Structural and ionic transport studies of $LiAl_yCo_{1+y}O_2$ nano-structured intercalation compounds

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Among the various systems with high operating voltage, lithium cobaltate with the α-NaFeO$_2$ pseudo-layered lattice is a positive electrode material grown by numerous synthesis methods. 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 $LiMe_yCo_{1-y}O_2$ (Me=Ni, Al, Mg, B). The system $LiNiO_2$-$LiCoO_2$ leads to successful results, while the $LiAlO_2$-$LiCoO_2$ solid solution has received less attention because the electrochemical inactivity of the sp element due its fixed oxidation state, leading to reduced specific capacity of the Li//$LiAl_yCo_{1-y}O_2$ cells.

We present the characterization and electrode behavior of $LiAl_yCo_{1-y}O_2$ ($0.0 \leq y \leq 0.3$) oxides prepared by wet-chemical method from the citrate precursor route. The phase evolution as a function of the Al substitution and the modification on the intercalation and deintercalation of Li ions are investigated.

X-ray diffraction patterns show that samples belong to the $LiCoO_2$-$LiAlO_2$ solid solution and have the layered rhombohedral R-3m structure. TG/TDA curves display the strong exothermic effect at 318 °C associated to the decomposition process of citric acid and acetate ions xerogel. The crystallization starts around 400°C; thus well-crystallized and impurity-free single phases have been obtained at 600°C. SEM studies reveal the nano-structured morphology of the powders. The influence of Al doping on particle size and morphologies is clearly evidenced (Fig. 1). FTIR vibrational spectra indicate the slight modification in the local structure related to the short-range environment of oxygen coordination around the cations in oxide lattices. The frequencies and relative intensities of the stretching bands are sensitive to the covalency of the (Al, Co)O$_2$ slabs.

The overall electrochemical capacity of the $LiAl_yCo_{1-y}O_2$ oxides have been reduced due to the sp metal substitution, however, a more stable charge-discharge cycling performances have been observed when electrodes are charged to 4.3 V as compared to the performances of the native oxide. Differences and similarities between $LiCoO_2$ and Al-substituted oxides are discussed therefrom. The rechargeability of the Li//$LiCo_{1-y}Al_yO_2$ cells appears better than $LiCoO_2$ because the lack of the two-phase behavior in the high-voltage region.

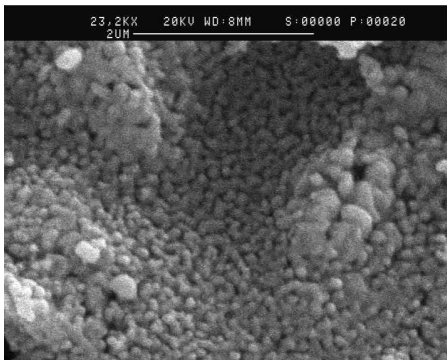Fig. 1. SEM photograph of $LiAl_{0.25}Co_{0.75}O_2$ grown by the wet-chemical method using the citrate route.

The high insertion capability has been confirmed also by measuring the chemical diffusion coefficients of Li$^+$ ions in $Li_xAl_yCo_{1-y}O_2$ cathode materials (Fig. 2). D_{Li} has been investigated in the compositional range $0.47 \leq x \leq 1.00$ corresponding to the single-phase region. Data show that the chemical diffusion coefficients for the $LiAl_yCo_{1-y}O_2$ powders exhibit an increase of more than one order of magnitude in the range 1×10^{-11}-5×10^{-9}-cm^2/s. During charging, D_{Li} increased continuously as lithium ions are extracted up to about x=0.7 and then slightly decreases. The decreasing values of D_{Li} for x<0.7 with lithium extraction (decreasing x) is probably due to a change in the bond covalency. Al substitution provides an increase of D_{Li} in the $LiAl_yCo_{1-y}O_2$ matrix due to an increase of the van der Waals interlayer spacing. The chemical diffusion coefficient can be expressed as $D_{Li}=\alpha W[(x_m-x)^2+\beta(x_m-x)x]$, where x_m is the full site occupancy for Li ions, α is the factor related with the probability for ion hopping and β represents an interaction factor. Fits give parameters $\alpha=8 \times 10^{-11}$ cm^2/s and $\beta=4.8$ for y=0.2, reflecting the relatively facile extraction process for Li ions from the layered structure grown by wet-chemical technique
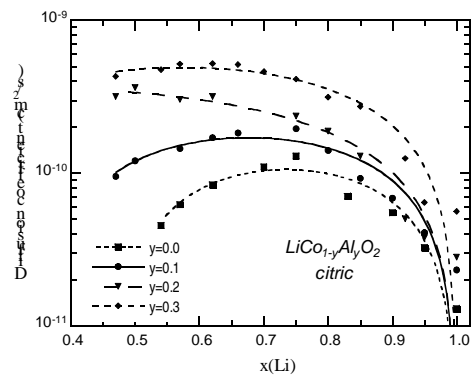

Fig. 2. Evolution of the chemical diffusion coefficients D_{Li} of Li$^+$ ions in $LiAl_yCo_{1-y}O_2$ powders synthesized by the wet-chemical citrate route.