

Development of Li-rich Layered Cathode Nanomaterials for High Energy Li-ion Batteries

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ABSTRACT

This study is on the development of a novel class of Li-rich layered oxide cathode nanomaterials based on $\text{Li}_x\text{Mn}_{0.75}\text{Ni}_{0.25}\text{O}_y$ ($1.5 \leq x \leq 1.6$, $y = 0.5x + 1.75$) with doping/co-doping and surface coating/treatments for high-performance Li-ion battery applications. A cost-effective, scalable synthesis process is employed to synthesize the cathodes, which could provide high voltage, high capacity, high rate and good stability. Microstructural and electrochemical characterizations were carried out to evaluate the properties and performance of the resultant cathode materials. Aegis Technology in cooperation with Bioenno Tech has established the capability in development and production of advanced electrode nanomaterials for high performance Li-ion batteries.

Keywords: energy storage, Li-ion battery, Li-rich cathode, high performance, large-scale production

1 INTRODUCTION

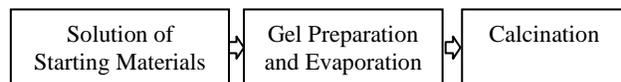
There is a great interest in developing energy storage systems based on more advanced lithium ion (Li-ion) battery technology, which has wide applications from small portable electronics to large scale systems. In this study, Aegis Technology Inc. has developed high-energy and high-capacity Li-rich manganese nickel oxide (LMNO) cathodes through material design, synthesis, optimization, and characterization, in order to significantly improve the utilization efficiency of cathode materials for Li-ion cells. This will lead to significant enhancements in energy performance of the resultant battery systems that can meet the demanding requirements from both military and civil applications.

In this development, the key technical issues related to material processing were well addressed. Preliminary optimization on material composition and processing parameters was conducted with an aim of achieving improved performance. Characterizations on both microstructure and electrochemical properties of the resultant materials were well carried out. Microstructure analysis indicated the formation of nanoscale LMNO particles. Electrochemical testing results showed that very promising performance had been successfully achieved, including extremely high capacity (>250mAh/g), good rate performance and cyclability.

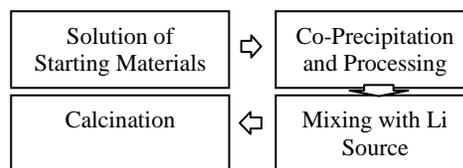
These results were among the best as reported in the latest literature. In addition, a potentially cost-effective and scalable material process method was established, which provided a solid basis for future mass production.

2 EXPERIMENTAL

Two methods, including a sol-gel-based method and a co-precipitation method, were established in order to prepare the cathodes and investigate the surface coating strategy. The processing investigations are aimed to a cost-effective and scalable material synthesis and processing method for the proposed material. Figure 1 shows the flow charts of the two methods employed.



(a) Sol-gel-based method



(b) Co-precipitation-based method

Figure 1: Flow charts of two established methods.

3 RESULTS

Three major strategies were employed in this investigation in order to develop advanced LMNO cathode chemistry with enhanced performance, including composition optimization, doping/co-doping, and surface coating/treatment.

3.1 Composition Optimization

It has been well acknowledged that material composition of LMNO exhibited a major influence on its performance, particularly in terms of capacity. Cathode composition optimization in this study was focused on the optimizations of Li content in the cathode formula, in order to determine the composition with the highest specific capacities. Samples of $\text{Li}_x(\text{Mn}_{0.75}\text{Ni}_{0.25})\text{O}_y$ with x values in the range of 1.50 to 1.60 (with an increment of 0.02) were investigated. In this investigation, a processing

method based on sol-gel technique was utilized. Preliminary optimization was also conducted on the processing parameters including acid concentration and pH value for the gel formation. After the LMNO samples were synthesized, examinations including scanning electron microscope (SEM) and X-ray diffraction (XRD) were performed in order to examine the microstructure including particle morphology and crystal structure. Figure 2 shows a representative SEM of a synthesized LMNO. Figure 3 shows the typical XRD patterns of the samples. From these figures, it can be found that the synthesized samples have good morphologies and pure phase crystal structures.

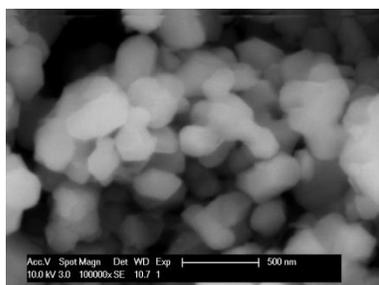


Figure 2: Representative SEM of a synthesized LMNO.

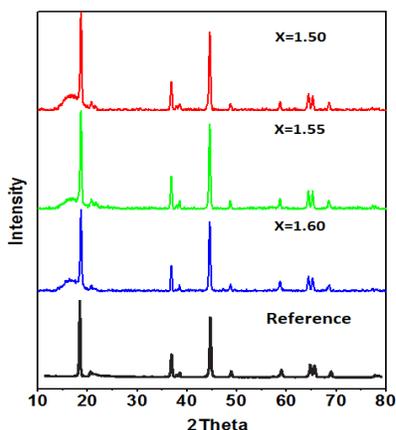


Figure 3: Representative XRD of typical LMNOs.

Electrochemical tests were conducted using CR2032 half cells. These cells are prepared, using the synthesized cathode materials [cathode composition: LMNO:C:PVDF = 80:10:10 wt.%; two Celgard 3501 separators; 1M LiPF₆-ethylene carbonate/dimethyl carbonate (EC/DMC) solution for electrolyte; galvanostatic charge-discharge experiments were performed at a voltage range of 2.0 volts to 4.9 volts; 1C capacity was calculated with ~250 mAh/g]. Figure 4 shows the typical rate performance of a LMNO sample (x=1.58), and Figure 5 shows the comparison of capacities of samples with varied x values (S01-S06 with x=1.50-1.60). The highest capacity (~270mAh/g) has been achieved with the cathode composition of x=1.58, *i.e.*, Li_{1.58}Mn_{0.75}Ni_{0.25}O_{2.5}. Therefore, Li_{1.58}Mn_{0.75}Ni_{0.25}O_{2.54} was selected as the baseline composition for the subsequent studies.

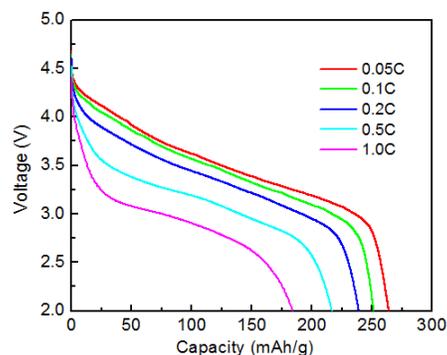


Figure 4: Typical rate performance of sample S05.

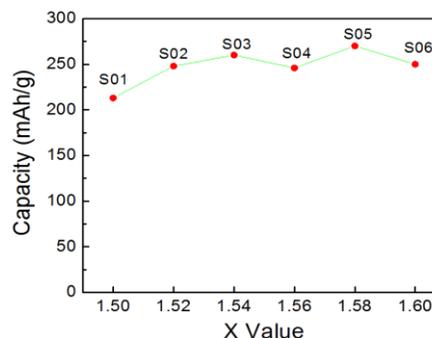


Figure 5: Capacities of samples with varied x values

3.2 Doping/Co-doping

Substitution doping (using single dopant) or co-doping (using multiple dopants) is another promising method to further improve the performance of LMNO-based cathodes. Recent studies indicated that a few kinds of dopants can be used, such as Co, Al, Na, F, *etc.* These dopants have been proposed based on different mechanisms. Doping/co-doping in this study was focused on substituting unstable transition metal ions (Mn and Ni) and/or Li, O ions in the cathodes with selected doping elements, in order to improve the crystal structural stabilities and electrical conductivities of cathode

SEM image of one representative Na-doped sample is shown in Figure 6. Good dispersion and uniformity of the particles are shown in the image. Also, Na-doped samples exhibit a relatively smaller average particle size when compared to the undoped sample.

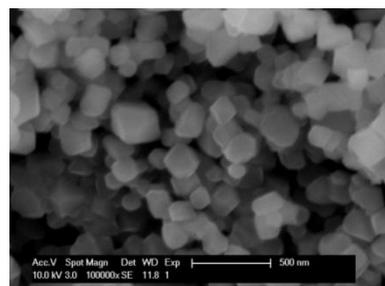


Figure 6: Representative SEM of a Na-doped sample.

Figure 7 shows the comparison of discharging profiles for four typical samples (with doping of 15 mol.%Co, 4 mol.% Na, and co-doping of 4 mol.%Na-4 mol.%Al, 6 mol.%Na-6 mol.%Al, respectively). Profiles for un-doped sample are also shown in each figure for the comparison purpose. From these figures, D03-15Co provided not only the highest capacity (~265 mAh/g vs. ~250 mAh/g of un-doped sample), but also the best rate performance (~170 mAh/g at 1C) among all these capacity samples. A possible reason is because of the presences of Co dopants such that the electrode polarization of the cathode can be significantly reduced, and at the meantime, the activation of the Li_2MnO_3 component (which is major contributor of capacities) is improved, as argued in literature [1]. Figure 8 shows the cycling performance of some representative doped/co-doped samples.

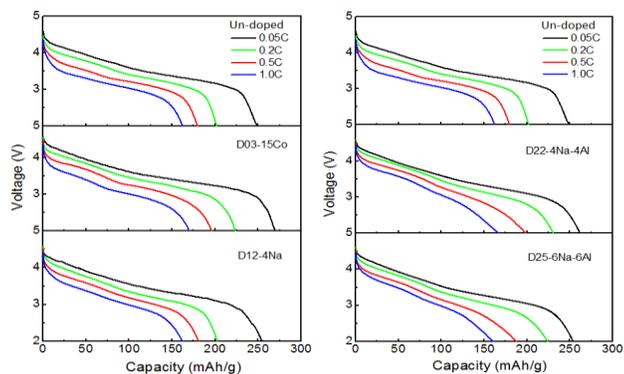


Figure 7: Typical rate performance of some doped samples.

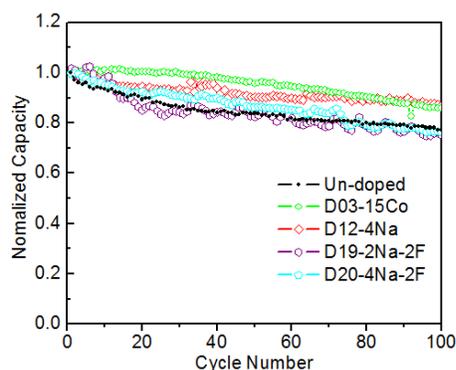


Figure 8: Typical cycling performance of some doped/co-doped samples.

3.3 Surface Coating/Treatment

Surface coating/treatment has long been regarded as a promising method to improve the performance of LMNO-based cathode materials. This can be attributed to the following reasons: 1) cathode active materials can be protected by the coating layer from the side reactions with electrolyte; 2) Li^+ intercalating sites can be effectively maintained because of the presence of a greater number of oxide ion vacancies that are protected by the coating layer; 3) surface transformation from layered-type to spinel-type

structure because of the interaction between the LMNO particle surface and the materials used, and the resultant spinel phase on the cathode surface facilitates the Li^+ intercalation. Therefore, it is expected that cathode performance can be improved in terms of capacity, rate capability, and cyclability.

In this study, two schemes of surface coating/treatment were investigated based on the same mechanisms as mentioned above but using different materials on cathodes with different particles dimensions. In the first scheme, surface coating materials such as MnO_x ($1.5 < x < 2$), AlF_3 , C, etc. and surface treating materials such as ammonium persulfate (or APS) and potassium permanganate (or PP) etc., were applied onto LMNO cathodes with relatively smaller particles (~200-500 nm), while in the second scheme, nanoparticles of $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4/\text{C}$ (LMFP/C) were coated to LMNO with relatively larger spherical particles (~2-5 μm , processed via co-precipitation).

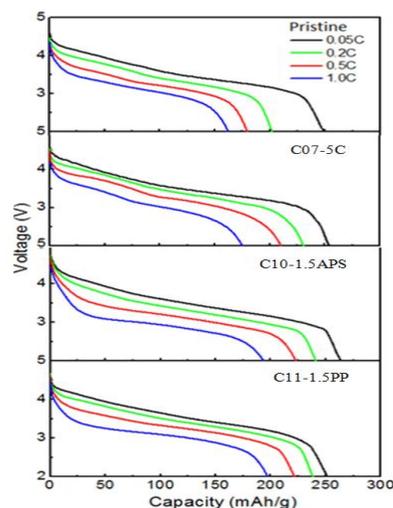


Figure 9: Comparison of discharge profiles between three surface coated/treated and pristine samples

Figure 9 shows the comparison of discharging profiles (at 0.05C, 0.2C, 0.5C, and 1C) for those three representative samples. For simplicity, profiles of other samples are omitted. As shown in the figure, C07-5C (with 5 mol.% C-coating) exhibited similar capacity and rate performance with those of pristine sample. However, the discharge voltages were enhanced (particularly at the early stages of the discharge processes). A possible reason for this higher voltage was explained by the presence of a small percentage of the spinel phase on the cathode surfaces as a result of surface-treatment via Super P, as argued in the literature [2]. Both surface-treated samples (C10-1.5APS and C11-1.5PP) provided attractive capacities (~264 and ~251 mAh/g, respectively) and higher rate performance (~194 mAh/g of C10 and ~197 mAh/g of C11 at 1C). In addition, when compared to C10-1.5APS, C11-1.5PP exhibited even better rate performance and higher discharge voltages, although its capacity was just a few percent lower. Based on these

results, surface treatment using both APS and PP are effective methods for LMNO cathodes enhancement. Also, comparing with APS, PP is better preferred when considering the similar price but tends to be environmentally benign than APS.

It is important to note that in order to achieve an effective coating (*i.e.*, covering all the exposed surfaces) on cathode samples that have small particles, more coating materials are needed because of the much larger surface areas when compared to those of cathodes with larger particles. However, too much amount of coating will significantly degrade the LMNO cathode performance, particularly lead to lower capacity and sometimes lower electrical conductivity. We have addressed the issue with the usage of LMNO cathodes with relatively larger particles, combined with coating materials consisting of active and conductive nanoparticles. For the coating material, LMFP/C nanoparticles were selected because of its smaller particle size and attractive electrochemical properties.

Figure 10 shows the discharging profiles (at 0.05C, 0.2C, 0.5C, and 1C) of samples P1 (pristine) and P2 (LMFP-coated). Both P1 and P2 samples had shown enhanced discharging voltage, suggesting the improved conductivities. In particular, when compared to P1-pristine, P2-coated sample provided further enhanced discharging voltage, which was attributed to the presence of conductive C in the coating layer, although the capacity (at 0.05C) of P2 was relatively lower because of lower capacity of LMFP (~140mAh/g). These results prove the effectiveness of the proposed surface-coating method.

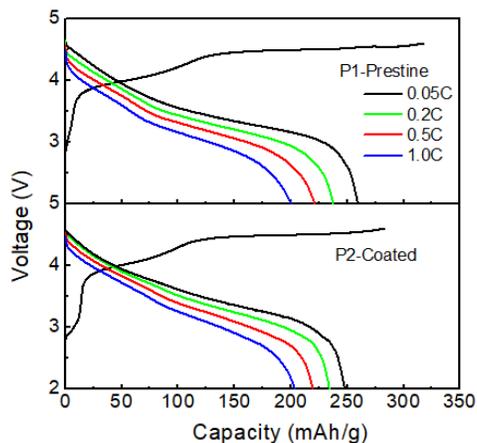


Figure 10: Comparison of discharge profiles of P1 and P2.

Cycling performances of P1-pristine and P2-coated are shown in Figure 11. P1-pristine underwent a degradation of capacity within 40 cycles, while P2-coated showed an enhanced cyclability, and it was even better when compared to that of un-doped samples (~81% of P2 vs. ~77% of un-doped and ~65% of P1 across 100 cycles). These results indicated the effectiveness of the proposed LMFP/C-coating strategy.

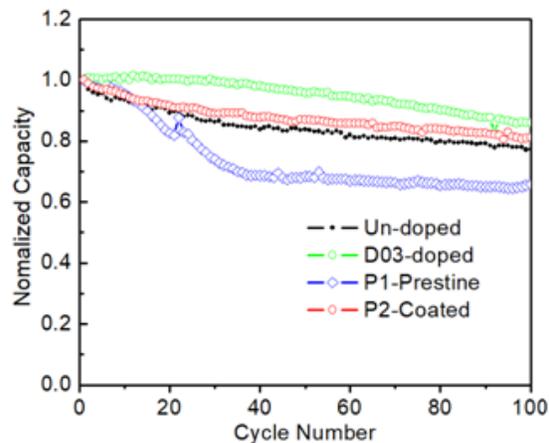


Figure 11: Comparison of cycling performance.

4 CONCLUSION

Systematic development of the proposed LMNO cathodes has been carried out via different strategies including composition optimization, doping/co-doping, and surface coating/treatments. The obtained results suggested that the proposed LMFP/C-coating on spherical LMNO cathode particles is a very effective strategy for enhancing the performance of Li-rich cathodes in terms of capacity, rate performance, discharge voltages, and 1st coulombic efficiency, although further improvement on cyclability is desirable. It is expected that through further optimization, it is quite feasible to achieve LMFP/C-coated LMNO cathodes with properties that suitable for practical applications, and eventually lead to the commercialization of this cathode technology.

5 ACKNOWLEDGEMENTS

This study was partially supported by an U.S. Army SBIR project (contract number#: W56HZV-13-C-0092; title High energy/capacity cathode materials)

6 REFERENCE

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