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Review article

Progress in aqueous rechargeable batteries

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Abstract

Over the past decades, a series of aqueous rechargeable batteries (ARBs) were explored, investigated and demonstrated. Among them, aqueous rechargeable alkali-metal ion (Li^+, Na^+, K^+) batteries, aqueous rechargeable-metal ion (Zn^{2+}, Mg^{2+}, Ca^{2+}, Al^{3+}) batteries and aqueous rechargeable hybrid batteries are standing out due to peculiar properties. In this review, we focus on the fundamental basics of these batteries, and discuss the scientific and/or technological achievements and challenges. By critically reviewing state-of-the-art technologies and the most promising results so far, we aim to analyze the benefits of ARBs and the critical issues to be addressed, and to promote better development of ARBs.

Keywords: Aqueous rechargeable batteries; Hybrid; Fundamental basics; Challenges

1. Introduction

The growing energy demands and the increasing environmental concerns drive the transformation of power generation from primarily fossil and nuclear sources to solely renewable energy sources and the search of efficient energy management systems (conversation, storage and delivery), to achieve a secure, reliable and sustainable energy supply [1–4]. The success is strongly dependent on the achievements in efficient electrochemical power sources that are also safe to operate, economically viable, and environmental friendly. Rechargeable battery technologies including lead-acid (Pb-acid), nickel-cadmium (Ni-Cd), nickel-metal hydride (Ni-MH), redox flow-cells (RFCs) and lithium ion batteries (LIBs) have found practical applications in various areas, however, the inherent limitations of these systems impede their applications in large-scale energy storage [5]. In which operational safety is of prime importance along with other desirable characteristics such as low installed cost, long cycling life, high energy efficiency and sustainability [6]. For example, the Pb-acid and Ni-Cd generally suffer from the limited energy density (~30 Wh kg^{-1}) [7], in addition to the employment of environmentally threatened electrode materials [8]. The nickel-iron battery is challenged by the poor charge/discharge efficiency (ca. 50–60%) and the self-discharge (20–40% per month) related to the corrosion and poisoning of the iron anode [9,10]. The Ni-MH possesses higher energy density, but delivers poor low-temperature capability, limited high-rate capability, and poor Coulombic efficiency [11,12]. Redox-flow cells can be easily piled up, however, the relatively low power/energy density and the special heat/temperature control requirements limit their widely applications [13,14]. Lithium ion batteries hold great promise, benefiting from higher energy density, lighter weight and longer life time [15,16]. However, incidents caused by the flammability of the organic electrolyte and the reactivity of

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the electrode materials with the organic electrolytes in the case of overcharging or short-circuiting raise serious safety concerns [17,18]. In addition, the LIBs technologies are comparatively high cost due to materials used (organic Li salts and organic electrolytes), the special cell designing and manufacturing processes, and auxiliary systems required for their operation [5,19,20]. Another challenge regarding LIBs is the limited rate capability and specific power that are restricted by the limited ionic conductivities of the organic electrolyte. All these, together, intrigue the development of novel battery systems that are safe to operate, economically viable, and environmental friendly.

Aqueous rechargeable batteries (ARBs) are of particular attractive for large-scale energy storage in terms of safe, economic and sustainable: i) inherently safe by avoiding the usage of flammable organic electrolytes, ii) the ionic conductivities of the aqueous electrolyte is about two orders of magnitude higher than that of nonaqueous ones, ensuring fast charge/discharge and high round-trip efficiency, and iii) the electrolyte salt and solvent are cheaper and the rigorous manufacturing requirements are avoided, and iv) environmentally benign [5,20–22].

In 1994, Dahn and co-workers proposed the first ARBs prototype using $LiMn_2O_4$ and β-VO_2 as positive and negative electrodes, respectively [23]. In which metal-ions are intercalated into or extracted from the active materials upon charge/discharge processes, identical to that of organic systems. It is therefore referred as "rocking chair" type or "intercalation-chemistry" type (Fig. 1a). Since then, significant progresses have been made in this intriguing area with more electrochemical redox couples are identified, more insights into fundamental chemistry are gained, and new battery chemistries are explored. More recently, hybrid design via coupling an intercalation cathode with a metal anode (Fig. 1b) or combining an intercalation anode with a metal oxides/sulphide (Fig. 1c), was introduced in ARBs with the appearance of a new class of aqueous hybrid batteries systems such as $LiMn_2O_4$//Zn [24], $Na_{0.44}MnO_2$//Zn [25], $Na_{0.61}Fe_{1.94}(CN)_6\cdot\square_{0.06}$//Zn (□ indexed as vacancy) [26], $Ni(OH)_2$//TiO_2 [27], and $Co_xNi_{2-x}S_2$//TiO_2 [28]. Differ from the "rocking chair" type batteries, these batteries operate based on two reversible electrochemical redox processes involved in anode and cathode parts separately, and the charge/discharge mechanism in one or two electrodes is not guest ion intercalation/de-intercalation (Fig. 1b and c). Instead, it can be the reaction of Zn^{2+} deposition-dissolution (Fig. 1b) and/or proton-induced oxidization/reduction (Fig. 1c). The electrolyte here acts as conducting ions and cooperates with the electrodes to store energy, rather than used as the simple supporting media in "rocking chair" type batteries. Here are denoted them as "hybrid chemistry" type batteries with abbreviation as ARHBs. These hybrid systems enrich the existing ARBs chemistry and open up new research era for high-performance ARBs design.

In this review, we summary the latest progresses in aqueous rechargeable batteries with an emphasis on i) "rocking chair" type ARBs based on intercalating cations such as Li^+ ions and Na^+ ions, as well as multivalent ions such as Mg^{2+}, Zn^{2+}, Ca^{2+}, and Al^{3+} ions; and ii) "hybrid chemistry" type ARBs such as interaction cathode//metal anode and metal oxide and/or metal sulfide cathode//intercalation anode (Tables 1 and 2). By critically reviewing state-of-the-art technologies and the most promising results so far, we aim to analyze the benefits of ARBs and the critical issues to be addressed, and to promote better development of ARBs.

2. Fundamental basics of aqueous rechargeable batteries

2.1. Safety working window & oxygen/hydrogen evolution

Since electrochemical redox reactions involved in ARBs take place in water environment, the electrochemical stability window is generally limited to be 1.23 V, beyond which H_2O is electrolysed with O_2 or H_2 gas evolution. Thus, materials with working potentials located between the H_2 evolution potential and O_2 evolution potential are promising electrode candidates for ARBs. In principle, electrodes with a working potential between 3 and 4 V (*vs.* Li^+/Li) can be used as cathode, and electrodes with a working potential between 2 and 3 V (*vs.* Li^+/Li) can be chosen as anode [29]. The potential diagram comparing with the stable potential window (*vs.* SHE) of water and working potential (*vs.* Li^+/Li, or Na^+/Na) of representative electrode materials as oxides, polyanionics, and other compounds on the same potential scale is shown in Fig. 2 [20]. Note that the H_2 evolution potential and O_2 evolution potential are strongly dependent on pH value,

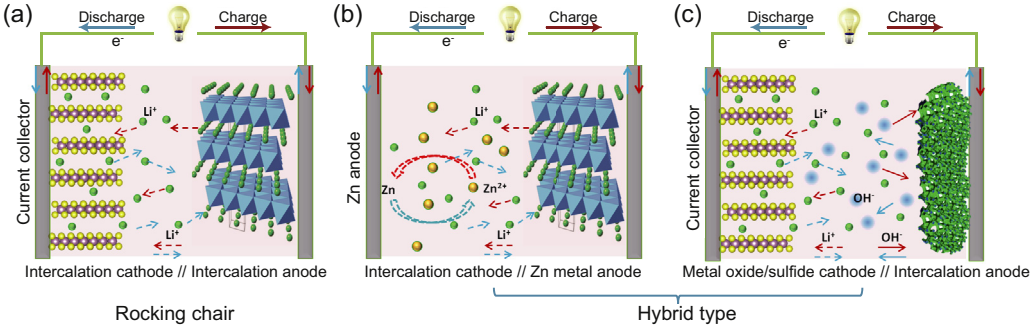

Fig. 1. Fundamental electrochemistry. Schematic illustration of "rocking chair" and "hybrid type" aqueous rechargeable batteries (ARBs).