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Review

Advanced Na metal anodes

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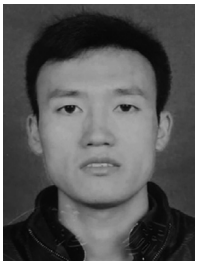
ABSTRACT

Na metal anode, benefiting from its high theoretical capacity and lowest electrochemical potential, is one of the most favorable candidates for future Na-based batteries with high energy density. Dendrite growth, volume change and high reactivity are the formidable challenges in terms of good cycling performance and high Coulombic efficiency as well as an expected safety guarantee of Na metal anode for the practical application. Solid electrolyte interphase (SEI) layer as an indispensable component of a battery, its formation and stability play the critical role in the feasibility of Na metal anode. In this review, we first discuss the current consideration and challenges of Na metal anode, and then summarize several strategies to suppress dendrite growth and improve electrochemical performance, including interface engineering, electrolyte composition, electrode construction, and so on. Finally, the conclusion and future perspective of potential development on Na metal anode are proposed.



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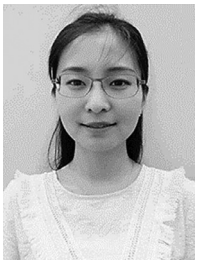

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1. Introduction

High-performance rechargeable battery systems are important to integrate renewable energy sources and energy storage systems. Li-ion batteries (LIBs) as the powerful energy storage and conversion devices have been widely applied from the portable electronics to electric vehicles (EVs) during the past 26 years, and the growth and utilization processes are developed rapidly [1,2]. The fast-growing consumer markets of LIBs are gradually urging the increment of cost on raw materials, and may cause lithium resource shortage due to its inhomogeneous distribution on the Earth's crust. The Earth abundant and low-cost Na-ion batteries (NIBs) are capable to offer long-term sustainability and high performance-price efficiency in the large-scale energy storage systems (EESs) [3–5]. However, a high-energy density is always desirable and needs much more attentions to meet the today's rapidly growing demand on this sustainable society [6].

The high-energy density is mainly derived from the high capacity of Na-intercalation/deintercalation electrodes in NIBs. Materials innovation toward the large-capacity and high-potential cathodes is a potential solution, however, it is a formidable challenge to realize more Na^+ transfer per transition metal with a capacity of ~300 mAh g^{-1} and a large electrochemical window well-matched with the electrolyte [3–5,7–9]. On the contrary, developing anode materials for NIBs can be easily available for their access to high capacity and low potential. The current anode materials for NIBs, including carbonaceous materials, titanium-based materials, alloy materials, chalcogen-based materials and organic materials are summarized in Fig. 1(a), according to specific capacity (mAh g^{-1}) and voltage (V). Carbonaceous materials, the well-known hard carbon materials, are the available anode in NIBs for their high capacity (~300 mAh g^{-1}) and relatively low potential on the immediate needs [10–14]. Merely, Na-deposition hazard can be caused in a low potential charge-discharge process, especially in - high power density and low temperature. Alloy and chalcogen compound anodes present the higher capacity suitable for the further development on high-energy-density NIBs, but the poor cycling performance and low Coulombic efficiency, as well as the uncontrollable volume change are the serious problems to be overcome in the practical application [10]. Alloy anodes often suffer from the huge volume expansion up to ~400% during (de)sodiation, which can cause the mechanical failure of electrodes and pulverization of active particles resulting in poor electrochemical performance [15,16]. Na metal can serve as the promising choice among all the anode materials because of its higher specific capacity of ~1165 mA h g^{-1} and lowest electrochemical potential (−2.714 V versus SHE) [17]. As a matter of the fact, Na metal anode is one of the key components for high-energy-density Na-based batteries such as Na-$NiCl_2$ ZEBRA batteries (Zeolite applied to Battery Research Africa), Na-S batteries, Na-O_2 batteries [18–32].

The advantages of using Na metal as anode is very obvious, however, not many researches are conducted on the room-temperature Na metal batteries due to its high reactivity, resulting in uncontrollable reaction with electrolyte, especially in the liquid electrolytes. Like other anode materials, the SEI layer always exists on the surface of Na metal anode and even much more serious owing to the highly negative electrochemical potential. This interface between Na anode and electrolyte plays an important role in regulating charge and mass transport, which is one of the critical components to determine the battery's performance and safety concerns. The relative electron energies of electrodes and electrolytes in a battery are shown in Fig. 1(b). When the electrochemical potentials of anode μ_A is above the energy of the lowest unoccupied molecular orbital (LUMO) of an electrolyte, electrons on the Na metal anode transfer to the LUMO of the electrolyte involving reduction reactions to generate some reductants attached to the surface of Na anode. The obtained species can stack up to a few dozen nanometers to form an SEI layer to prevent the further decomposition of liquid electrolytes [33,34]. The stability of composition, morphology and structure for passivating SEI layer is of great importance for Na plating and stripping; meanwhile, a high ionic conductivity and electronic insulation capability, are also the critical factor. However, the thermodynamic SEI layer can't be in fact easily formed, which will be thickened, broken, and collapsed during cycling. As a result, the SEI layer on the surface of metal anode will be a mechanical failure due to volume expansion, dendrite formation and growth and even the battery short circuit. Possible problems may happen with the Na metal anode illustrated in Fig. 1(c).

As high chemical and electrochemical reactivity, Na metal can easily react with liquid electrolyte in a very short time to form a loose and fragile SEI layer in the process of battery assembly. During the Na plating, Na^+ prefers to deposit persistently on sites with the higher electric field, where this uneven deposition results in the Na plating crack [35]. Further plating would cause failure of the SEI protective layer to induce the Na dendrite formation and growth. The fresh Na metal dendrite will react with the surrounding electrolyte to produce the SEI layer to cover the surface. When stripping, a part of dendrite may lose connection to the Na plate due to the Na^+ migration from the anode to cathode resulting in the formation of isolated Na or 'dead' Na wrapped in SEI passivation layers; another part of dendrite will grow steadily and penetrate the separator to cause the short circuit of a battery. Even if the short circuit does not happen, lots of dead Na would no doubt produce a porous Na metal electrode and increase the thickness of SEI layer, fading the batteries' performance. The related consideration and challenges of Na metal anodes will be discussed in Section 2.

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