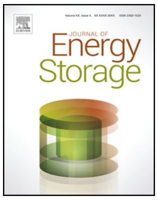
Journal of Energy Storage 15 (2018) 304–328

Contents lists available at ScienceDirect

Journal of Energy Storage

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



An overview of progress in electrolytes for secondary zinc-air batteries and other storage systems based on zinc

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ARTICLE INFO

Article history:
Received 2 February 2017
Received in revised form 5 December 2017
Accepted 6 December 2017
Available online xxx

Keywords:
Zinc-Air battery
Zinc-based batteries
Aqueous
Non-aqueous batteries
Battery's electrolytes

ABSTRACT

The revived interest and research on the development of novel energy storage systems with exceptional inherent safety, environmentally benign and low cost for integration in large scale electricity grid and electric vehicles is now driven by the global energy policies. Within various technical challenges yet to be resolved and despite extensive studies, the low cycle life of the zinc anode is still hindering the implementation of rechargeable zinc batteries at industrial scale. This review presents an extensive overview of electrolytes for rechargeable zinc batteries in relation to the anode issues which are closely affected by the electrolyte nature. Widely studied aqueous electrolytes, from alkaline to acidic pH, as well as non-aqueous systems including polymeric and room temperature ionic liquids are reported. References from early rechargeable Zn-air research to recent results on novel Zn hybrid systems have been analyzed. The ambition is to identify the challenges of the electrolyte system and to compile the proposed improvements and solutions. Ultimately, all the technologies based on zinc, including the more recently proposed novel zinc hybrid batteries combining the strong points of lithium-ion, redox-flow and metal-air systems, can benefit from this compilation in order to improve secondary zinc based batteries performance.

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https://doi.org/10.1016/j.est.2017.12.004

1. Introduction

Nowadays, lithium-ion batteries are the most widely used secondary batteries for portable consumer electronics. However, its low theoretical energy density (100–200 Wh kg^{-1}) is insufficient to meet the demands of large-scale applications [1]. The potentialities for high performance power sources demand a system which efficiently stores and/or generates more energy. In this context, the energy storage requires the development of sustainable, inexpensive, and high energy density electrochemical storage devices.

Batteries traditionally have not widely been used for large scale energy storage, they are mainly used for energy and power applications. Energy applications involve the storage system discharge over periods of hours with correspondingly long charging periods. Power applications involve comparatively short periods of discharge, short recharging periods and often require many cycles per day [2]. On the other hand, battery technologies can be distinguished in the way they storage the energy; namely, static, flowing and fuel cells. The static cells store energy within the electrode structure and the electrolyte is static and it is hold into the cell, whereas redox flow batteries store the energy in the reduced and oxidized electroactive species in the electrolyte system which is recirculated through the cell [3–5]. There are various types of developed flow cells, namely (1) Redox flow battery (*e.g.* zinc-halide); (2) Hybrid flow battery, where one or more electroactive components deposited as a solid layer (*e.g.* zinc-bromide, zinc-cerium [6] or zinc ferro-ferricyanide [7]); and (3) Membrane-less flow battery, in which two liquids are pumped through a channel where the flow naturally separates the liquids, eliminating the need for a membrane (*e.g.* zinc-quinone [8]). Other type of battery is the fuel cell. In this type the energy is stored in reactants external to the cell such as hydrogen, alcohol or even zinc-slurries (zinc-air fuel battery cell) [9–11].

Classical secondary batteries, such as lead-acid, nickel-cadmium or lithium-ion can be deployed for stationary energy storage applications. However, such current technologies cannot fully satisfy the requirements for this application in terms of *e.g.* performance, economic issues, environment regulations, etc. In this context, flow batteries become attractive as stationary storage device [10] (*viz.* aqueous zinc based flow batteries like zinc-bromide, zinc-cerium, nickel-zinc or zinc-air [12,13]) in spite of the high size and low energy density in comparison to other electrochemical devices. Unfortunately, insufficient consideration of redox flow battery design and engineering has limited their performance and hindered their scale-up resulting in restricted confidence in large-scale, long-term, low-maintenance operation [14].

On the other hand, among emerging battery technologies, metal-air batteries are being considered as preferable technologies with regards to energy density needs, while *e.g.* redox flow batteries are favorable with respect to power density requirements [15]. An advantage implementing metal-air batteries is the fact that the active material at the cathode is oxygen from the air which is abundant, free, and does not require a heavy casing (simple design provide significant cost advantages [16]) to keep it inside which increases the energy density of the system. This fact has supported an increasing interest of companies and researchers in developing further this technology as an energy storage system [17–25]. Furthermore, metal-air batteries offer a promising alternative because of their theoretical energy densities; typically flat discharge voltages; very long shelf lives (when properly

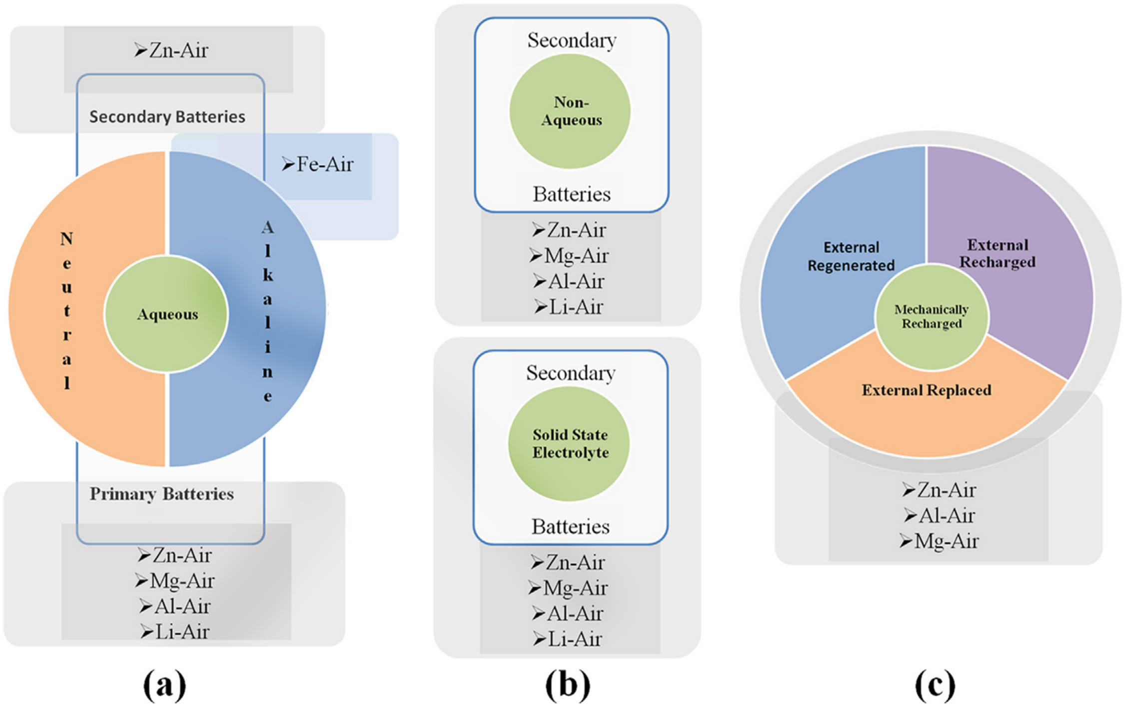

Fig. 1. Classification of metal-air batteries and electrolyte types used: (a) aqueous electrolytes (neutral and alkaline), (b) non-aqueous electrolytes, and (c) mechanically recharged.