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Advances in modeling and simulation of Li–air batteries

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ABSTRACT

Li–air batteries have potential to be the next generation power sources for various applications, from portable devices to electric vehicles and microgrids, due largely to their significantly higher theoretical energy densities than those of the existing batteries. The commercialization of this technology, however, is hindered by a variety of technical hurdles, including low obtainable capacity, poor energy efficiency, and limited cycle life. Breakthrough to these barriers requires a fundamental understanding of the complex electrochemical and transport behaviors inside the batteries. Mathematical modeling and simulation are imperative in gaining important insight into the mechanisms of these complex phenomena, which is vital to achieving rational designs of better materials for high-performance batteries. In this paper, we present a comprehensive review of the latest advances in modeling and simulation of Li–air batteries and offer our perspectives on new directions of future development. Unlike previous reviews that centered mainly on continuum modeling of non-aqueous Li–air batteries, the present paper focuses on mathematical descriptions of the detailed transport and electrochemical processes in different types of Li–air batteries. We start with a brief introduction to the working principles of Li–air batteries. Then, the governing equations for mass transport and electrochemical reactions in non-aqueous Li–air batteries are formulated, including lithium ion and oxygen transport in the porous air electrode, the formation of solid discharge products, the kinetics of electrode reactions, the evolution of electrode structure, the distribution of active sites, the effect of the side reactions during cycling, the phenomena of the volume change, and the charge process. In addition, the mo\deling and simulations of aqueous and hybrid Li–air batteries are reviewed, highlighting the phenomena that are different from those in the non-aqueous ones. Finally, the challenges facing the modeling and simulation of Li–air batteries are discussed and perspectives for the development of a new generation of Li–air batteries are outlined.

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1. Introduction

The rapid development of advanced electronic devices and electric vehicles results in a great demand for high-energy-density storage systems [1]. To date, rechargeable lithium-ion batteries are the most widely used power sources for portable and mobile applications because of their reasonable energy density, rate capability, and cycle life [2]. During charge, lithium ions are extracted from a positive electrode material (e.g., a layered intercalation compound $LiFePO_4$ or $LiCoO_2$) and inserted into or reacted with a negative electrode material (e.g., graphite). During discharge, all the electrochemical processes proceed in the reverse direction [3]. The low theoretical capacity of the positive electrode materials, however, limits the energy density of the existing lithium-ion batteries to about 500–700 Wh kg^{-1}, which is insufficient for many emerging applications (e.g., electric vehicles) [4]. Thus, the exploitation of new energy storage technologies with much higher energy density is still a grand challenge.

Among various emerging energy storage technologies, metal–air batteries have the greatest potential for dramatically enhancing energy density, especially lithium–air, aluminum–air, and zinc–air batteries [5]. In these types of batteries, a pure metal is used as the negative electrode rather than an intercalation compound. Different from the intercalation reaction mechanism, oxygen enters the porous air electrode and participates in the oxygen reduction reaction (ORR) during the discharge process. The charge process is the reversed one through the oxygen evolution reaction (OER) to produce metal and oxygen. As oxygen can be obtained directly from ambient air, minimizing the required mass and volume of the air electrode, the energy density of a metal–air battery theoretically relies on the metal electrode only. Among the metal–air batteries, the lithium–air (Li–air) battery has garnered the most attention, due largely to the lowest equivalent weight of lithium metal, corresponding to a theoretical energy density of ~11,680 Wh kg^{-1}, which is close to that of gasoline (~13,000 Wh kg^{-1}) [6].

A prototype rechargeable Li–air battery was demonstrated by Abraham and Jiang in 1996 [7], in which a polymer electrolyte composed of a lithium salt and carbonate-based solvents was used, and the reversibility was achieved through the hypothesized formation and decomposition of lithium oxides. Since then, many advancements have been made due to worldwide attention, and various types of Li–air batteries have been proposed and developed [6]. During discharge, lithium metal is oxidized at the lithium electrode (or anode), producing electrons and lithium ions. Oxygen is reduced at the air electrode (or cathode) and combined with lithium ions in the electrolyte to form the discharge product. During charge, the electrochemical processes are reversed. The discharge product is electrochemically oxidized at the air electrode, producing electrons, lithium ions, and oxygen [8]. Notably, the discharge product depends on the type of electrolytes used in the battery. In aqueous electrolytes, the product dissolves first and starts to precipitate when reaching its solubility. In non-aqueous electrolytes, on the contrary, the product is insoluble and deposits on the electrode surface from the beginning. Accordingly, careful design of the air (positive) electrode is vital to the performance of Li–air batteries based on different types of electrolytes.

The development of a high-performance rechargeable Li–air battery requires a profound understanding of the electrochemical and transport processes, the utilization of suitable electrolyte and electrode materials, and the design of proper battery structures. Tremendous efforts have been made in the recent decade to make Li–air batteries commercially viable. Various electrolyte and electrode materials have been fabricated and tested [9,10]. The reaction, degradation, and failure mechanisms have been investigated and proposed [11]. Advanced characterization techniques and devices have been developed and utilized [12,13]. Although some breakthroughs have been made, the development of Li–air batteries is still in the early stage with many technical difficulties, such as the relatively low obtainable discharge capacity, poor rate capability, low energy efficiency, and limited cycle life [11]. In addition to the experimental explorations, modeling is a powerful and economical tool for understanding the working processes, evaluating the material capabilities, and improving the battery performance [14].