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Challenges and benefits of post-lithium-ion batteries

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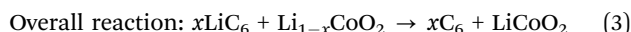
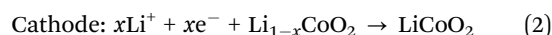
At present, rechargeable batteries composed of sodium, magnesium and aluminum are gaining attention as potentially less toxic and more economical alternatives to lithium-ion batteries. From this perspective, the last two decades have seen a surge of reports on various anodes and cathodes for post-lithium-ion batteries, including sodium-, magnesium-, and aluminum-ion batteries. Moreover, the new electrochemical concept of dual-ion batteries, such as magnesium–sodium and aluminum–graphite dual-ion batteries, has recently attracted considerable attention. In this focus article, the operational mechanisms of post-lithium-ion batteries are discussed and compared with lithium-ion technology, along with core challenges currently limiting their development and benefits of their practical deployment.

Introduction

To decrease carbon dioxide emissions, unprecedented research is being undertaken to develop efficient and inexpensive electric vehicles and stationary energy-storage systems for energy generated by intermittent (renewable) sources such as wind and solar power.^{1,2} In this regard, increasingly batteries based on sodium (Na), magnesium (Mg), and aluminum (Al) are drawing attention due to the high abundance of these elements on Earth and therefore their potentially overall lower cost compared to lithium (Li)-ion batteries (LIBs), which represent the current commercial standard.^{3,4} However, replacing Li-ions with Na-, Mg-, or Al-ions requires deep revision and re-exploration of the cathode and electrolyte materials and electrochemistry of such batteries. Herein, we briefly review emerging battery technologies based on Earth-abundant elements—excluding already mature systems such as lead–acid and sodium–sulfur batteries as well as post-Li-ion batteries based on sulfur/air cathodes—and discuss their respective advantages and disadvantages. It is recognized that batteries based on potassium (K) begin attracting attention as a low-cost battery technology,⁵ but for the sake of conciseness it will be omitted from this short focus article.

The operating principle of a rechargeable battery is based on a reversible redox-reaction between an anode material (negative electrode, “reductant”) and a cathode material (positive material, “oxidant”). The anode and the cathode material are spatially

separated but connected electrically through an external electrical circuit and ionically through the electrolyte. Fig. 1a shows the fundamental operating principle for a battery with graphite as the anode material and lithium cobalt oxide (LiCoO₂) as the cathode material (the materials used in most commercial LIBs). For a LIB, the transfer of electrons from the anode to the cathode side is accompanied by the extraction of Li-ions from the anode material and their insertion into the cathode material to balance the charge. Hence, anode and cathode need to be connected ionically by a Li-ion containing electrolyte. The reactions that occur during discharge of the battery are:



Upon charging, the processes are reversed and both Li-ions and electrons are extracted from the cathode and reinserted into the anode material. Because the same ions migrate during both charge and discharge processes, such devices are often referred to as “rocking-chair” cells. Importantly, despite its high capacity metallic Li is not used in commercial rechargeable LIBs for safety reasons. Li is prone to forming branch-like structures (dendrites) during cycling, which can result in short-circuiting of the cell and consequently even explosion of the battery.^{6–8} Important electrochemical parameters that determine the energy density (E_{cell}) of such a cell are the specific/volumetric capacities of the anode and cathode materials (C_{Anode} and C_{Cathode} , respectively) and cell voltage (U_{cell}), which are related by $E_{\text{cell}} = C_{\text{cell}}U_{\text{cell}}$, where $C_{\text{cell}} = C_{\text{Anode}}C_{\text{Cathode}}/(C_{\text{Anode}} + C_{\text{Cathode}})$. C_{Anode} and C_{Cathode} express the amount of charge that can be extracted from the respective electrodes per unit of their mass/volume. U_{cell} is determined by the difference between

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Fig. 1 (a) Schematic illustrating the operating principle of a rechargeable LIB with graphite as the anode material and LiCoO₂ as the cathode material. (b) Galvanostatic charge/discharge curves of LiCoO₂ and graphite measured in combination with metallic lithium as counter and reference electrodes (half-cell configuration).

the average charging voltage of the anode (delithiation) and the average discharge voltage of the cathode (lithiation), which are both measured *versus* metallic Li (Fig. 1b). Apart from E_{cell} of a cell, there are numerous important electrochemical criteria that have to be considered such as long-term cycling performance (cycle life), coulombic efficiency, energy efficiency, and power density. Moreover, because values such as energy and power densities are related to the mass/volume of the electrode materials, the mass/volume of all the components in practical cells has to be considered. For instance, while the theoretical energy density of a graphite/LiCoO₂ cell is *ca.* 400 W h kg⁻¹, to estimate its practical energy density, this value should be decreased by 40–60% to account for the weight of inactive components of the cell such as the electrolyte, current collectors, separator, and packaging.⁹ For practical applications, further equally important factors are safety, environmental friendliness, and capital cost (\$ per kW h) of the battery.

Sodium-ion batteries

Sodium-ion batteries (SIBs) have the most similarities with LIBs in terms of their typical electrode materials and electrolyte formulations. However, despite their proximity in the periodic table, the electrochemistries of Na- and Li-ions are often very different because the radius of an Na ion is ~50% larger than that of an Li ion. For instance, sodium cobalt oxide (NaCoO₂), which is the direct Na-ion analog of LiCoO₂, shows poorer electrochemical cycling performance and has much lower discharge/charge voltages than those of LiCoO₂.¹⁰ Nevertheless, new efficient Na-ion cathode materials have been successfully developed, such as Na_{1.5}VPO_{4.8}F_{0.7}¹¹ and Na₄Co₃(PO₄)₂P₂O₇,¹² which show electrochemical performance comparable with that of the best Li-ion cathodes. The issue at hand for SIBs has been the development of high-performance anode materials. Similar to metallic Li, the use of elemental Na as an anode is not possible because of the problem of Na dendrite formation (Fig. 2). In addition, graphite, which serves as an anode material for LIBs, shows negligible capacities of 30–35 mA h g⁻¹ for Na-ion storage.¹³

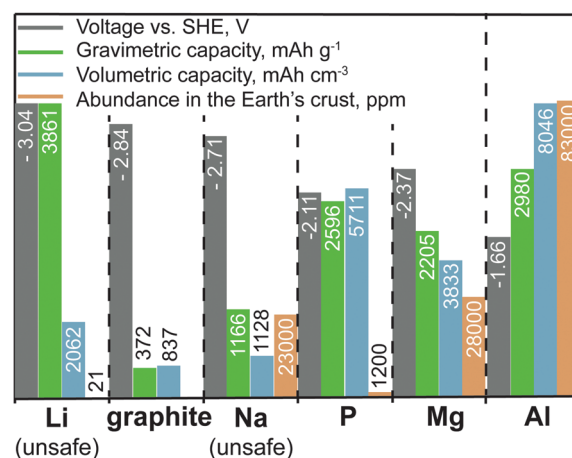


Fig. 2 Comparison of the voltage vs. standard hydrogen electrode (SHE), specific and volumetric capacities, and Earth abundance of various anode materials. As elemental lithium and sodium cannot be used safely in rechargeable batteries because of dangerous dendrite formation, graphite (for Li-ion storage) and phosphorus (for Na-ion storage) are listed as potential substitutes.^{19,20} The voltages given for graphite and phosphorus correspond to their lithiated (graphite) and sodiated (phosphorus) state. We note that unlike in aqueous systems, where the Al³⁺/Al potential is -1.66 V vs. SHE, its value shifts markedly in chloroaluminate ionic liquid electrolytes to about -0.7 V vs. SHE (2.3 V vs. Li⁺/Li).²¹ Even though graphite is a naturally occurring material, its abundance is not given in the graph. We also note that high-quality graphite is available as an industrial side product.

Other carbonaceous materials such as hard carbon exhibit capacities of less than 300 mA h g⁻¹ at rather low current rates and suffer from low tap density. Although they often exhibit lower capacities for Na- than for Li-ion storage, alloying-type anodes composed of elements such as tin (Sn), antimony (Sb), or phosphorus (P), have also been intensively studied as promising anode materials.^{14–17} However, such anodes often suffer from poor cycling stability caused by their massive volume changes upon discharge/charge (alloying/dealloying), which leads to rapid mechanical deterioration of the electrodes. For instance, in the



Similar to metallic Mg, Al is a highly abundant, non-toxic, and inexpensive metal that can be used safely in rechargeable

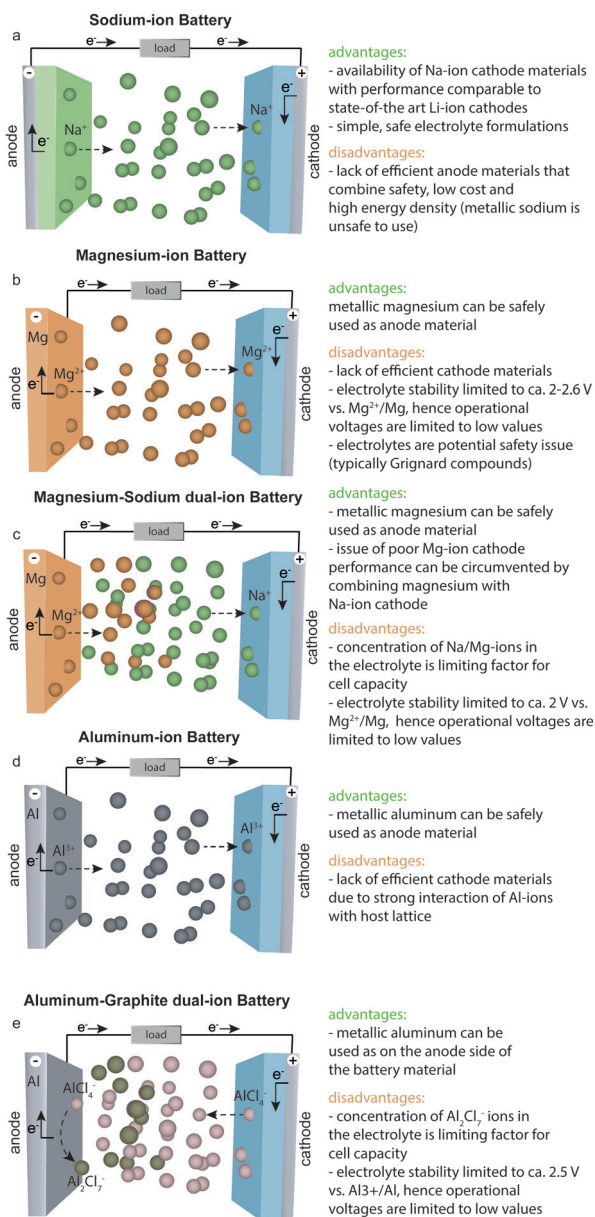
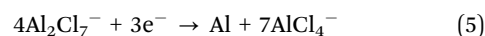


Fig. 3 Schematic working principle of sodium-ion (a), magnesium-ion (b), magnesium–sodium dual-ion (c), aluminum-ion (d), and aluminum–graphite dual-ion (e) batteries and the respective advantages and disadvantages of each system.

aluminum-ion batteries (AIBs) because of its dendrite-free electrodeposition.¹⁹ Furthermore, Al has extremely high volumetric and gravimetric capacities of 8046 mA h cm⁻³ and 2980 mA h g⁻¹, respectively. However, the Al³⁺/Al redox potential is shifted to more positive value than that of the Mg²⁺/Mg couple (see also Fig. 2), resulting in lower overall cell voltage compared with that of MIBs. An additional complication is the fact that although efficient Al plating/stripping occurs in chloroaluminate ionic liquids, they are corrosive and often have a limited operation voltage window of about 2.5 V. With respect to reversible Al-ion storage, various materials have been explored so far, such as sulfides,^{60–73} selenides,^{74,75} Prussian blue analogs,^{76,77} transition

metal oxides,^{78–91} phosphite,⁹² carbide,⁹³ molybdate,⁹⁴ vanadate,⁹⁵ sulfur,^{96–98} selenium,⁹⁹ iodine,¹⁰⁰ and oxygen.¹⁰¹ Although reversible Al-ion storage has been demonstrated, most of the reported compounds showed relatively low charge-storage capacity, low average discharge voltage, high polarization, and short cycle life. Similar to the case for MIBs, the intercalation of Al-ions, which are much smaller than Li-ions, has proved to be difficult because of their strong coulombic interaction with the host cathode material.²⁹ In this context, finding suitable Al-ion cathodes with high capacity and high operating voltage remains a great challenge.

Apart from AIBs, aluminum-graphite dual-ion batteries (Al-GDIBs) have attracted considerable attention recently. Al-GDIBs are composed of highly abundant elements (H, O, N, C, and Al) and have appropriate energy densities ($30\text{--}70\text{ Wh kg}^{-1}$).^{102–106} The basic architecture of an Al-GDIB consists of a graphite cathode, metallic Al current collector, and $\text{AlCl}_3\text{-1-ethyl-3-methylimidazolium chloride}$ ([EMIM]Cl) ionic liquid anolyte, as shown in Fig. 3. Thus far, various forms of natural and synthetic graphite/carbon such as natural graphite flakes,^{107,108} kish graphite flakes,¹⁰⁹ graphitic foams,^{102,110} graphene nanoribbons,¹¹¹ few-layer graphene aerogels,¹¹² graphene mesh network,¹¹³ large-sized few-layer graphene,¹¹⁴ and carbon paper (of graphitic nature)^{115–117} have been used as the cathode materials of Al-GDIBs, providing capacities of $60\text{--}150\text{ mA h g}^{-1}$, average discharge voltages of $1.7\text{--}2\text{ V}$, and long-term cyclic stability for up to 10 000 cycles. However, it should be noted that the working principle of such batteries is different from that of rocking-chair metal-ion batteries. In this battery concept, during charge, the following half-reactions occur at the positive and negative electrodes, respectively:



Reaction (4) represents the intercalation of AlCl_4^- species into the graphite cathode during its oxidation. Reaction (5), which occurs at the anode, relies on the presence of Al_2Cl_7^- and is only observed in acidic melts (molar ratio of AlCl_3 to $[\text{EMIM}]\text{Cl} > 1$). During the charging process, Al species are depleted from the chloroaluminate ionic liquid and taken up by both electrodes. Therefore, severe limitations are imposed on the amount of chloroaluminate ionic liquid because it acts as a capacity-limiting liquid anode (anolyte). We note that graphite dual-ion batteries are not limited to the use of Al plating/stripping reactions on the negative electrode.^{118,119} Other presently pursued alternative anodes include graphite,¹²⁰ carbonaceous materials,^{121–124} Sn,^{125,126} Sb¹²⁵ or Pb.¹²⁵

Conclusion and outlook

Despite the fact that post-LIBs based on Na, Mg, or Al potentially offer substantial electrochemical and economic advantages, numerous challenges still hinder the practical utility and commercial deployment of these technologies. In short, enormous effort is required to develop low-cost Na-ion anodes that possess low desodiation potential and high charge-storage capacity to achieve comparable performance with that of graphite anodes

in LIBs. The greatest challenges for MIBs and AliBs lie, however, in finding electrolytes with higher electrochemical oxidation stability and the development of cathode materials with high charge-storage capacity at high potentials. With respect to magnesium-sodium and aluminum-graphite dual-ion batteries, much room for improvement also remains regarding the gravimetric and volumetric charge-storage capacities of electrolytes (anolytes), their cycle life, and oxidation stability. In the context of the effects of electrolytes, separators, and current collectors on the overall energy density of post-LIBs, further research should be focused on quantifying their practical amounts. Generally, batteries in academia are designed to test proof-of-principle and often neglect cost or the mass/volume of the entire battery (including all the inactive components). However, such factors are crucial for commercialization. The technological immaturity of these alternative battery systems in this regard makes it very difficult to predict which battery type might emerge as a commercial product. It should also be noted that none of the presented battery technologies is currently capable of competing with LIBs in terms of energy density and will most likely not be in the future. This is in stark contrast to Li-sulfur, Li-air or solid-state batteries with metallic lithium that are fuelled by the promise of higher energy density compared to the present state of the art. The prospective benefit of such non-Li-ion-based batteries might be—given their further optimization—as viable energy-storage systems for applications where parameters such as cost and environmental friendliness are more important than energy density.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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