

Ionic transport versus morphology for Al-doped Li-Ni-Co-O nano-structured compounds

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Intensive investigations have been reported on LiCoO₂ which is considered as prototypal electrode material for Li-ion batteries. This oxide leads to successful results with high operating voltage. In view of its optimization for the use in Li-ion batteries, a large amount of work has been carried out to synthesize materials by substituting monovalent or multivalent cation for cobalt to form solid solutions LiMe_yCo_{1-y}O₂ (Me=Ni, Al, Mg, B).

Doping with extra non-transition metal such as aluminum has gained in interest for several reasons. Some important advantages of the aluminum are its low cost, low toxicity and low density. Since α -LiAlO₂ is isostructural with LiCoO₂ (R $\bar{3}$ m) and the ionic radii of Al³⁺ and Co³⁺ are very close (^{VI}r_{Al}³⁺ = 0.535 Å; ^{VI}r_{Co}^{3+(l.s.)} = 0.545 Å), a wide range of solid solution exists for LiCo_{1-x}Al_xO₂. It has predicted and verified experimentally that aluminum substitution for transition-metal oxides lead to higher lithium intercalation potentials, as the remaining 3+ valence of aluminum forces more electron exchange with oxygen [1-2]. Aluminum can also have a stabilizing effect of the layered structure when doped into LiCoO₂ or LiNiO₂ which extends the cyclability and enhances the capacity of the electrochemical cells.

In this study, we have used a wet-chemical method based on a typical sol-gel reaction, employing succinic acid as chelating agent to prepare LiCo_{1-y}Al_yO₂ and LiNi_{0.5-y}Al_yCo_{0.5}O₂ samples. Results show the solid solubility of aluminum in the LiCoO₂ oxide and in the mixed cobalt-nickel compound LiNi_{0.5}Co_{0.5}O₂. The effects of the aluminum doping on the structural, compositional and electrochemical properties of the resulting materials are presented. The net effect of Al doping is the decreasing particle size of the oxide as shown in the SEM picture (Fig. 1).

The electrochemical features of the synthesized materials were studied for the Li//LiNi_{0.5-y}Al_yCo_{0.5}O₂ cells cycled in the potential range from 2.5-4.2 volts. The overall capacity of the oxides have been reduced due to the sp metal substitution, however, a more stable charge-discharge cycling performances have been observed as compared to the performances of the native oxides. At 4.2 V cut-off, the charge capacity of the Li//LiNi_{0.35}Al_{0.15}Co_{0.5}O₂ cell is ca. 115 mAh/g. Kinetics were characterized by the galvanostatic intermittent titration technique. Al substitution also provides an increase of the chemical diffusion coefficients of Li ions in the LiNi_{0.5-y}Al_yCo_{0.5}O₂ matrix (Fig. 2).

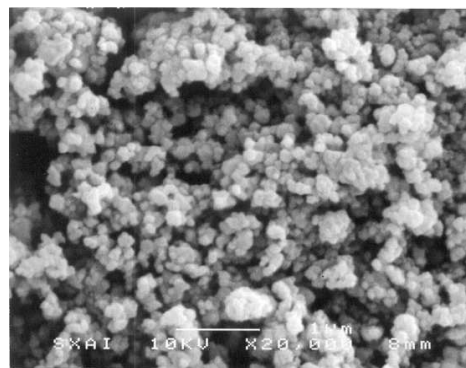


Fig. 1. SEM photograph of LiNi_{0.2}Al_{0.3}Co_{0.5}O₂ grown by the wet-chemical method using the succinate route.

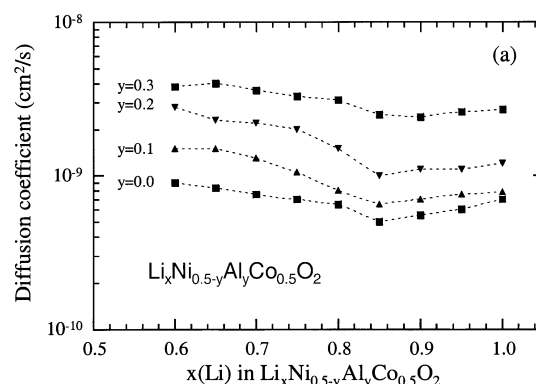


Fig. 2. Evolution of the chemical diffusion coefficients D_{Li} of Li⁺ ions in LiNi_{0.5-y}Al_yCo_{0.5}O₂ powders synthesized by the wet-chemical succinate route.

References

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