

IMPURITIES INFLUENCE ON THE RECYCLING PROCESS OF NCM ACTIVE MATERIALS

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MOTIVATION

Due to growing importance of lithium-ion batteries (LIB) as a key energy storage technology the demand for metals such as lithium, cobalt and nickel increases rapidly. EU-wide annual demand for these metals for LIBs production is forecast to be 38,000 tons of Li, 34,000 tons of Co and 112,000 tons of Ni. This is a significant growth compared to 2018, as it then amounted to 2,000 tons for Li and Co, and 6,000 tons Ni [1]. To prevent resources shortages and fulfil the growing demand, a proper waste management is required. Therefore, the recycling of these raw materials is becoming increasingly relevant.

One of the challenges for the future of lithium battery recycling technology is to obtain a stable resynthesis process of recycled metals, which leads to new usable active materials (e.g., NCM). Furthermore, this process must be robust to contaminations coming from battery casings, current collectors, or electronic circles. However, small amounts of impurities can remain and affect the resynthesis process afterwards. The impurities can indeed be incorporated during the coprecipitation of NCM precursors, leading to an irreversible contamination in the cathode active material. The effects however might vary. Depending on the impurity itself and on its content in the NCM-structure, the impurities can have positive and negative effects on the active materials. Therefore, a robust concept and masking strategies are required to allow an acceptable concentration of impurities to incorporate into the active materials without critical disadvantages. The preliminary research to investigate the influence of impurities on the NCM active materials is shown in the current work. The literature study revealed the most relevant impurities, their origin and the scale that can be tolerated in the synthesized active material:

- Cu from current collectors - < 0.05 % [2]
- Al from current collectors, casing material - < 1.5 % [3]
- Fe from casing material - < 0.25 % [4]

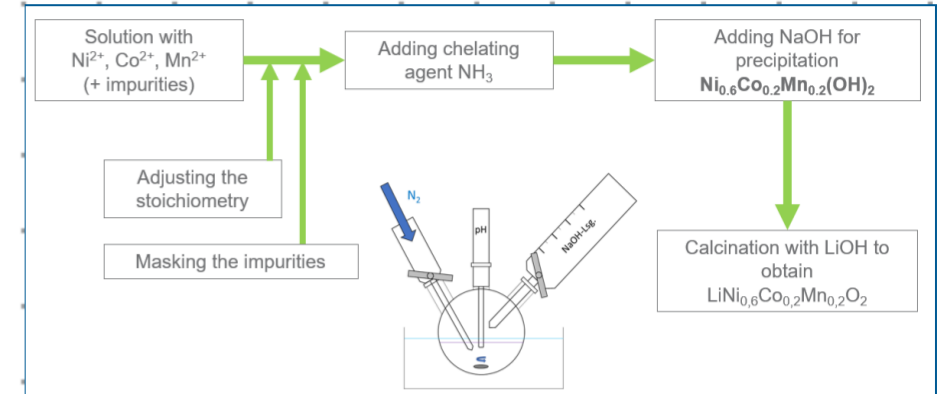


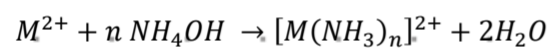
Fig. 1: Schematic overview of the direct coprecipitation of NCM-precursors. Impure leached solutions must be adjusted regarding the stoichiometry of desired active materials and treated with masking additives to prevent the participation of impurities in the resynthesis process. Afterwards, the Ni, Co and Mn are being chelated, precipitated and calcinated to active materials.

EXPERIMENTAL

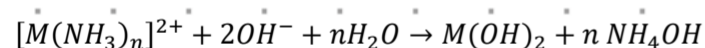
Coprecipitation

The schematic overview from the leached metal solution the calcinated active material is represented in Fig. 1. To precipitate active material precursors from leached solutions containing Ni, Co and Mn ions the stoichiometry of these ions must be adjusted according to the required composition of the active material. However, the first experiments were carried out using a metal sulphates solution with the Ni:Co:Mn ratio of 6:2:2.

A lab-scale process for the synthesis of NCM was set up the following. Ammonia solution (25 %) was added to the metal solution as a chelating agent to form a complex with the metal ions. This step is important for better reaction control and uniform precursor particle growth.



The coprecipitation was performed at 50 °C with a sodium hydroxide solution. The pH value of 11.0 was maintained constant during precipitation (Fig. 2). The precursor was filtered, washed, and dried.



Calcination

The calcinations were performed using a lithium salt and the obtained precursor with a ratio of 1.05:1. They were mixed and preheated at 500 °C for 5 h. The calcination took place at 800 °C for 11 h. The synthesized active materials are being characterized by XRD, SEM and the particle size distribution.

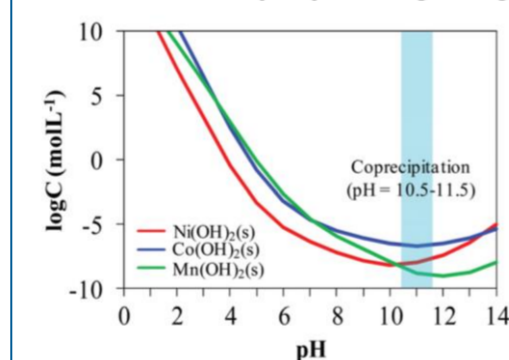


Fig. 2: Experimental setup for the coprecipitation and the optimal pH range for the precipitation of NCM precursors from literature [5]

RESULTS

First-synthesis results

- Composition of precipitated NCM-622 precursors (Fig. 3)
- XRD image of the NCM-622 phase measured from calcinated active material (Fig. 4)
- SEM images and EDX spectrum to observe possible impurities during precipitation (Fig. 5 and 6)

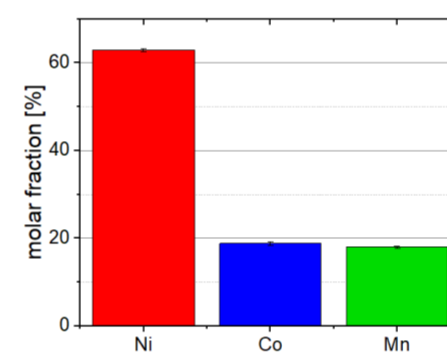


Fig. 3: Ratio of Ni, Co, and Mn in the precipitated precursors determined by XRF

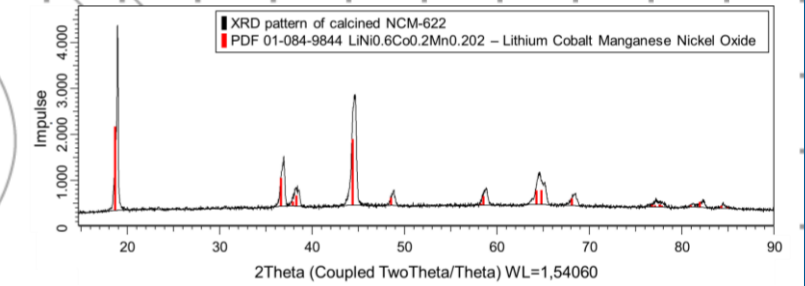


Fig. 4: XRD pattern of the calcined active material NCM-622 (black line) compared to XRD pattern NCM-622 from database (red peaks). It confirms the successful synthesis process of said active material

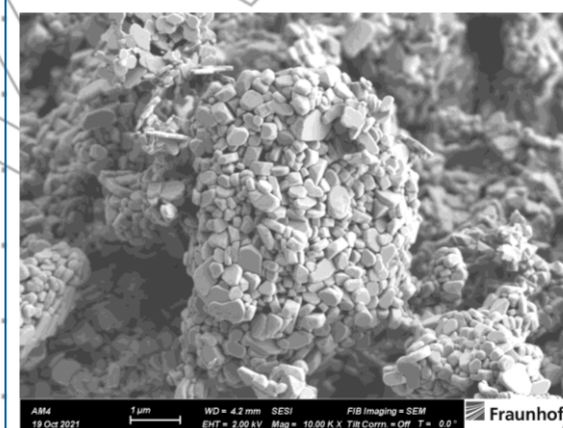


Fig. 5: SEM image of the synthesized NCM-622

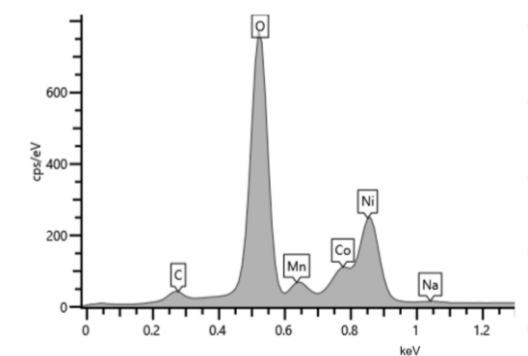


Fig. 6: EDX spectrum of NCM-622 active material, which has subtle signs of sodium impurity after precipitation

OUTLOOK

Further research and challenges

- Coprecipitation with < 1 mol% impurity ions (Fe, Al, Cu)
- Ball-milling processes to achieve smaller and homogeneous particle size of the synthesized active materials
- Electrochemical characterizations of synthesized NCM-622 in coin-cells to compare its performance with commercially available NCM-622 active materials

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