



Modeling discharge deposit formation and its effect on lithium-air battery performance

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ABSTRACT

Lithium-air batteries show a great promise in electrochemical energy storage with their theoretical specific energy comparable to gasoline. Discharge products such as Li_2O_2 or Li_2CO_3 are insoluble in several major nonaqueous electrolytes, and consequently precipitate at the reaction sites. These materials are also low in electric conductivity. As a result, the reduced pore space and electrode passivation increase the reaction resistance and consequently reduce discharge voltage and capability. This work presents a modeling study of discharge product precipitation and effects for lithium-air batteries. Theoretical analysis is also performed to evaluate the variations of important quantities including temperature, species concentrations, and electric potentials. Precipitation growth modes on planar, cylindrical and spherical surfaces are discussed. A new approach, following the study of ice formation in PEM fuel cells, is proposed. Validation is carried out against experimental data in terms of discharge voltage loss.

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1. Introduction

Due to the growing concerns on fossil fuels' depletion and climate change, lithium-based battery technologies have received a great deal of attention in recent years owing to their relatively high efficiency and energy density. A successful example is lithium-ion batteries that have been widely used in nowadays portable and automotive applications. A major hurdle to battery development, however, is the insufficient low energy capability as opposed to fossil fuels. The gasoline's specific energy is about 13,000 Wh/kg, an order-of-magnitude higher than that of Li-ion batteries. Li-air batteries are an emerging area, showing a great promise of high specific energy storage. Their unique feature is that the cathode active material – oxygen is not stored inside the batteries, but obtained from the ambient environment. In addition, pure lithium metal, rather than Li intercalated graphite (LiC_6) as that in Li-ion batteries, is used as the anode material. The open circuit potential (OCP) of Li-air batteries can reach around 3.0 V. As a result, the theoretical specific energy reaches around 11,680 Wh/kg, comparable to gasoline and higher than methanol [1]. Fig. 1 shows schematic of a Li-air battery and its operation. Prior to their full commercialization stage, however, many scientific and technical challenges must be overcome.

Early concept of Li-air batteries can be traced back to the 1970s, originally proposed for automotive applications [2]. Abraham and Jiang reported one of the first nonaqueous Li-air batteries that show rechargeability [3]. The electrode and electrolyte are laminated to produce a battery of about 300 μm thick. The cell can be recharged when using cobalt phthalocyanine catalyst. In recent years, Li-air batteries received a growing interest of research and development. Most studies were focused on material design and performance characterization for the cathodes [4–10]. A major challenge in the cathode is the precipitation of discharge product such as Li_2O_2 and Li_2CO_3 . These materials have low solubility in several major electrolytes, therefore are deposited over the reaction surface during discharging operation. These discharge products are poor electric conductors, leading to passivation, and increase reaction resistance. As the product accumulates in the cathode electrode with time, the discharge voltage drops (see Fig. 2). Several studies have attempted to understand the discharge product's effects. Albertus et al. presented both experimental and modeling studies on Li-air batteries with a special effort on investigating discharge product effect [11]. They used both flat and porous electrodes in experiment. They showed the cell voltage starts around 2.6 V, followed by a gradual decrease at initial stage and a rapid drop when close to 2.0 V. Their modeling followed the approach of lithium-ion batteries and accounted for the passivation effect. Viswanathan et al. studied the electric conductivity of Li_2O_2 both experimentally and theoretically [12]. They treated the charge transport in the Li_2O_2 film following that in a biased metal insulator metal (MIM) junction. A Fc/Fc^+ redox couple [13] was used to probe the electric

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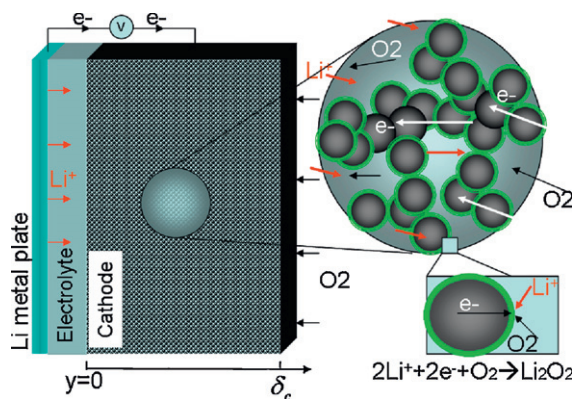


Fig. 1. Schematic of a Li-air battery and its discharge operation with discharge product Li_2O_2 as an example.

resistance. They indicated that electron tunneling [14,15] may play an important role in sustaining the cathode electrochemical activity.

In polymer electrolyte fuel cells (PEFCs, also called PEM fuel cells), a similar phenomenon occurs under subfreezing condition, i.e. ice formation. Water is a byproduct of PEFCs by the oxygen reaction reduction (ORR) [16]. At subfreezing temperature, product water freezes to form ice, which is deposited in the electrode and causes cell voltage loss (see Figs. 3 and 4; [17]). Fig. 3 shows the evidence of ice accumulation in fuel cell electrodes. As a result of ice formation, the voltage decreases (as shown in Fig. 4). A theory has been developed to delineate various mechanisms of voltage loss caused by ice formation [18,19]. In this paper, we will also examine the effects of discharge product formation in Li-air batteries by extending the knowledge of PEFCs to Li-air batteries. Analysis will be performed on the spatial variations of important quantities such as species concentrations, temperature, and phase potentials. Comparison with literature experimental data will be presented. The results benefit both Li-air battery and PEFC developments.

2. Theoretical analysis

Lithium metal is used as the anode active material. Li dendrite/moss formation may occur upon battery cycling due to the preferential deposition of lithium metal, which may lead to shorts between the anode and cathode. A thin Li^+ -conductive artificial layer is usually used to improve lithium anode stability. During

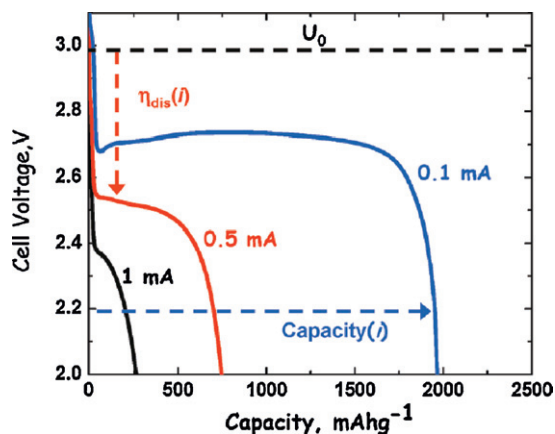


Fig. 2. Discharge curves at different current densities [1].

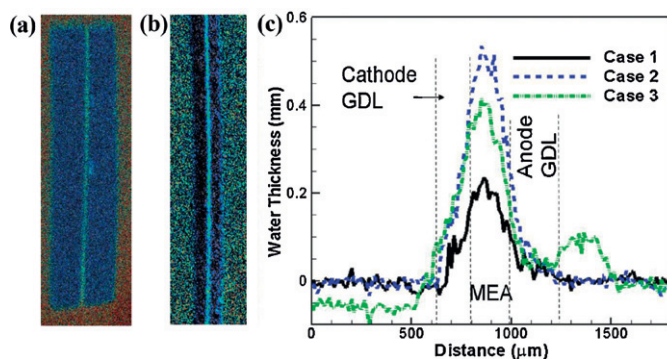
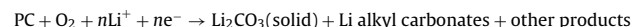


Fig. 3. Neutron images of ice formation in a fuel cell: (a) water content neutron image; (b) close-up image; and (c) water thickness in the PEFC detected by high-resolution neutron imagery. Cases 1–3: Cooling from 100, 50, 50% RH and cold start at 0.04, 0.04, and 0.094 A/cm^2 , respectively [17].

discharge, the following electrochemical reaction occurs at the lithium–electrolyte interface:



The produced Li ions transport through the thin artificial layer and electrolyte to the cathode. The produced electrons are conducted through out circuit toward the cathode, where they combine with Li^+ ions and oxygen to form Li oxides or Li-based composites depending on the cathode electrochemistry detail. The battery electrolyte plays a critical role in determining the cathode electrochemistry. Li_2O_2 and Li_2CO_3 are the primary products when using several major nonaqueous electrolytes, e.g. organic and carbonate solvents, respectively. The exact reaction routes can be complex, involving several intermediates. The overall cathode reactions with Li_2O_2 and Li_2CO_3 , respectively, as product can be rewritten by [1,3,11,12]:



Both Li_2O_2 and Li_2CO_3 are usually insoluble in the corresponding electrolytes and exhibit low electric conductivity. As a result, the discharge materials are deposited over the carbon surface and form a thin film, hampering species transport and the electrochemical activity, and leads to cell voltage loss.

During discharging, irreversible processes occur, reducing the energy conversion efficiency. Comparing with Li-ion batteries, the operating efficiency of current Li-air battery technology is relatively low, around 50%. The rest of the energy is released in form of waste heat. Temperature has profound effects on Li-air battery performance due to its importance on overcoming the activation barriers of reactions. The principle mechanisms include the reversible, irreversible, and ohmic heating. The reversible and irreversible sources are released at the reaction interface during energy conversion, whereas the ohmic heating arises from the resistance to the electric current flows including ion movement. These sources lead to spatially varying temperature inside a battery. To evaluate the upper bound of temperature variation, one can assume all the heating sources were uniformly distributed inside the electrode, the temperature variation can be evaluated by [18]:

$$\Delta T = \frac{I(E_0 - V_{\text{cell}})\delta_c}{2k_{\text{eff}}} \quad (3)$$

where E_0 is defined as $-\Delta\bar{h}/2F$ and represents the EMF (electromotive force) that all the energy from Li–oxygen reaction, the ‘calorific value’, heating value, or enthalpy of formation, were transformed into electrical energy. The effective thermal conductivity of

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