


Perspective

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Could potassium-ion batteries become a competitive technology?

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Abstract

Potassium-ion batteries (PIBs) have attracted significant attention as a complement to lithium-ion and sodium-ion batteries (SIBs). PIBs can theoretically provide higher specific energy and power density than SIBs due to lower standard electrode potential of K/K⁺ and faster K⁺ ion diffusion, maintaining the benefits of low-cost and sustainability. However, research on PIBs is in its infancy; therefore, further efforts are necessary to enhance their performance and position them as a competitive technology. In this perspective, the remaining challenges and possible strategies to advance the development of PIBs are presented.

Keywords: Sustainability, energy storage, potassium-ion batteries, electrolyte, cathode, anode

STATE-OF-THE-ART

To achieve climate neutrality, the number of renewable energy sources and clean energy carriers should



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significantly increase, reducing the dependence on fossil fuel consumption. In parallel, novel efficient energy storage solutions must be developed for grid and household applications along with the implementation of sustainable and smart technologies in transportation systems. The electric vehicle industry is growing considerably, as are stationary energy storage systems (EES), which will become a key facet towards the realization of a sustainable society. Environmentally friendly, efficient, and powerful energy storage devices are required. In this context, batteries are a key technology, with lithium-ion batteries (LIBs) being the preferred choice for electromobility due to their high energy density. However, they utilize toxic (i.e., cobalt) or critical raw materials, i.e., cobalt, natural graphite, and lithium^[1]. As a consequence, the feasibility of LIBs for application in large-scale renewable EES is uncertain. This necessitates the development of alternative EES composed of earth-abundant elements that meet the cost, sustainability, availability, and good performance metrics.

Sodium-ion batteries (SIBs) are a competitive technology because they are environmentally friendly, sustainable, and cost-effective^[2]. Sodium-based electro-active materials are made from non-critical raw materials, such as manganese- and iron-based layered oxides or Prussian Blue analogs (PBAs) as cathodes and biowaste-derived hard carbon anodes^[3]. In addition, aluminum can be used as anode current collector because sodium does not alloy with aluminum at low potential^[4]. The main challenge of SIBs is to enhance their energy and power density to be more competitive with LIBs. Experimental energy densities of 711 W·h·kg⁻¹ and more than 1,450 W·h·kg⁻¹ have recently been reported for LIBs at the cell level (with practical batteries around 350 W·h·kg⁻¹)^[5]. Nevertheless, Contemporary Amperex Technology Co., Limited (CATL) announced the commercialization of SIBs with 160 W·h·kg⁻¹ and more than 2,000 cycles by 2023^[6].

In theory, potassium-ion batteries (PIBs) can achieve superior energy and power densities than SIBs, considering their lower standard electrode potential and faster ion diffusion^[7]. Austin-based PIB startup Group 1 aims for a large-scale launch of PIB production by 2027 due to comparable energy density to lithium iron phosphate (LFP)-based LIBs^[8]. For the research-based development of PIBs, further advances are necessary in electrode and electrolyte design, understanding of the interfacial chemistry, and manufacturing potassium full cells to enhance their viability.

POTASSIUM-ION BATTERY ADVANTAGES

The main expected advantages of PIBs in comparison to other technologies, such as LIBs and SIBs, include affordability and environmental friendliness resulting from the material replacement in PIBs *vs.* LIBs, along with higher power density, high energy density, and safety of PIBs *vs.* SIBs due to the more negative voltage of reduction of K metal [Figure 1]^[9,10]. However, these properties are not supported by experimental data. In fact, the current performance and safety of PIBs are inferior to that of both LIBs and SIBs [Figure 1]. Recent energy density calculations hardly reach 160 W·h·kg⁻¹ for PIBs^[11]. Regarding the inferior safety of PIBs, the literature points out the highest reactivity of K metal with respect to Li and Na. While it is understood that PIBs do not contain metallic K, the risk of metal plating on the anode exists for low-voltage anode materials when using high currents, making PIBs less safe. Nevertheless, research on PIBs is still in its infancy; thus, the potential for them to become a feasible technology remains open.

Low-cost and environmentally friendly technology

PIBs can be made with abundant and non-critical raw materials, such as aluminum, iron, manganese, potassium, *etc.*, avoiding the use of critical raw and scarce elements (i.e., lithium, cobalt, copper, nickel, natural graphite) used in LIBs^[1]. An aluminum current collector can also be used in both electrodes because potassium does not alloy with aluminum to thermodynamically form intermetallic compounds, thus reducing battery cost and weight^[12]. For example, in the case of SIBs, 55% and 3% of battery mass and cost

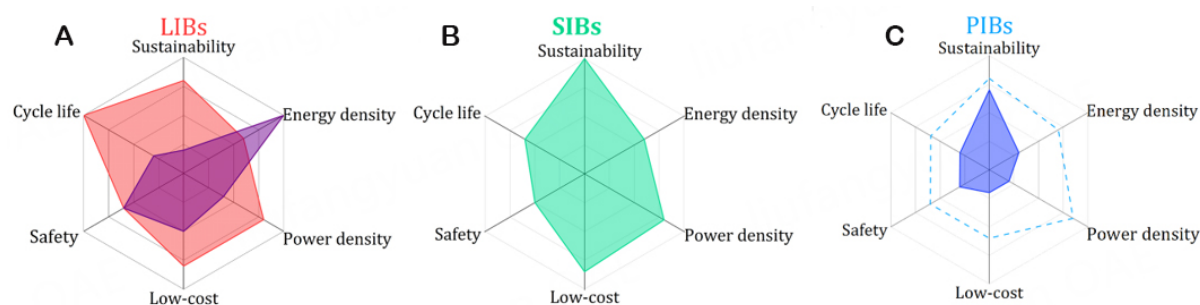


Figure 1. Radar plot of electrochemical, sustainability, and cost properties of (A) LIBs (red: LFP-based and purple: lithium nickel manganese cobalt oxides (NMC)-based LIBs), (B) SIBs, and (C) PIBs (cyan dots: theoretical values and blue line: experimental values)^[9,10].

reduction can be obtained by replacing 10 μm thick copper with 15 μm thick aluminum^[13]. A similar outcome could be expected for PIBs.

Potential high power and energy density

PIBs could provide high power densities because K^+ ions diffuse faster than Li^+ and Na^+ ions in liquid electrolytes^[14]. This is due to weaker Lewis acidity and Coulombic interactions with the anions and solvents. The K^+ ion exhibits smaller Stokes radii (3.6 Å) in propylene carbonate (PC) than Na^+ and Li^+ ions (i.e., 4.6 Å and 4.8 Å, respectively). In addition, the K^+ ion shows lower desolvation energy; thus, PIBs might exhibit enhanced rate capability. Nevertheless, the K^+ ion diffusion in the electrolyte is not the only factor to be considered. Indeed, the power capability is still poor compared to LIBs and SIBs due to the limited K^+ ion kinetics within the electro-active materials.

Moreover, PIBs could also be considered high energy density batteries, mainly due to the low standard electrode potential of K/K^+ (-2.93 V vs. SHE), even lower than Li/Li^+ in organic electrolytes^[14], leading to high operating average voltages.

Potassium metal reactivity

A controversial opinion remains in the research field regarding the safety properties of PIBs due to the higher reactivity of K metal than Li or Na. However, the lower standard electrode potential of K/K^+ compared with Li/Li^+ and Na/Na^+ could reduce the chances of K metal plating due to overpotential at low voltages. In addition, the higher reactivity of K metal (compared to Li and Na metal) may have a positive impact, similar to the way metallic Al reacts when it comes into contact with oxygen^[15]. This reaction facilitates easy interaction with the liquid electrolyte, rapidly forming a coherent solid electrolyte interphase (SEI) to protect the electrode surface from further decomposition reactions.

CHALLENGES OF POTASSIUM-ION BATTERIES

Although PIBs possess several advantages, the experimental results are far from the theoretical properties. Consequently, several challenges must be overcome for their practical implementation [Figure 2].

Low K^+ ion diffusion and poor K^+ ion reaction kinetics

It is expected that PIBs possess a high rate capability due to the weak Lewis acidity and small Stokes radii in solvents. However, poor ion diffusivity and kinetically limited reactions are commonly reported in electro-active materials with small tunnels or interlayer cavities, such as polyanion compounds and layered oxides^[16,17]. The main reason is the larger ionic radius of unsolvated potassium in comparison to lithium and sodium. As examples, K^+ ions can be poorly inserted in polyanion compounds, i.e., olivine phase

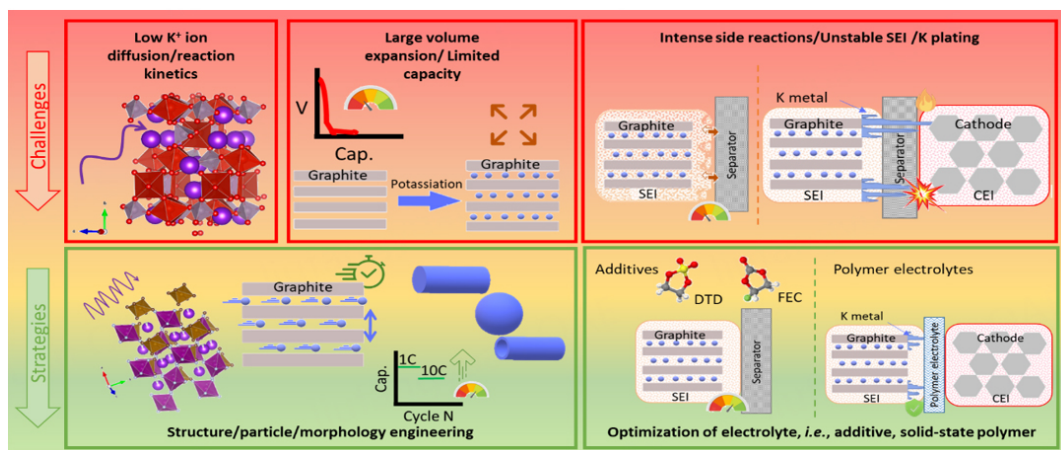


Figure 2. Challenges of PIBs and possible strategies to resolve the issues.

$\text{Li}_{1-x}\text{K}_x\text{FePO}_4$ ($0 < x < 0.03$)^[16], while in P3-layered oxides, they usually show slow K^+ ion mobility at high voltages, inducing rapid capacity fading^[17].

Larger volume changes upon K^+ ion (de)insertion/(de)intercalation

The large size of the K^+ ion also induces poor long-term stability due to the large volume change upon cycling. Therefore, large cavity electro-active materials must be designed to improve the structural stability and extend the lifetime of PIBs.

The anode of choice for PIBs is graphite due to the possibility of intercalating K^+ ions and forming KC_8 , which delivers a reversible capacity of 279 mAh g^{-1} ^[18]. However, the large volume expansion of graphite after potassiation (61%), which is six times larger than for lithiation, results in relatively fast capacity decay. Similar behavior is observed for K-based layered oxide cathodes, where the large volume expansion upon cycling induces permanent structural changes, high hysteresis, and poor cycling stability^[19].

In-situ investigations of electrode materials during battery operation can provide very useful information with respect to structural transitions or changes in the oxidation state of transition metals and are particularly informative with respect to the crystallographic volumetric expansions^[7,20].

Side reactions, electrolyte consumption, SEI formation

The commonly used liquid electrolytes of LIBs and SIBs, i.e., carbonate- or ether-based solvents, are unstable at low potential. Furthermore, the high reactivity of K metal with liquid electrolytes easily induces electrolyte decomposition, delivering low Coulombic efficiencies. In addition, the formed SEI is often unstable, increasing polarization and reducing long-term stability. Many studies have demonstrated the importance of electrode-electrolyte formulation to avoid unfavorable side reactions and achieve good electrochemical performances. For example, potassium bis(fluorosulfonyl)imide (KFSI) salt leads to the formation of stable SEI due to the decomposition products of the anion and the reduction of free solvents due to the stronger solvation^[21,22]. In contrast, the potassium hexafluorophosphate (KPF_6) decomposition products do not stabilize the SEI.

Solvent selection is also critical; cyclic carbonates, i.e., ethylene carbonate (EC) and PC, form stable SEI and provide higher Coulombic efficiencies. Meanwhile, the linear carbonates (dimethyl carbonate (DMC) or diethyl carbonate (DEC)) are not appropriate for stabilizing the SEI, leading to poor capacity retention as

reported for graphite anodes and KVPO_4F and KVOPO_4 polyanion cathodes^[23,24]. Nonetheless, SEI studies should also be performed on full cells since cross-contamination from very unstable SEI on metallic K may lead to misinterpretations.

Battery safety hazards

PIBs are considered to present safety hazards due to the high reactivity and low melting point (63 °C) of K metal. However, it has been reported that the heat generation during thermal runaway in PIBs is lower than in LIBs^[25]. In addition, the K metal reactivity towards liquid electrolytes can be decreased by using electrolytes, such as triethyl phosphate (TEP) or trimethyl phosphate (TMP), or ionic liquids due to the formation of a protective layer^[26,27]. Another strategy is to substitute liquid electrolytes with solid-state electrolytes, such as ceramics or polymers^[28], which are non-flammable and could suppress/reduce dendrite growth.

OVERCOMING THE CHALLENGES

Electrolytes: from liquids to polymers

Research on PIB electrolytes is dominated by fluorinated organic salts dissolved in liquid carbonate or ether solvents, as in LIBs and SIBs. If a fire or explosion occurs, the fluorinated salt can release toxic fluoro-organic compounds, i.e., bis(2-fluoroethyl)-ether^[29] and hydrofluoric acid^[30]. Moreover, ether solvents limit the upper voltage cut-off to < 3.8 V vs. K/K⁺, restricting the use of high-voltage cathode materials. The surface modification of active materials or the addition of electrolyte additives can reduce side reactions and stabilize the SEI. The electrolyte additives decompose at a higher potential than solvents, forming a stable SEI and preventing further side reactions. For example, it is known that vinylene carbonate (VC) and fluoroethylene carbonate (FEC) are good additives for lithium- and sodium-ion systems, respectively^[31,32]. However, they significantly decrease the capacity and stability of PIBs due to the formation of high concentrations of insoluble KF and K_2CO_3 , which increase the interfacial resistance and hinder K⁺ ion transport through the SEI^[33]. In contrast, it has been demonstrated that sulfur-based additives, such as ethylene sulfide (DTD), can suppress the side reactions and form a stable SEI on graphite anodes and PBA cathodes^[34,35].

Replacing flammable carbonate- and ether-based electrolytes could also enhance the stability of PIBs. If non-flammable solvents are used, the PIB safety profile is also ameliorated. TEP and TMP are well-known non-flammable solvents for SIBs and PIBs; they form a robust and stable SEI, enhancing cycling stability^[36]. Ionic liquids are another non-flammable alternative. For example, KFSI or potassium bis(trifluoromethanesulfonyl) imide (KTFSI) mixed with pyrrolidinium-based ionic liquid form effective SEI, leading to good electrochemical performance^[37].

Finally, polymer electrolytes could overcome the side reactions and safety challenges of PIBs^[38]. Incipient research in solid-state PIBs shows that the main challenges are the low ionic conductivity at room temperature and the interfacial charge transfer due to low wetting and compatibility. However, for example, Ni_3S_2 @Ni cathode electrodes exhibit higher capacity retention in PEO-KFSI solid electrolytes than in carbonate-based electrolytes, suggesting further investigations on the use of solid electrolytes for long-term cycling PIBs^[39]. In addition, the ionic conductivity could be improved by adding inorganic fillers, such as Al_2O_3 , SiO_2 , etc.^[40]. Moreover, mixing with additives such as carbonate solvents or ionic liquids, which result in gel electrolytes, can enhance ionic conductivity at room temperature and reduce the electrolyte-electrode charge transfer resistance^[41].

3D structure cathode materials

PBAs are the most promising materials among the families of 3D materials proposed as cathodes for PIBs, i.e., layered oxides, phosphates, and PBAs^[42]. Their 3D open framework structure provides suitable channels and interstitial sites for large K^+ ion diffusion, allowing faster K^+ ion kinetics. One of the main drawbacks of layered oxide and polyanion compounds is the low K^+ ion content in the structure. This is related to the strong K^+ - K^+ repulsion in the interlayer and small cavities^[43]. Particle morphology engineering could facilitate ionic transport, shortening the ion diffusion distance and allowing faster K^+ ion diffusion. Furthermore, this engineering could be suitable for controlling the volume expansion upon cycling, preventing the SEI cracking upon (dis)charge, and delivering superior cycle life.

Among the PBAs, the Fe-/Mn-based Prussian White (PW), $K_2Mn_2[Fe(CN)_6]$ ^[44], is the most promising. It exhibits the reversible insertion of two K^+ ions *per* formula unit at a voltage of 4.0 V *vs.* K/K^+ . Cycle life approaches 8,000 cycles when controlling the crystallinity and defect content. However, PBAs have two limitations: low bulk density and low electron conductivity, originating from their structure and chemical bond^[43], resulting in lower specific capacity and inferior performance compared to layered oxides. The low bulk density of PBAs is difficult to overcome. Modifying the mixing conditions of electrode components and using large particle sizes and additives can improve the density and homogeneity of the electrode. Meanwhile, metal substitution and/or carbon coating could overcome their poor electronic conductivity. Unfortunately, the latter strategy requires temperatures above the thermal stability of PW. One possible approach is a hybridization or coating of the PW active material with electronically conducting polymers, acting as conducting additives and binders^[45].

Alternative anode materials

Graphite reversibly (de)intercalates K^+ ions around 250 mAh·g⁻¹ in liquid electrolytes^[14]. However, low initial Coulombic efficiencies, severe capacity fading, and moderate rate capabilities are observed, related to the 61% volume change during K^+ ion (de)intercalation. In addition, the very low insertion voltage implies a risk of K metal plating at high C-rates, yet it remains the anode of choice for PIBs.

Other carbon-based materials can be used as anodes. For example, hard carbon anodes deliver ~215 mAh·g⁻¹ with negligible hysteresis due to the weaker interaction of K^+ ions with the terminal functional groups^[42]. The potassium full cell based on a hard carbon anode and $K_{0.3}MnO_2$ layered oxide shows encouraging electrochemical properties over 100 cycles with a Coulombic efficiency of 99%^[46]. Nevertheless, hard carbons still have several limitations, such as low (initial) Coulombic efficiencies and low specific capacity. The former can be enhanced by optimizing the electrode-electrolyte configuration, such as replacing the conventional carbonate-based electrolytes with glyme, TEP, TMP, or ionic liquids, which might provide better electrochemical performances, as shown in SIBs^[47,48]. Meanwhile, the latter can be addressed *via* structure/morphology engineering^[49] or N, P, S, *etc.*, doping. Indeed, the P-doped hard carbon delivers higher reversible capacity than un-doped hard carbon, which was attributed to the improved adsorption of K^+ ions due to the P-O and P-C bonds^[50,51]. One of the advantages of hard carbons as anode materials is that bio-waste precursors can be used^[52], supporting the circular economy, recycling, and lowering production costs. However, hard carbons derived from bio-waste usually generate a large specific surface area, leading to high first cycle irreversible capacity. Therefore, to avoid highly porous hard carbons, the synthesis route should be controlled, i.e., pre-/post-treatments and pyrolysis parameters (temperature and time).

As alternative anode materials, metal oxides are interesting for high-power PIBs. In particular, titanium-based oxides exhibit high density and low-cost. Furthermore, the K^+ ion insertion typically occurs at higher voltages than in carbon-based anodes, enabling a fast charge without the risk of K metal plating.

Nanostructured layered materials prepared through hydrothermal processes followed by high-temperature calcination show some degree of K^+ ion insertion, suggesting surface adsorption rather than bulk insertion. Regarding tunneled oxides, the hollandite-type structures (e.g., $K_{0.17}TiO_2$) enable fast bulk diffusion, delivering $60 \text{ mAh}\cdot\text{g}^{-1}$ at $5C$ ^[53]. Fine-tuning the metal doping in known hollandites and hexagonal bronzes will optimize the ionic and electron transport properties. In addition, particle morphology control could minimize the dimension along which K^+ ions and electrons travel, enhancing the power capability.

Alloying materials (Sn, P, Bi, Sb, Pb, Ge, *etc.*) also represent a large class of anode materials with high reversible capacities and high energy densities^[54]. However, they do not stand out as the most sustainable and abundant materials and, therefore, are not candidates for sustainable large-scale batteries. Meanwhile, organic electro-active materials are often produced through low-cost synthesis methods while delivering competitive electrochemical performance^[55]. Potassium terephthalates (PETs) deliver reversible capacities of $250 \text{ mAh}\cdot\text{g}^{-1}$ at an average voltage of 0.3 V vs. K/K^+ , making them suitable for use as anodes^[56]. Even more sustainable, PETs derived from recycled plastic films show similar capacities at a slightly higher voltage of 0.7 V vs. K/K^+ ^[57].

TOWARD SUSTAINABLE POTASSIUM-ION BATTERIES

Electrode material chemistry

PIBs can be considered sustainable and low-cost devices because electrodes can be based on non-critical raw materials. As a negative electrode, although potassium can be intercalated into graphite, more sustainable carbon-based species could be implemented, such as bio-waste-derived hard carbons. For example, Mn-/Fe-based PW and bio-waste-derived hard carbons can be synthesized by low energy routes, i.e., PW by room temperature precipitation and hard carbons at a lower temperature than graphite ($< 1,500 \text{ }^\circ\text{C}$)^[44,52].

Electrode manufacturing

The standard electrode processing is based on a polyvinylidene difluoride (PVDF) binder, which is soluble in hazardous, irritating, and teratogenic N-methyl-2-pyrrolidone (NMP)^[58]. Therefore, additional focus on alternative electrode processing using a low-cost and low-carbon footprint system should be performed [Figure 3A]. For example, bio-sourced aqueous binders should be employed to ensure the reuse and recycling of electrode materials^[58]. In addition, several reported works demonstrated superior electrochemical performance in terms of Coulombic efficiencies and cycling using water-soluble binders, i.e., carboxymethyl cellulose (CMC) and sodium polyacrylate (PAANa). This enhancement has been attributed to the formation of an effective SEI^[59].

The recycling and separation of the different components found in LIBs have yet to be standardized^[60]. The metallurgical routes and processes employed are energy-consuming. In some cases, the waste derived from processes such as lixiviation, e.g., mother liquors and gaseous emissions, is harmful and far from being environmentally friendly. The recycling of PIBs using sustainable materials should enable the realization of such batteries to satisfy the requirements of a (battery) circular economy.

Advanced characterization tools to extend the lifetime of PIBs

The manufacture of reliable long-cycle life PIBs should also be targeted. The study of the stability of the electrode and electrolyte materials, the interfacial chemistry, relevant ion diffusion mechanisms, and the formation and decomposition of the SEI are important for developing high specific energy/power devices with extended lifetime. PIBs are still at an early stage of development; hence, little is known about the formation, composition, and evolution of SEI. Similar to LIBs and SIBs, advanced analytical tools are requisite to probe ion transport across the electrode-electrolyte interfaces. As the SEI is a nanoscale heterogeneous, disordered, and reactive layer, standard characterization tools are limited in their

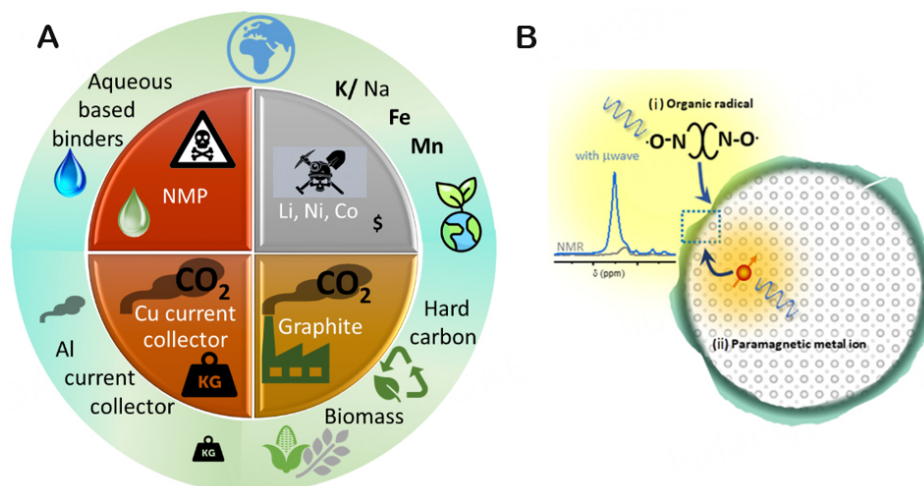


Figure 3. (A) Scheme towards more sustainable PIBs. (B) A schematic showing the paths for enhancing NMR signals from chemical environments in the SEI through DNP from different polarizing agents: in (i), organic biradicals are used as an exogenous source of polarization, and in (ii), paramagnetic metal ions are introduced as dopants into the bulk of the material. In both cases, microwave irradiation results in polarization transfer from the unpaired electrons to the nuclei in the sample, thereby enhancing their polarization and making them easily detectable in NMR.

applicability. For example, solid-state nuclear magnetic resonance (ssNMR) spectroscopy might be a versatile technique, providing an atomic-molecular scale insight into the composition and structure of the electrode-electrolyte interface^[61]. Leveraging the successful developments of this approach to probe interphases in LIBs, the nuclear magnetic resonance (NMR) methodology could also be adapted and developed to investigate the SEI on PIB anodes. Dynamic nuclear polarization (DNP) could be employed to increase the sensitivity of ssNMR to detect hidden and buried interfaces [Figure 3B]^[62,63]. In DNP, the large electron spin polarization is transferred to surrounding nuclear spins, increasing the sensitivity of their detection in ssNMR by up to four orders of magnitude. In combination with X-ray photoelectron spectroscopy (XPS) for investigating the SEI chemical composition in PIBs^[64] and advanced transmission electron microscopy (TEM) for evaluating changes in the electrode surface structure, detailed chemical composition maps and structural insights into the architecture of the SEI can be gained. The correlation between electrochemical performance and chemical and morphological properties of the SEI will provide valuable information about potential strategies to enhance the lifetime of PIBs. Besides, *in-situ* and *ex-situ* ssNMR approaches can be employed to monitor K⁺ ion transport across the electrode-electrolyte interface. The correlation of ion exchange rates with the SEI composition can guide the choice of beneficial electrode-electrolyte formulations.

Advanced characterization techniques and *in-situ* and *operando* experiments will be crucial to understanding the degradation mechanism and the correlations among structures, morphology, K⁺ ion transport, and performance. This will allow the discovery of advanced anode and cathode materials with enhanced K⁺ ion kinetics and high energy/power densities. In addition, future research directions must involve designing alternative electrolyte formulations (non-flammable liquid electrolytes or solid-state electrolytes) that enable the formation of a stable SEI and mitigate side reactions, providing extended cycle life. Finally, the practical potential of PIBs should be investigated by manufacturing real cells (i.e., full cells). Resolving these standing problems can realize PIBs as a competitive technology in the near future.

DECLARATIONS

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Availability of data and materials

Not applicable.

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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REFERENCES

1. RMIS - raw materials information system. Available from: <https://rmis.jrc.ec.europa.eu/?page=crm-list-2020-e294f6/> [Last accessed on 14 Aug 2023].
2. Goikolea E, Palomares V, Wang S, et al. Na-ion batteries - approaching old and new challenges. *Adv Energy Mater* 2020;10:2002055. DOI
3. Hasa I, Mariyappan S, Saurel D, et al. Challenges of today for Na-based batteries of the future: from materials to cell metrics. *J Power Sources* 2021;482:228872. DOI
4. Murray JL. The Al-Na (aluminum-sodium) system. *Bull Alloy Phase Diag* 1983;4:407-10. DOI
5. Li Q, Yang Y, Yu X, Li H. A 700 Wh kg⁻¹ rechargeable pouch type lithium battery. *Chin Phys Lett* 2023;40:048201. Available from: <https://iopscience.iop.org/article/10.1088/0256-307X/40/4/048201/meta> [Last accessed on 14 Aug 2023].
6. CATL news. The first-generation sodium-ion battery launch event. Available from: <https://www.catl.com/en/news/685.html> [Last accessed on 14 Aug 2023].
7. Xu Y, Titirici M, Chen J, et al. 2023 roadmap for potassium-ion batteries. *J Phys Energy* 2023;5:021502. DOI
8. Energy storage news. Available from: www.energy-storage.news/potassium-ion-battery-startup-group1-lfp-is-our-benchmark/ [Last accessed on 14 Aug 2023].

9. Xu Z, Wang J. Toward emerging sodium-based energy storage technologies: from performance to sustainability. *Adv Energy Mater* 2022;12:2201692. DOI
10. Liu M, Wang Y, Wu F, et al. Advances in carbon materials for sodium and potassium storage. *Adv Funct Mater* 2022;32:2203117. DOI
11. Sun L, Li G, Zhang S, et al. Practical assessment of the energy density of potassium-ion batteries. *Sci China Chem* 2022. DOI
12. Songster J, Pelton AD. The Al-K (aluminum-potassium) system. *JPE* 1993;14:366. DOI
13. Vaalma C, Buchholz D, Weil M, Passerini S. A cost and resource analysis of sodium-ion batteries. *Nat Rev Mater* 2018;3:18013. DOI
14. Komaba S, Hasegawa T, Dahbi M, Kubota K. Potassium intercalation into graphite to realize high-voltage/high-power potassium-ion batteries and potassium-ion capacitors. *Electrochem Commun* 2015;60:172-5. DOI
15. Greenwood NN, Earnshaw A. Chemistry of the elements. Oxford: Pergamon Pub; First edition 1984, reprinted 1989, p. 253.
16. Madram AR, Daneshtalab R, Sovizi MR. Effect of Na⁺ and K⁺ co-doping on the structure and electrochemical behaviors of LiFePO₄/C cathode material for lithium-ion batteries. *RSC Adv* 2016;6:101477-84. DOI
17. Nathan MGT, Yu H, Kim GT, et al. Recent advances in layered metal-oxide cathodes for application in potassium-ion batteries. *Adv Sci* 2022;9:e2105882. DOI PubMed PMC
18. Jian Z, Luo W, Ji X. Carbon electrodes for K-ion batteries. *J Am Chem Soc* 2015;137:11566-9. DOI PubMed
19. Zhang X, Wei Z, Dinh KN, et al. Layered oxide cathode for potassium-ion battery: recent progress and prospective. *Small* 2020;16:2002700. Available from: <https://onlinelibrary.wiley.com/doi/abs/10.1002/sml.202002700> [Last accessed on 23 Aug 2023].
20. Yang J, Muhammad S, Jo MR, et al. In situ analyses for ion storage materials. *Chem Soc Rev* 2016;45:5717-70. DOI
21. Zhang Q, Mao J, Pang WK, et al. Boosting the potassium storage performance of alloy-based anode materials via electrolyte salt chemistry. *Adv Energy Mater* 2018;8:1703288. DOI
22. Wang H, Wang H, Chen S, et al. A depth-profiling study on the solid electrolyte interface: bis(fluorosulfonyl)imide anion toward improved K⁺ storage. *ACS Appl Energy Mater* 2019;2:7942-51. DOI
23. Zhao J, Zou X, Zhu Y, Xu Y, Wang C. Electrochemical intercalation of potassium into graphite. *Adv Funct Mater* 2016;26:8103-10. DOI
24. Chihara K, Katogi A, Kubota K, Komaba S. KVPO₄F and KVOPO₄ toward 4 volt-class potassium-ion batteries. *Chem Commun* 2017;53:5208-11. DOI PubMed
25. Zhang W, Liu Y, Guo Z. Approaching high-performance potassium-ion batteries via advanced design strategies and engineering. *Sci Adv* 2019;5:eaav7412. DOI PubMed PMC
26. Zeng G, Xiong S, Qian Y, Ci L, Feng J. Non-flammable phosphate electrolyte with high salt-to-solvent ratios for safe potassium-ion battery. *J Electrochem Soc* 2019;166:A1217. DOI
27. Silvester DS, Jamil R, Dobliger S, Zhang Y, Atkin R, Li H. Electrical double layer structure in ionic liquids and its importance for supercapacitor, battery, sensing, and lubrication applications. *J Phys Chem C* 2021;125:13707-20. DOI
28. Zhu X, Ali RN, Song M, Tang Y, Fan Z. Recent advances in polymers for potassium ion batteries. *Polymers* 2022;14:5538. DOI PubMed PMC
29. Hammami A, Raymond N, Armand M. Lithium-ion batteries: runaway risk of forming toxic compounds. *Nature* 2003;424:635-6. DOI PubMed
30. Sloop SE, Pugh JK, Wang S, Kerr JB, Kinoshita K. Chemical reactivity of PF₅ and LiPF₆ in ethylene carbonate/dimethyl carbonate solutions. *Electrochem Solid-State Lett* 2001;4:A42. DOI
31. Hekmatfar M, Hasa I, Eghbal R, Carvalho DV, Moretti A, Passerini S. Effect of electrolyte additives on the LiNi_{0.5}Mn_{0.3}Co_{0.2}O₂ surface film formation with lithium and graphite negative electrodes. *Adv Mater Interfaces* 2020;7:1901500. DOI
32. Komaba S, Ishikawa T, Yabuuchi N, Murata W, Ito A, Ohsawa Y. Fluorinated ethylene carbonate as electrolyte additive for rechargeable Na batteries. *ACS Appl Mater Interfaces* 2011;3:4165-8. DOI PubMed
33. Eills AW, May R, Marbella LE. Potassium fluoride and carbonate lead to cell failure in potassium-ion batteries. *ACS Appl Mater Interfaces* 2021;13:53841-9. DOI PubMed
34. Liu G, Cao Z, Zhou L, et al. Additives engineered nonflammable electrolyte for safer potassium ion batteries. *Adv Funct Mater* 2020;30:2001934. DOI
35. Hosaka T, Fukabori T, Matsuyama T, Tatara R, Kubota K, Komaba S. 1,3,2-dioxathiolane 2,2-dioxide as an electrolyte additive for K-metal cells. *ACS Energy Lett* 2021;6:3643-9. DOI
36. Liu S, Mao J, Zhang Q, et al. An intrinsically non-flammable electrolyte for high-performance potassium batteries. *Angew Chem Int Ed* 2020;59:3638-44. DOI
37. Yoshii K, Masese T, Kato M, Kubota K, Senoh H, Shikano M. Sulfonamide-based ionic liquids for high-voltage potassium-ion batteries with honeycomb layered cathode oxides. *ChemElectroChem* 2019;6:3901-10. DOI
38. Elmanzalawy M, Sanchez-ahijón E, Kisacik O, Carretero-gonzález J, Castillo-martínez E. High conductivity in a fluorine-free K-ion polymer electrolyte. *ACS Appl Energy Mater* 2022;5:9009-19. DOI
39. Fei H, Liu Y, An Y. Safe all-solid-state potassium batteries with three dimensional, flexible and binder-free metal sulfide array electrode. *J Power Sources* 2019;433:226697. DOI
40. Schaefer JL, Morganty SS, Archer LA. Nanoscale organic hybrid electrolytes. *Adv Mater* 2010;22:3677-80. DOI
41. Zheng J, Li W, Liu X, Zhang J, Feng X, Chen W. Progress in gel polymer electrolytes for sodium-ion batteries. *Energy Environ Mater* 2022;6:e12422. DOI

42. Kubota K, Dahbi M, Hosaka T, Kumakura S, Komaba S. Towards K-ion and Na-ion batteries as “beyond Li-ion”. *Chem Rec* 2018;18:459-79. DOI PubMed
43. Rajagopalan R, Tang Y, Ji X, Jia C, Wang H. Advancements and challenges in potassium ion batteries: a comprehensive review. *Adv Funct Mater* 2020;30:1909486. DOI
44. Deng L, Qu J, Niu X, et al. Defect-free potassium manganese hexacyanoferrate cathode material for high-performance potassium-ion batteries. *Nat Commun* 2021;12:2167. DOI PubMed PMC
45. Zhou M, Tian X, Sun Y, et al. Pillar effect boosting the electrochemical stability of Prussian blue-polypyrrole for potassium ion batteries. *Nano Res* 2023;16:6326-33. DOI
46. Vaalma C, Giffin GA, Buchholz D, Passerini S. Non-aqueous K-ion battery based on layered $K_{0.3}MnO_2$ and hard carbon/carbon black. *J Electrochem Soc* 2016;163:A1295. DOI
47. Pan J, Sun YY, Yan Y, et al. Revisit electrolyte chemistry of hard carbon in ether for Na storage. *JACS Au* 2021;1:1208-16. DOI PubMed PMC
48. Arnaiz M, Huang P, Ajuria J, Rojo T, Goikolea E, Balducci A. Protic and aprotic ionic liquids in combination with hard carbon for lithium-ion and sodium-ion batteries. *Batteries Supercaps* 2018;1:204-8. DOI
49. Wu J, He J, Wang M, et al. Electrospun carbon-based nanomaterials for next-generation potassium batteries. *Chem Commun* 2023;59:2381-98. DOI
50. Qiann Y, Jiang S, Li Y, et al. *In situ* revealing the electroactivity of P-O and P-C bonds in hard carbon for high-capacity and long-life Li/K-ion batteries. *Adv Energy Mater* 2019;9:1901676. DOI
51. Wu X, Li Z, Liu J, Luo W, Gaumet J, Mai L. Defect engineering of hierarchical porous carbon microspheres for potassium-ion storage. *Rare Met* 2022;41:3446-55. DOI
52. Li W, Li Z, Zhang C, et al. Hard carbon derived from rice husk as anode material for high performance potassium-ion batteries. *Solid State Ion* 2020;351:115319. DOI
53. Jo JH, Kim HJ, Yaqoob N, et al. Hollandite-type potassium titanium oxide with exceptionally stable cycling performance as a new cathode material for potassium-ion batteries. *Energy Stor Mater* 2023;54:680-8. DOI
54. Imtiaz S, Amiin IS, Xu Y, Kennedy T, Blackman C, Ryan KM. Progress and perspectives on alloying-type anode materials for advanced potassium-ion batteries. *Mater Today* 2021;48:241-69. DOI
55. Zhang W, Huang W, Zhang Q. Organic materials as electrodes in potassium-ion batteries. *Chemistry* 2021;27:6131-44. DOI PubMed
56. Lei K, Li F, Mu C, et al. High K-storage performance based on the synergy of dipotassium terephthalate and ether-based electrolytes. *Energy Environ Sci* 2017;10:552-7. DOI
57. Kang Z, Sun K, Sun CF, Liu Q. A plastics-derived organic anode material for practical and sustainable potassium-ion batteries. *Int J Electrochem Sci* 2023;18:100222. DOI
58. Bresser D, Buchholz D, Moretti A, Varzi A, Passerini S. Alternative binders for sustainable electrochemical energy storage - the transition to aqueous electrode processing and bio-derived polymers. *Energy Environ Sci* 2018;11:3096-127. DOI
59. Wu X, Xing Z, Hu Y, et al. Effects of functional binders on electrochemical performance of graphite anode in potassium-ion batteries. *Ionics* 2019;25:2563-74. DOI
60. Harper G, Sommerville R, Kendrick E, et al. Recycling lithium-ion batteries from electric vehicles. *Nature* 2019;575:75-86. DOI
61. Haber S, Leskes M. What can we learn from solid state NMR on the electrode-electrolyte interface? *Adv Mater* 2018;30:e1706496. DOI PubMed
62. Leskes M, Kim G, Liu T, et al. Surface-sensitive NMR detection of the solid electrolyte interphase layer on reduced graphene oxide. *J Phys Chem Lett* 2017;8:1078-85. DOI
63. Haber S, Rosy, Saha A, et al. Structure and functionality of an alkylated $Li_xSi_yO_z$ interphase for high-energy cathodes from DNP-ssNMR spectroscopy. *J Am Chem Soc* 2021;143:4694-704. DOI
64. Ji S, Li J, Li J, et al. Dynamic reversible evolution of solid electrolyte interface in nonflammable triethyl phosphate electrolyte enabling safe and stable potassium-ion batteries. *Adv Funct Mater* 2022;32:2200771. DOI