electrolytes and forms thick and unstable surface layers, depending on the electrolyte formation.15 It was reported that the polarization on K stripping/plating is much larger than that of Li or Na, which could result in inaccurate evaluation of the electrochemical properties of electrolytes and electrodes. Moreover, the reactive side-products from the K metal and electrolyte can be transferred to the working electrode materials, which affects the SEI formation and leads to electrolyte decomposition and electrode degradation. Therefore, K metal is not a reliable reference or counter electrode. The issues of K metal can be solved by pre-treating the K metal electrochemically in a compatible electrolyte. Komaba et al. found that a highly concentrated electrolyte of 3.9 M KFSI/DME shows a small polarization of 25 mV for K metal, and demonstrated that pre-treated K metal in this electrolyte can be reliably used as a reference or counter electrode in half cells to evaluate the performance of electrode materials.114 It is beyond doubt that a great challenge in the evaluation of effective electrolytes in half cells is the side reactions between the electrolyte and K metal. Therefore, it is a good idea to adopt the re-treated K metal to evaluate the developed electrolytes in half cells. However, the effectiveness of PIB electrolytes should be further evaluated in full cells in which no potassium metals are employed.

Conflicts of interest

There are no conflicts of interests to declare.

Acknowledgements

Financial support provided by the Australian Research Council (ARC) (LP160101629, DP200101862, FL210100050) is gratefully acknowledged.

References