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Effects of Operating Temperature on the Electrical Performance of a Li-air Battery operated with Ionic Liquid Electrolyte

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ABSTRACT

Li-air cell operated with ionic liquid electrolytes is a very promising energy storage technology for electric vehicle and plug-in hybrid electric vehicle due to several favorable characteristics of ionic liquids. However, Li-air cells that employ room temperature ionic liquid (RTIL) electrolytes exhibit poor performance due to limited oxygen solubility and low reactant species mobility. To circumvent these aforementioned drawbacks, we investigated the electrical performance of a Li-air cell with ionic liquid electrolytes operating at high temperature. A continuum based model is used to quantify the performance of the Li-air cell, with an ionic liquid (MPPY-TFSI) electrolyte, as a function of operating temperature. Simulations at the atomistic scale, such as molecular dynamics (MD) and density functional theory (DFT) calculations are used to obtain key properties for the continuum model. These properties include electron transfer reaction rate constant, species diffusivity and oxygen solubility. The MD simulations indicate that oxygen solubility in ionic liquid increases with temperature, which is very favorable for high temperature operation. The continuum based cell level simulation results show that the battery performance can be improved significantly by increasing operating temperature. For instance, specific capacity as high as 3000 mAh/g can be achieved at 110 °C operating temperature, which is almost 25 times higher than its counterpart at room temperature. Simulation results also reveal that by increasing the operating temperature, the specific capacity can be improved significantly for high load current density, which is one of the most critical drawbacks in RTIL based Li-air battery. We also studied the effect of cathode thickness on the performance of Li-air battery at different operating temperatures. The transport limitation of oxygen and lithium ions can be alleviated at higher operating temperatures, suggesting that even thicker cathode materials can be used to enhance the cell capacity at elevated temperature.

1. Introduction

Even though recent developments in Li-ion battery have revolutionized the portable electronics market, it still falls short of meeting the demands of the automobile industry for electric vehicles and hybrid electric vehicles. For instance, the current driving range of most Li-ion based electric vehicles is limited to 200 km, which is practically useless for any long distance trip [1]. The successful development of electric vehicles requires breakthrough in battery technology that leads to very high specific capacity as well as cell capacity at reasonable price. The Li-air battery, which has a theoretical energy density comparable to that of gasoline [2], has the potential to meet the demand of auto industry and supply power for longer driving range. As a matter of fact, the specific energy of lithium-air battery can be 10 times as high as that of lithium-ion battery. This high specific energy can be attributed to a light cathode employed in Li-air battery, where the principal reactant (oxygen) is taken directly from atmosphere rather than stored in heavy cathode materials, such as $LiMn_2O_4$, $LiFePO_4$, and $LiCoO_2$ [3]. The superior performance of Li-air battery has been reported in recent studies where organic solvent was used as electrolytes [4,5]. However, the cyclic performance of those batteries was very low since lithium carbonate is produced from organic electrolytes during discharge [6]. Owing to the very high chemical stability of lithium carbonate, high electric potential is required to recover lithium ions from lithium carbonate during charging process. This high charging potential can oxidize the electrolyte, which results in the degradation of electrolytes as well as formation of insulation layer on the electrode surface [7]. Another major drawback of widely used

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organic electrolytes is flammability due to their characteristic high vapor pressure. The flammability of these electrolytes can lead to major safety hazard, especially in the Li-air battery due to its open form architecture.

To overcome aforementioned drawbacks, ionic liquids have been used as electrolytes in lithium-air batteries [8]. Ionic liquids have low vapor pressure and they are chemically and thermally stable solvents. However, the performance of RTIL based Li-air battery was inferior compared to that of organic electrolytes because of high viscosity and low diffusivity at room temperature. Moreover, the oxygen solubility and diffusivity are much lower in ionic liquid electrolytes compared to organic liquids, which severely affect the electrical performance of Li-air battery [9]. Furthermore, lithium ion mobility is limited in ionic liquids because of the formation of charged clusters between lithium ion and ionic liquid anions [10]. However, in a recent work, Deshpande et al. [10] have shown that diffusivities of lithium ions increase with temperature in ionic liquid electrolytes, which can improve the lithium ion mobility. As a matter of fact, Kuboki et al. [8] have demonstrated the feasibility of high temperature (over 80 °C) operation of Li-air battery using ionic liquid electrolyte. While higher specific capacity was obtained at elevated temperature, the battery was tested at very low current density conditions ~0.1 A/m^2, which is not suitable for most applications. In this work, the performance of Li-air batteries with ionic liquid electrolytes is studied at high temperatures since species transport properties, such as diffusivity and mobility, of the electrolytes could be improved at higher operating temperatures. Here, MD and DFT calculations are performed to calculate properties of ionic liquids and reaction constants, and continuum level analysis is carried out to predict the battery performance at different load current densities. Furthermore, the effects of varying cathode thickness are studied to demonstrate the species transport behavior in ionic liquid electrolytes and its consequence on cell performance at different working temperatures.

2. Model

2.1. Model System

A typical Li-air cell consists of lithium anode, porous separator and catalyst loaded porous carbon cathode as shown in Fig. 1. Here, porous cathode and separator are filled with electrolyte, which provides route for lithium ion and oxygen transportation. Typically, solid lithium foil is used as anode material since it can decrease the anode weight by eliminating structural materials (e.g. graphite), and anodic reaction takes place only at the interface between lithium foil and electrolyte. On the other hand, cathodic reaction occurs in the entire porous cathode surface. During the discharge state, lithium metal is oxidized and dissolved into electrolyte continuously by releasing an electron as

$$Li \rightarrow Li^+ + e^- \quad (1)$$

The electron released from lithium metal moves to cathode side through outer loop while lithium ions pass through the electrolyte to cathode region. The lithium ion is subsequently reduced at the cathode side (Fig. 1) in presence of electron and oxygen derived from atmospheric air through the gas diffusion layer (GDL) as [11]

$$O_2 + e^- \rightarrow O_2^- \quad (2)$$

$$O_2^- + Li^+ \rightarrow LiO_2 \quad (3)$$

$$2LiO_2 \rightarrow Li_2O_2 + O_2 \quad (4)$$

Thus, the overall reaction for a Li-air battery can be represented as

$$2Li + O_2 \rightarrow Li_2O_2 \quad (5)$$

During the charge process, the anodic and cathodic reactions are reversed. In other words, lithium peroxide is oxidized at the

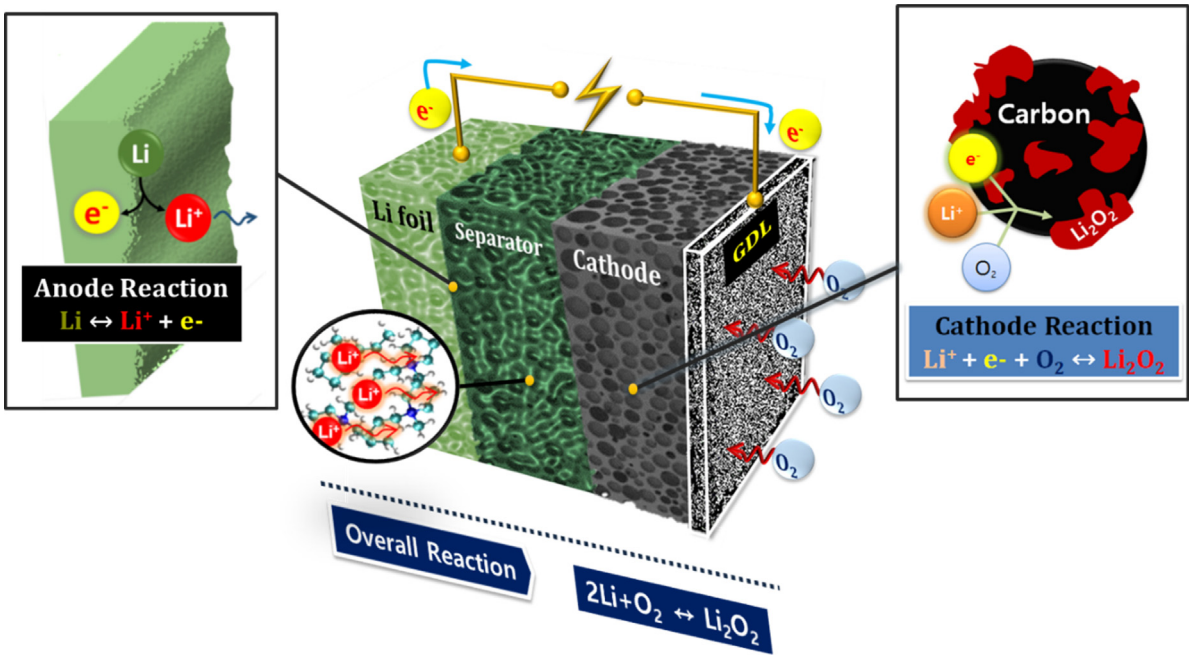

Fig. 1. Schematic illustration of Li-air battery with corresponding electrochemical reactions at anode and cathode side is provided. Li ion dissolves into electrolyte due to oxidation at anode while it reduces with oxygen at cathode during discharge stage. Oxygen is introduced continuously to the cell through the air-breathing cathode.