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Modeling separator membranes physical characteristics for optimized lithium ion battery performance

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ABSTRACT

The effect of varying separator membrane physical parameters such as degree of porosity, tortuosity and thickness, on battery delivered capacity was studied in order to optimize performance of lithium-ion batteries. This was achieved by a theoretical mathematical model relating the Bruggeman coefficient with the degree of porosity and tortuosity. The inclusion of the separator membrane in the simulation model of the battery system does not affect the delivered capacity of the battery. The ionic conductivity of the separator and consequently the delivered capacity values obtained at different discharge rates depend on the value of the Bruggeman coefficient, which is related with the degree of porosity and tortuosity of the membrane. Independently of scan rate, the optimal value of the degree of porosity is above 50% and the separator thickness should range between 1 μm and 32 μm for improved battery performance.

1. Introduction

Taking into account the rapid technological advances in portable electronic devices, such as mobile-phone, computers, e-labels, e-packaging and disposable medical testers, there is an increasing need for improving the autonomy and performance of batteries independently of the battery type [1]. One of the types of the battery with the best properties is the lithium ion batteries, as they are lighter, cheaper, with higher energy density (210 Wh kg^{-1}), no memory effect, prolonged service-life and higher number of charge/discharge cycles when compared to other battery solutions [2].

In order to improve the autonomy and performance of lithium-ion batteries new advances in novel materials for improved delivery capacity, lifetime and safety are necessary [3,4].

In all battery devices, the separator membrane is located between the anode and cathode and its main function is transferring the charge and prevent over-potential [5,6].

The main characteristics of separator membranes for lithium ion batteries are thickness, permeability, porosity and pore size, wettability by liquid electrolyte, and mechanical and dimensional stability [7,8].

The separator is typically constituted by a polymer matrix, in which the membrane is soaked by the electrolyte solution, i.e., salts are dissolved in solvents, water or organic molecules.

For optimizing separator and electrode materials (cathode and anode) the use of computer simulations of the battery performance is essential and critical [9].

These computer simulations are based on mathematical models that take into account the physico-chemical properties of the materials to be used as electrodes and separators, the organic solvents for electrolytes, and the geometry and dimensions of the battery components [10,11].

The computer simulation of the separator/electrolyte includes the correlation of ionic conductivity of the polymeric membrane and the conductivity of the electrolyte solution. Also the effective diffusivity is related to the Bruggeman coefficient. This correlation is described through the Bruggeman equation which reflects the importance of porosity and tortuosity of the material [12], the Bruggeman exponent being 1.5 for ideal electrodes [7] and 2.4 at 4.5 for different electrolyte solutions and polymer membranes [13,14]. In relation to electrode materials, experimental results indicate that the complexity of the porous electrodes induces tortuosity values that greatly deviate from the classical Bruggeman ideal [15].

For the same degree of porosity and polymer membrane, it was revealed through the utilization of the different salts, such as $LiBF_4$ and LiTFSI, in the electrolyte solution that tortuosity value varies between 3.3 and 4.1 [16].

In [17] the Bruggeman parameters for commercial separator membranes differ from the parameters reported in previous studies on separator tortuosity.

It has been proven, on the other hand, that this exponent in not valid for real electrodes or separator materials [12]. This is mainly due to effects in the separators that are typically not accounted for. In this way, diffusion limitations in thick cells have been reported [13], which become more prominent as the thickness of the electrodes increases.

It is thus necessary for a proper description of separator performance, to take into account the morphology parameters of separators that are important for the performance of separator membranes such

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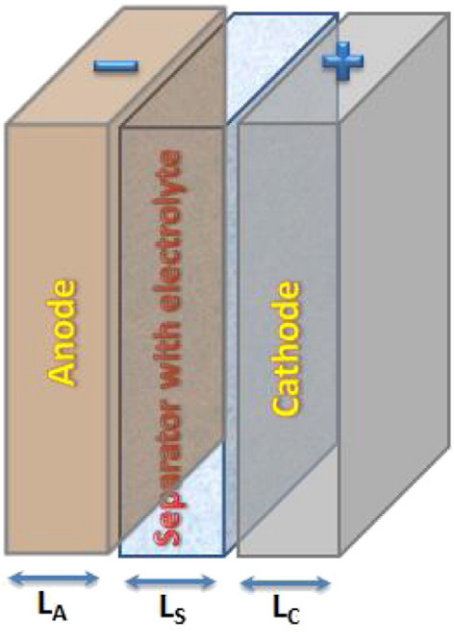

Fig. 1. Schematic representation of the main structure of a lithium ion battery.

as porosity, pore size, tortuosity and thickness [18]. The relevance of this work is to include these parameters in the computer simulation models in order to optimize and improve battery performance.

A finite element method simulation has been thus carried out in order to quantitatively evaluate the effects of the dimensions of separator, porosity and tortuosity towards optimization of its performance in lithium-ion batteries for the same electrodes (anode and cathode) and independently of the electrolyte solution.

2. Theoretical model

2.1. General model

Anode, cathode and separator are the components of the lithium ion batteries (Fig. 1). Each constituent has a specific function in the operation of a lithium-ion battery. The fundamental equations governing the main phenomena of the operation process of a lithium-ion battery are based on the Doyle/Fuller/Newman model [14]. Table 1 shows the main equations governing the different constituents (cathode, anode and electrolyte/separator) in the operation of a lithium-ion battery as well as the boundary conditions. The model takes into account all the variables corresponding to the phenomena occurring in the electrodes and electrolyte/separator, including: the diffusion and ionic conductivity of lithium ions in the electrolyte and electrodes, the relation between the potential of the electrolyte and the local current density on the electrodes (Ohm's law), the relation between the potential of the electrolyte and the local current density on electrolyte/separator (Ohm's law), the diffusion of lithium ions in the active material, the kinetics of the heterogeneous reaction at the electrode/electrolyte interface, the open circuit voltage and the mass transport flux (Table 1).

2.2. Separator

The effective conductivity of the separator is described through the following equation:

$$\kappa_f = \kappa_l \cdot \varepsilon_s{}^p \tag{1}$$

Table 1
Summary of the fundamental equations governing the different processes involved in lithium-ion batteries and boundary conditions. Nomenclature is indicated at the end.

	Governing equation	Boundary conditions
Electrodes (anode and cathode)	$\varepsilon_{a,c}\frac{\partial C_L}{\partial t} = \frac{D_{ef,c,a}}{\delta^2}\frac{\partial^2 C_L}{\partial x^2} + a(1-t_+^0)$ $-\frac{\sigma_{ef,c,a}}{\delta^2}\frac{\partial^2 \varphi_E}{\partial x^2} = -FaJ_{Li+}$ $-\frac{K_{ef,c,a}}{\delta^2}\frac{\partial^2 \varphi_L}{\partial x^2} = Faj_{Li+} + \frac{2kRT}{F}(1-t_+^0)\frac{\partial^2 \ln C_L}{\partial x^2}$ $k_{ef,c,a} = k_l\varepsilon_{c,a}^{brugg}, brugg = 1.5$ $\sigma_{ef,c,a} = \sigma_{c,a}(1-\varepsilon_{c,a}-\varepsilon_{f,c,a})$ $D_{ef,c,a} = D_l\varepsilon_{c,a}^{brugg}, brugg = 1.5$	Cathode: $\frac{\partial C_L}{\partial x}\Big\|_{x=L_a+L_s+L_c} = 0$ $\frac{\partial C_L}{\partial x}\Big\|_{x^+=L_a+L_s} = \frac{\partial C_L}{\partial x}\Big\|_{x^-=L_a+L_s}$ $D_{ef,s}\frac{\partial C_L}{\partial x}\Big\|_{x=L_a+L_s{}^-} = D_{ef,c}\frac{\partial C_L}{\partial x}\Big\|_{x^-=L_a+L_s{}^+}$ $D_{ef,c}\frac{\partial C_L}{\partial x}\Big\|_{x=L_a+L_s+L_p} = 0$ $\frac{\partial \varphi_E}{\partial x}\Big\|_{x=L_a+L_s+L_c} = -\frac{I_{TOTAL}}{\sigma_{ef,c}}$ $\varphi_E\Big\|_{x=L_a+L_s} = \varphi_{E,0}$ $k_f\frac{\partial \varphi_L}{\partial x}\Big\|_{x=L_a+L_s{}^-} = k_{ef,c}\frac{\partial \varphi_L}{\partial x}\Big\|_{x=L_a+L_s{}^+}$ $k_{ef,c}\frac{\partial \varphi_L}{\partial x}\Big\|_{x=L_a+L_s+L_c} = 0$ Anode: $\frac{\partial C_L}{\partial x}\Big\|_{x=0} = 0, \quad \frac{\partial C_L}{\partial x}\Big\|_{x^+=L_a} = \frac{\partial C_L}{\partial x}\Big\|_{x^-=L_a}$ $D_{ef,c}\frac{\partial C_L}{\partial x}\Big\|_{x=0} = 0$ $D_{ef,a}\frac{\partial C_L}{\partial x}\Big\|_{x=L_a{}^-} = D_{ef,s}\frac{\partial C_L}{\partial x}\Big\|_{x=L_a+}$ $\varphi_E\Big\|_{x=0} = 0, \quad \frac{\partial \varphi_E}{\partial x}\Big\|_{x=L_a} = 0$ $k_{ef,a}\frac{\partial \phi_L}{\partial x}\Big\|_{x=L_a{}^-} = k_f\frac{\partial \phi_L}{\partial x}\Big\|_{x=L_a{}^+},$ $k_{ef,a}\frac{\partial \varphi_L}{\partial x}\Big\|_{x=0} = 0$
Separator/electrolyte	$\varepsilon_s\frac{\partial C_L}{\partial t} = \frac{D_{ef,s}}{\delta^2}\frac{\partial^2 C_L}{\partial x^2}$ $-\frac{k_f}{\delta^2}\frac{\partial^2 \varphi_L}{\partial x^2} = Faj_{Li^+} + \frac{2kRT}{F}(1-t_+^0)\frac{\partial^2 \ln C_L}{\partial x^2}$	$D_{ef,a}\frac{\partial C_L}{\partial x}\Big\|_{x=L_a{}^-} = D_{ef,s}\frac{\partial C_L}{\partial x}\Big\|_{x^-=L_a{}^+}$ $D_{ef,s}\frac{\partial C_L}{\partial x}\Big\|_{x=L_a+L_s{}^-} = D_{ef,c}\frac{\partial C_L}{\partial x}\Big\|_{x^-=L_a+L_s{}^+}$ $k_{ef,a}\frac{\partial \varphi_L}{\partial x}\Big\|_{x=L_a{}^-} = k_f\frac{\partial \varphi_L}{\partial x}\Big\|_{x=L_a{}^+}$ $k_f\frac{\partial \varphi_L}{\partial x}\Big\|_{x=L_a+L_s{}^-} = k_{ef,c}\frac{\partial \varphi_L}{\partial x}\Big\|_{x=L_a+L_s{}^+}$
Active material	$\frac{\partial C_E}{\partial t} = D_{Li}\left[\frac{\partial^2 C_E}{\partial r^2} + \frac{2}{r}\frac{\partial C_E}{\partial r}\right]$	$\frac{\partial C_E}{\partial r}\Big\|_{r=0} = 0, \quad \frac{\partial C_E}{\partial r}\Big\|_{r=R_{sp}} = -\frac{J_{Li^+}}{D_{Li}}$