Influence of KCl and NaCl Proportions in $Li(Ni_{0.8}Co_{0.1}Mn_{0.1})O_2$

Molten Salt Synthesis for Li-ion Batteries

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1 Abstract

2 Introduction

Lithium Ion batteries are a key technological tool for the sustainable mobility development all around the world. The performance of these batteries are highlly influenced by the materials composition, morphology, crystal structure and synthesis parameters, specially for the postive electrode material and the electrolyte.

In this report, we are going to focus on the NMC811 material. Currently, the aim of development for this material is to increase the amount of nickel in the structure, increasing the capacity and reducing costs, but the increase of nickel might also deteriorate the structure mainly by positive electrode mixing, which means that the nickel might take the Lithium sites. [4]

Specific capacity theoretical (mAh/g)	280
Average Voltage in discharge (V)	3.7
Row 3, Col 1	Row 3, Col 2

Currently, there is a great need to avoid any waste form industry, specially if you are working with scarce materials. The European Critical Raw Materials Act describes lithium, nickel and cobalt as crucial for the economy and asks for the implementation of a sustainable independent supply chain. [3] Therefore some efforts have been done to repurpose the waste of Li-ion batteries plants and turn them into a usable material. This project, attached to LEPMI laboratory and VERKOR, aims to repurpose byproduct carbonates ($MnCO_3$, $CoCO_3$ and $NiOH_a(CO_3)_b$) to synthesize NMC811 by solid state sintering.

This experiment will evaluate the morphology and performance of molten salt sintered NMC 811 for lithium-ion technologies. The presence of a liquid phase during calcination aids the whole process kinetics serving as a faster diffusion media for particle growth and homogenization. When solidified, the presence of this aiding phase is no longer wanted, to assure the purity of the target material. Therefore, salts are used, due to the capacity of easy dissolution on water, the salt can be washed off the target material [2].

From previous research, a mix of NaCl and KCl is chosen to be used since the mix between both salts depresses their melting point, allowing a purely liquid phase at the processing temperature of NMC. In addition to the low price of the compounds and the fact that the ion size is too large to take lithium sites in the materials lattice when washed. The aim of this study is to evaluate the influence of the salt mixture proportions on the final morphology and performance of the synthesized NMC positive electrode material material [5].

The characterization techniques used are Scanning Electron Microscopy (SEM), X-Ray Dirfraction spectroscpoy to identify the material phases and electrochemical characterization techniques on coin cells.

3 State of the art

3.1 Positive electrode materials

Todays positive electrodes are mostly intercalation or composite electrodes, they consist in a solid network that can host lithium ions with intercalation during discharge and deintercalation during discharge. These compounds can be devided into several different structures; layered, olivine and spinel. [4]

Some common cathode materials in lithium-ions technologies are:

3.1.1 Layered structures

$LiCoO_2$ (LCO). This material has low capacity compared to the theoretical one the extraction of more than half the lithium content leads to structural instabilities. It's use is also restricted due to the high cost of cobalt and its scarcity. [4] [**?**]

$Li(Ni_{0.8}Co_{0.1}Mn_{0.1})O_2$ (NMC811). NMC811 has more nickel and less cobalt than NMC111, which is better for the environment by reducing reliance on cobalt. However, this higher nickel content makes NMC811 batteries less stable and more prone to degradation and overheating compared to NMC111. [4]

$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA). This material increases the charge capacity by changing the Co content with Ni and using aluminum as a stabilizer. This reduces slightly the average cell voltage compared to LCO. [4]

3.1.2 Spinel structures

$LiMn_2O_4$ (LMO).The specific lattice structure of LMO, allows diffusion on three dimensions, which leads to faster charge - discharge rates. It is also a greener solution compared to to Co based positive electrode materials. The disadvantage of LMO is t its low charge retention and low cyclability. [4]

3.1.3 Olivine structures

$LiFePO_4$ (LFP). This is also a greener material than the Co based structures. LFP has a really high thermal stability but only counts with one dimensional diffusion. Therefore the voltage of discharge is too low. [**?**]

3.2 Synthesis methods

The choice of synthesis method plays a critical role in determining the final properties of NMC materials. Key attributes such as tap density, particle size distribution, particle morphology (both primary and secondary shapes), and crystallinity are strongly influenced by the synthesis process. Additionally, the method chosen impacts the presence of impurities, the overall quality of the final product, and its electrochemical performance.

Various synthesis methods are available for producing NMC, including co-precipitation, solid-state reaction, sol-gel processes, hydrothermal methods, and spray pyrolysis [1].

Each approach has its own advantages and limitations, influencing the structure and performance of the material in different ways. Below is an overview of the most commonly used methods for NMC synthesis:

3.2.1 Co-precipitation

This is today the most popular and cost effective production method, on an industrial scale . The method consists on the simultaneous precipitation of the transition metals and a subsequent sintering with a lithium source. The parameters important for this process is the pH of the solution, the stirring rate and the used chealing agent this highly affects the particle size and morphology [1]. There are three types of co-precipitation depending on the precursors used;

- Carbonate co-precipitation: This type of precipitation doesn't need an inert atmosphere because the oxidation state of the metals can be stabilized by CO. The problem is that the control of the final morphology is limited.
- Hydroxide co-precipitation: The final product of this process is really cost effective and has high tap density. When sintered, the particle size doesn't change so much but it is possible to get impurities from manganese oxides.

- Oxalate co-precipitation: This method is considered more environmentally friendly than the other two, and even cheaper. It does not require an inert atmosphere. The only problem is that the oxalate salts that are used have low solubility in water, therefore the production rate would be lower [1].

3.2.2 Solid state reaction

This is one of the most classical methods to synthesize any kind of ceramic material. It consists on the correct mixing of the precursors, and then heating the powder below the fusion temperature of the material. This activates the diffusion of the material due to surface energy phenomena, finishing on the coarsening of larger particles in expense of smaller ones. The disadvantage of this method is the high dependence on the initial particle size distribution and the homogeneity of the mixture [1].

Use of molten salts

This process commonly requires really high energy input. One alternative to this is to introduce a liquid diffusion media into the process, which is done in this project. A salt is used because is a substance that is liquid at the sintering temperature, it does not interact chemically with the active material and can be removed easily after sintering [1].

3.2.3 Sol-gel

Sol-gel method is used on laboratory scale conditions. It consists on forming a gel from transition metal salts and a chealing agent that is then dried and sintered. It provides really good morphology and control over the stoichiometry [1].

3.2.4 Spray pyrolysis

Spray Pyrolysis consists on atomizing the precursor in a solution at a really high temperature. This yields on a quite homogenous layer of mixed materials (not better that CVD or PVD). Here the properties depend on the solution concentration, the droplet size and the temperature of the process [1].

3.3 Characterization methods

There are several techniques to extract information from positive electrode materials, these evaluate physical, chemical and electrochemical properties to evaluate the stability, morphology and performance of the material. Here is an overview of the characterization techniques used on this project.

3.3.1 Scanning Electron Microscopy (SEM)

This technique is useful to get high resolution imaging of the materials morphology. It consists on a beam of electrons that scans the surface of the sample and the collection of three different signals; secondary electrons, backscattered electrons and X-rays. With the primary electrons being the ones emitted by the source.

- Backscattered electrons: These electrons are the ones that interact with the materials atoms and get back to the sensor, the intensity of the signal can be related to the element's atomic mass. Heavier elements will scatter more electrons to the sensor. Therefore, this signal is useful to get the composition and phases of the material. The strength of this signal is also dependant on the topography of the samples surface, therefore a topographic image can be obtained.

- Secondary electrons: The secondary electrons are the ones that interact in an inelastic way with the material, therefore they arrive to the sensor with less energy. This signal is useful to get the morphology of the material because only the electrons that interact with the surface are collected. The energy when collected is related to the surface morphology and an image is created.

- X-rays: Are a byproduct generated when a primary electron removes an electron from the inner shell of an atom. The energy of the X-ray is related to the atomic number of the element. This signal is useful for the creation of composition maps overlaying the SEM images.

3.3.2 X-Ray Diffraction (XRD)

X-Ray Diffraction is a non destructive technique used to characterize crystalline materials. It provides information about the crystal phases, structural parameters (ize of crystals, crystallinity and defects) and the orientation of the crystals.
This method works by comparing the of the xray beam (with a wavelength λ) and the lattice planes called θ. The reflected beam has an angle of 2θ, and this is the one that is meassured.

$$2d\sin(\theta) = n\lambda$$

The Bragg's law is used to calculate the distance between the lattice planes (d) , characteristic of the crystal structure. The intensity of the diffracted beam is related to the number of atoms in the crystal, the atomic number and the distance between the planes.

Today, databases can compare the diffraction spectra with the ones of known materials, to identify the phases present in the sample.

3.3.3 Electrochemical characterization

4 Methodology

4.1 NMC 811 electrode synthesis

4.1.1 Active material synthesis

Step 1: precursor mixing:
Precursor mixtures were prepared with the stoichiometry of NMC811 with excess lithium 15%, and with the target of 4g of precursors. As three salt ratios are tested, three NMC precursors need to be made. Each species was weighted as stated in Table 1 in the three samples, and the salts were then added with different mass for each mixture according to Table 2.

Species	Mass (g)
$MnCO_3$	0.589
$CoCO_3$	0.610
$Ni(OH)_a(CO_3)_b$	4.508
LiOH	2.828

Table 1: Mass of each components used for NMC 811 synthesis other than the salts.

Step 2: Ball milling:
Each sample is then mixed with ball milling, using 60 ZrO2 4.5mm beads in a 45 mL bowl air and 4 cycles of the following programme: rotations at 250 rpm during 5 min, then 10 min rest.

Salt ratio (NaCl:KCl)	Mass of NaCl (g)	Mass of KCl (g)	Total mass (g)
1:1	2.971	3.791	6.762
6:4	3.566	3.033	6.598
4:6	2.377	4.549	6.926

Table 2: Masses of NaCl and KCl for different salt ratios used in NMC synthesis.

Step 3: Pre-annealing:
The three mixtures obtained are then heated at 500°C in an oven: first, a ramp of 5°C/min during 100 min to reach 500°C, then this temperature is held during 3h. This step aims to melt the LiOH in the precursors, as this Li-source melting point is 462°C. [6]

Step 4: Annealing:
The pre-annealed samples are then calcinated in an oven at 800°C for 12h, after a ramp of ??. The salt mix melts, as its melting point is at 660°C, but not the NMC material as it melts above 800°C. When the samples are annealed, they are then cooled down naturally.

Step 5: With or without ball milling:
Each annealed NMC precursor are grounded in a morter and divided in two samples: an A one and a B one, that will follow different protocols. The samples B have a additionnal ball milling step, with the same parameters as before: 4 cycles of rotations at 250 rpm during 5 min cut by 10 min rest, using 60 ZrO2 4.5mm beads in a 45 mL bowl air. The goal is to homogenize the grains again. As for samples A, they are not ball milled and go directly to the next step of the protocol.

Step 6: Washing:
Each one of the grounded or ball-milled NMC samples are then washed using vacuum filtration. The filters used are 47 mm Milipore Express PLUS 0.22µm PES Membrane, and the powder is added on top. It is rinced several times with distilled water to remove the salt from the NMC material, with approximately 250 mL of water in total. NaCl and KCl then dissolve in the water as Na^+, K^+ and Cl^- and pass through the filter, leaving the NMC powder. The solid material is dried in the air after the washing, to remove the water.

Step 7: Last annealing:
After the washing step, the samples are once again heated in the oven, this time at 600°C for 3h with a prior ramp of ??. This last step of the NMC 811 materials synthesis aims to release the CO2 gas that can still remains in the powder, or even some carbonates. It is also a way to effectively dry the material previously washed.

4.1.2 Ink preparation

4.2 Coin cell protocol

4.3 Characterization precaution

5 Results and discussion

5.1 ICP results

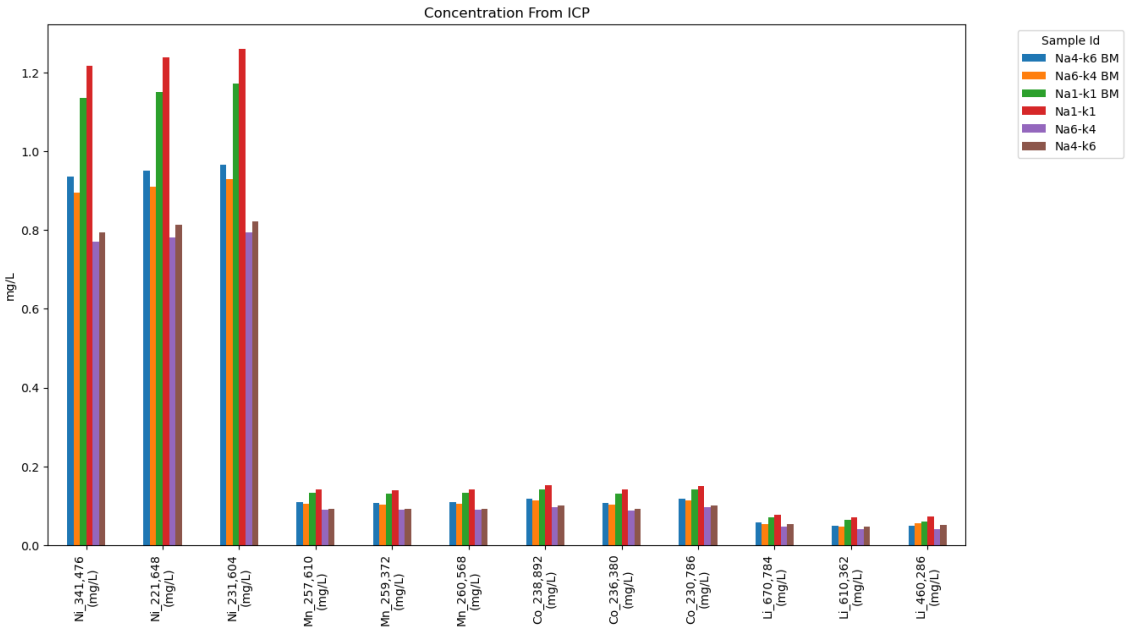

Figure 1: Most representative ICP readings for every sample.

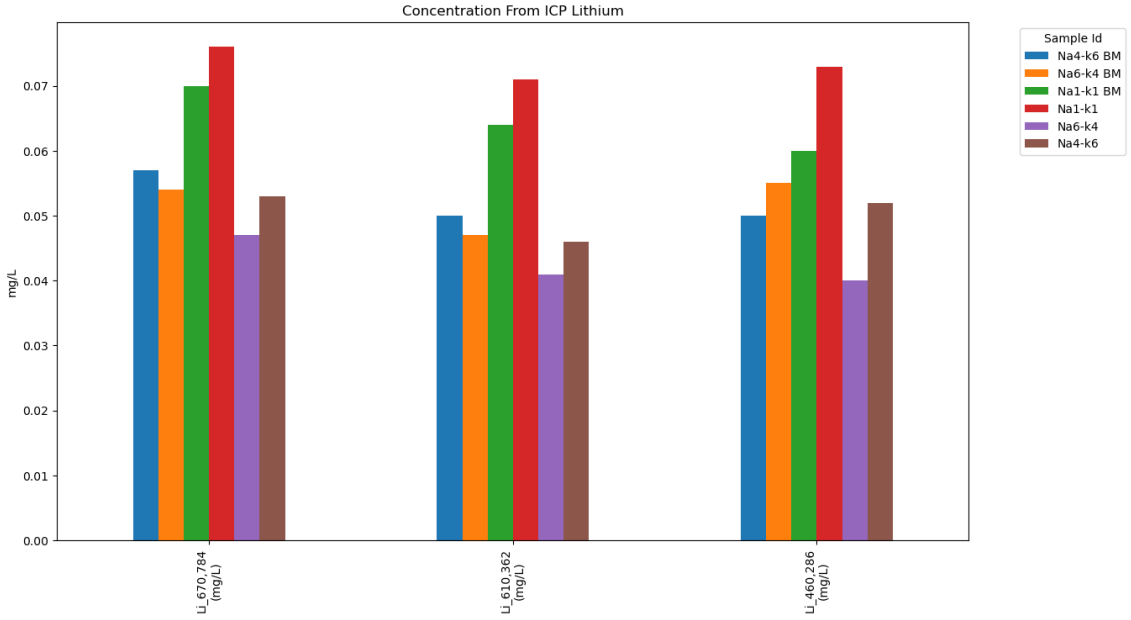

Figure 2: Lithium specific ICP readings.

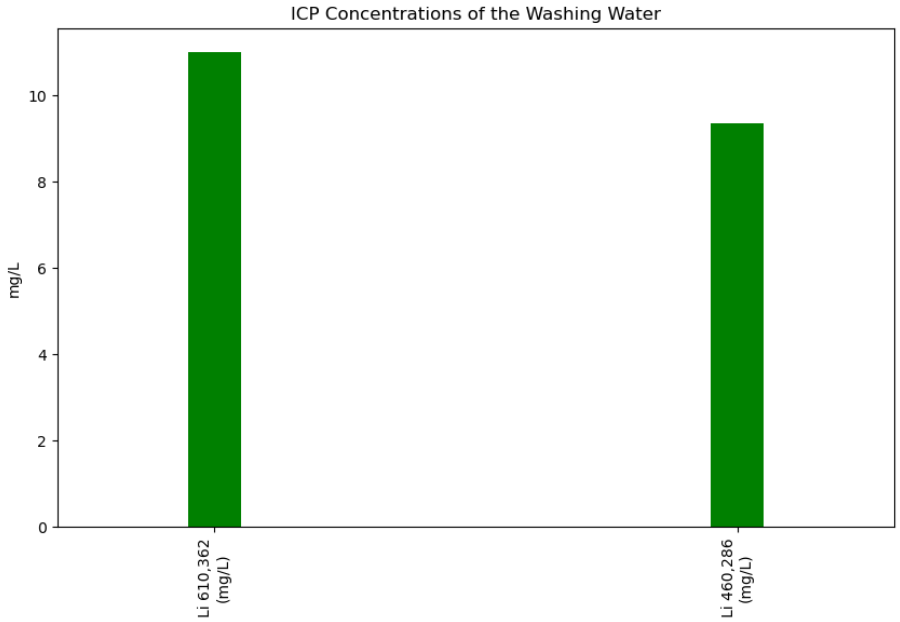

Figure 3: ICP readings for the washing water.

6 Conclusion

List of Figures

References

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