Impact of Stoichiometry and Solid Solution Limits on the Electrochemical Performance of Li_xCoO_2

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Although $LiCoO_2$ has been utilized in commercial systems for over a decade, the available products still exhibit a large disparity in stoichiometry and electrochemical performance. Many questions remain regarding the basic relationships existing between the materials stoichiometry and cycling stability. Utilizing Li_xCoO_2 materials of differing bulk crystallographic and morphological properties, we aimed at the identification of the governing failure mechanism, mainly bulk vs. surface, of Li_xCoO_2 electrodes cycling up to 4.2 and limited to 35% DoD.

The Li_xCoO_2 samples were fabricated at elevated temperature from nominal mixtures of Li_2CO_3 and Co_3O_4 with nominal Li/Co molar ratios ranging from 0.95 to 1.20 (Li/Co= 0.95, 0975, 1.00, 1.05, 1.10 and 1.20). Using a combination of x-ray diffraction, Fourier transform infrared spectroscopy, transmission electron microscopy and thermogravimetric analysis, we showed the stoichiometric sample was single phase, whereas residual Co_3O_4 and Li_2CO_3 existed in the materials fabricated from all the non-stoichiometric mixtures with Li/Co<1 and Li/Co>1, respectively (Fig.1).

Various surface characterization techniques revealed at least part of the residual Li_2CO_3 phase present in the materials fabricated from lithium excess mixtures forms a layer at the surface of the Li_xCoO_2 particles (Fig.2).

The stoichiometric $LiCoO_2$ electrode exhibited the highest electrochemical performance under the applied protocol (Fig.3). All samples with nominal Li/Co≤1 also showed excellent cycling stability over 1500 cycles whereas lithium excess promoted fast electrochemical degradation (Fig.3).

The sample fabricated with nominal Li/Co=1.05, which cycled poorly and exhibited differing bulk crystallographic properties, was made to cycle well under the applied protocol as long as the Li_2CO_3 surface phase was not present.

Finally, preliminary results obtained by EIS impedance spectroscopy performed during cycling will be introduced.
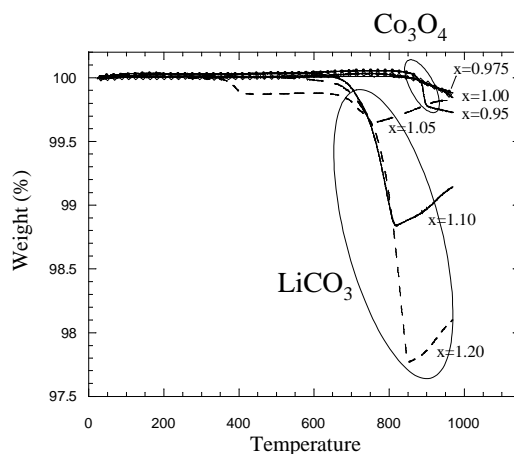

Figure 1. TGA curves of the as fabricated Li_xCoO_2 powders showing evidence for the presence of $LiCO_3$ in the overstoichiometric samples and Co_3O_4 in the lithium deficient samples.
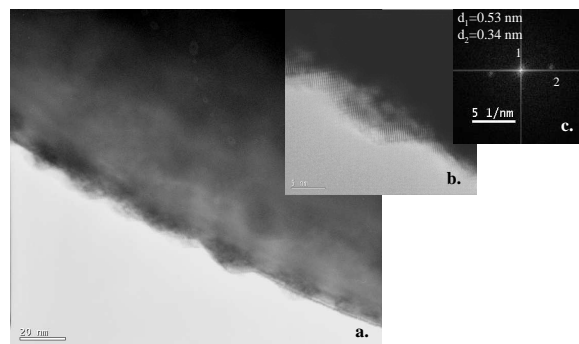
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Figure 2. High-resolution transmission electron micrographs (a) and (b) of the as fabricated $Li_{1.05}CoO_2$. (c) FFT identifying the layer existing in (b) as Li_2CO_3.
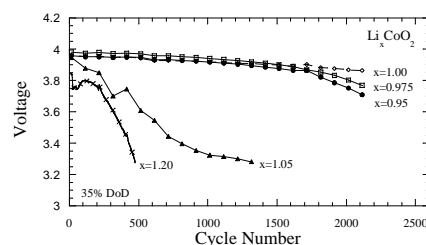

Figure 3. End of discharge potential as a function of cycle number of the as-fabricated Li_xCoO_2 samples (x=0.95, 0.975, 1.00, 1.05 and 1.20) tested in Li metal coin cells.