Optimizing the Electrochemical Performance of Cathode Materials for Lithium Ion Rechargeable Batteries

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Introduction:
In recent years, the environmental impact of petroleum-based transportation has led to greater interest in alternatively powered transportation. Electric vehicles (EVs) and plug-in hybrid electric vehicles (PHEVs) are fast becoming a viable alternative, because they are capable of being fueled by electricity from sustainable power sources. In order for EVs to compete with current gas-powered cars, they must provide comparable performance, so their batteries need large capacity and good capacity retention. In our study, we used spray pyrolysis to synthesize cathode materials. The desired product is a layered-layered composite material of the form xLi$_2$MnO$_3$(1-x)Li(MnNiCo)$_{1/3}$O$_2$, where x = 0.5. We focused on identifying the optimal spray pyrolysis furnace temperatures that yielded the best electrochemical performance.

Experimental Procedure:
Precursor Preparation. In order to obtain the desired powder, a precursor solution was prepared by dissolving specific amounts of metal nitrates to obtain the correct stoichiometry. The product is a layered-layered material of the form xLi$_2$MnO$_3$(1-x)Li(MnNiCo)$_{1/3}$O$_2$, where x = 0.5, or Li$_{1.2}$Mn$_{0.53}$Ni$_{0.13}$Co$_{0.13}$O$_2$.

Spray Pyrolysis. Spray pyrolysis is the process by which precursor droplets thermally decompose to create solid particles. The precursor solution, containing the aqueous metal nitrates, was aerosolized with an ultrasonic nebulizer. The aerosolized droplets were then introduced to a carrier gas, saturated with air. The air carried the droplet towards the preheater, which was heated to 200°C. The preheater dried the layer of water surrounding the droplets before they entered the furnace. The furnace temperature was set at 350°C, 450°C, 550°C, 575°C, and 650°C, respectively. The dry precursor droplets thermally decomposed, removing the aqueous portion of the precursor droplet, leaving a dry metal oxide. The powder was collected downstream via vacuum filtration.

Battery Fabrication and Testing. The powder obtained from the spray pyrolysis process was annealed at 900°C for two hours in a box furnace, to improve crystalline structure and remove any residual moisture. A slurry was prepared by mixing the annealed powder with a 7% binder solution, and then cast upon an aluminum current collector to create our film. The binder solution consisted of 3.5% carbon black, 3.5% polyvinylidene fluoride (PVDF), and 93% N-Methyl-2-pyrrolidone (NMP). The carbon black assisted in electron transportation from the metal oxides to the aluminum current collector, the PVDF adhered the powder to the aluminum, and the NMP was the solvent.

After the film was made, it was allowed to dry overnight at room temperature and then another night in a vacuum oven to allow the NMP to evaporate. After drying, cathode disks, 13 mm in diameter, were prepared for battery fabrication. The batteries were assembled in an argon-filled glove box. Pure lithium disks were used as the anode to study the performance of the cathode material without side effects arising from the anode. The batteries were subjected to cycle and rate tests on MTI battery testers.

Results and Discussion:
We recorded x-ray diffraction (XRD) spectra of the products synthesized at different temperatures (Figure 1). The exact distances separating the peaks and the ratios of peak intensities indicated a lack of contaminants, and showed the superlattice layered-layered structure

Figure 1: XRD spectra.
characteristic of $x\text{Li}_2\text{MnO}_3(1-x)\text{Li(MnNiCo)}_{1/3}\text{O}_2$. We produced exclusively our desired product at all temperatures.

The cycle test results (Figure 2) indicated that the battery produced at 575°C yielded the highest reversible charge and discharge capacity. In Figure 2, the x-axis is the cycle number and the y-axis is specific capacity in mAh/g. C/10 and C/3 are the current densities of charge and discharge of each cycle, where C = 200 mA/g. Since the practical capacity of batteries made from layered-layered materials is 200 mAh/g, a battery would be fully charged if charged at a rate of 1C for one hour.

We ran the majority of the cycle test at a rate of C/3 considering that three hours was a reasonable amount of time to recharge a PHEV battery. Each cycle consisted of charging and discharging the battery; and the 575°C battery displayed slightly higher capacity than the other batteries, remaining above 200 mAh/g after 100 cycles.

Rate capability tests (Figure 3) determined how flexibly the material may be discharged at various current rates. The battery began by charging and discharging at a rate of C/10.

We then began charging and discharging at higher rates, to simulate acceleration and deceleration of EVs. As expected, the capacity of the battery diminished as it was cycled at a higher rate. The 450°C and 575°C batteries had the best performance with capacities above 170 mAh/g at a rate of 1C.

Figure 4 shows voltage profile evolution over time. We observed that with increasing synthesis temperatures, the change in the voltage plateau indicated by the arrows became smaller, showing better voltage profile retention. The x-axis displays specific capacity, while the y-axis displays voltage. The 650°C battery had a much lower voltage drop when compared to the 575°C battery. This is favorable because the voltage output from a certain specific capacity diminishes less over time for the 650°C battery, suggesting higher performance. Not only is it important to have high specific capacity, it is also important to have high output voltages corresponding to those capacities.

Conclusions and Future Research:
Layered-layered materials deliver very high reversible capacities. The highest capacity was achieved when the reactor temperature was 575°C. Increasing the reactor synthesis temperature improved the voltage profile without compromising the electrochemical performance. The relationship between increased reactor temperature and decreased voltage decay must still be studied. Future work will continue with higher synthesis temperatures as well as doping and variation of lithium concentration. The results will be discussed in an upcoming publication of the group.

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