Energy Storage Materials 4 (2016) 103–129

Contents lists available at ScienceDirect

Energy Storage Materials

journal homepage: www.elsevier.com/locate/ensm

Emerging non-lithium ion batteries

Yanrong Wang[a,1], Renpeng Chen[a,1], Tao Chen[a], Hongling Lv[a], Guoyin Zhu[a], Lianbo Ma[a], Caixing Wang[a], Zhong Jin[a,*], Jie Liu[a,b,**]

[a] Key Laboratory of Mesoscopic Chemistry of MOE and Collaborative Innovation Center of Chemistry for Life Sciences, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China
[b] Department of Chemistry, Duke University, Durham, NC 27708, USA

ARTICLE INFO

Article history:
Received 30 December 2015
Received in revised form
4 April 2016
Accepted 7 April 2016
Available online 13 April 2016

Keywords:
Electrochemical energy storage
Non-lithium ion batteries
Rechargeable secondary batteries
Cathode and anode materials
Electrolytes

ABSTRACT

Li-ion batteries have dominated the field of electrochemical energy storage for the last 20 years. It still remains to be one of the most active research fields. However, there are difficult problems still surrounding lithium ion batteries, such as high cost, unsustainable lithium resource and safety issues. Rechargeable batteries base on alternative metal elements (Na, K, Mg, Ca, Zn, Al, *etc.*) can provide relatively high power density and energy density using abundant, low-cost materials. Therefore, non-lithium ion batteries are regarded as promising candidates to partially replace lithium ion batteries in near future. In recent years, the research on non-lithium rechargeable batteries is progressing rapidly, but many fundamental and technological obstacles remain to be overcome. Here we provide an overview of the current state of non-lithium rechargeable batteries based on monovalent metal ions (Na^+ and K^+) and multivalent metal ions (Mg^{2+}, Ca^{2+}, Zn^{2+} and Al^{3+}). The needs and possible choices of superior electrode materials and compatible electrolytes beneficial for ion transport were emphatically discussed in this review.

Contents

Abbreviations: AIBs, aluminum ion batteries; CIBs, calcium ion batteries; LIBs, lithium ion batteries; MIBs, magnesium ion batteries; NASICON, sodium super ionic conductor; PBAs, Prussian blue analogues; PIBs, potassium ion batteries; SEI, solid-electrolyte interface; SHE, standard hydrogen electrode; SIBs, sodium ion batteries; XRD, X-ray diffraction; ZIBs, zinc ion batteries

* Corresponding author.
** Corresponding authors at: Key Laboratory of Mesoscopic Chemistry of MOE and Collaborative Innovation Center of Chemistry for Life Sciences, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China.
E-mail addresses: zhongjin@nju.edu.cn (Z. Jin), j.liu@duke.edu (J. Liu).
[1] Both authors contributed equally to this work.

http://dx.doi.org/10.1016/j.ensm.2016.04.001
2405-8297/

1. Introduction

High-efficiency electrochemical energy storage devices have become an urgent demand over the past few decades along with the rapid increase of global energy consumption, the drain of fossil fuels and the aggravation of environmental problems [1–3]. Significant attention has been drawn to the research of alternative eco-friendly energy systems based on renewable resources to alleviate these crises [4–6]. The secondary batteries, especially rechargeable lithium-ion batteries (LIBs), are capable of storing and releasing electric energy for many times [7,8]. While the application of LIBs as a major power source in portable devices and electric vehicles is rapidly expanding, the current LIB technology is still facing several difficult challenges, such as resource limitation, high cost, potential safety issue and insufficient energy density [9,10]. In particular, the rarity and uneven distribution of global lithium reserves results in rising cost [11]. Graphite has long been used as anode material in commercial LIBs with a low operating voltage closed to 0 V *vs.* Li/Li^{+}, which has a beneficial effect on the energy density, but also lead to the formation of potentially risky lithium dendrite [12]. The dendritic deposition of lithium metal may result in short circuits leading to internal overheating and even flaming [13,14]. Furthermore, it is imperative to develop rechargeable batteries with higher energy density for electric vehicles to get better mileage. The state-of-art commercial LIBs are difficult to satisfy the practical needs [15,16]. Even though lithium metal has a high theoretical volumetric capacity of 2062 mA h mL^{-1} and a highly negative reduction potential of −3.04 V *vs.* standard hydrogen electrode (SHE), as shown in Table 1, these unresolved problems motivated researchers to make considerable effort to develop new types of rechargeable batteries with high sustainability and performances beyond LIBs.

A possible solution for overcoming the disadvantages of LIBs would be the non-lithium batteries based on alternative metal ions [17], such as alkali metals (Na^{+} and K^{+}), alkaline earth metals (Mg^{2+} and Ca^{2+}), group IIIA metal (Al^{3+}) and transition metal (Zn^{2+}). Non-lithium ion based batteries with high energy density, good environmental benignity and low cost have great potentialities for energy storage in future [18–23].

Secondary batteries based on monovalent alkali metal ions, including Na^{+} and K^{+}, have the advantages of high abundance and low price. Nonetheless, several obstacles still need to be overcome before these batteries can become a practical, commercial reality. The challenges include how to improve the insufficient cycle life and how to design new anode and cathode materials with high specific energy capacity [24–26]. Other rechargeable batteries based on multivalent metal ions (such as Mg^{2+}, Ca^{2+}, Zn^{2+} and Al^{3+}) could transfer more electrons in a single redox couple, hence possibly helpful to obtain high volumetric energy density that is desirable for portable devices [17,27,28]. In addition, multivalent metal anodes do not appear to be troubled by dendrite formation to the same degree as lithium metal anodes. Moreover, air and moisture exposure is a much lesser safety problem for multivalent metal ion batteries compared to LIBs [5]. However, rechargeable batteries based on multivalent metal ions also need to overcome several difficulties before usage in practical applications. The biggest challenge is the lack of suitable electrode materials in which multivalent metal ions can diffuse with fast kinetics and the lack of high-voltage electrolytes compatible with electrodes [29,30].

In this review, we summarized the recent progresses and hurdles encountered by secondary batteries based on non-lithium ions. We expect that this review may provide some new insights into the further development of rechargeable batteries beyond LIBs and reveal their immense potential in electrochemical energy storage aspect.

Table 1
Theoretical capacities, reduction potential and effective ionic radius of various metals.

Species	Volumetric capacity (mA h mL^{-1})	Specific capacity (mA h g^{-1})	Reduction potential (*V vs.* SHE)	Effective ionic radius (Å)
Li	2026	3861	−3.04	0.76
Na	1128	1165	−2.71	1.02
K	591	685	−2.93	1.38
Mg	3833	2205	−2.37	0.72
Ca	2073	1337	−2.87	1.00
Zn	5851	820	−2.20	0.74
Al	8040	2980	−1.67	0.54

2. Sodium ion batteries

Sodium ion batteries (SIBs) were originally developed in the late 1980s, approximately in the same time period as LIBs [31]. In recent years, SIBs have drawn increasing attention for large-scale energy storage, because of the natural abundance, low cost and environmental benignity of sodium [4,32–34]. Worldwide research on SIBs is now flourishing, and SIBs are considered as one of the most appealing alternative rechargeable batteries to LIBs. SIBs have a theoretical specific capacity of 1165 mA h g^{-1} with a negative reduction potential of −2.71 V *vs.* SHE (Table 1). Since the size of Na^{+} (radius ~1.02 Å) is larger than Li^{+}, most materials don't have sufficiently big interstitial space to host Na^{+}, leading to sluggish diffusion kinetics of Na^{+} in electrode materials [9]. Therefore, a great challenge for developing SIBs is to find appropriate electrode materials capable of hosting Na^{+} with high capacity and fast diffusion kinetics [35]. Up to now, many different electrode materials have been synthesized, but the capacities and the rate performances of assembled SIBs are still not satisfactory for practical applications.