Understanding Limitations in LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ Electrode

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LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ (NMC) electrode is one of the promising materials for Li-ion batteries in automotive applications for its large capacity and high energy density. The rate capability of NMC has been studied at the particle scale on thin (6 to 11 µm) electrodes [1]. The results showed that NMC is a high-rate material capable of charge and discharge at rates exceeding 100C. However, battery electrodes used for electric vehicles are usually in the order of 100 µm thick in order to increase the energy density. To improve battery performance and optimize battery design, it is important to understand the rate limitations on thick, porous electrodes.

The layered NMC cathode system has been modeled based on Newman's porous electrode model [2,3] with the aim of predicting the performance at high rates. While the macro-homogeneous models can describe the behavior of battery electrodes at low rates, further increase in current leads to significant deviation in the model predictions when compared to experimental data. The purpose of this study is to understand the cause for these deviations.

Experiments were performed on NMC electrodes in a half-cell configuration with a Li-metal counter electrode. The results obtained from the thin and thick NMC electrode (Fig. 1) showed that at low rates (less than 1C) the system is limited to the solid phase of the active material. This is evident in the end-of-discharge capacity that gradually decreases with increasing rates which reflects the decreasing of the diffusion coefficient of lithium in the solid particles toward the end of discharge [1]. As the discharge rate was increased further, the thicker electrodes showed a rapid capacity loss, suggesting the change in the electrode limitation as the thickness increases. Re-plotting Fig. 1 as the electrode utilization against the current density based on the cross-sectional area of the porous electrode (Fig. 2) shows an apparent deviation of the thick electrodes from the thin electrode at the same current density. This deviation suggests that the limitation occurs on the electrolyte phase within the porous electrode, rather than, say, in the separator or the Li-metal electrode.

Modeling results show that at rates larger than 1C the calculated electrode potentials and capacity deviate from the experimental data. The prediction of the model can be improved by using appropriate effective transport properties that describe the transport of ionic species in the solution phase of the porous electrode. The effective transport properties are related to the bulk values of the electrolyte and the electrode structure such as porosity and tortuosity. Therefore, understanding the electrolyte transport properties the electrode structure is required to accurately predict the electrode capacity as well as the potential at high rates.

This presentation will present the results of the experimental study, and the model comparisons to shed light on the limitations in this cathode.
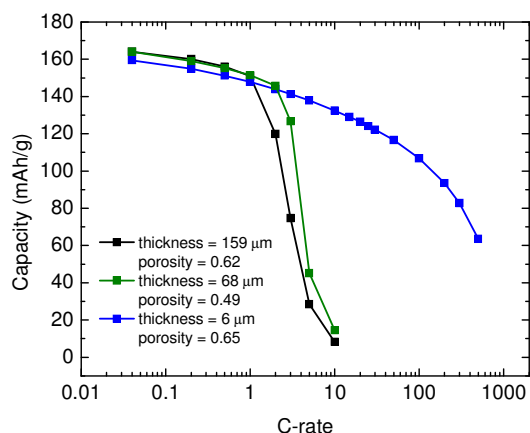

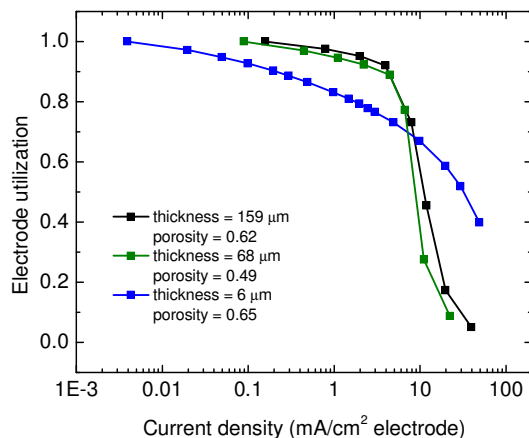Figure 1. Experimental capacity of electrodes with different thickness as a function of discharge rate.

Figure 2. Normalized electrode utilization of electrodes with different thicknesses as a function of current density.

References
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