Limitations and Potential Li-Air Batteries: a Simulation Prediction

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Abstract— **Li-air batteries are attracting much attention because of their relatively high theoretical energy densities compared to other types of batteries and storage devices. This interest in this area is driven not only by industries requiring high electric power such as the electric car industry who requires fundamental improvements in the current Li-ion technology in order to extend the driving range of current electric vehicles, but also by many low-power and portable electronics industries which require light, high-capacity energy storage devices. In this article we first make a comparative analysis between modeling and simulation (M&S) of semiconductor devices and the M&S of electrochemical systems, then discuss about the potential and limitations of Li-air batteries and show how computer simulations can help increasing even more the energy density and overcome some of the limitations of these batteries.**

Keywords-Li-air batteries, modeling, simulation, specific capacity.

I. Transport in Electrochemical systems vs. Semiconductor Devices

The M&S of semiconductor devices and the M&S of electrochemical systems (including fuels cells, Li-ion, Li-air, and other metal-ion batteries, etc.) are areas of research that were traditionally performed by different research groups throughout the world. The M&S of electrochemical systems has mostly been conducted by research in chemical engineering, while the M&S of semiconductor devices has mostly been guided by research in electrical engineering (including technical institutes and departments with a focus in electrical engineering). So far, there was relatively limited interaction between the two groups, which lead to the development of conceptually similar but differently formulated theories for the two systems. More recently, driven in part by the demand in low-power electronics, the systems became more and more integrated on the same device and represent *the major limit factors for the further development of portable electronic devices*. This fact is bringing the two communities together, which seems to be a rather slow process. In then first part of this article we present the main similarities and differences in the modeling and simulations of the two types of systems, and discuss the issues that make the two areas hard to unite from an M&S viewpoint. We do not focus on language differences between the two communities, but on differences between the structure of the transport equations in the two systems, numerical approaches, and on differences in the experimental validation and verification in the two areas. In the second part of the article we discuss about the potential and limitations of Li-air batteries and present numerical simulations.

Semiconductor devices are usually modeled by the Poisson equation coupled with various types of transport models such as the drift-diffusion model, the Boltzmann transport equation, or other semi-classical (e.g. the density-gradient model) or quantum based models [1]. The charge transport is given by mobile electrons and holes in the *semiconductor crystal*. In electrochemical devices the charge transport is given by at least two types of ions that travel between anode and cathode in a solid and, most often, *liquid electrolyte*, and by electrons that travel through carbon or other conducting materials. The transport medium is usually a porous material, and the transport equations are often given by modified drift-diffusion models, which are coupled with the mass transport equations for the other species in the system [2]. The number of transport equations is usually much larger in electrochemical systems than in semiconductor devices.

One major difference between the transport in semiconductor devices and in electrochemical systems is that the number of electrons and holes that are involved in transport in semiconductor devices is relatively small, which allows one to use approximations for low-concentration transport. In the case of electrochemical systems, the ion concentration is relatively high and demands theories appropriate for *concentrated solutions* (for instance, the mass of the ions involved in the transport in a Li-air battery accounts for more than 30% of the mass of the whole cell). An important simplification in the case of electrochemical systems is that the charge density can be approximated to zero almost everywhere in electrolytes. Hence, the Poisson equation is rarely if ever solved in electrochemical systems, and the transport system is somewhat simplified [2].

The *generation-recombination* rates in semiconductor systems appear as source terms in the continuity equations and correspond to the *reaction rates* in electrochemical systems. However, if the form of the generation-recombination rate equations is relatively well established in the semiconductor theory, the same cannot be said about the reaction rates in

electrochemical systems. In these systems, the reaction rates are usually written in the form of Butler-Volmer equations, however, the number and structure of these equations depend on the exact reaction steps and mechanisms, which are often unknown in many electrochemical systems. For this reason one often uses empirical expressions for the reaction rates in electrochemical systems, which are most often limited to the "empirical" Tafel equation, in which the coefficients are measured experimentally [3]. The generation-recombination processes can take place both in the bulk and on surfaces in semiconductor devices. In the case of electrochemical systems the chemical reactions take place mostly at interfaces, where the electrons can react with various ions in the electrolyte. In order to increase the power density of the electrochemical systems one needs to increase the surface-to-volume ratio as much as possible, which usually requires *complex, porous structures* that complicate the modeling and simulation significantly.
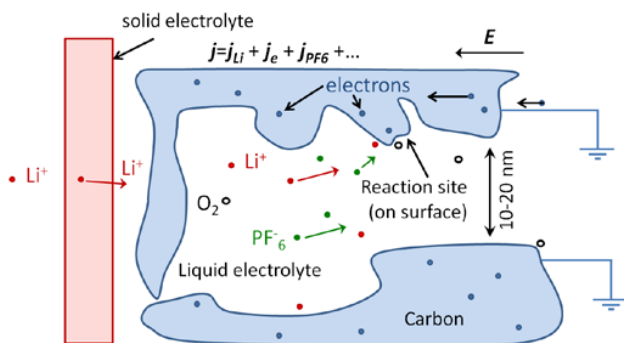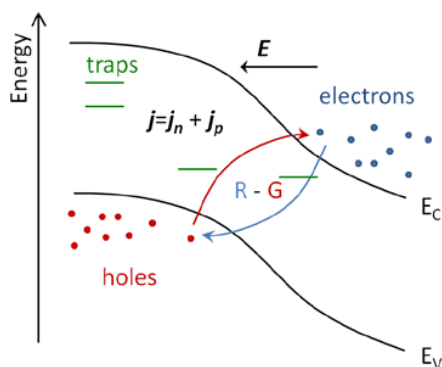

Figure 1   Transport in semiconductor devices (up) and electrochemical systems (down).

The *electron and hole mobilities* defined in semiconductor devices, translate to the ion mobilities in electrochemical systems. However, the concept of ion mobility has more of a theoretical than practical value in electrochemical systems, where it is almost always replaced by *transference coefficients*, which are numbers between 0 and 1 that describe the "relative mobility" of a given ion with respect to the other ions that participate in the transport. The simple form of the

Einstein relationships (i.e. $D = V_T\mu$) holds relatively well in non-degenerate semiconductors, however it produces wrong results in most electrochemical systems, where it needs to be established experimentally.

The M&S of electrochemical systems is enormously complicated by the *fast degradation of materials* in the system. For instance, cycling a rechargeable Li-air battery for 10 times might decrease its specific capacity by more than a half; many diffusion and conductivity coefficients of the species involved in the transport might change significantly even during one full discharge of the battery. These facts bring many problems for the experimental validation and verification of the models used in electrochemical systems.
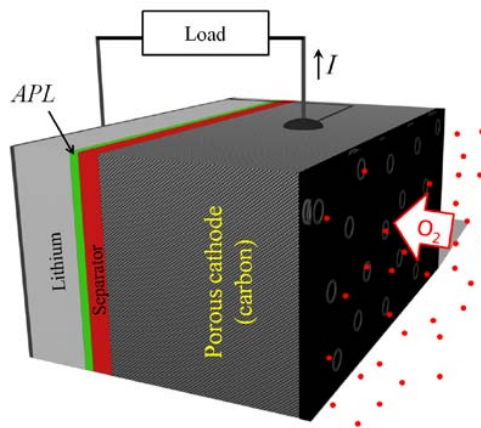

Figure 2   Li-air battery with organic electrolyte

II.   BASIC EQUATIONS AND SIMULATION PROCEDURE

The model used in this article is based on a model recently developed by our group and used for the simulation of the Li-air batteries with organic [3] and dual electrolyte [4,5]. It is based on the drift-diffusion and mass transport equations of the species involved in the transport and uses the theory of concentrated solutions [2] to describe the transport of Li^+/PF_6^- and Li^+/OH^- ions and the diffusion of the O_2 in the anode protective layer (APL), separator, and cathode electrolyte. We consider a binary monovalent organic electrolyte in the APL and organic (in the case of batteries with organic electrolyte) and aqueous (in the case of batteries with dual electrolyte) electrolyte in the cathode, with no convection. The model equations and simulation procedure are relatively similar to the classical (drift-diffusion based) modeling of semiconductor devices.

A.   Li-Air batteries with organic electrolyte

Li-air batteries with organic electrolyte are made of a Li metallic anode, a solid separator, and a porous carbon cathode filled with organic electrolyte (see Fig. 1). External air penetrates the pores of the cathode, diffuse through the electrolyte, and react with the Li ions according to reaction $2Li^+ + O_2 + 2e^- \rightarrow Li_2O_2$. The reaction product is insoluble in

the electrolyte and deposits on the solid surface of the cathode in this way filling in the pores and eventually stopping the flow of the oxygen inside the battery. The governing equations are the Li conductivity, Li diffusion, and O_2 diffusion [3]:

$$\nabla \cdot \left(\kappa_{eff} \nabla \phi_{Li} + \kappa_D \nabla \ln c_{Li} \right) - R_C = 0 \tag{1}$$

$$\frac{\partial \left(\varepsilon c_{Li} \right)}{\partial t} = \nabla \cdot \left(D_{Li,eff} \nabla c_{Li} \right) - \frac{1 - t^+}{F} R_C - \frac{\boldsymbol{I}_{Li} \cdot \nabla t_+}{F} \tag{2}$$

$$\frac{\partial \left(\varepsilon c_{O_2} \right)}{\partial t} = \nabla \cdot \left(D_{O_2,eff} \nabla c_{O_2} \right) - \frac{R_C}{2F} \tag{3}$$

where κ_{eff} is the effective electric conductivity of Li^+ in the solid or liquid electrolyte, κ_D is the diffusional conductivity, c_{Li} is the Li^+ concentration, and R_C is the reaction rate, ε is the porosity, $D_{Li,eff}$ and $D_{O2,eff}$ are the effective Li^+ and O_2 diffusion coefficients, t^+ is the transference number, F is the Faraday constant, and $\boldsymbol{I}_{Li} = -\kappa_{eff} \nabla \phi_{Li} - \kappa_D \nabla \ln c_{Li}$ is the Li current density. Besides equations (1)-(3) that are solved in all three regions (APL, separator, and cathode), the following two equations are solved in the cathode region to compute the potential of electrons (ϕ) and the change in the local porosity:

$$\nabla \cdot \left(\sigma_{eff} \nabla \phi \right) + R_C = 0 \tag{4}$$

$$\frac{\partial \varepsilon}{\partial t} = -R_C \frac{M_{Li_2O_2}}{2F \rho_{Li_2O_2}} \tag{5}$$

where σ_{eff} is the effective conductivity of electrons in the cathode, and $M_{Li_2O_2}$ and $\rho_{Li_2O_2}$ are the molecular weight and mass density of Li_2O_2.

The reaction rate in the cathode region is given by the Buttler-Volmer equation

$$R_C = \frac{dFk\varepsilon c_{O_2}}{\overline{r}_p} \times \left(e^{\frac{1-\beta}{V_T}\eta} - e^{-\frac{\beta}{V_T}\eta} \right) \tag{6}$$

where F is the Faraday's constant, $k = 1.77 \times 10^{-10}$ cm/s is the reaction rate constant, $\beta = 0.5$ is a symmetry factor, $\eta = V_0 - V$ is the over-potential, V_0 is the open cell voltage, $\overline{r}_p$ is the average radius of the pores inside the cathode, and d is a coefficient that depends on the shape of pores. In general d varies from 2 when the pores are cylindrical to 3 when they are spherical. The average radius of the pores depend on the initial pore radius $\overline{r}_{p,0}$, and the initial porosity ε_{i0} according to $\overline{r}_p = \overline{r}_{p,0} \left(\varepsilon / \varepsilon_{i0} \right)^{1/d}$. The reaction rate in the anode and separator regions is zero. More details about the derivation of transport equations can be found in [3, 4].

B. Li-Air batteries with aqueous electrolyte

The structure of Li-air batteries with aqueous electrolyte is relatively similar to the structure of Li-air batteries with organic electrolyte, however, the organic electrolyte in the cathode is replaced with aqueous electrolyte containing of Li^+ and OH^- ions. The chemical reactions in the cathode and the nature of the discharge product depend on the concentration of Li^+ ions in the aqueous electrolyte, c_{Li}. If c_{Li} is smaller than the concentration of saturation of Li^+OH^- in water ($c_{LiOH,sat}$) we have $4Li^+ + O_2 + 2H_2O + 4e^- \rightarrow 4Li^+ + 4OH^-$ and the reaction product dissolves in the electrolyte; if $c_{Li} > c_{LiOH,sat}$ the cathode reaction becomes $4Li^+ + O_2 + 6H_2O + 4e^- \rightarrow 4LiOH\text{-}H_2O_{(deposit)}$. The transport equations depend on whether the electrolyte is saturated or not and are relatively similar to eqs. (1)-(4) [4]. The porosity changes only when $c_{Li} > c_{LiOH,sat}$ according to [4]

$$\frac{\partial \varepsilon}{\partial t} = -4R_C \frac{M_s}{F\rho_s - c_{LiOH,sat}FM_s} \tag{7}$$

where M_s and ρ_s are the molecular weight and mass density of deposited $LiOH \cdot H_2O$.
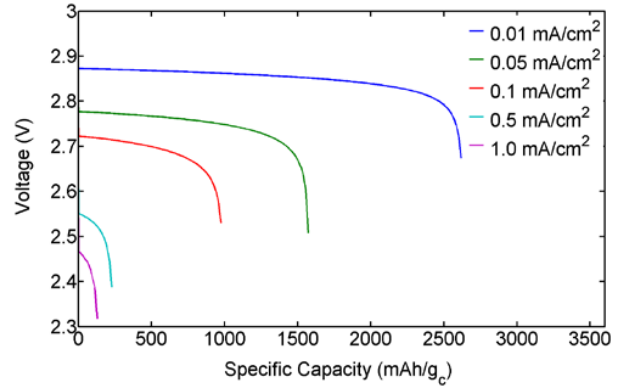

Figure 3   Discharge curves for a Li-air battery with organic electrolyte.

III. SIMULATION RESULTS AND ANALYSIS

The model equations presented in the previous section have been implemented numerically in RandFlux [6] and solved to analyze the potential and limitations of Li-air batteries or organic and aqueous electrolytes. Figure 3 shows typical discharge characteristics for a standard Li-air battery with organic electrolyte having a cathode width of 0.5 mm, separator width of 50 μm, and cross-sectional area of 1 cm². In all the simulations we have assumed that the oxygen is coming from the air at 1 atm and the solubility factor of the oxygen in the electrolyte is 0.345. The initial porosity was 0.75 and the we have neglected the resistivity of the deposited layer. The effective oxygen diffusion coefficient in the cathode was assumed to satisfy Bruggemann's relation $D_{O_2,eff} = \varepsilon^{1.5} D_{O_2}$ where $D_{O_2} = 7 \times 10^{-6}$ cm²/s is the diffusivity in the electrolyte, the reaction rate constant $k = 1.77 \times 10^{-10}$ cm/s, $V_0 = 2.96$, the initial average pore radius $\overline{r}_{p,0} = 20$ nm, and $d = 2$.

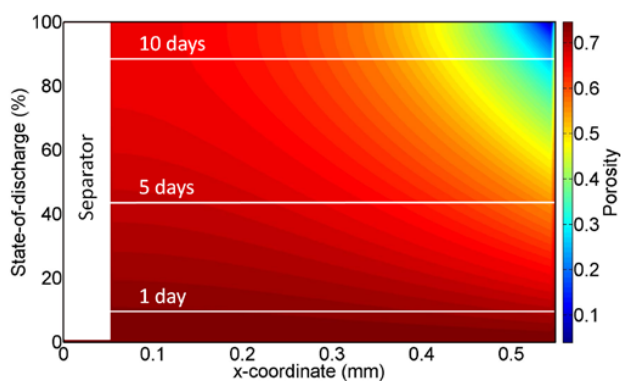Figure 4   The porosity as a function of the state of discharge and position when the cell is discharged at constant current I = 1 mA/cm^2.
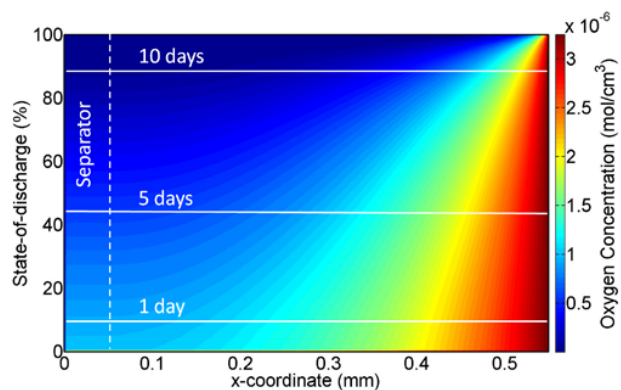

Figure 5   The oxygen concentraiton as a function of the state of discharge and position when the cell is discharged at constant current I = 1 mA/cm^2.

The operation of the Li-air batteries is limited by the oxygen diffusion in the porous cathode; the rest of the parameters related to the Li conductivity and diffusion, electron conductivity, and reaction rate at the anode do not affect significantly the results presented in this section. For details about the values of the other parameter we recommend [3] for Li-air batteries with organic electrolyte ad [4] for Li-air batteries with aqueous electrolyte. It is apparent from the simulations shown in Figure 3 that the specific capacity of Li-air batteries is about one order of magnitude larger then in commercial Li-ion batteries when the discharge currents are relatively small (< 0.1 mA/cm^2). At higher discharge currents, the specific capacity becomes smaller and the maximum specific capacity is limited by the ability of the oxygen to diffuse inside the cathode. As shown in Figures 4 and 5, the deposited lithium peroxide fills in the pores of the cathode at the entrance of the oxygen and stops the flow of the oxygen inside the cell. Figure 6 shows the reaction rate inside the cathode as a function of the state-of-discharge of the battery. Note again that the chemical reactions take place in the cathode, mostly at the entrance of the oxygen, in this way poisoning the battery.

Figure 6 shows the variation of the minimum porosity of a lithium air battery with the specific capacity. Since the Li$^+$OH$^-$

is soluble in the water at low electrolyte concentrations, the reaction product does not deposit at the cathode during the first period of the discharge process. After Li reaches the saturation concentration $c_{LiOH,sat}$ the reaction product starts discharging on the porous carbon and the porosity decreases with time. This fact makes Li-air batteries with aqueous electrolyte promising for designing Li-flow batteries that operate for $c_{Li} < c_{LiOH,sat}$.
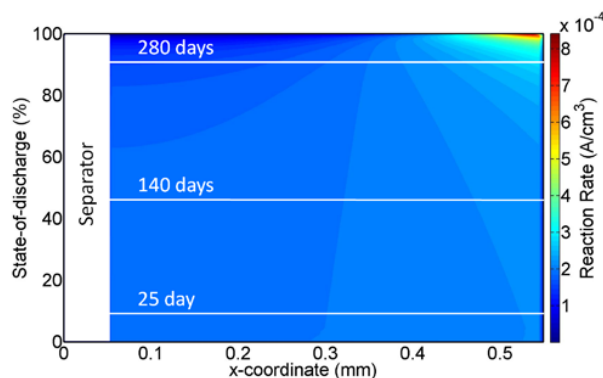

Figure 6   The reaction rate as a function of the state of discharge and position when the cell is discharged at constant current I = 0.1 mA/cm^2.
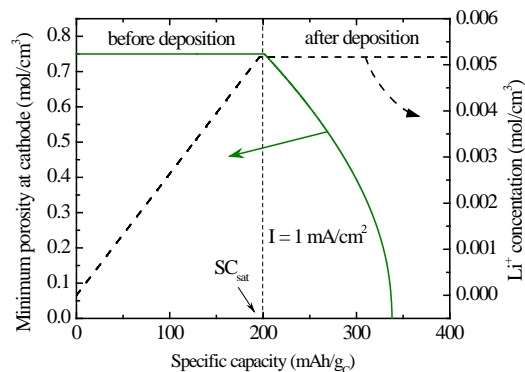

Figure 7   Minimum porosity in the cathode as function of the specific capacity in a Li-air battery with aqueous electrolyte.

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