NMC microparticles with core-shell structure for cathodes in Li-ion batteries

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The increasing necessity for improvement in energy storage technologies, especially of the mature Lithium-Ion Batteries (LIBs), relies on the advances in the characterization techniques and the materials used in the device. Advanced microscopy and spectroscopy techniques, including *in-situ* measurements, can provide valuable insights to face some of the challenges that this technology faces. In recent years, Ni-Mn-Co (NMC)-based cathodes have gained relevance due to their high specific capacity and thermal stability leading to an improvement of the performance of the LIBs. So far, different approaches have been pursued to improve the synthesis mechanisms, and diverse characterization techniques have been employed in the study of the NMC materials at the microscale.

In this work, NMC core-shell microparticles have been studied by a combination of techniques including scanning and transmission electron microscopy (SEM, TEM), X-ray diffraction (XRD), energy dispersive x-ray spectroscopy (EDS), Raman spectroscopy and X-Ray Photoelectron Spectroscopy (XPS), including i*n-situ* techniques as well. Micro-Raman and XRD results indicate the formation of Li-Ni-Mn-Co-O complex oxides presenting the usual layered structure of NMC (R-3m) with the presence of reduced quantities of other structures like spinel phases. This layered structure is directly related to the high capacity and structural stability of NMC cathodes when the battery is cycled. In-situ thermo XRD measurements indicate an enhanced formation of NiO as the temperature increases up to 900 ºC. The analyzed microparticles exhibited a rounded appearance with an average diameter of 4 μm and variations in their morphology as a function of the temperature used during the synthesis, as observed by SEM and TEM. In-situ SEM observations also lead to assess the morphology evolution of the particles with increasing temperature. 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 can mitigate 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. Micro-Raman spectroscopy was also used to understand the variations in the crystalline structure of the particles as a function of the synthesis route and the Li insertion. Finally, in-situ XPS measurements at temperatures up to 500 ºC and a variable pressure, shows variations in the Mn(3s) and O(1s) core levels, as well as in the electrical conductivity of the samples. These results can lead to achieve a deeper knowledge of the properties of the NMC microparticles in the search of improved performance in LiBs.