Characterization of Flowing Aqueous Solid Dispersions of Electroactive Lithium-Ion Battery Materials

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Abstract

While there are many material characterization techniques that are employed for the quality control processes of lithium-ion battery active material powders, eventually the materials must be validated electrochemically in battery cells. This requires making the cells including slurry mixing, slurry coating and drying, electrode calendaring and pairing, and final cell assembly. Fabricating cells requires significant equipment and material expense and, in some cases, significant time. Additionally, the cells must be electrochemically tested which depending on the protocol can take multiple days. A technique that provides insights into the electrochemical properties of battery materials without cell fabrication and electrochemical evaluation could improve battery active material powder quality control and potentially reduce the time and cost involved in material validation. Our lab has been working on a technique where dispersions of battery active materials are evaluated electrochemically during collisions with current collectors. The technique has been referred to as dispersed particle resistance (DPR), and in previous studies we have shown that DPR measurements provide an indicator of the rate capability of lithium-ion battery active materials. DPR has a significant advantage with regards to timescale for material evaluation because the method takes only a few minutes and has the option of high throughput analysis due to a flow-through configuration. We have also adapted the technique to characterization of the particles in aqueous dispersions, and in this presentation we will demonstrate that the technique is effective with aqueous dispersions of cathode materials, including water-sensitive layered metal oxides with high nickel content such as $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$.

Material Preparation

The cathode material used in this study was $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$, which will be referred to as NCM. The material was synthesized by first coprecipitating an oxalate precursor by mixing 1.0 L of 0.10 M NaC_2O_4 with a blend of transition metal sulfates (80 mM Ni, 10 mM Co, and 10 mM Mn). The solution was stirred at 60 °C for 30 minutes, filtered, rinsed, and dried. The resulting oxalate powder was mixed with LiOH with a 1.05:1 lithium to transition metal ratio and fired under 5 conditions: 770 °C with no hold, 770 °C with 10 hour hold, 770 °C with 20 hour hold, 820 °C with 10 hour hold, and 820 °C with 20 hour hold. The collected powders were characterized and processed into electrodes after the firing treatment.

X-Ray Diffraction on Layered Cathode Materials

Powder x-ray diffraction (XRD) on the NCM materials indicated that all firing conditions resulted predominantly in layered NCM material. The relative intensities of the (003) and (104) peaks were compared, as higher values for this relative intensity has previously been associated with increased cation ordering. The outcome of this analysis can be found in the table to the right.

NCM Firing Condition	I003/I104
820 °C 20 h	1.64
820 °C 10 h	1.38
770 °C 20 h	1.23
770 °C 10 h	1.23
770 °C No Hold	0.59

Relative intensity of the (003) to the (104) peak for the different NCM firing conditions.

Rate Capability in Coin Cells

2032-type coin cells were fabricated using the different NCM active materials in the cathode in a composite electrode and pairing with a lithium foil anode. The electrolyte was 1.2 M LiPF_6 in a blend of ethylene carbonate and ethyl methyl carbonate. All charge cycles were conducted at C/20 (7.5 mA/g NCM), and discharges were conducted at the indicated values (with 1C assuming to correspond to 150 mA/g NCM). Error bars represent the standard deviations of 5 discharge cycles each over 3 independent coin cells.

Comparison Between Dispersion Resistance and Rate Capability

NCM Sample	DPR (Ω)
820 °C 20 h	3770
820 °C 10 h	4236
770 °C 20 h	4500
770 °C 10 h	10135
770 °C No Hold	11428

Dispersion Characterization Cell

The dispersed particle resistance (DPR) was measured in the custom electrochemical cell depicted above. A 2.0 vol% dispersion of particles was flowed through a channel containing a serpentine current collector. Chronoamperometry experiments of sequentially increasing steps in potential were conducted, and the average steady-state current was calculated. The applied voltage and measured current were used to determine the resistance associated with the electrochemical reactions of the particles colliding with the current collector.

Conclusions

1. Aqueous dispersions of high Ni content NCM materials (exemplar case 80% Ni) rapidly characterized using stepwise chronoamperometry of flowing dispersions in electrochemical cells. Water sensitivity of Ni-rich materials does not seem to impact the comparative measurements.
2. Resistance measurements on the suspensions were found to correlate to rate capability, with lower resistance corresponding to higher rate capability. XRD suggests cation ordering and intrinsic material conductivity likely determined the relative rate capability of the active materials.

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