Theoretical Analysis of the Discharge Behavior of the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ Electrode

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The layered $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ active material has gained popularity in recent years due to its high theoretical capacity (278 mAh/g) and specific energy (1100 Wh/kg, assuming 4.0 V).[1-4] In addition, it is thought to be both a lower cost material compared to $LiCoO_2$, due its lower cobalt content, and safer. Previous research has resulted in a comprehensive understanding of the structure of the material[5, 6] and its performance under various operating conditions.[3]

While the theoretical values are high, the practical capacity is considerably lower and dependent on the voltage to which the electrode is charged. While charging to 4.3 V results in a capacity of 165 mAh/g, as much as 210 mAh/g can be obtained when charged to 5.0 V. However, it has been noted that electrodes charged to these voltages exhibits capacity fade.[2] It has been suggested that this is caused by a side reaction, possibly related to electrolyte decomposition.[2] In addition, the material exhibits a large 1st cycle irreversible capacity loss (as much as 15%) after which the loss becomes negligible. Recent reports have suggested that this is caused by a SEI formation reaction which consumes current at higher voltages.[7]

However, little is as yet known about the cause for the performance limitations in this material, especially under high rates. Such an understanding would be very critical in assessing the capability of this electrode and in suggesting design changes that can be used to improve the performance. In this talk we attempt to answer these questions using a mathematical modeling approach.

The model is similar to those developed previously and consists of description of ionic transport using concentrated solution theory, charge and mass balance in the porous electrode using porous electrode theory, and the thermodynamics and kinetics of reaction at the electrode/electrolyte interface.[8-10] The intercalation of lithium into the lattice of the active material is accounted for by solving for the diffusion equation in spherical coordinates using the Duhamel's superposition theorem.[10]

The properties of the electrolyte used (1 M $LiPF_6$ in 1:1 EC:DEC) were taken from literature values. The diffusion coefficient of lithium in the solid phase has been measured and has been reported to increase with decrease in lithium content by an order of magnitude. However, incorporating this feature would require the need for a more complicated model using a pseudo two-dimensional approach and hence a constant value was used that provides a reasonable prediction of the behavior of the cell.

The prediction was based on experimental constant-current data over a large current range. The results are shown in Figure 1. The model was fit to the utilization at the current density of 3.99 mA/cm^2 in order to extract a diffusion coefficient, and this value was used at all the other currents. The excellent fits suggest that the constant value used here (2.7×10^{-12} cm^2/s) can approximate the behavior of the electrode adequately.

This talk explores the development of the model, the comparison to experiments, the impact of the varying diffusion coefficient, the limiting processes, and design changes that can help improve performance. In addition, full-cell simulations with a natural graphite negative electrode where system optimization is performed is discussed and the ability of this chemistry to be used in high-energy and high-power applications is assessed.

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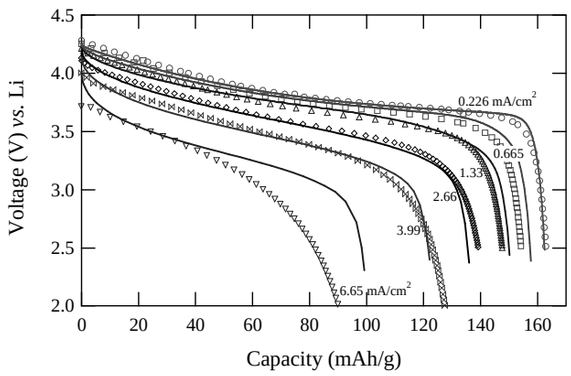

Figure 1. Comparison of the model (lines) to experimental (symbols) rate data on half-cells with a Li reference electrode. The electrode thickness was 75 □m and loading was 7.9 mg/cm^2.