Stabilized NMC811 to Enable High Energy Density Lithium Ion Batteries

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by:

Yuxin Gao (ME)

Logan Visser (ME)

Approved:

Prof. Yan Wang, Project Advisor

Abstract

Over the past decade, the performance of lithium ion batteries (LIBs) has improved greatly and costs have dropped significantly. However, emerging battery applications (EVs) demand increasingly higher energy density, lower cost, longer cycle life, and higher safety, which cannot be met simultaneously by current LIB technology. Specifically, cathode material is recognized as the key limiting component for both energy density and cost. Commercial cathode materials (LiCoO2, LiFePO4, Li2Mn2O4, LiNi1/3Mn1/3Co1/3O2) normally offer a specific capacity in the range of 130-160mAh/g. Currently, both industry and academia are searching for next generation cathode materials with a specific capacity of >200mAh/g for xEV applications, and LiNi0.8Mn0.1Co0.1O2 (NMC811) is viewed as a promising candidate in this space. However, along with the energy density benefits, its high nickel content also poses technical issues including cracking, low thermal stability, cation mixing, and parasitic reactions which result from interactions between the electrolyte and the highly reactive delithiated cathode surface at high potentials. These issues have thus far stalled the commercialization of these materials. In this project, an integrative approach including doping and coating was adopted to solve the above issues of NMC811.

Acknowledgements

Completing this project would not have been possible without the help and guidance of several people during the course of this year. We are very thankful to these people who have spent so much time advising, teaching, and working alongside us during this project:

Professor Yan Wang: Thank you for providing the initial idea for this project and advising our project throughout this year. We appreciate the time you invested into teaching us, reviewing our experiments, and discussing results with us. We have enjoyed working in your laboratory and have benefitted immensely from this experience.

Yangtao Liu: Thank you for your continued investment into our project this year. Thank you for teaching us how to prepare and use the chemical reactor, cast our samples, assemble our coin cells, and analyze our data. We have learned a lot from you, and we greatly appreciate the many hours you dedicated to helping us, and for your continued patience with us and our many questions.

Mengyuan Chen: Thank you for teaching us about the sintering and doping processes, and for providing your previous research data for us to review.

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Background

While the market for large, stationary batteries is currently dominated by lead acid and nickel-based batteries (Albright, Edie, & Al-Hallaj, 2012), lithium-ion batteries (LIBs) have recently become much more popular for portable, rechargeable applications, due to their comparably high energy density and low cost. LIBs have grown to account for approximately 63% of the worldwide (Tarascon & Armand, 2001), and from 2006-2016 increased in market share by 16% per year (Pillot, 2015). There are several types of LIBs which are widely commercialized, including lithium-cobalt oxide (LiCoO2), which has a high energy density and low discharge rate, and is used in most handheld electronics; lithium-iron phosphate (LiFePO4) and lithium-ion manganese oxide (Li2Mn2O4), both of which have low energy density but longer life and are often used for electric tools and medical equipment. All of these commercial batteries typically offer a specific capacity in the range of 130-160 mAh/g.

In the future, LIB applications are projected to continue to grow, with the market size projected to at least double for applications in consumer tablets and mobile phones (Goldman Sachs, 2015), as well as for electric vehicles (Citibank, 2012). Li-ion popularity has grown due to their high capacity and low cost, but as applications in electric vehicles demand lighter, smaller, higher-capacity, and safer batteries, the limits of li-ion battery performance are very clear. These increasing requirements cannot be all met by the current LIB technology. Therefore, newer, more undeveloped types of LIB cathodes, especially LiMO2, are being researched. There are two types of LiMO2 cathode materials, depending on the nickel content—same content Ni/Mn materials (LiNi0.4Mn0.4Co0.2O2 for example), and Ni-rich (such as LiNi0.8Mn0.1Co0.1O2) (Zhao et. al, 2017). The capacity retention and lifetime of these batteries depend on the structure and long-term stability of the materials (Li, Murphy, Winnick, & Kohl, 2001). LiNi0.8Mn0.1Co0.1O2 (NMC811) is regarded as a promising candidate, as it shows potential to have a specific capacity of over 200mAh/g. However, while Ni-rich Li-ion batteries demonstrate an initial high capacity, they end up fading quickly due to problems with poor rate capacity retention. Other technical issues with NMC811 include cracking, inferior cycle stability, and instability in air, low thermal stability, cation mixing, and parasitic reactions which result from interactions between the electrolyte and the highly reactive delithiated cathode surface at high potentials. These issues are formidable and have thus far stalled the commercialization of these materials. In this project, an integrative approach including doping and coating is being adopted to solve the above issues of NMC811.

Methodology

To begin this research, the process to synthesize the precursor Ni0.8Mn0.1Co0.1(OH)2 material was determined. Several iterations, as explained below in greater detail, were performed to determine and hone in on appropriate experiment parameters to synthesize the precursor materials. First the uncoated precursor was developed, then the coating process was added.

Uncoated Precursor NMC811

For each experiment, the same general process was used to prepare the reactants for the reaction. There were two reactants in the synthesis process, 2M metal sulfate (MSO4) and 5M sodium hydroxide (NaOH). The metal sulfate was created by mixing 189.22 grams of NiSO4, 15.12 grams of MnSO4, and 25.3 grams of CoSO4 with 300 mL of water in a beaker and stirring the two together overnight to make sure the powder was completely dissolved, then adding distilled water to create a total of 500 mL of 2M solution. Similarly, the sodium hydroxide was mixed by measuring 100 grams of NaOH with 300 mL of water in a beaker and stirring the two together overnight to make sure the powder was completely dissolved, then adding distilled water to create a total of 500 mL of solution. The reaction also required a 3.5M solution of ammonia water (Na4OH) as a complexing agent. The ammonia water was prepared by measuring 52.8 mL of ammonia and adding distilled water until 250 mL of solution was ready.

For each reaction a small batch chemical reactor (shown in Figure 1) with a reservoir volume of 550 mL was used. The reservoir was filled with 750 mL of 2.75M ammonia water, and the reactor was flushed for 1 hour, with the stirrer running at 650 RPM as 150 psi of nitrogen was fed in. After the reactor had been flushed, the reaction was started by turning on the pumps to add the prepared solutions at the rates described below.

The chemical reaction during this step is as follows:

$$\text{Ni0.8Mn0.1Co0.1SO4} + \text{2NaOH} \rightarrow \text{Ni0.8Mn0.1Co0.1(OH)2} + \text{NaSO4}$$

After the reactions were complete, the contents of the reactor was drained and the resulting material was filtered and rinsed thoroughly with DI water to remove as much ammonia solution and byproduct NaSO4 as possible. The samples were then dried overnight in the furnace to remove all liquids from the material. Approximately 20 grams of each sample was collected.

These dried materials then were examined by an SEM to see the particle structure. The resulting images from these SEM tests are shown below, along with the explanations of the experiment parameter iterations.

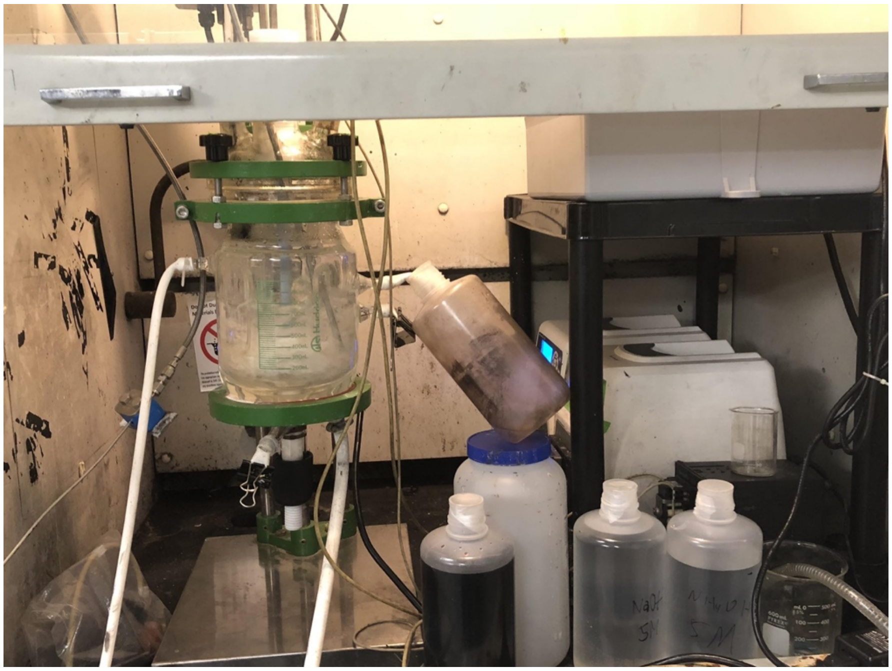

Figure 1. Chemical Reactor and Reaction Setup

The first parameters were determined based off of several small previous experiments conducted in Professor Yan Wang’s material processing lab by several PhD students, Zhangfeng Zheng and Mengyuan Chen.

After the reactor had been flushed, the reaction was started. The metal sulfate (MSO4) was fed into the reactor at 0.55 mL/min, the sodium hydroxide (NaOH) as needed (determined by the pH sensor), and the ammonia water (Na4OH) at 0.17mL/min.

The reaction temperature was kept constant at 55°C, the stirring speed at 650 RPM, the and the pH at 11 throughout the duration of the reaction. The residence time was 5 hours. The reaction was run for a total of 6 hours. These parameters are shown in Table 1, and the resulting precursor material is shown in Figure 2.

Table 1. Parameters for Uncoated Material #1

Residence time	5 hours
Reaction time	6 hours
Flow rate MSO4 (2M) NH4OH (3.5M) NaOH (5M)	0.88 mL/min 0.264 mL/min auto
Temperature	55℃
Stirring speed	650 RPM
pH	11

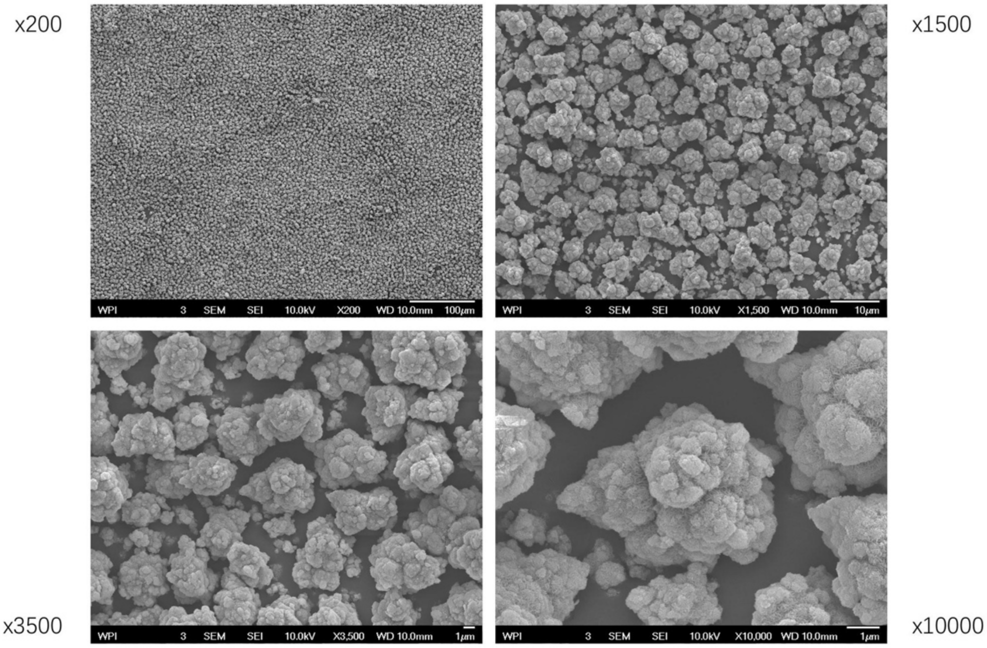

Figure 2. Uncoated Material #1

The resulting precursor was poorly formed, with a highly irregular surface and a particle size of about 4-5µm diameter, which was smaller than desired. (The goal for the particle size was an average diameter of 10µm.)

In order to attempt to form smoother, more uniform particles, the residence time was increased to 10 hours, and the required flow rates were recalculated as necessary. The parameters we used are shown in Table 2, and the resulting precursor is shown in Figure 3.

Table 2. Parameters for Uncoated Material #2

Residence time	10 hours
Reaction time	6 hours
Flow rate MSO4 (2M) NH4OH (3.5M) NaOH (5M)	0.40 mL/min 0.2 mL/min auto
Temperature	55℃
Stirring speed	650 RPM
pH	11

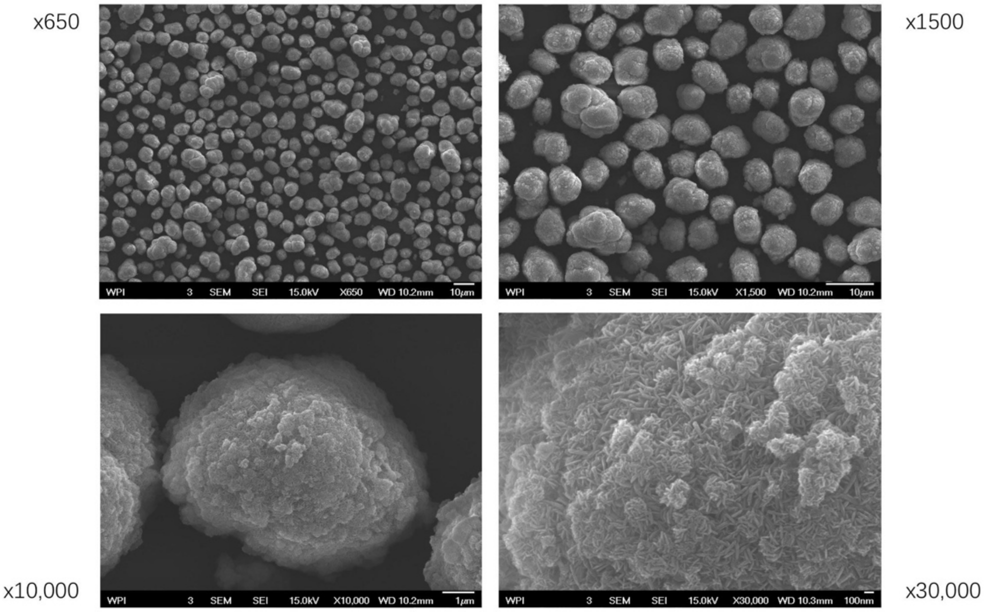

Figure 3. Uncoated Material #2

The resulting material looked much better, both in size (8-9µm in diameter) and in structure (more of a uniform spherical shape) than the last reaction (shown in Figure 2) but was somewhat on the dense side—too dense to accept the coating layer. Therefore, some slight adjustments were made to the third reaction.

Since the particles were too dense, the residence time was reduced down to 8 hours, and the flow rates were recalculated. A sample was collected halfway through the reaction, at 3 hours, to help decide if the 6-hour reaction time was the optimal length.

The reaction temperature was kept constant at 55°C, the stirring speed at 650 RPM, the and the pH at 11 throughout the duration of the reaction. The residence time was 8 hours. The reaction was run for a total of 6 hours, with a sample collected at 3 hours. These parameters are shown in Table 3, and our resulting precursor is shown in Figure 4.

Table 3. Parameters for Uncoated Material #3

Residence time	8 hours
Reaction time	6 hours (sample collected at 3 hours)
Flow rate MSO4 (2M) NH4OH (3.5M) NaOH (5M)	0.55 mL/min 0.17 mL/min auto
Temperature	55℃
Stirring speed	650 RPM
pH	11

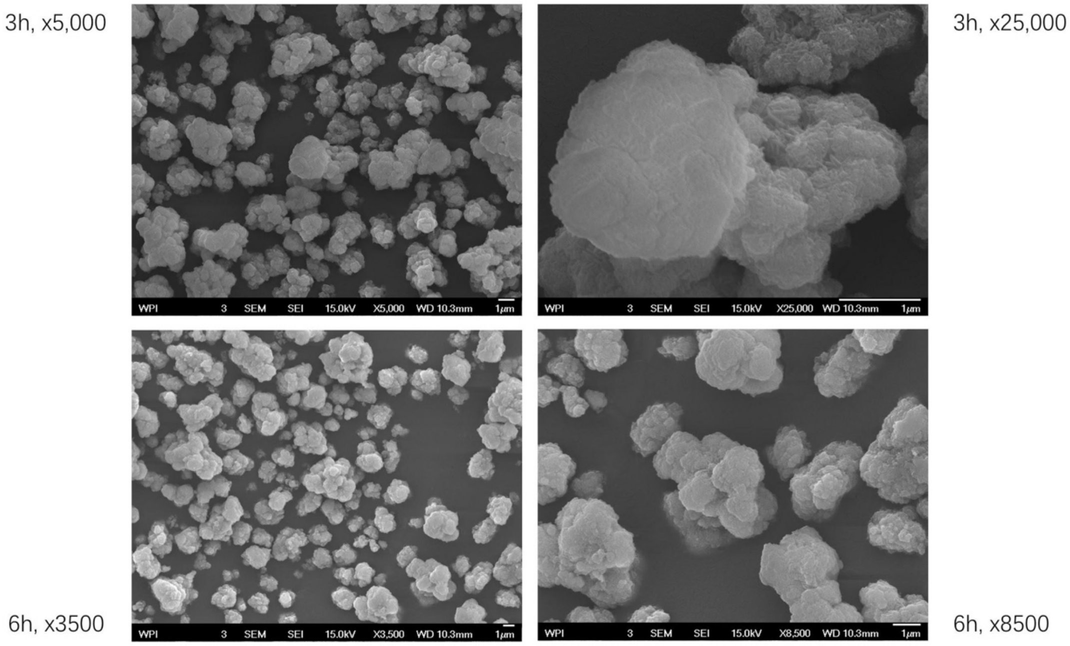

Figure 4. Uncoated Material #3

The third reaction failed and did not produce results that were usable. The reason why the reaction did not work is unknown, but the reaction produced an odd color (blue instead of milky green) for the first 2 hours of the reaction. The best guess was that there was something odd going on with the DI water that was used. After new water was obtained, the experiment was repeated with the same parameters (Table 3), and the resulting precursor is shown in Figure 5.

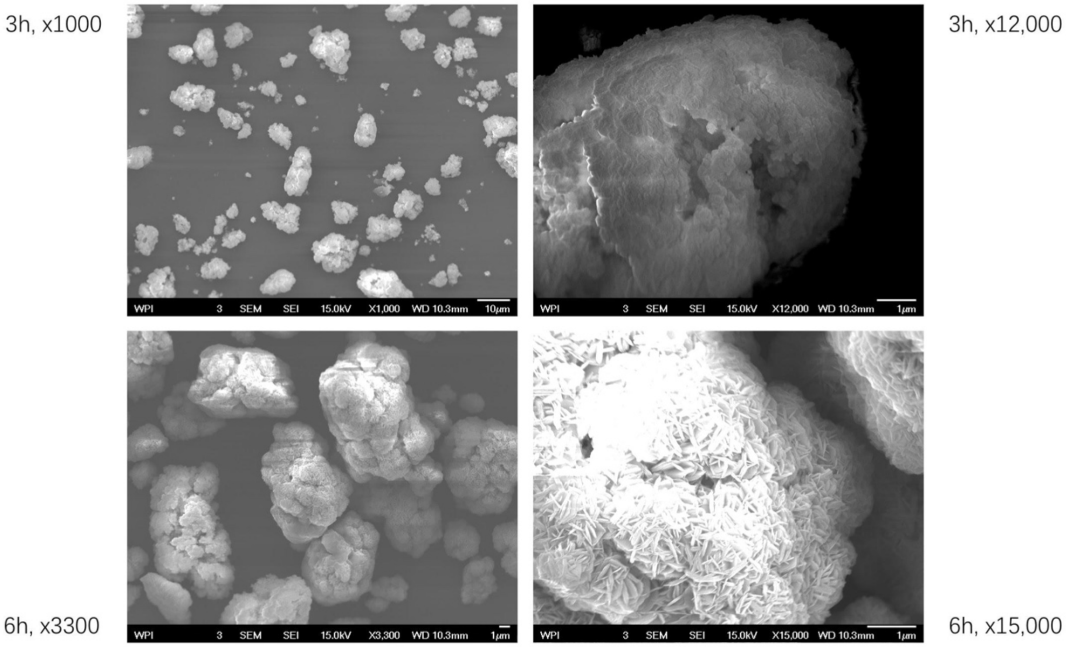

Figure 5. Uncoated Material #4 (Repeat of third reaction)

The precursor resulting from this reaction still was somewhat irregular in shape, but the porosity appeared to be reasonable, so although this uncoated material was not perfect, the best use of time seemed to be to move on and try to add the coating to this material.

Coated NMC811

The coated material was created in a similar way to the precursor sample. The precursor reaction was repeated, then after the 6-hour reaction the reactants were changed to create the coating on the surface of the precursor material. The parameters used to create this coating are as follows:

The two reactants used to create the coating were 0.1M metal sulfate (MSO4) and 3.5M sodium hydroxide (NaOH). The metal sulfate for coating consisted of MnSO4 and CoSO4 in 9:1 rate. We used 0.375M sodium hydroxide to control the pH of the reaction. These solutions were prepared similarly to the solutions above. The coating chemical reaction is as follows:

$$Mn_{0.9}Co_{0.1}SO_4 + 2NaOH \rightarrow Mn_{0.9}Co_{0.1}(OH)_2 + NaSO_4$$

For the coating, the metal sulfate was fed into the reaction at 3.5 mL/min, the ammonia water at 2 mL/min, and the sodium hydroxide as needed to maintain the pH. The reaction temperature was kept constant at 55°C, the stirring speed at 650 RPM, and the pH at 10.5 (Adjusted by adding H_2SO_4 at beginning) throughout the duration of the reaction. The residence time was 8 hours. The reaction was run for a total of 4 hours. (These parameters are shown in Table 4.) Once the reaction was complete, the reactor was drained, and the resulting material was filtered, rinsed thoroughly with DI water, collected, and dried in the furnace overnight. The resulting SEM images for this coating reaction are shown in Figure 6.

Table 4. Parameters for First Coating Reaction

Residence time	8 hours
Reaction time	4 hours
Flow rate MSO_4 (0.1M) NH_4OH (3.5M) NaOH (.375M)	3.5 mL/min 2 mL/min Auto
Temperature	55℃
Stirring speed	650 RPM
pH	10.5

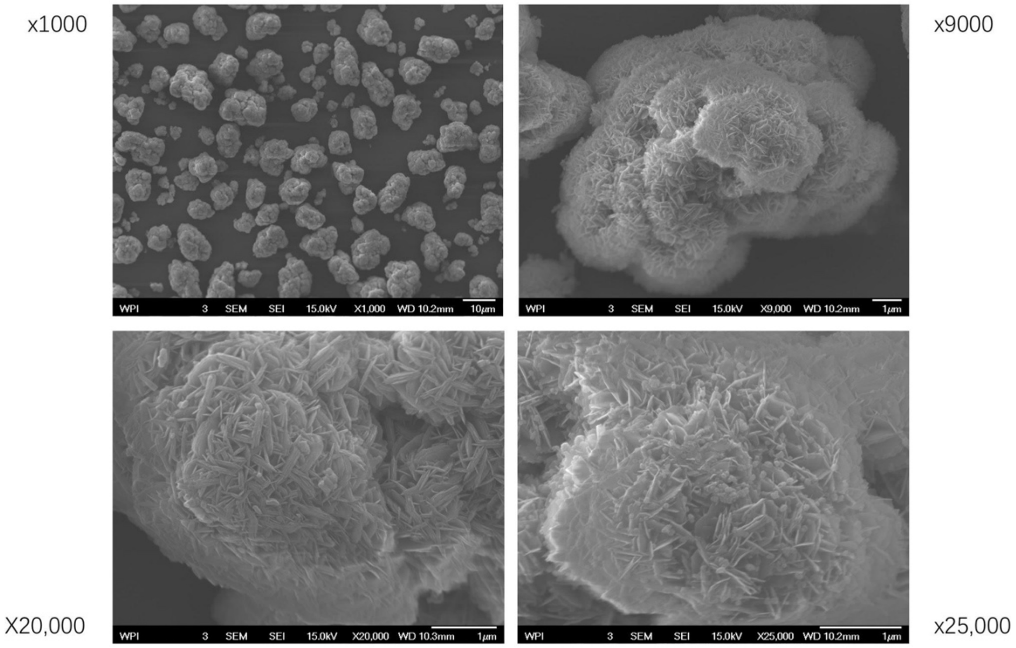

Figure 6. Coated Material #1

The results for the coating appeared to be satisfactory. Since the uncoated material was non-uniform, these particles after the coating were also irregular. The coating did appear to adhere to the base material well, though, so the entire process, with the exact parameters (as shown in Table 4), were repeated to produce the second coated material. The resulting uncoated material (Figure 7) and coated material (Figure 8), are shown below.

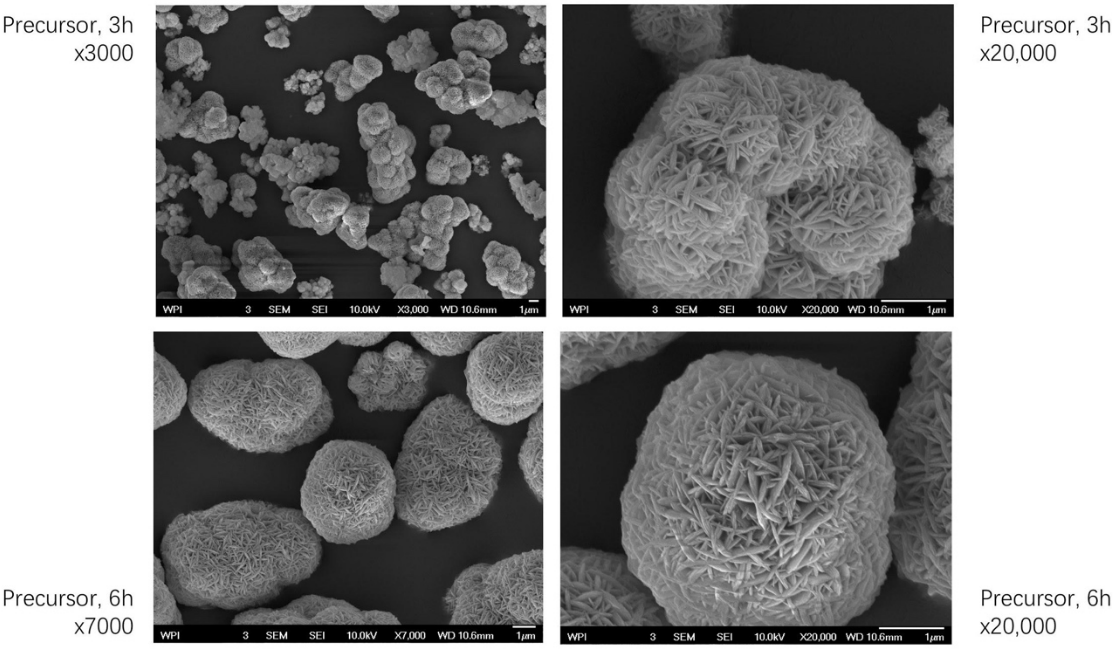

Figure 7. Uncoated Material for Coating Reaction #2

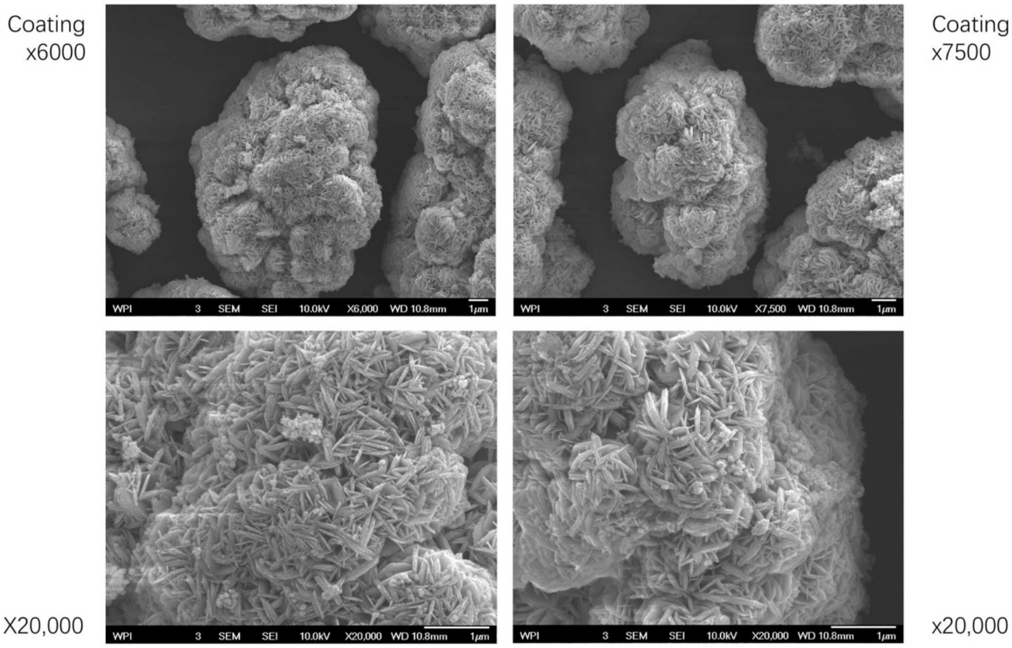

Figure 8. Coated Material #2

The sample collected at 3 hours (top two images of Figure 7) contained irregular and small particles, but the precursor particles collected after the full 6-hour reaction time (bottom two images of Figure 7) were of satisfactory shape, size, and density. The coated sample appeared irregular but did seem to have a reasonably even coating of the MC91 material on all the particles.

After this reaction, the precursor materials were all completed and ready to move on to produce the NMC811 material. The uncoated precursor from Figure 3 and the coated precursor from Figure 8 were used for the following processes and testing.

Sintering and Doping

Four samples of each precursor sample (uncoated and coated) were prepared and sintered in air. During the sintering process, several samples were prepared to test the influence of doping on the cathode material properties. For both coated and uncoated samples, we introduced varying weight percentages of sodium carbonate (NaCo3) into the samples. In total, 8 samples were mixed—a pure sample (no NaCo3), 1 wt% NaCo3, 3 wt% NaCo3, and 5 wt% NaCo3—for both the coated and uncoated precursor samples.

To prepare each sample, 2.1g of lithium carbonate (LiCO3) was first combined with a weight percentage of sodium carbonate (NaCO3), depending on which sample it was. (The pure sample contained no NaCO3, the 1% sample contained 0.021g NaCO3, the 3% sample contained 0.063g NaCO3, and the 5% sample contained 0.105g NaCO3.) The LiCO3 and NaCO3 were thoroughly mixed for over 5 minutes with a mortar and pestle to ensure they were well combined. 5g of the precursor material was then measured and thoroughly combined into the mixture and mixed for 10-15 minutes. Each prepared sample was then transferred to a crucible and placed in the very back of the muffle furnace (Figure 9) to benefit from the most consistent and accurate furnace temperature. The sintering reaction is as follows:

$$Ni_{0.8}Mn_{0.1}Co_{0.1}(OH)_2 + Li_2CO_3 \rightarrow LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$$

Figure 9. Thermo Scientific Muffle Furnace Used for Sintering

The samples underwent two heating cycles. The first cycle started at 25°C and increased temperature at a rate of 2°C/min until it reached 450°C, where it remained for 6 hours. After 6 hours, the temperature was gradually reduced at a rate of 2°C/min until it reached room temperature. The second cycle was similar, but this time was increased to 750°C and remained constant at that temperature for 15 hours before being slowly lowered to room temperature. These parameters are shown graphically in Figure 10. Some of the final NMC811 samples are shown in Figure 11.

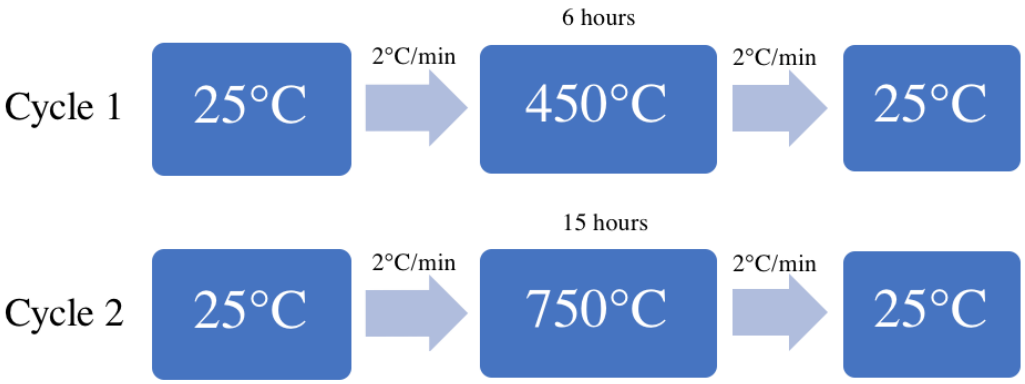

Figure 10. Sintering Parameters

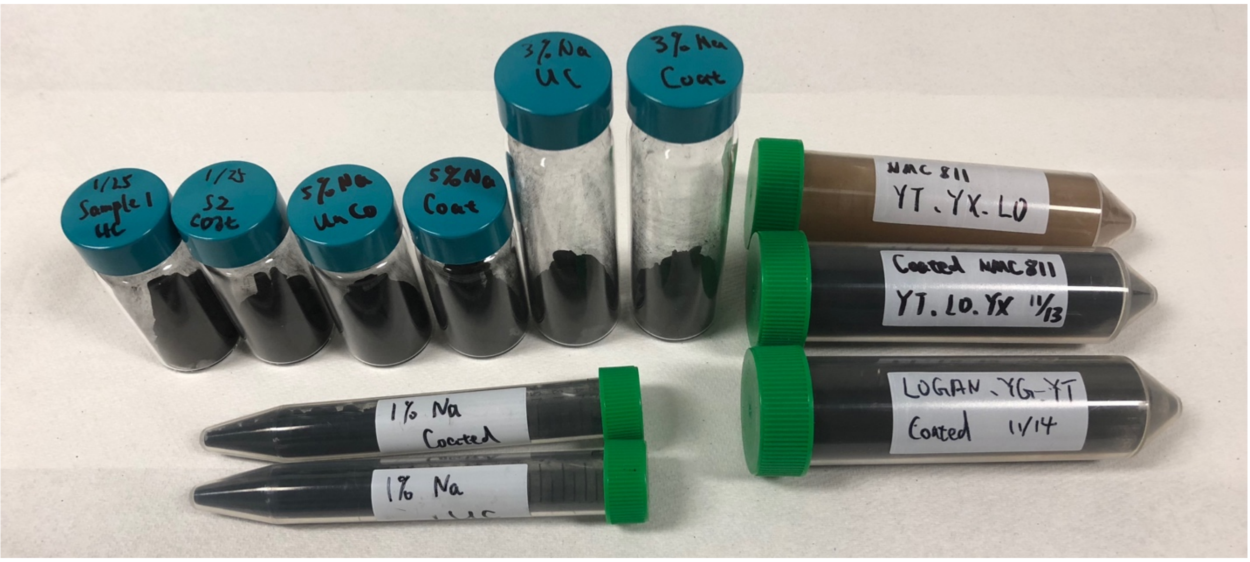

Figure 11. Various NMC811 Samples

Casting

To create the electrode slurry, 0.4g NMC811 powder and 0.05g Super-S carbon black were thoroughly mixed with a mortar and pestle, then thoroughly mixed with 0.77mL of 6 wt% PVDF and 0.6 mL of solvent until the slurry was completely smooth and of a consistency similar to thick paint or honey. The electrodes were made by coating this prepared slurry on aluminum foil with a 20 µm notch bar spreader. The electrode was dried in air overnight at a temperature of 60°C in the Automatic Film Coater (shown in Figure 12). The electrode was punched with a 14mm punch, then each punched electrode circle was flattened under a pressure of 2500 psi (Figure 13), measured for thickness and weight, and dried overnight at 60°C in a vacuum oven.

Figure 12 (L) & Figure 13 (R). Automatic Film Coater and Hydraulic Press

Coin Cell Assembly

After the cathodes were punched, pressed, and dried, they were ready to be assembled into coin cells. They were all assembled in the glove box (Figure 14) under vacuum pressure.

Figure 14. Glove Box used to Assemble Coin Cells

To begin the assembly, a bottom battery shell was placed on the working board. Then a spring was placed inside with a spacer covered on it. One thin piece of polished lithium was stacked on the spacer. (The lithium disk needed to be polished with brush to remove the oxide layer.) Next, two drops of electrolyte were added on lithium. One separator paper was carefully placed on top of the electrolyte, then two more drops of electrolyte were added. The punched electrode was placed face down (black side down) and one more spacer was laid to flatten the electrode. Finally, a battery cap covered everything inside the coin cell, and was sealed under 1,000 psi in a hydraulic press. Each battery was carefully labeled for identification during testing. And all the tools used were cleaned before assembly. Several of the final coin cells are shown in Figure 15.

Figure 15. Final Assembled Coin Cells

Cell Testing

According to the weight and thickness measured from punched electrodes, weights of real active material in batteries could be calculated. The weights of real active material were used to estimate the current and voltage should be applied during the test.

For the rate test, the current and voltage were calculated under various C-rates, such as 0.1C, 0.3C, 0.5C, 1C, 10C, etc. The higher C-rate applied, the shorter the charging time should be. This test showed the capacity of batteries under different C-rate. For the cycle test, the current and voltage were set as increasing value. This test showed the capacity retention of batteries after around one hundred cycles.

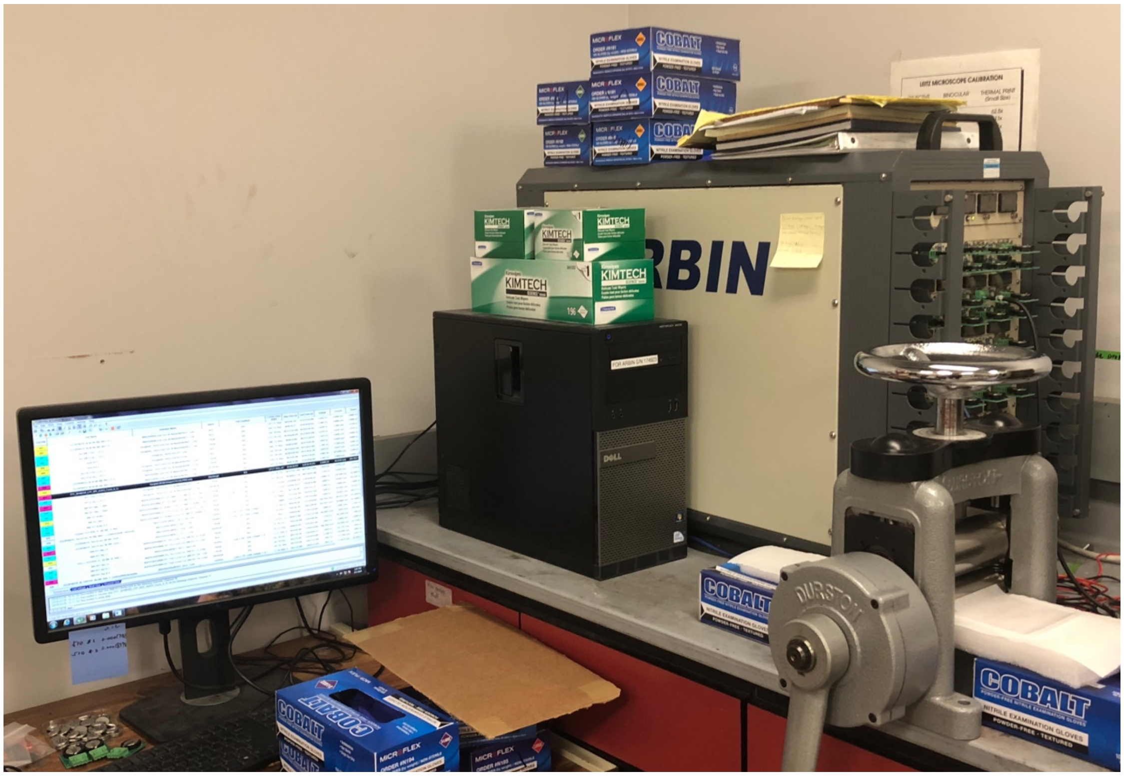

Figure 16. Arbin Battery Testing Machine

After the estimated data was entered into the testing software on the computer, assembled batteries were inserted into the Arbin testing machine (Figure 16) and the channels were started. The testing machine charged and discharged the batteries continuously as set in testing software; meanwhile, it recorded the resulting data such as applied current, voltage, cycles, and capacity. The recorded data was received after the testing had produced sufficient data (about one week) and was analyzed according to the weight of real active material to show the performance of tested batteries.

Results

Rate Testing

By comparing the testing data of NMC811 samples with different wt% sodium, we found the doping with sodium did not improve the capacity of the batteries. As shown in Figures 17-19, each of the no Na (no doping), 1% Na, and 3% Na samples had capacities around 150 mAh/g (uncoated), or 140 mAh/g (uncoated). The 5% Na samples all failed in the rate testing, therefore no data for those samples are provided in this report.

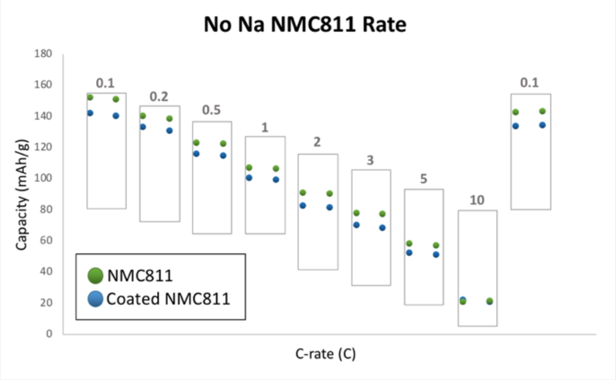

Figure 17 *(Top L)*. Rate Test Results for Sample with no Doping

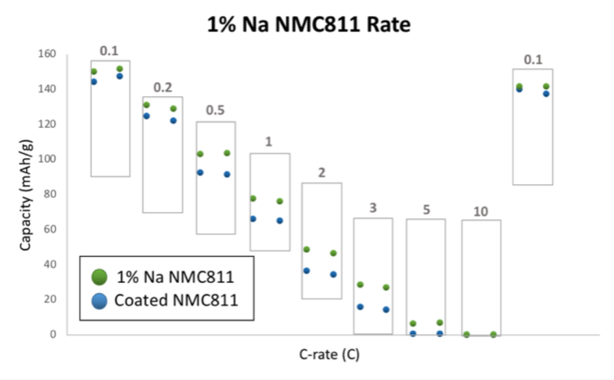

Figure 18 *(Top R)*. Rate Test Results for 1% Na Doping Sample

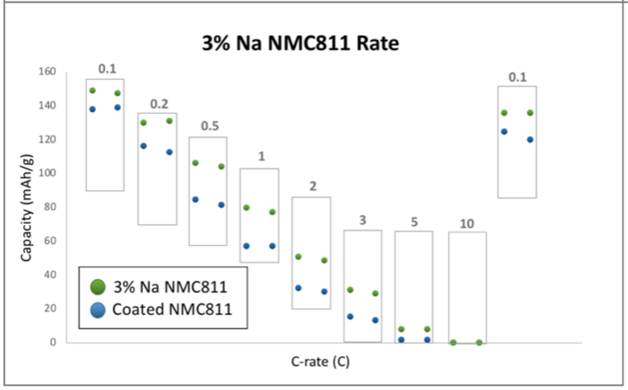

Figure 19 *(Bottom L)*. Rate Test Results for 3% Na Doping Sample

The undoped and 1% doping samples showed that the batteries retained capacity well, with the final 0.1 C-rate test retaining 94% of the original capacity. The coated 3% sample, however, performed much worse, retaining only 87% of its initial capacity from the beginning of the rate test to the end.

Cycle Testing

The cycle tests provided somewhat inconclusive data. In the undoped sample (Figure 20), one of the coated samples shows a higher capacity retention than the uncoated sample, however another coated sample provided lower results. The other samples, 1% Na doping

(Figure 21) and 3% Na doping (Figure 22), showed the uncoated material to hold higher capacity retention than the coated material. The 5% Na samples failed in the cycle testing, therefore no data for those samples are provided in this report.

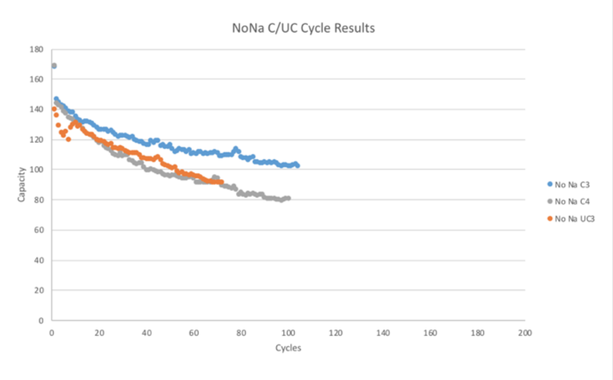

Figure 20 *(Top L)*. Cycle Test Results for Sample with no Doping

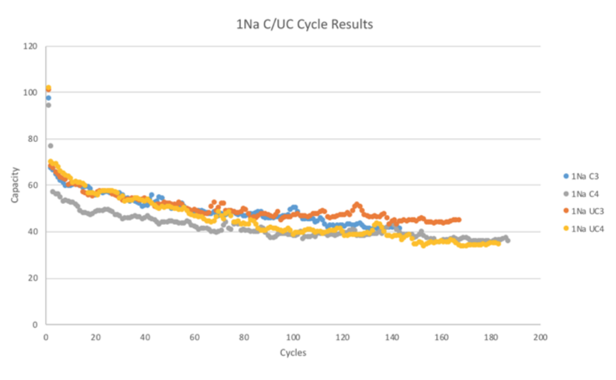

Figure 21 *(Top R)*. Cycle Test Results for 1% Na Doping Sample

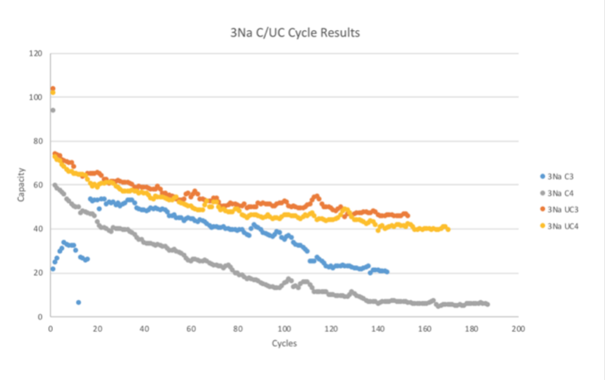

Figure 22 *(Bottom L)*. Cycle Test Results for 3% Na Doping Sample

Discussion and Conclusions

The coated NMC811 material demonstrated to have a lower capacity than the uncoated material. This was expected, because the MC91 coating has lower capacity properties than the NMC811 material, therefore lowering the average capacity of battery that contained the coated samples. This can be seen in Figures 17-19.

The coating appeared to improve capacity retention in the undoped sample (Figure 20). However, the uncoated 1% Na and 3% Na samples performed better than the coated samples.

The doping process did not improve the capacity or the cycle performance properties of the battery samples (as seen in Figure 21 and Figure 22). The doping was most likely unsuccessful in showing any material improvement because these materials were sintered in air rather than in oxygen, which disrupted the reaction during the sintering process.

Overall, these results demonstrated that these materials had a low (Figure 21 and Figure 22) to commercial-level capacity (Figures 17-19). By comparing with the result from previous experiments conducted in Professor Yan Wang's material processing lab by PhD students, we believe this may be caused by:

1. No aging time after the reaction to polish the material particles
2. The ideal parameters for the precursor coating were not used, resulting in a less-than-ideal coating layer on the particles.
3. NMC811 samples were sintered in air rather than in pure oxygen.
4. Part of springs and spacers used in coin cell have worse performance than expected
5. According to information from PhD students in Professor Wang's lab, the *Arban* battery testing machine may have been functioning improperly during this research and wrongly reading former test settings. Thus, the data we received from testing machine may not be accurate.

In order to produce more advantageous results in the future, we recommend that these problems be addressed in future projects.

Future Work

The following works and improvements are recommended for the future research groups:

- Synthesize precursor in larger reactor, where can polish the particles better.
- Repeat coating under different wt% coating material and pH numbers to produce a better coating material on the material particles
- Sinter precursor NMC811 in oxygen
- Evaluate battery components thoroughly for quality before battery assembly
- Add aging time in synthesis of precursor NMC811 material

Appendix: What we learned from this MQP

Before we entered Professor Wang's lab for MQP, we had never had the chance to get close to kinds of unfamiliar but high-tech experiment instruments. When we got access using them to synthesize new battery material, for the first time, we felt we were doing something great and meaningful. Just like engineers who can make change and contribution to the world, we were also trying to make something progress.

It was really an exciting process when we saw our experimental product gradually appeared after several hours' reaction. With the help from professor and PhD students in the lab, we learned how to do the SEM and analyze those images. Seeing the results changed every time due to small differences on the experiment parameters, we realized this was how engineers should work, "be patient and always keep trying to find a better way out." Of course, things couldn't always go smoothly. During the repeated experiments, we also met accidents which ruined the product and made worse SEM images. But this experience reminded us, "Accident may happen anytime, but what we should do is try to manage it and never give up.

In our last term, we were finally able to put our battery material into real button cells to test the performance of new material. We really felt a sense of achievement when we took the own-assembled batteries in our hands and saw they had voltage shown under voltmeter which mean the battery could really be put into use. After collecting and analyzing the test data from cell battery testing machine, we found the batteries' performance was not as good as expected, even worse than commercial ones. After discussed with professor, we made several possible assumptions for the result. And Professor Wang told us, "I don't require you to create something really great. What's more important is what you learned from the process. Failure always happens before success and at that time, just find reasons and keep going." So for us, besides how to synthesize electrodes' material and assemble batteries, we learned the spirit of an engineer.

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