PROBING THE FEASIBILITY OF HYDROGEN-BASED RECYCLING FOR NMC CATHODES

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ABSTRACT

- As the demand for lithium-ion batteries continues to rise so will the need to recycle them. The current recycling process separates the cathode material into Li_2O and metal oxide after which it is further processed to produce the same virgin material it will be incorporated with. One of the disadvantages of this process is the high energy consumption required to refine the powder back into the virgin material
- The internship's objective was to explore the potential reduction of $Li(Ni_{0.33}Mn_{0.33}Co_{0.33})O_2$ (NMC 111) and $Li(Ni_{0.6}Mn_{0.2}Co_{0.2})O_2$ (NMC 622) using hydrogen, to determine if it is a feasible method to be used in cathode material recycling and what the conditions required for a high-yielding reduction to occur

MOTIVATION

- This project has the potential of reducing the energy usage required to recycle NMC cathode material by producing a product that is ready to be incorporated into the current battery manufacturing pipeline

METHODS

- Raman spectroscopy – used to probe what bonds were present in the Virgin NMC powders and how they changed after the powder was reduced
- Powder size analysis – Compared the particle size and shape of the NMC powers before and after reduction
- Thermogravimetric analysis – Used to reduce the NMC powders at temperatures of 350, 375 and 400 °C

RAMAN ANALYSIS

- Raman spectroscopy of the samples has identified two peaks of interest at 577-594 cm^{-1} and 1088-1097 cm^{-1}. The latter peak was shown to increase in intensity when the sample was reduced at a higher temperature leading to believe that it is the product of the reduction given that the peak was not present in the spectrum of the virgin sample. The source of the peak has been identified to be the formation of LiOH [1]
- By comparing the intensity ratio for the two peaks we can establish how successful the reaction is at different reduction temperatures. As shown in Figure 1, LiOH was shown to form at a higher rate in NMC 622 as the intensity of the 1088-1097 cm^{-1} peak increased with temperature, but NMC 111 showed a much lower formation of LiOH as the ratio stayed around the same, with the exception that at 375°C where much less LiOH formed

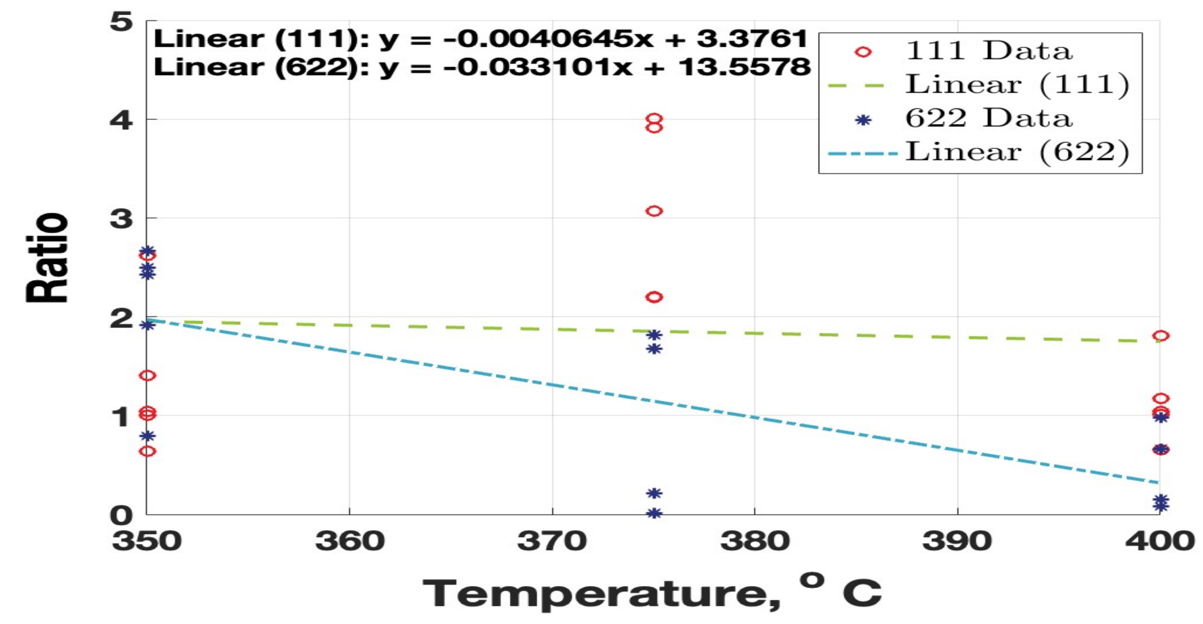

Figure 1: Relative change in peak intensity ratios between the peaks at 577-594 cm^{-1} and 1088-1097 cm^{-1}

SEM AND EDX ANALYSIS

- It was observed that for the samples reduced at 350 °C, there was no noticeable difference present. At 375 °C formation of string-like particles was observed to have formed from the surface of the NMC powders as shown in Figures 2 and 3. Additionally, the surface has also become more porous
- EDX of the string-like particles in Figure 3 has shown that they mostly consisted of oxygen and have a much lower presence of Mn, Co and Ni, than the surrounding NMC particles, as shown in Figure 5. This suggests that the oxygen has been absorbed out of the powder and formed a phase that branched away from the powder
- At 400 °C the string-like particles appeared to have coalesced into small droplets as shown in Figure 4, which adhered to the powder particles. Because of this, it was expected that the particle size would be larger than the reading at 350 °C, but given that the particle size has been decreasing and the shape of the reported particles has remained the same. It is assumed that when LiOH forms, it absorbs the oxygen from the powder causing it to reduce in size, and as LiOH is water soluble it would explain why the particle size has decreased and the shape hasn't changed. A pH test before and after the powder was added, observed a change from 6 to 12, indicating further evidence that LiOH has formed

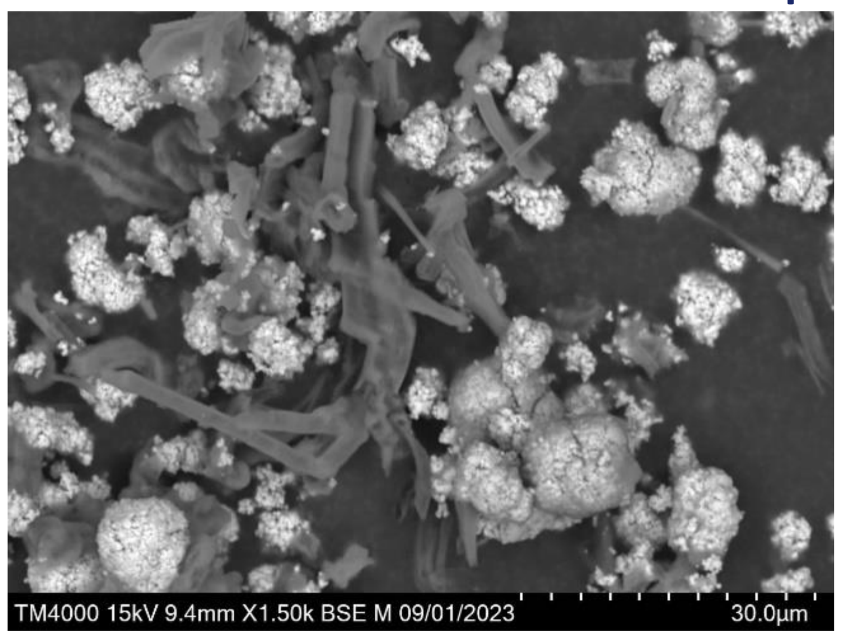

Figure 2: NMC 111, reduced at 375 °C

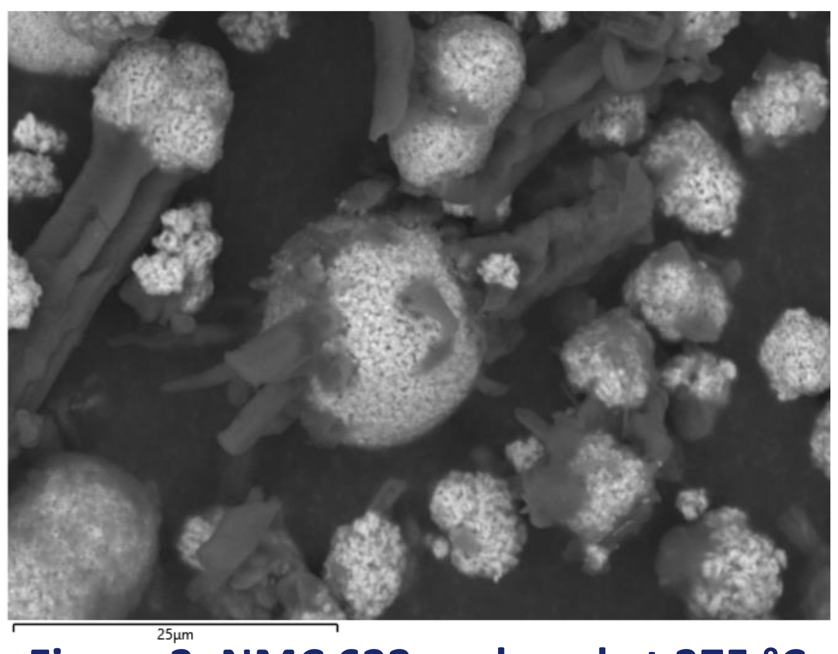

Figure 3: NMC 622, reduced at 375 °C

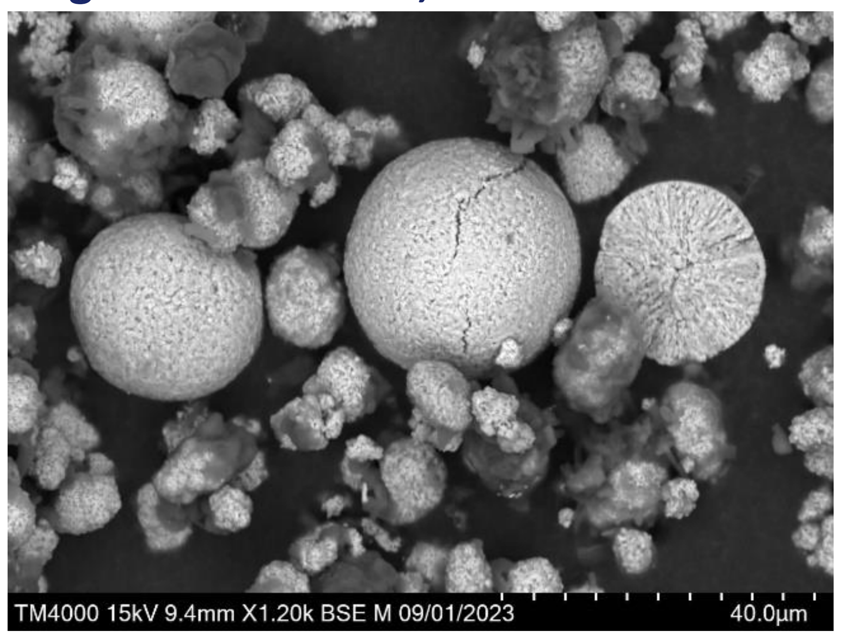

Figure 4: NMC 622, reduced at 400 °C

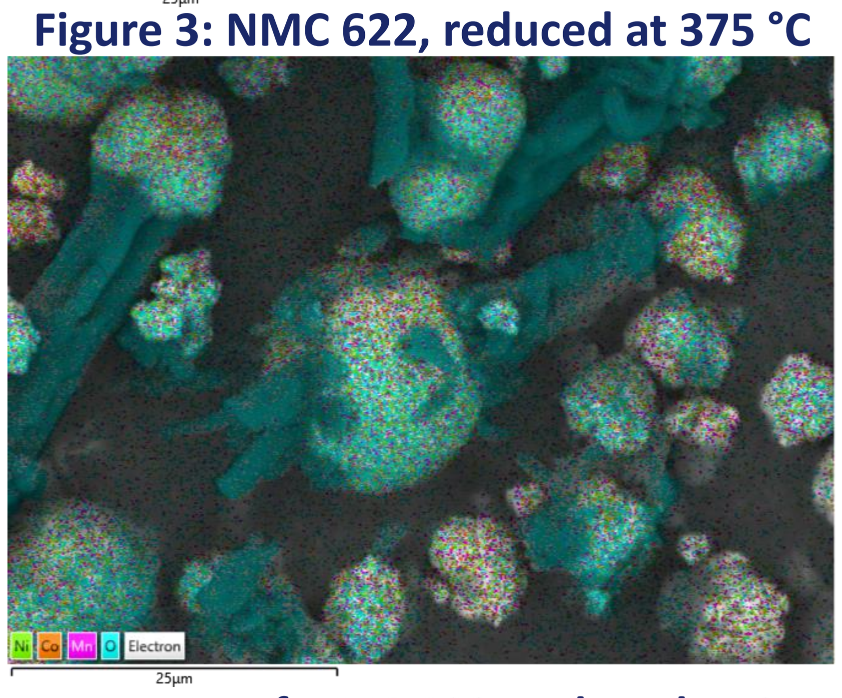

Figure 5: EDX of NMC 622, reduced at 375 °C

PARTICLE SIZE ANALYSIS

- Tables 1 and 2 show the particle size distribution where the average particle size for each powder is D50
- The particle size has generally been observed to decrease with an increase in temperature. However, for 350 °C the particle size is much smaller than the Virgin powder reading as some data points had to be excluded due to the larger particles which have coalesced and have proven difficult to break up, which is believed to be because of electrostatic attraction
- PSA has also observed little to no change in particle shape

Table 1 : PSA of NMC 111 reduced at various temperatures

Particle percentiles	Sample size (μm)			
	Virgin powder	Reduced at 350°C	Reduced at 375°C	Reduced at 400°C
D10	5.14	4.64	8.95	6.07
D50	8.87	7.57	16.65	10.59
D90	14.04	12.67	32.09	17.87

Table 2 : PSA of NMC 622 reduced at various temperatures

Particle percentiles	Sample size (μm)			
	Virgin powder	Reduced at 350°C	Reduced at 375°C	Reduced at 400°C
D10	8.61	7.55	9.78	8.88
D50	14	12.68	15.7	14.34
D90	21.03	19.45	23.42	22.23

CONCLUSIONS

- The reduction reaction was found to form LiOH, and the yield of the reaction was observed to increase proportionally with the reduction temperature
- The formation of LiOH was found to absorb the oxygen from within the powder particles and form string-like phases on the surface of the NMC particles. The absence of oxygen resulted in a decrease in particle size
- The reduction reaction was found to exhibit greater success in NMC 622 as compared to NMC 111

IMPACT / NEXT STEPS

- The next step would be to conduct further experiments to narrow down the conditions required to produce a powder that has a D50 particle size of 10 μm as that is what current battery manufacturing processes are using, allowing it to be incorporated straight into the current manufacturing route

REFERENCES

[1] Gorelik VS, Bi D, Voinov YP, Vodchits AI, Gorshunov BP, Yurasov NI, Yurasova II. (2017) Raman spectra of lithium compounds. Journal of Physics: Conference Series Vol. 918, No. 1, p. 012035.

INTERN BIO

Jakub is a second-year Materials Science student at the University of Birmingham, pursuing a Meng with a year in industry. He is interested in exploring pathways toward greener and low-carbon power generation, with a particular focus on the renewable and nuclear industries

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