

Performance of stoichiometric, over-lithiated and doped LiCoO₂ electrode materials for Li-ion batteries

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Since the commercialization of Li-ion batteries in 1991, lithium cobalt oxide (LiCoO₂, LCO) has been used as positive electrode material in them. Even now, a few decades later, LCO is still one of the most used materials in Li-ion batteries for portable applications as it exhibits high operating potential, low self-discharge and high reversibility. As the result of three decades of investigation, several procedures to improve the performance of LCO have been proposed. These include e.g. particle morphology variation, doping and over-lithiation [1,2,3]. The modifications have enhanced the cyclability and widened the voltage ranges of LCO cycling. However, it is difficult to compare these modification procedures because the synthesis methods and materials are not convergent. In this work, the properties of stoichiometric, over-lithiated and Mg-Ti doped LCOs as positive electrode materials for Li-ion batteries are investigated and compared. The same precursors and synthesis method were used to prepare all the LCO materials to ease the comparison. The electrochemical tests were performed in both half-cells and LCO/graphite pouch cells.

The particle morphology is similar for all the LCO materials, the particles being oval shaped with an average particle diameter of 16 μm. However, the doped LCO has slightly smaller crystallite size than the other two materials, which is most likely caused by the doping. The doped material has superior rate capability properties that are attributed to the smaller particle size and a larger lithium diffusion coefficient value of the material.

The cycle life tests performed in LCO/graphite pouch cells show that the doped LCO has also the longest cycle life of the three materials. This is observed in both the studied voltage ranges of 3.0–4.2 V and 3.0–4.4 V. The over-lithiated LCO shows the shortest cycle life in the voltage range of 3.0–4.2 V. However, in the voltage range of 3.0–4.4 V, the stoichiometric and over-lithiated LCOs have approximately the same capacity retention up to 80 % of the initial capacity. After this, the capacity drop of the stoichiometric material is the fastest. The differences in the cyclabilities are attributed to charge transfer impedances of the LCO materials induced by changes in the structures. The possibility of a Li-rich layer on top of the over-lithiated LCO particles is also discussed. The next step in this work is to perform *post mortem* studies for the cells in order to further investigate the causes for the different behaviours of the materials. Electrochemical tests for the LCO electrodes of the cycled LCO/graphite pouch cells are also planned.

References:

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