

Improvement of Lithium Ion Batteries with Selected Dopants

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Introduction:

For electric vehicles to be a feasible option for the general public, batteries need to deliver higher capacities, higher rate capabilities, and longer cycle life at a fraction of the current cost. Nanostructured lithium-ion battery cathode material formed through spray pyrolysis is promising because of its beneficial morphology along with the scalability of the process for mass production. We focused on the layered $\text{Li}_{1.2}\text{Mn}_{0.53}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ composition due to its excellent capacity of over 250 mAhg^{-1} . However, this specific structure suffers from voltage fade upon cycling. The purpose of our investigation was to determine the effects of dopant substitution on the voltage fade characteristics of the batteries. Through this study, we hoped to achieve a better understanding of the voltage fade phenomena to aid in the commercial implementation of these materials in electric vehicles.

Experimental Procedure:

The precursor solutions were made of nitrate solutions dissolved in deionized water for use in spray pyrolysis. The precursor solution was placed in a nebulizer, which created a fine mist. The aqueous droplets were carried into a preheater using air as the carrier gas. There, they underwent rapid drying and then were conveyed into a hot furnace reactor heated to 575°C , where they decomposed, forming oxide particles. The particles were collected downstream of the reactor on porous polycarbonate filters. After each hour, the material was collected and weighed. The as-synthesized particles were then annealed at 900°C for two hours in a box furnace. The powders were converted into a thin film using the doctor blade method. The binder solution contained 10% carbon black, 10% PVDF (poly-vinylidene-fluoride) and 1-methyl-2-pyrrolidinone. The

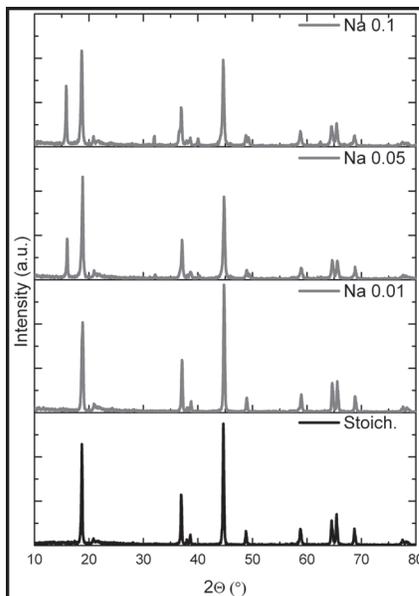


Figure 1: XRD.

cathodes were then tested in 2032 type coin cells using 1M LiPF_6 in ethylene-carbonate:diethyl-carbonate:dimethyl-carbonate (EC:DEC:DMC, 1:1:1).

Battery tests included rate capability tests, cycling tests, and voltage fade tests. All electrochemical testing was performed at room temperature. Rate capability tests demonstrated how well the structure responded to different charge and discharge rates. The rates chosen were C/10, C5, C2, C1, and then C/10 again (where 1C = 200 mA/g). Cycle tests demonstrated the cell's ability to maintain capacity over extended cycling. The entire test spanned over 100 cycles. The cycle test was used for seven different doped batteries, along with an undoped battery cell for comparison. The rates used for this test were C/10 and C/3. The activation cycle was between 2.0-4.8V at

C/10 and subsequent cycles were between 2.0-4.6V for cycle and rate tests. Voltage fade tests were performed for 30 cycles, but have not yet been completed. After an initial activation cycle between 2.0-4.8V at C/20, the remaining cycles were performed at C/10.

The powders were characterized using both powder x-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD, as seen in Figure 1, was used to verify the crystal structure of the powders. At low dopant levels, the crystal structure should not have strayed far from the undoped material. However, when the dopant level was too high for the structure to accommodate the dopants, it formed a separate phase, indicated by additional peaks in the diffraction spectrum. Figure 1 shows four different particle compositions, where part of the lithium was substituted for different Na levels.

It is clear that when the 0.05 Li atoms are replaced by Na atoms additional peaks start to occur in the XRD spectra, which become more pronounced as the concentration increases.

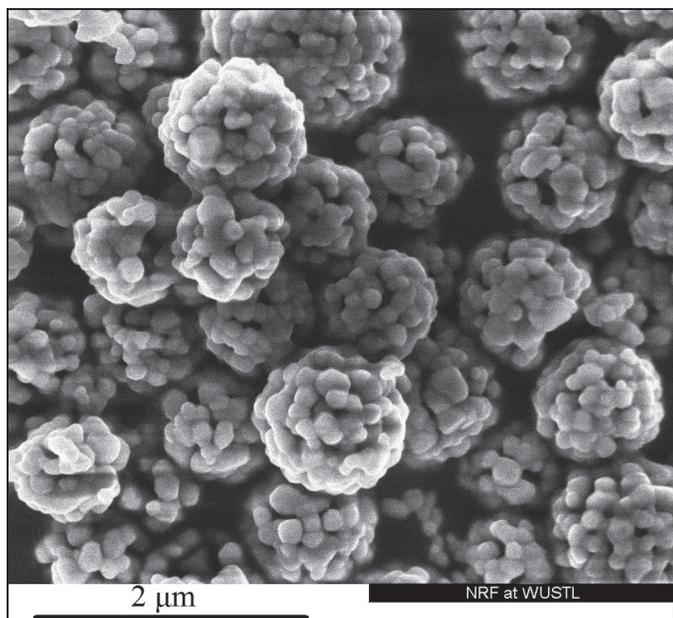


Figure 2: SEM.

Figure 2 shows an SEM image of chromium-doped particles. The particles are primarily spherical in shapes and have 200-400 nm size primary grains, while forming loosely aggregated secondary particles, which range between 0.5-5.0 μm .

Results:

Figure 3 shows the results of the rate test of selected materials compared to the undoped composition. Although there were not significant differences, the battery with the strontium-doped cathode material seemed to outperform the undoped battery in the final C/10 segment by maintaining a high capacity.

Cycle test results are displayed in Figure 4. From these initial results, no significant difference could be observed in the capacity fade behavior of the various dopants. However, the battery with the aluminum-doped cathode material maintained a higher capacity than the undoped sample after 100 cycles. As it can be seen from Figure 4, some of the dopants, most notably magnesium, may have reduced the capacity of the cell. This could be the consequence of exchanging transitional metal ions, which have multiple oxidation states by metal ions, which only have a single oxidation state. This way the host structure may become electrochemically inactive. However these results may indicate that the capacity and stability can be tuned to optimal performance for specific battery applications.

The voltage fade studies that are underway will help determine the dependence of this relationship to dopant levels.

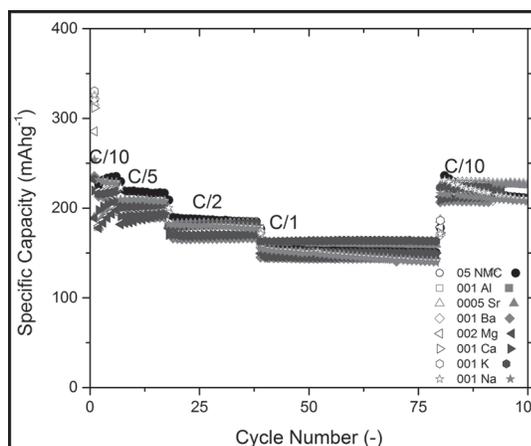


Figure 3: Rate test.

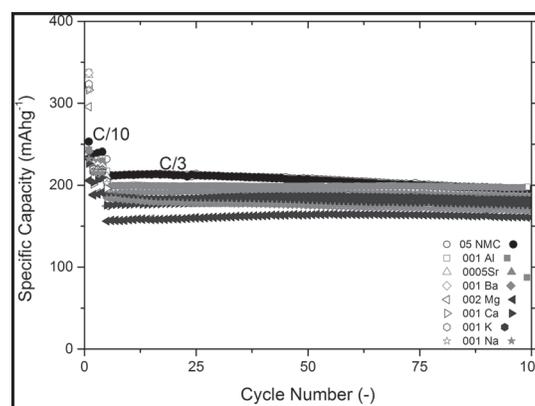


Figure 4: Cycle test.

Future Work:

Future work will focus on evaluating results from the voltage fade study. These results will be used in conjunction with impedance spectroscopy to determine more detailed data about diffusion mechanisms within the material and optimize the composition to reduce and hopefully eliminate the voltage fade of these materials. Studies focusing on two or more dopants will be performed based upon the results of the current study.

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