Characterization of NNC microparticles with controlled composition for cathodes in Li-ion Batteries

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The advent of modern Lithium Ion Batteries (LIBs) and energy storage technologies will rely on innovative materials and improved techniques allowing to achieve a deeper understanding of the battery performance while overcoming the challenges that still faces this technology. In that sense, increasing efforts are being invested in the development of safer, high energy density, high voltage capable, and long-term cycling components for which a deeper knowledge on the materials used as LIB electrodes is still required. In this frame, cathodes based on Ni-Mn-Co system (NMC) are gaining increasing attention as they have proven to yield enhanced specific capacity and thermal stability, as well as improved LiB performance, as compared with other conventional cathodes. Different approaches are being followed so far in the design and study of NMC cathodes, including improved synthesis mechanisms, characterization of the structure and chemical composition at the microscale, and analysis of the electrical performance.

In this work, the chemical synthesis of core-shell NMC microparticles was achieved in two steps combining a co-precipitation route and a solution evaporation process. The as-synthesized NMC microparticles were investigated by a combination of electron microscopy and spectroscopy techniques, including scanning electron microscopy (SEM), x-ray diffraction (XRD), energy dispersive x-ray spectroscopy (EDS) and Raman spectroscopy. During the synthesis, Li-Ni-Mn-Co-O complex oxides are formed by the combination of $LiMO_2$ (M=Ni, Mn, Co) compounds that present a layered structure (R-3m), as confirmed by XRD and Raman spectroscopy This layered structure allows to reach high capacity and structural stability when NMC is used as cathode material in LIBs. Initially, the synthesized NMC particles exhibit a rounded appearance and dimensions around 4 µm, with some cracks on their surface. EDS analysis with variable beam acceleration voltage confirms the presence of a Ni-rich core and a Mn-rich shell with submicrometric dimensions. The presence of Ni allows for a higher capacity but a lower structural stability when cycling, while Mn allows for higher structural stability but lower capacity. Co in small quantities mitigates the cation disordering inside the crystal structure. SEM and EDS measurements confirm that the morphological and compositional properties of the particles were maintained after the Li introduction, despite the weak morphological changes observed at their surface. Raman spectroscopy was used to assess the correct introduction of the Li ions inside the particles and the formation of the ternary oxides with spinel structures into the R-3m structure of the NMC. The analysis of the Raman spectra before adding Li indicates the formation of different ternary oxides with spinel structure (Fd-3m) at the particles and the possible presence of NiO. Raman spectra after Li introduction present vibrational modes around 500 cm^{-1} characteristic of the layered R-3m structure of NMC. A deeper knowledge of the incorporation of Li in the NMC microparticles can lead to improved performance in the fabrication of NMC-based cathodes for LiBs.