Journal of Power Sources 274 (2015) 762–767

Contents lists available at ScienceDirect

Journal of Power Sources

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

Gas transport evaluation in lithium–air batteries with micro/nano-structured cathodes

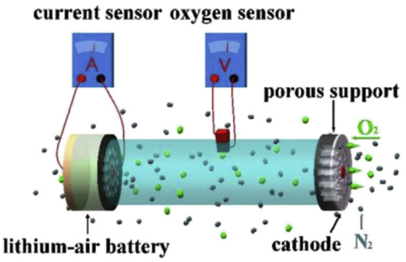
Xiaoning Wang [a], Kechun Wen [a], Yuanqiang Song [a], Luhan Ye [a], Kelvin H.L. Zhang [b], Yu Pan [a], Weiqiang Lv [a], Yulong Liao [c], Weidong He [a, *]

[a] *School of Energy Science and Engineering, University of Electronic Science and Technology, Chengdu, Sichuan 611731, PR China*
[b] *Department of Chemistry, Chemistry Research Laboratory, University of Oxford, Mansfield Road, Oxford OX1 3TA, United Kingdom*
[c] *School of Microelectronics and Solid-State Electronics, University of Electronic Science and Technology, Chengdu, Sichuan 611731, PR China*

HIGHLIGHTS

- Designs a device to measure the cathode diffusivity in the lithium–air battery.
- Evaluates the performance of the lithium–air battery with nanoscale cathodes.
- Analyze correlation between limiting current density/polarization and important battery parameters.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 4 August 2014
Received in revised form
25 September 2014
Accepted 17 October 2014
Available online 23 October 2014

Keywords:
Lithium–air battery
Diffusivity
Concentration polarization
Limiting current density
Porous cathode

ABSTRACT

Inefficient gas transport in the porous cathode is disastrous for the lithium–air battery to achieve a high electrochemical performance. Previous evaluation of the cathode diffusivity relies on indirect calculations based on multiple V–I data obtained over the intact battery system, which inevitably induces evaluation uncertainty and material waste. In this report, an electrochemical device is designed for the out-of-cell diffusivity measurement in the lithium–air battery with micro/nano-sized cathodes. With the measured diffusivity, a few electrochemical parameters including the limiting current density and the concentration polarization associated with the porous cathodes can thus be directly evaluated. The work facilitates the development of highly-efficient cathode materials in the general field of metal–air battery field.

1. Introduction

Metal–air batteries, especially the lithium–air battery, own a number of attractive characteristics including high energy density and high theoretical specific capacity [1], which together have made such battery systems promising power-supply resources for a variety of applications, such as automotive applications, mobile phone and laptop [2]. In particular, the advances in the lithium–air battery field have been multifold, and many high-performance materials have been designed and realized in recent years to improve the overall electrochemical performance of the battery system. For instance, alloying anode materials have been synthesized to enhance the capacity and the safe operation of the lithium–air battery [2]. In addition, endurable and highly ionic-conducting electrolyte materials such as hydrophobic room temperature ionic liquid electrolyte are prepared to achieve better discharge capacity in the battery system [3]. As for the cathode, Xiao et al. [4] have reported hierarchically porous graphene to be

---

* Corresponding author.
E-mail address: weidong.he@uestc.edu.cn (W. He).

http://dx.doi.org/10.1016/j.jpowsour.2014.10.117
0378-7753/

employed as the cathode electrode in the battery system, Sun et al. [5] have prepared graphene nanosheets as cathode catalysts to improve the performance of lithium–air battery, and Li et al. [6] use nitrogen-doped carbon nanotubes as cathode to improve the specific discharge capacity. With such cathode materials, high specific capacity and long cycling life for lithium–air battery have been shown to be realizable. Compared to those promising advances in the lithium–air battery materials, much still has remained to be explored to directly evaluate the gas transport in the porous cathodes of the lithium–air battery, a parameter that largely correlates with the porosity, tortuosity and the oxygen partial pressure of the lithium-battery system [7–9]. At the cathode side, oxygen diffuses from the porous carbon and reacts with Li ions at the cathode–electrolyte interface. Oxygen diffusion in the cathode is of significant importance to the performance of the lithium–air battery since the over-potential, which is dependent on the reaction kinetics, is dominated by oxygen diffusion. A slow oxygen diffusion rate results in a large over-potential while fast oxygen diffusion leads to a small over-potential. The efficient operation of a lithium–air battery depends largely upon the fast diffusion of oxygen, which is then determined by the parameters including the cathode porosity, the cathode tortuosity, the oxygen partial pressure, and the cathode thickness [10]. There are models focused on the oxygen diffusion in the lithium–air battery. For instance, Sandhu et al. proposed a limiting-diffusion model, and studied the effects of oxygen partial pressure and current density on the specific capacity of the lithium–air battery. The model assumes an average pore size ~4 nm as the pore diameter of the cathode [11]. In this report, an electrochemical device is designed based on a few known gas transport models for measuring, in an out-of-cell fashion, the oxygen diffusivity in the micro/nano-structured cathode of the lithium–air battery. The pore diameters used in this work range from 0 to 500 nm, and cover a large range of practical values. The limiting current density and the concentration polarization associated with the lithium–air battery are then pre-evaluated subsequently. The work based on the quantitative analysis facilitates further development in the general field of the metal–air battery with highly-efficient micro/nano-sized electrode materials.

2. Electrochemical device

An electrochemical device is designed, as shown in Fig. 1, to measure the diffusivity of oxygen in the cathode of the lithium–air battery in the air environment. The device contains five components: a lithium–air battery, an oxygen sensor, a current sensor, a tube, and a porous cathode composed of porous carbon loaded with catalyst. Due to the nanoscale thickness of the cathode, a porous support is designed under the cathode as mechanical support, the pore size of which is large enough so that the diffusion of cathode gas is not impeded.

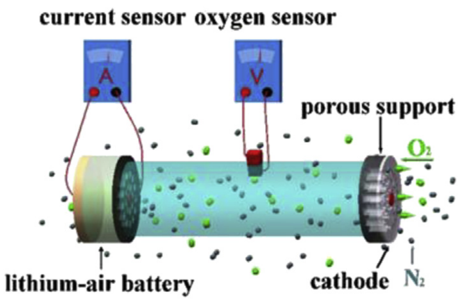


Fig. 1. The schematic of an electrochemical device for the out-of-cell measurement of cathode diffusivity in the lithium–air battery.

In the diffusivity measurement, a constant current density (i) is applied to the lithium–air battery. Then, there occurs the reaction $O_2 + 2e^- = O_2^{2-}$ [12], which leads to the decrease in the partial pressure of oxygen in the tube. An oxygen flux along the oxygen concentration gradient is then formed through the porous cathode. The Nernst potential is obtained through the oxygen sensor at a fixed temperature. The correlation of the Nernst potential (E) with the partial pressure of oxygen outside the tube (p_o), and the partial pressure of oxygen inside the tube (p_i) is given in Eq. (1).

$$p_i = p_o \exp\left(\frac{-2EF}{RT}\right) \tag{1}$$

where F is the Faraday constant, R is the ideal gas constant, T is the operating temperature, and p_o is the oxygen partial pressure outside the tube, as set at 0.21 atm [13,14].

In the measurement, there is no nitrogen concentration gradient, and nitrogen is not involved in the diffusion. The air transport through the porous cathode can be described in Eqs. (2)–(4), where 1 and 2 represent O_2 and N_2, respectively, J_1 is the flux of oxygen, n_1 is the concentration of oxygen, X_1 is the molar fraction of oxygen, J is the total flux, $D_{1\,K}^{\text{eff}}$ is the effective Knudsen diffusivity of oxygen, D_{12}^{eff} is the effective binary diffusivity, p is the total pressure, B_0 is the permeability, t is the viscosity, and D_1 is the total effective diffusivity [13].

$$J_1 = -D_1 \nabla n_1 + X_1 \delta_1 J - X_1 r_1 \left(\frac{nB_0}{t}\right) \nabla p \tag{2}$$

$$\delta_1 = \frac{D_{1\,K}^{\text{eff}}}{D_{1\,K}^{\text{eff}} + D_{12}^{\text{eff}}} \tag{3}$$

$$r_1 = 1 - \delta_1 = \frac{D_{12}^{\text{eff}}}{D_{1\,K}^{\text{eff}} + D_{12}^{\text{eff}}} \tag{4}$$

The cathode pore size is typically less than 10 times the oxygen mean free path [13]. Therefore, the Knudsen diffusivity and the binary diffusivity are both taken into account, and the value of $X_1 \delta_1 J$ is close to zero [16]. The total pressures inside and outside the tube are the same, and $\nabla p = 0$. Based on the oxygen pressure difference between inside and outside of the tube, Eq. (2) can be reduced as Eq. (5) [13].

$$J_1 = -D_1 \nabla n_1 \tag{5}$$

The correlation between the oxygen flux and the current density is depicted in Eq. (6). Based on the ideal gas equation as depicted in Eq. (7), Eq. (8) is then obtained. Integrating Eq. (8) gives rise to Eq. (9), where l is the cathode thickness [13].

$$J_1 = \frac{i}{2F} \tag{6}$$

$$n_1 = \frac{p_1}{k_B T} \tag{7}$$

$$\frac{i}{2F} = -D_1 \frac{\nabla p_1}{k_B T} \Rightarrow \frac{i N_A \mathrm{d}x}{2F} = -D_1 \frac{\mathrm{d}p_1}{k_B T} \tag{8}$$

$$p_i = p_o - \frac{iRTl}{2FD_1} \tag{9}$$

The oxygen partial pressure inside the tube is resulted from the change in the value of current density, leading to the changes in the value of the Nernst potential and the value of p_i based on Eq. (1). By