Energy xxx (2015) 1–5

Contents lists available at ScienceDirect

Energy

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

A new insight into the oxygen diffusion in porous cathodes of lithium-air batteries

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ARTICLE INFO

Article history:
Received 11 August 2014
Received in revised form
21 February 2015
Accepted 23 February 2015
Available online xxx

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

ABSTRACT

Slow air transport in the cathodes limits the performance of the metal-air battery. In this work, the diffusion mechanisms in the lithium-air battery have been investigated. It has been found that Knudsen diffusivity can be influenced dramatically by the different pore sizes while bulk diffusivity is almost a constant at a fixed temperature. Limiting current density and concentration polarization, both limited by impeded gas diffusion in the porous cathode, have been evaluated systematically. The analysis of the correlation between those electrochemical parameters and diffusivities improves the quantitative evaluation of gas-based batteries at various materials and operation conditions.

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1. Introduction

Efficient energy storages with excellent capacity are urgently demanded in the modern society. Among all current-available energy storages, metal-air batteries, especially the lithium-air battery, have drawn extensive attention due to its huge energy density [1–4]. High electrochemical performance of the lithium-air battery has been achieved by employing various advanced materials. For instance, Xiao et al. (2011) have reported highly-porous nanostructured hierarchically porous graphene to be employed as cathode in the non-aqueous lithium-air battery system [5]. A capacity of 15,000 mAh/g was obtained in their work. As for the highly stable lithium-air battery, Peng et al. (2013) have obtained 98% capacity retention after 100 cycles using stable TiC-based cathodes [6]. Despite those promising advances in the lithium-air battery materials, much still has remained unexplored regarding the cathode. For example, the deposition of Li_2O_2 on the cathode surface and the decomposition of metal lithium related to the penetration of H_2O and CO_2 are big issues to be solved for the development of non-aqueous lithium-air battery. The stability of the lithium-air battery induced by many factors largely limits its capacity and safety [7,8]. Furthermore, high energy loss and low maximum output energy caused by the insufficient O_2 diffusion are yet to be addressed, especially for the ambiently-operating lithium-air battery with a protected gas diffusion layer [9].

Cathode materials with different pore sizes and materials heterogeneities lead to different air transport channels. The difference affects largely the diffusion mechanism in the cathode [10,11]. Previous studies on the fuel cells investigated the gas diffusion in the cathode comprehensively. For instance, Zhao et al. (2003) and He et al. (2012) employed the direct measurement of effective diffusivity to explore the limiting current density and concentration polarization associated with electrode parameters [12,13]. Zhao et al. (2003) also measured one of the important diffusion coefficients, bulk diffusivity in their work by neglecting Knudsen diffusivity. In the process of air transport, one or more

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http://dx.doi.org/10.1016/j.energy.2015.02.072
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Please cite this article in press as: Ye L, et al., A new insight into the oxygen diffusion in porous cathodes of lithium-air batteries, Energy (2015), http://dx.doi.org/10.1016/j.energy.2015.02.072

diffusion mechanisms including Knudsen diffusion and bulk diffusion govern the gas transport process. If the Knudsen number K_n, the ratio of the gas mean path to the size of pores of an electrode is much smaller than 0.1, bulk diffusion is dominant in the gas transport. If K_n is much greater than 10, Knudsen diffusion becomes dominant. As K_n ranges between 0.1 and 10, both mechanisms govern the gas transport [14]. As a matter of fact, the latter two situations typically occur in the mesoporous/nanoporous air diffusion layer of lithium-air batteries [15]. However, previous reports in the fuel cell field mainly take bulk diffusion into account. In addition, there is still a lack of quantitative equations for evaluating the air diffusion in the lithium-air battery field. The lack of cathode air diffusion models limits the quantitative evaluation and development of cathode materials in the lithium-air battery field. In this report, based on the previous work on the gas diffusion in large pore cathodes of fuel cells, gas diffusion and electrochemical performance of the lithium-air battery are explored *via* an amended mathematical diffusion model. Based on our derivation and analysis, important parameters including limiting current density and concentration polarization are evaluated with respect to the combination of two diffusivities. The work facilitates the development of the metal-air battery with highly-efficient cathode materials.

2. Theoretical analysis

Gas transport through a porous sample can be described in Eqs. (1)–(5), [12].

$$J_1 = -D_1\nabla n_1 + X_1\delta_1 J - X_1 r_1\left(\frac{nB_0}{\mu}\right)\nabla p \tag{1}$$

$$J_2 = -D_2\nabla n_2 + X_2\delta_2 J - X_2 r_2\left(\frac{nB_0}{\mu}\right)\nabla p \tag{2}$$

$$\delta_1 = 1 - r_1 = \frac{D_{1K}^{\text{eff}}}{D_{1K}^{\text{eff}} + D_{12}^{\text{eff}}} \quad \text{and} \quad \delta_2 = 1 - r_2 = \frac{D_{2K}^{\text{eff}}}{D_{2K}^{\text{eff}} + D_{12}^{\text{eff}}} \tag{3}$$

$$\frac{1}{D_1} = \frac{1}{D_{1K}^{\text{eff}}} + \frac{1}{D_{12}^{\text{eff}}} \quad \text{and} \quad \frac{1}{D_2} = \frac{1}{D_{2K}^{\text{eff}}} + \frac{1}{D_{12}^{\text{eff}}} \tag{4}$$

$$n_1 = \frac{p_1}{k_B T} \tag{5}$$

where 1 denotes O_2, 2 denotes N_2, J_1 and J_2 are the fluxes of gas species 1 and 2, J is the total flux, n_1 and n_2 are the concentrations of gas species 1 and 2, n is the total gas concentration, X_1 and X_2 are the molar fractions of gas species 1 and 2, μ is the viscosity, B_0 is the permeability, p is the total pressure, D_{1K}^{eff} and D_{2K}^{eff} are the effective Knudsen diffusivities of gas species 1 and 2, D_1 and D_2 are the combined effective diffusivities of gas species 1 and 2, D_{12}^{eff} is the effective binary diffusivity, the diffusivities are combined into δ_1 (δ_2) and r_1 (r_2) as presented in Eq. (3) to simplify the expression, p_1 is the partial pressure of oxygen, T is the absolute temperature and k_B is the Boltzmann constant. In a typical lithium-air battery operated in the ambient condition, the ratio between permeability and viscosity is particularly small and only O_2 transports into the cathode [16,17]. Thus the correlation between the gas flux and diffusivities can be reduced as Eq. (6). Based on charge balance, the flux is correlated with the current density, as given in Eq. (7), where i is the current density and F is the Faraday constant. Combining Eq. (6) and Eq. (7) gives Eq. (8).

$$J_1 = -\frac{D_{1K}^{\text{eff}} D_{12}^{\text{eff}}}{\left(D_{12}^{\text{eff}} + D_{1K}^{\text{eff}}\right)k_B T}\nabla p_1 + \frac{D_{1K}^{\text{eff}} p_1}{\left(D_{12}^{\text{eff}} + D_{1K}^{\text{eff}}\right)p} J_1 \tag{6}$$

$$J_1 = \frac{i}{2F} \tag{7}$$

$$\frac{idx}{2Fp} = \frac{-D_{12}^{\text{eff}} D_{1K}^{\text{eff}} dp_1}{\left(D_{1K}^{\text{eff}} + D_{12}^{\text{eff}}\right)p - D_{1K}^{\text{eff}} p_1} \tag{8}$$

Due to the oxygen reduction reaction, the oxygen partial pressure at the interface between electrolyte and cathode, expressed as p_i, is smaller than that in the outer cathode side, as shown in Fig. 1. As $x = 0$, the oxygen partial pressure in the outside of the battery system, p_1, is equal to p_0, and as $x = l$, the oxygen partial pressure inside the battery system, p_1, is equal to p_i. Integration of Eq. (8) gives Eq. (9). Since the cathode thickness and current density are both small in typical lithium-air batteries, $iRTl/2Fp$ is much less than 1. Therefore, Eq. (9) can be simplified as Eq. 10

$$D_{1K}^{\text{eff}} p_i = \left(D_{1K}^{\text{eff}} + D_{12}^{\text{eff}}\right)p - \left[\left(D_{1K}^{\text{eff}} + D_{12}^{\text{eff}}\right)p - D_{1K}^{\text{eff}} p_0\right]\exp\left(\frac{iRTl}{2FpD_{12}^{\text{eff}}}\right) \tag{9}$$

$$p_i = p_0 - \left(\frac{p}{D_1} - \frac{p_0}{D_{12}^{\text{eff}}}\right)\frac{iRTl}{2Fp} \tag{10}$$

where R is the ideal gas constant. Setting the left item (p_i) in Eq. (10) at 0, the limiting current density (i_{cs}) at the cathode is then expressed in Eq. (11). Accordingly, the concentration polarization at the cathode is given in Eq. (12).

$$i_{cs} = \frac{2Fpp_0}{RTl\left(\frac{p}{D_1} - \frac{p_0}{D_{12}^{\text{eff}}}\right)} \tag{11}$$

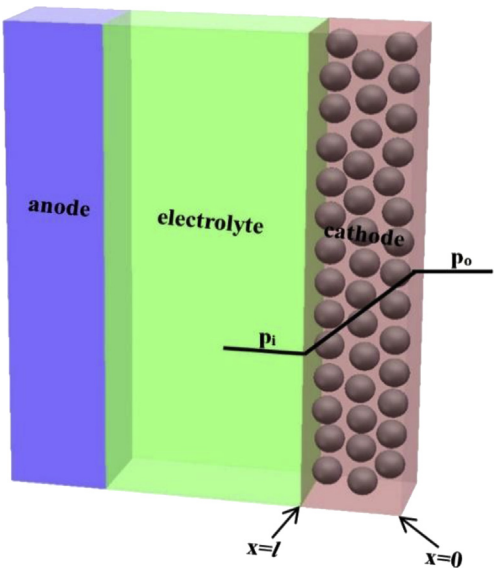

Fig. 1. A schematic of a typical lithium-air battery along with the partial pressure gradient of oxygen across the cathode.

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