Influence of Electrode Kinetics on Lithium-ion Battery Characteristics

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Introduction: The purpose of this work is to show whether an important difference in Lithium solid phase and electrolyte concentrations can be observed in a Lithium-ion battery model, when considering either Butler-Volmer kinetics or Tafel kinetics at the electrodes (including a boundary layer between the electrolyte and the electrode particles). The mathematical model is based on [1,2].

Computational Methods: This study is performed by using the Equations Based Model with the following equations:

$$\frac{\partial(\varepsilon_e c_e)}{\partial t}$$
$$= \nabla \cdot \left(D_e^{eff} \nabla c_e \right) + \frac{a_s \boldsymbol{i_e}(1 - t_+^0) - \boldsymbol{i_e} \cdot \nabla t_+^0}{F}$$
$$\frac{\partial(\varepsilon_s c_s)}{\partial t} = \frac{a_s \boldsymbol{i_e}}{F}$$
$$\frac{D_s}{l_{se}}(\bar{c}_{se} - c_s) = \frac{\boldsymbol{i_e}}{F}$$
$$\nabla \cdot \left(\kappa^{eff} \nabla \phi_e \right) + \nabla \cdot \left(\kappa_D^{eff} \nabla \ln(c_e) \right) + a_s \boldsymbol{i_e} = 0$$
$$\nabla \cdot \left(\sigma^{eff} \nabla \phi_s \right) - a_s \boldsymbol{i_e} = 0$$

Butler-Volmer kinetics

$$\boldsymbol{i_e} = i_0 c_e^{\alpha_a}(c_{s,max} - \bar{c}_{se})^{\alpha_a} \bar{c}_{se}^{\alpha_c}\left[e^{\left(\frac{\alpha_a F}{RT}\eta\right)} - e^{\left(-\frac{\alpha_c F}{RT}\eta\right)}\right]$$

Tafel kinetics

$$\boldsymbol{i_e} = nFke^{\left(\pm\frac{\alpha_{a/c}F}{RT}\eta\right)}$$

Results: The current is considered to flow through the tabs on the top of the two electrodes. During discharge, the lithium ions insert into solid particles of the positive electrode and de-insert from the solid particles of the negative electrode. It is assumed that interfacial chemical equilibrium exists in the electrolyte phase due to a large value of the mass diffusivity of the electrolyte.

Also, interfacial electrical equilibrium is assumed to exist in both the electrolyte and solid active material phases due to either large values of their electronic conductivities or a small size of active material particles.
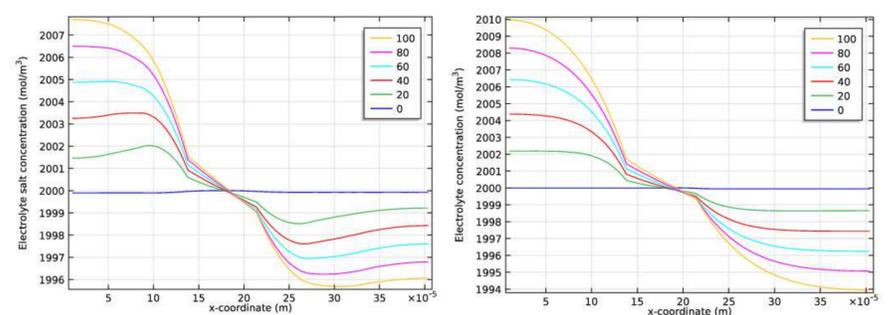

Figure 1. Electrolyte concentrations for Butler-Volmer kinetics (left) and Tafel kinetics (right); the legend shows the corresponding times in s.
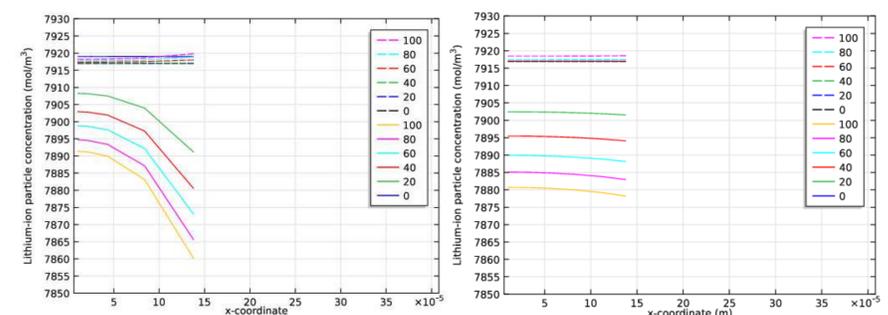

Figure 2. Lithium solid phase concentrations in the anode for Butler-Volmer kinetics (left) and Tafel kinetics (right); the legend shows the corresponding times in s; solid lines for the surface and dashed lines for the center

Conclusions: We can see clearly the differences in the results between using the Tafel equation and the Butler-Volmer equation. This implies that neglecting low overpotential is not to be suggested in Lithium-ion batteries of the kind studied in this work.

References:
1. W.B. Gu and C.Y. Wang, "Thermal-electrochemical modeling of battery systems,"J. Electrochem. Soc., 147(8), 2910-2922 (2000)
2. C.Y. Wang, W.B. Gu, and B.Y. Liaw, "Micro-Macroscopic Coupled Modeling of Batteries and Fuel Cells I. Model Development" *J. Electrochem. Soc.*, 145, 3407-3417 (1998)