



Research paper

Modeling of the lithium-air battery cathodes with broad pore size distribution



Artem V. Sergeev^a, Alexander V. Chertovich^a, Daniil M. Itkis^{b,*}

^a Physics Department, Lomonosov Moscow State University, Moscow 119991, Russia

^b Chemistry Department, Lomonosov Moscow State University, Moscow 119991, Russia

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ABSTRACT

Achieving theoretical promises of 1000 W h/kg specific energy for lithium-air batteries is quite challenging due to limited transport in the cathode along with electrode passivation. Transport can be enhanced in the electrodes with complex hierarchical pore architecture. Here, using computer simulations we analyze the effects of cathode pore size distribution (PSD) on capacity and discharge curve shape. Calculations considering a broad PSD revealed that even small discharge product resistivity prevents larger pores from accumulating the discharge product and thus turning them into non-clogging oxygen supply channels. Thus optimization of cathode architecture by adding of large-scale cavities enables cell capacity enhancement.

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1. Introduction

Today there is a huge demand for high energy density electrochemical storage, which is driven a lot by the automotive industry. Currently these demands are fulfilled mainly by mature Li-ion technology, however, as it is already reaching its limits, many groups focused their research on new technologies. Li–O₂ or Li-air batteries, being one of those, theoretically can provide specific energy of up to 3.5 kW h/kg of active components (lithium and oxygen). Implementing only a quarter of its theoretical capacity would be a major breakthrough for electric vehicles and other applications.

Naturally, Li–O₂ chemistry has drawn lot of attention over recent years. Christensen et al. [1] estimated practically achievable cell level specific energy to be about 1.3 kW h/kg taking the masses of all cell components into account. Understanding of processes occurring in this system is still limited, however, and there are lots of fundamental and engineering issues on a way towards implementation of Li-air batteries. Although the sustainable cyclability problem seems to be the most critical, experimentally achieved values of specific capacity are, nevertheless, far below theoretical expectations. Meini et al. [2] using different carbon blacks as cathode materials reached capacity of 2168 mA h/g_{carbon} at rather low current density of about 0.05 mA/cm². Another work [3] demonstrated smaller values – about 1100 mA h/g_{carbon} at 0.02 mA/cm².

Higher current densities, which are more useful for practice, often lead to even lower capacities. Cathode with gradient porosity designed for optimized oxygen transport demonstrated only 250 mA h/g_{carbon} at 0.5 mA/cm² [4]. Electrodes prepared of non-carbonaceous material – TiC nanopowder [5] – yielded about 500 mA h/g_{TiC} at 1 mA/cm². On the other hand, previous simulation study [6] that considered limited oxygen diffusion but not surface passivation, predicted that about 3000 mA h/g at 1 mA/cm² under 1 atm oxygen pressure can be reached. Such estimations are close to theoretical predictions by Andrei et al. [7]. Accounting for other cell components (such as separator, electrolyte and cell case) has led to cell level specific energy estimations around 350 W h/kg [6] as the pore filling factor derived from simulations turned out to be only 10–30%, which is much lower than 65% assumed in earlier estimations [1]. Further development should handle the oxygen diffusion problem making pore filling more uniform and complete, and, therefore, enabling achievement of higher specific energy.

Generally, there are two mechanisms of capacity limitation currently under discussion: surface passivation [8,9,2] and pore clogging (oxygen diffusion limitation) [10,11,1]. The former implies that a thin layer of an insulating product covers the porous electrode surface inhibiting electron transfer. The product film thickness was found to be only 10 nm or less (several monolayers) [2,8], which explains very low cell capacity. Using a computer simulation and experimental data on product film resistivity it was shown [9] that neglecting the Ohmic potential drop across the film (i.e. considering only oxygen diffusion limitations) results in more than one order of magnitude higher capacity. There is still some

* Corresponding author at: Chemistry Department, Lomonosov Moscow State University, Leninskie Gory, Moscow 119991, Russia.

E-mail address: daniil.itkis@gmail.com (D.M. Itkis).

discussion, whether the passivation is only caused by the discharge product, lithium peroxide, or, as some works suggest [2,12], by some byproducts formed due to side reactivity of the electrode materials and electrolytes.

Although electrode passivation can potentially lead to more serious specific capacity limitations, slow oxygen diffusion and pore clogging also prevent the achievement of the desired cell performance [6]. Besides increasing oxygen diffusion coefficient and oxygen solubility of the solvent used, which is much challenging especially taking into account the chemical stability requirements, the alternative approach is to optimize cathode structure. There are several experimental works studying hierarchically structured and specifically organized materials [13–16] that demonstrate noticeably higher cell specific capacity in comparison to conventional cathode materials prepared of Super P carbon black. Proposed cathode designs provide enough pore volume to accumulate lithium peroxide, which is a main discharge product, and at the same time maintain some oxygen transport channels remaining not clogged. Macroscopic distribution of the discharge product across the cathode thickness is another important point. While some papers report suppressed reaction rates at the separator (anode) side of the cathode [4,11], anomalous product distributions with discharge product excess at the both sides of the cathode were also demonstrated in some experiments [17] suggesting that lithium diffusion limitation can also take place.

Mathematical modeling and numerical simulations are actively used today to analyze the issues associated with Li-air cell design [18]. In most of the simulations published [7,9,19–24], pores of a single size were considered, however, that is loosely connected to the real structure of the cathode materials. Some groups has taken into account pore size distribution [18,25–27], though it was assumed to be very narrow and included pores with radii less than 100 nm only. So far the most elaborate scheme is proposed in [28], and it considers the presence of cavities ('halls') much larger than 100 nm.

In this work we investigate the effect of pore size distribution (PSD) on the shape of the discharge curves and the cathode specific capacity using a continuum mathematical model and computer simulation. Firstly qualitative analysis of the effects caused by presence of large pores in the cathode structure is performed. We simulate a discharge of the cathode with log-uniform PSD (uniform in logarithmic length scale) and show that such a broad PSD leads to more gentle slope of the discharge curves in comparison to single pore size case. We also employ bimodal PSD to demonstrate the roles of smaller and large pores in the discharge process and to evaluate influence of the discharge product resistivity on the functioning of pores with different sizes. We further solve an optimization problem and find an optimal volume fraction of large cavities that enables higher discharge capacity. It is anticipated that the demonstrated role of large cavities and macroscopic channels in cathode structure is as important for the cell performance as the inherent porosity of the used cathode material, and thus a special attention should be paid to this issue in electrode preparation technology.

2. Model development

General model, which was used, is described in detail in our previous study [6] and employs theory and approaches developed by Newman and Thomas-Alyea [29]. The alterations introduced here concern consideration of the passivation layer resistivity and pore size distribution.

Fig. 1 schematically represents the simulated cathode structure. Liquid (electrolyte solution) and solid (carbon material) phases interpenetrate providing ionic and electronic conductivity, respec-

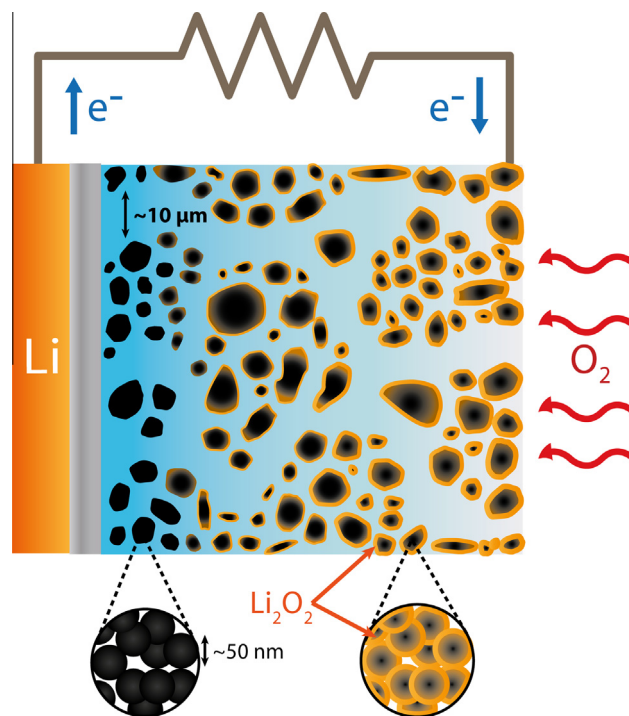


Fig. 1. Schematic representation of a partially discharged Li–O₂ cell. The cathode consist of electrically connected agglomerates of carbon black resulting in two pore types – large channels between carbon black particle agglomerates, and smaller ones, which are the voids inside the agglomerates.

tively. Lithium peroxide, which is supposed to be the only reaction product, precipitates as a resistive layer on the surface of carbon. Whole structure is handled as a homogeneous porous media. Mass-transport of species (ions and oxygen) is governed by drift-diffusion equations, while Butler-Volmer equation is used to calculate local reaction rates. Product precipitation decreases volume fraction of the liquid phase (porosity) and gradually inhibits the species transport. All equations are solved numerically by a finite difference method.

Experiments on Li–O₂ cell discharge are usually conducted at 0.05–1 mA/cm² discharge current densities. According to Adams et al. [30] at higher current densities film growth dominates over Li₂O₂ crystallization in the solution bulk. In our simulation, we set current density to 1 mA/cm² as it is closer to practically required values. Therefore, film growth mechanism is adopted in our model, i.e. the product is assumed to precipitate on the walls of cylindrical pores. Thus, the local ohmic voltage drop depends on both local product layer thickness and local current density. Variation of the effective product resistivity allows qualitative simulation of partial product crystallization in the electrolyte bulk and control of maximum product layer thickness. We also consider simulated discharge curves with zero product layer resistivity using them as a reference demonstrating the role of diffusion limitations alone.

Wide PSD is simulated by a set of pore radii. Concentrations of the species and electric potentials of the phases are assumed to be common for the interpenetrating pore subsystems, though individual values of porosity, surface area, product layer resistivity and reaction rate are assigned to each one. The log-uniform distribution is emulated by a set of 15 pore radii that represent a geometric sequence with common ratio equals 2, while the values of initial porosity are the same.

The parameters used for simulations are summarized in Table 1 (variables naming is consistent with Ref. [6]).

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