Journal of Energy Storage 8 (2016) 35–50

Contents lists available at ScienceDirect

Journal of Energy Storage

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

Zinc regeneration in rechargeable zinc-air fuel cells—A review

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ARTICLE INFO

Article history:
Received 23 May 2016
Received in revised form 8 September 2016
Accepted 20 September 2016
Available online 30 September 2016

Keywords:
Zinc-air fuel cell
Rechargeable alkaline fuel cell
Zinc regeneration
Zinc deposition
Metal-air cell
Zinc deposition additives

ABSTRACT

Zinc-air fuel cells (ZAFCs) present a promising energy source with a competing potential with the lithium-ion battery and even with proton-exchange membrane fuel cells (PEMFCs) for applications in next generation electrified transport and energy storage. The regeneration of zinc is essential for developing the next-generation, i.e., electrochemically rechargeable ZAFCs. This review aims to provide a comprehensive view on both theoretical and industrial platforms already built hitherto, with focus on electrode materials, electrode and electrolyte additives, solution chemistry, zinc deposition reaction mechanisms and kinetics, and electrochemical zinc regeneration systems. The related technological challenges and their possible solutions are described and discussed. A summary of important R&D patents published within the recent 10 years is also presented.

Contents

1. Introduction

The concepts of "metal-air fuel cell" and "metal-air battery" are normally defined as follows. If both metallic fuel and oxidant, such as oxygen or air, are added to the system from outside the cell, the system should be referred to as a "metal-air fuel cell". If the

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http://dx.doi.org/10.1016/j.est.2016.09.007
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chemical energy from metallic fuel is still confined within the cell, the system should be regarded as a "metal-air battery". Recently, the research on metal-air has gradually emerged as a hot-topic, which is attributed to their remarkably high theoretical specific energy densities [1–4]. The theoretical specific energy density of the available metal-air batteries reaches 13,300Wh/kg for Li/O_2 [5], 8140 Wh/kg for Al/O_2 [6], 6462 Wh/kg for Mg/O_2 [7] and 1084 Wh/kg for Zn/O_2 [1]. A comparison of the specific energy densities of some representative types of primary/rechargeable batteries, metal–air batteries, H_2–air fuel cell with gasoline is shown in Fig. 1 [2]. Clearly, the H_2-air fuel cell, i.e. proton-exchange membrane fuel cell (PEMFC), possesses the best theoretical specific energy density. This is one of key factors explaining why all car manufacturing companies in the world have their strong interest and have invested heavily into the PEMFC vehicle for future clean transportation.

However, in reality, due to respective technical barriers, the difference in practical specific energy density between PEMFC and metal-air batteries, as shown in Figs. 1 and 2, is not very striking. Although it is difficult to compare directly a "PEM fuel cell" with a "metal-air battery", the Ragone plot [8] in Fig. 2 shows candidly that the advanced metal-air batteries have equivalent (or even slightly higher) power values than PEMFCs do. In comparison with the primary/rechargeable batteries presented in Fig. 1, metal-air fuel cells also have attractive energy densities, which results from the high ratio of valence electrons to atomic nuclei of anodic metals while cathodic oxygen is virtually unlimited (as oxygen is not stored in the cell but comes from the air) [2,3,9,10].

Among the metal-air fuel cells and batteries, alkaline-based cell systems, such as Zn-air, are well balanced with respect to energy density, kinetics, stability and reversibility, as illustrated in Fig. 3. The Zn-air battery system was intensively developed in the past, as it is relatively simple, easy to operate, inexpensive to manufacture, and has excellent reliability, recycle-ability, and recharge-ability [10]. Thus far, the practical specific energy density of the Zn-air system has reached 350 Wh/kg in industry (MetAir) [11] and 580–750 Wh/kg in academia (data published sporadically from 2013 till now). Compared with the market dominating Li-ion battery, the Zn-air system exhibits certain advantages. Firstly, it is more cost efficient, going for less than a third of its Li-ion counterpart [12]. Secondly, it is constructed using safer materials, while Li-ion batteries are vulnerable to catch fire [13,14]. Thirdly, the currently achieved specific energy density of the Zn-air system is superior to that of its Li-ion competitors (typically within 100–250 Wh/kg) [15]. Compared with other high-energy battery systems such as the sodium-sulfur or sodium-metal chloride, which work at elevated operating temperatures (300 °C) and contain highly reactive and potentially polluting components, the Zn-air system is environmentally friendly and has a low safety risk [16]. The widespread accessibility, recyclability and abundant natural resources of raw zinc materials further guarantee its long-term use on the mass market. Therefore, these days the Zn-air system is considered as one of the most promising metal-air power sources.

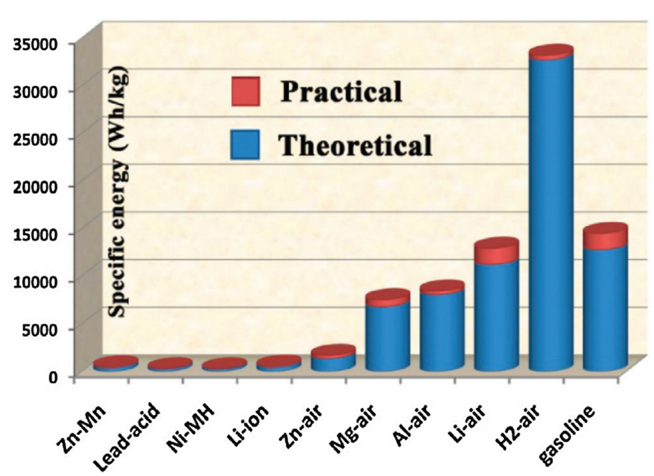

Fig. 1. Comparison of the specific energy density of some representative types of primary/rechargeable batteries, metal–air batteries, H_2–air fuel cell and gasoline (Reprint with permission from Royal Society of Chemistry, the theoretical values are calculated on the basis of thermodynamics of active materials [2]).

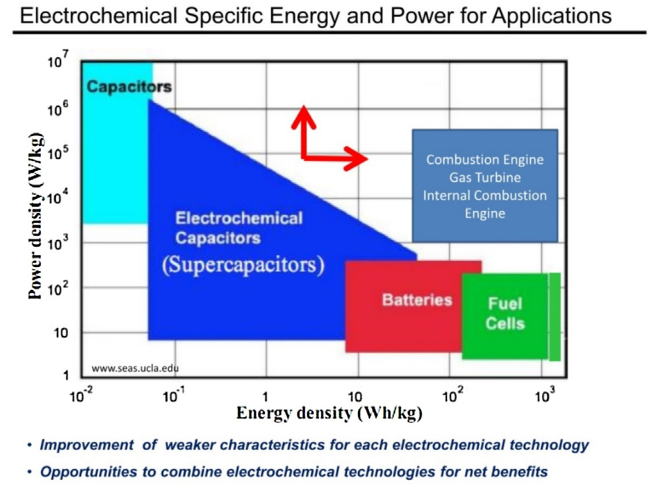

Fig. 2. The Ragone plot [8] of the practical power density *versus* the practical specific energy density.

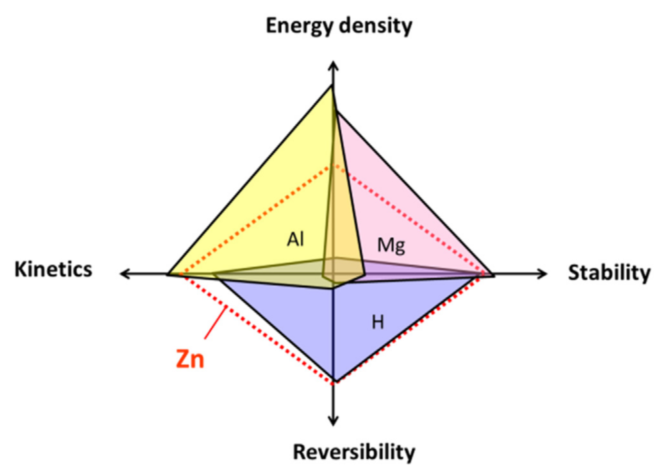

Fig. 3. Revealed zinc property regimes (Reprint with permission from Dr. G.X. Zhang and the National Research Council of Canada). Note that C and organics are not reversible, H has a low specific energy density, Al, Mg, Si, Ti are not reversible, Fe, Cd, Pb have low specific energy density, and Li, Na, K, Ca are neither stable nor reversible.

At present, Zn-air batteries already have certain applications, for example, in hearing-aids and miniature medical devices [5,17,18]. However, certain technological challenges are still hindering their success on the competing market. The main obstacles can be briefly summarized as follows: (i) poor recharge-ability, (ii) low utilization of the anode, (ii) sluggish kinetics of the cathode, (iii) longevity challenge. Compared with the Zn-air battery, the Zn-air fuel cell (ZAFC) offers several benefits, such as higher specific energy density, more attractive costs, better environmental compatibility and faster on-site refueling which requires only a standard electrical supply [1–4,16,19,20]. It also has