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Effects of Diffusive Charge Transfer and Salt Concentration Gradient in Electrolyte on Li-ion Battery Energy and Power Densities

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ABSTRACT

The simulation of lithium-ion batteries based on a fundamental multi-physicochemical model requires extensive computational resources and remains sluggish for real-time or battery pack analysis applications. In these applications, simplification of the model is required to reduce computational costs while maintaining the model accuracy in estimation of one or more performance parameters. In this study, the effects of neglecting the lithium-ion diffusive charge transfer and the salt concentration gradient in electrolyte on the model accuracy are investigated. The results indicate the feasibility of simplifying the model for a range of cell designs and discharge rates without sacrificing the preciseness of the cell energy and power density predictions.

1. Introduction

Among rechargeable electrochemical energy storage systems, lithium-ion batteries (LIBs) with high energy and power densities are becoming increasingly popular for various applications in portable electronic devices and electric vehicles [1–4]. The literature reveals many studies that can be found regarding the development of fundamental multi-physicochemical models to estimate LIB behavior in adequate detail [5,6]. First, Newman and Tiedmann [7] developed the porous electrode theory to simulate batteries, assuming that the function of penetrated electrolyte into the void spaces of an electrode follows the concentrated solution theory [8]. Based on this, Doyle [9] and Fuller [10] *et al.* built a general isothermal model to describe the galvanostatic charge and discharge of lithium-ion-insertion batteries. Later, Doyle and Newman [11,12] used this general model to simulate the whole cell for design and optimization of LIBs. To carry out the simulation, the experimental characterization methods of transport, thermodynamic, and design-adjustable parameters were introduced by them. The experimental data, obtained from cells with several configurations, were compared to the simulation results and exhibited acceptable compatibility. However, for this general model, it is required to designate numerous parameters and solve many differential equations with complicated numerical techniques. The extensive computational resources required limit practical application toward real-time or battery pack analysis. Therefore, simplification of this model to reduce its complexity is required. Thus far, some model simplifications were practiced based on various viewpoints [13–19]. Doyle and Newman [13,14] considered the system as an ohmically-limited cell (no concentration gradients) and simplified the model. Then, they derived analytic expressions for the cell potential, specific energy vs. specific power (Ragone plot), and specific capacity vs. discharge rate. Subramanian *et al.* [4,16,18] developed a reduced-order model applying a combination of perturbation, volume-average integration, and intuition-based methods to simplify the simulation of LIBs in real time applications. Afterwards, Dao *et al.* [19] employed the volume-average integration and Galerkin's approximation techniques to simplify the general LIB model.

This investigation, considers the possibility of simplifying the LIB model, with regards to the treatment of electrolyte. There are three driving forces that influence the lithium-ion transfer in the electrolyte of LIBs, namely electric field, concentration gradient, and bulk motion of the electrolyte, which produce the phenomena of migration, diffusion, and convection, respectively [8]. Usually, the convection term in the electrolyte of LIBs is insignificant, which

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Nomenclature

c-rate	discharge rate, h^{-1}
C_{salt}	electrolyte salt concentration, mol L^{-1}
D	salt diffusion coefficient, cm^2 s^{-1}
DMR	lithium-ion diffusion to migration ratio in the electrolyte
E_{cell}	specific energy of the cell, Wh kg^{-1}
F	Faraday's constant, 96, 487 C mol^{-1}
i_{cell}	total current density drawn from the cell, mA cm^{-2}
i^{el}	total ionic current density, mA cm^{-2}
i^{el}_{diff}	ionic current density due to diffusion, mA cm^{-2}
i_{local}	local rate of charge generation per unit active area, A m^{-2}
i^{el}_{mig}	ionic current density due to migration, mA cm^{-2}
Li^+	lithium-ion
M	electrode active material
P_{cell}	specific power of the cell, W kg^{-1}
Q_{cell}	capacity of the cell, Ah
$R_{contact}$	contact resistance between the cell components, Ωm^2
R_u	universal gas constant, 8.3143 J $mol^{-1}K^{-1}$
S	surface area per unit volume of the electrode active area, m^2 m^{-3}
t	time, s
T	temperature, K
t_+	lithium-ion transference number
t_d	cell discharge time, s
V_{cell}	cell voltage, V
Greek	
δ	thickness, μm
κ	ionic conductivity of the electrolyte, S cm^{-1}
ν	volume fraction
ρ	density, kg m^{-3}
Φ	potential, V
ω_{cell}	total mass per unit area of the cell, kg cm^{-2}
Subscripts	
|	interface
a	negative-electrode or anode
b	binder
c	positive-electrode or cathode
cc	current collector
cm	conductive material
j	compartment of the cell (negative-electrode, separator, or positive-electrode)
s	separator
Superscripts	
0	initial
ed	electrode
eff	effective
el	electrolyte
f	end of discharge

can be eliminated [20]. Thus, the ion transfer in the electrolyte is mainly due to the migration and diffusion processes. In this study, the LIB model based on the porous electrode and concentrated solution theories developed by Newman's group [11,21] is considered and the simplification is proceeded by evaluating the contribution of the diffusion with respect to the migration in the lithium-ion transfer in electrolyte. Then, the effects of the assumptions of no diffusive charge transfer and no salt concentration gradient on the accuracy of the prediction of the cell energy and power densities at various cell designs and discharge rates are investigated. The cell design parameters considered in this investigation are initial salt concentrations in the electrolyte, electrolyte volume fraction in the electrodes, and the electrode thickness. Finally, the validity and limitations of these assumptions are discussed.

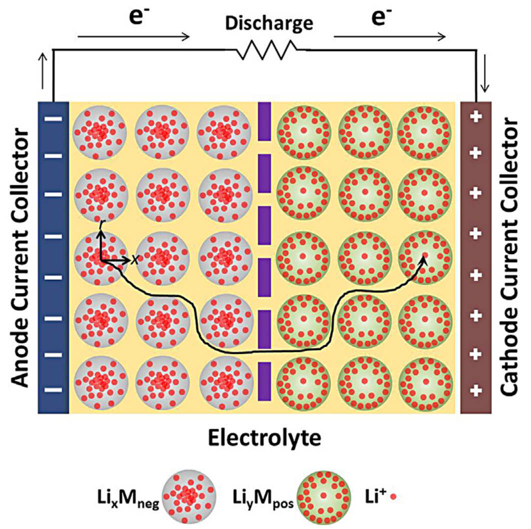

Fig. 1. Scheme of the lithium-ion transfer in electrolyte during the cell discharge process (the yellow color represents the electrolyte).

2. Modeling and Simulation

As mentioned before, the Newman's group model [11] is employed for computer simulation of the lithium-ion cell. In this model, it is assumed that both negative and positive electrodes of the cell are made of uniform-sized solid spherical particles. These particles are the active material of electrodes. The size of these particles is assumed to be unchanged during the cell charging and discharging processes. The volume fraction of electrolyte in electrode and the electrode porosity are also assumed to be identical. Reactions R1 and R2 take place in the negative and positive electrodes, respectively; and all side reactions in the cell are neglected.

$$Li_{x_1}M_{neg} \xrightarrow{discharge} Li_{x_2}M_{neg} + (x_1 - x_2)Li^+ + (x_1 - x_2)e^- \qquad \text{(R1)}$$

$$Li_{y_1}M_{pos} + (y_2 - y_1)Li^+ + (y_2 - y_1)e^- \xrightarrow{discharge} Li_{y_2}M_{pos} \qquad \text{(R2)}$$

In reactions R1 and R2, M_{neg} and M_{pos} represent the active materials of the negative and positive electrodes, respectively.

It is assumed that the effective electron and ion conductivities and lithium-ion diffusivity that take both porosity and tortuosity of electrodes into account are estimated from the Bruggeman correlation [12]:

$$\kappa^{eff} = \kappa \times \left(\nu^{el}\right)^{1.5} \qquad (1)$$

$$D^{eff} = D \times \left(\nu^{el}\right)^{1.5} \qquad (2)$$

The lithium-ion transfer in the electrolyte is resulted from two simultaneous mechanisms (see Fig. 1). One is due to the electric field, which causes migrations of ions from the high voltage to the low voltage. Another mechanism is due to the concentration gradient of electrolyte, leading to the diffusion of lithium-ions. Therefore, the total ionic transfer of lithium-ion in the electrolyte can be stated as follow:

$$i_j^{el} = i_{j,\,mig}^{el} + i_{j,\,diff}^{el} \quad j \in \{a,\ c,\ s\} \qquad (3)$$