Maximum theoretical power density of lithium–air batteries with mixed electrolyte

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HIGHLIGHTS

- Mathematical models for the discharge voltage and power density are derived.
- Limits for the maximum power density in mixed Li–air batteries are determined.
- Internal ohmic resistances currently account for one fourth of the power loss.
- Oxygen diffusion length is under 1 μm at maximum discharge power.

ARTICLE INFO

ABSTRACT

An analytical model is developed for the discharge voltage of Li–air batteries with mixed organic/aqueous electrolyte and used to analyze the effects of the oxygen dissolution, solubility, pressure, and diffusivity, reaction rates, and internal resistance on the power density of Li–air batteries. By carefully identifying the model parameters using experimental data it is shown that, for discharge currents above 25 mA cm^{-2} the power of these batteries is mainly limited by the large internal resistance of the membrane and membrane/electrolyte interfaces (which is currently larger than 100 Ω cm^2), while for smaller discharge currents the power is limited by the low oxygen concentration at the reaction sites. The maximum power density can be increased by approximately 1.5 times if the internal resistance is decreased from 100 Ω cm^2 to 25 Ω cm^2. This relatively small increase in the power density is due to the low dissolution rate and solubility of the oxygen in the liquid electrolyte. Finally, when the battery is operated at maximum discharge power, the oxygen diffusion length in the aqueous electrolyte is under 1 μm, which shows that one needs to use partly wet cathodes in order to achieve high power densities in these batteries.

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1. Introduction

Li–air batteries have recently attracted the research community because of their high specific capacities and energy densities. Depending on the type of the electrolyte and excluding the mass of the oxygen, the theoretical specific capacity of Li–air batteries is 3828 mA h g^{-1} in batteries with organic electrolyte [1], 129 mA h g^{-1} in batteries with mixed organic/aqueous-basic electrolyte [2,3], and ranges between 95 and 316 mA h g^{-1} in batteries with organic/aqueous-acid electrolyte [3]. These large specific capacities make Li–air batteries attractive for applications in the areas of electric vehicle transportation, grid storage, and portable electronic devices. However, although praised for their high theoretical specific capacities, Li–air batteries suffer from a number of deficiencies that reduce their power density significantly:

1. the low solubility and oxygen diffusivity in liquid electrolyte result in low oxygen concentration at the reaction sites and reduce the maximum power density of Li–air batteries [4,5];
2. internal ohmic losses at the separator and inside the electrolyte further reduce the power density, particularly in Li–air batteries with mixed electrolyte; these ohmic losses are usually due to the high resistivity of the separator and solid electrolytes [6–8];
3. the resistivity of the deposit products in the cathode are also responsible for increasing the ohmic losses in the battery [9,10];

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4. the solid deposition of the reaction products decreases the cathode porosity making it more difficult for oxygen to flow through the pores of the cathode. Often, the pores at the air side get filled first with deposit product, completely interrupting the flow of the oxygen from the atmosphere and making the battery nonoperational before it is fully discharged [11–13].

Among the various types of lithium−air batteries, lithium−air batteries with mixed organic/aqueous electrolyte have become the focus of much research lately because, at low electrolyte concentrations, the reaction products are soluble in the electrolyte and do not deposit on the surface of the cathode. In this way, the last two of the mentioned deficiencies can be avoided by using aqueous electrolyte in the cathode and constantly refreshing it so it never reaches saturation. This observation led a number of research groups to develop flow batteries, in which the electrolyte is continuously circulated between the reaction unit and an electrolyte storage unit [2,3,14]. In this article we analyze the voltage losses in Li−air batteries with mixed electrolyte by looking at the first two deficiencies: the low solubility and oxygen diffusivity in liquid electrolyte and the internal ohmic losses in the battery. The novelty of this article in deriving a closed-form equation for the maximum power density of these batteries and in analyzing the factors that can hinder the achievement of this power density. Numerical results are shown for Li−air batteries with aqueous/basic catholyte (i.e. LiOH) but the model can be extended to other metal-air batteries by properly calibrating the material constants and geometrical dimensions. Finally, it should be noted that, although Li−air batteries are known for their low power density and there are many experimental attempts to increase their discharge rates, most of the existing analytical models in the literature refer to energy density of these batteries and not to their power density. The reason behind this fact is that it is usually much easier to estimate the energy density of electrochemical systems (for instance by using the masses and available volumes of different components) but it is much more difficult to estimate their power density.

Li−air batteries with mixed electrolyte are made of a Li metallic anode, a solid separator, and a porous carbon cathode filled with aqueous electrolyte (see Fig. 1). The space between anode and separator is usually filled with 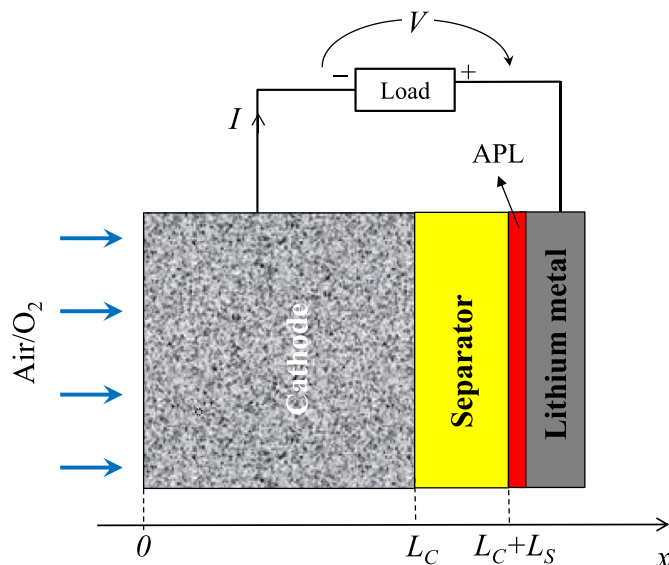a thin layer of organic electrolyte, while the separator consists of a solid electrolyte. In the cathode, external oxygen penetrates the pores, diffuses through the electrolyte, and reacts with the Li-ions coming from the anode. In the case of Li−air batteries with lithium hydroxide electrolyte at the cathode, if the electrolyte concentration is below the concentration of saturation of Li^+ and OH^- ions in water, which is 12.5 g of LiOH per 100 g of water, the cathode reaction is [3,9]:

$$4Li^+ + O_2 + 2H_2O + 4e^- \rightarrow 4Li^+ + 4OH^- \tag{1}$$
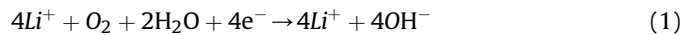
When the concentration of the electrolyte reaches saturation, c_{sat}, the cathode reaction becomes $4Li^+ + O_2 + 6H_2O + 4e^- \rightarrow 4LiOH \cdot H_2O_{(deposit)}$ and the reaction product deposits on the surface of the carbon, thus filling the pores of the cathode and eventually interrupting the flow of O_2 in the cathode. In this article we analyze the operation of the battery during the first period of the discharge, i.e. when there is no solid deposition in the cathode, and develop an analytical model for the discharge voltage of the battery. We also develop a compact model for the power density (expressed in W cm^{-2}) and show that the maximum power density depends not only on the internal ohmic resistance but also on the oxygen pressure, solubility, and diffusivity in the electrolyte.

It should be mentioned that finite element models for the simulation of Li−air batteries with mixed electrolyte have been developed before by various research groups [15–17]. Most of the existing work in the literature has focused on evaluating and predicting the energy density of Li−air and there is very limited research in predicting the maximum theoretical power density of these batteries. The existing finite element models are based on solving the mass and charge transport equations numerically, including oxygen diffusion, electrolyte diffusion and migration, electron conductivity, and the reaction product deposition in the cathode, which are coupled with Bulter−Volmer kinetics. Due to the high complexity of the finite element models, it is practically impossible to derive a closed-form solution for the discharge characteristics analytically, and one should rely on numerical simulations to compute the discharge voltage. For instance, Fig. 2 presents the variation of the electrolyte concentration as a function of the discharge capacity for a Li−air battery with mixed electrolyte computed using the finite element model presented in Ref. [15]. The geometrical dimensions, porosity, and other
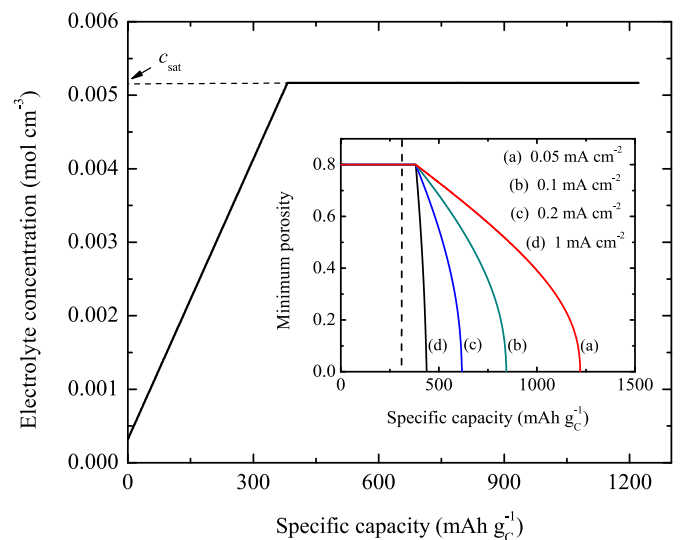

Fig. 1. Schematics of the Li−air batteries showing the porous carbon, separator, and anode regions.

Fig. 2. Variation of the electrolyte concentration during the discharge of Li−air battery with dual electrolyte. The inset shows the variation of the minimum porosity as a function of the discharge capacity for different discharge currents.