Structural and Electrochemical Properties of LiCoO$_2$ and LiA$_{y}$Co$_{1-y}$O$_2$ (y = 0.1 and 0.2) Oxides: A Comparative Study of Electrodes Prepared by the Citrate Precursor Route

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Abstract. We present the characterization and electrode behavior of LiCoO$_2$ and Al-doped LiA$_{y}$Co$_{1-y}$O$_2$ (y = 0.1 and 0.2) oxides prepared by wet-chemical method from the citrate precursor route. We study the phase evolution as a function of the aluminum substitution and the modification on the intercalation and deintercalation of Li ions. Characterization methods include XRD, SEM, and FTIR. X-ray diffraction patterns show that samples belong to the LiCoO$_2$-LiA$_2$O$_2$ solid solution and have the layered α-NaFeO$_2$ structure. FT-infrared vibrational spectroscopy indicates 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 bands are sensitive to the covalency of the (Al, Co)O$_2$ slabs. The overall electrochemical capacity of the LiA$_{y}$Co$_{1-y}$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.

1. Introduction
Lithium-ion batteries are now being widely studied and developed as rechargeable energy sources, the most important of which is for high energy density batteries [1]. However the demands on battery performance have required further improvements in lithium intercalation electrodes. Among the various systems with high operating voltage, lithium cobaltate (LiCoO$_2$) with the pseudo-layered α-NaFeO$_2$ lattice is a material grown by numerous synthesis methods [2-3]. In view of applications, a large amount of work has been carried out to optimize the positive electrodes formed by solid solutions LiMe$_x$Co$_{1-y}$O$_2$ (Me = monovalent or multivalent cation). The system LiNiO$_2$-LiCoO$_2$ leads to successful results [4-5], 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//LiA$_{y}$Co$_{1-y}$O$_2$ cells [6-17].

The crystal chemistry of LiA$_{y}$Co$_{1-y}$O$_2$ oxides show that these compounds crystallize with the α-NaFeO$_2$ structure (R$\bar{3}$m S.G.) similarly to the native oxide LiCoO$_2$. They are formed by slabs of (Co, Al)O$_2$, where the lithium ions reside in 3b sites between the slabs and the transition metals are located in 3a sites. The oxygen anions are coordinated with three lithium and three transition metal cations and occupy the 6c sites. A schematic view of the structure in Fig. 1 shows the -ABCABC- type stacking of the -O-Li-O-Co-O-Li-O- triangular sheets. A strong bond covalency in LiCoO$_2$, with reduced Co-O bond distance, results in stabilization of Co$^{3+}$ in low-spin ground state, [d$^6$ = (t$_{2g}$)$^2$(e$_g$)$^4$, S = 0], and reduces the electronic conductivity of the compound (bandgap of 2.7 eV) [18].
Fig. 1. Structure of the rhombohedral elementary cell of LiAl$_{1-y}$Co$_y$O$_2$ oxides (R$\overline{3}$m space group).

It is to worth mentioning the several features reported on lithium intercalation in Al-substituted LiCoO$_2$ materials [6-17]. Ohzuku et al. observed that doping with Al improves overcharge resistance in LiAl$_{0.25}$Ni$_{0.75}$O$_2$ [6]. Nazri et al. found that 95 % Li intercalation was possible during the first discharge in LiAl$_{0.35}$Ni$_{0.65}$O$_2$ [7]. Jang et al. [10] have shown that the open-circuit voltage and working voltage increase with Al content as predicted by ab-initio calculations [19]. Recently, Yoon et al. reported significant improvement in capacity and cyclability of Al-doped LiCoO$_2$ synthesized by sol-gel process, revealing that the large capacity fading of LiAl$_{0.25}$Co$_{0.75}$O$_2$ is strongly related to the remaining Co$^{4+}$ ions and the local structure distortion [16-17].

In this work, we present the characterization and electrode behavior of LiAl$_{1-y}$Co$_y$O$_2$ (0.0 ≤ y ≤ 0.2) prepared by wet-chemistry via the citrate precursor route. Characterization methods include X-ray powder diffraction (XRPD), thermogravimetry analysis (TG-DTA), scanning electron microscopy (SEM), and Fourier transform infrared (FTIR) spectroscopy. The electrochemical charge-discharge profiles of Li//LiAl$_{1-y}$Co$_y$O$_2$ cells are investigated when electrodes are cycled in the potential range 2.5-4.3 V. Differences and similarities between LiCoO$_2$ and Al-substituted oxides are discussed therefrom.

2. Experimental Description

2.1. Synthesis and Analysis of LiAl$_{1-y}$Co$_y$O$_2$ Oxides. The native LiCoO$_2$ and Al-doped LiAl$_{1-y}$Co$_y$O$_2$ (0.1 ≤ y ≤ 0.2) powders were prepared at low-temperature by a sol-gel method. The synthesis was carried out from metal acetates via inorganic polymerization reactions in solution according to the method reported by Julien et al. [20-21], namely, the citric acid-assisted sol-gel technique. Stoichiometric amounts of acetate hydrates of Li, Co and Al (Fluka, purum p.a. grade) were dissolved in triple distilled water and mixed well with an aqueous solution of citric acid (Fluka, MicroSelect grade). The complexing agent, citric acid ($\text{C}_6\text{H}_7\text{O}_7$), dissolved in aqueous solution was functioned as a fuel. DTA-TG curves of the gel precursor were obtained using a Netzsch STA 409 thermogravimetric analyzer at the heating rate of 10 °C/min under oxygen flow. The XRD patterns were obtained using a Philips PW1800 X-ray powder diffractometer XRD profiles were measured between 10° and 90° 2θ using a monochromatized CuKα radiation source ($\lambda = 1.5406$ Å). The morphologies of the sample particles were examined with a Philips XL30 scanning electron microscope. The FTIR absorption spectra were recorded using a Bruker IFS113v Fourier transform interferometer in the wavenumber range 120-1200 cm$^{-1}$ at a spectral resolution 2 cm$^{-1}$. Samples were ground to fine powders and dispersed into ICs pellet.

2.2. Electrochemical Studies of Electrodes. The composite electrode consisted of 80 % active material, 15 % graphite, and 5 % poly(vinylidene fluoride) (PVDF), which were blended to form the slurry that was deposited on the aluminum disk. The lithium anode was made by pressing the lithium foil on stainless steel disk. The liquid electrolyte (Merk product) consisted of dissolved LiPF$_6$ (1 M) in a blended solvent of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 volume ratio). Electrochemical measurements were carried out at room temperature following the experimental procedure previously described using Teflon laboratory-cell hardware and Mac-Pile system [20]. Quasi open-circuit voltage curves were recorded using current pulse of 0.1 mA/cm$^2$ applied for 1 h followed by a relaxation period of 0.5-1.0 h.

3. Synthesis and Thermal Analysis

According to the citric acid-assisted sol-gel preparation process, ($\text{C}_6\text{H}_8\text{O}_6$)$_n$, Li(OAc)$_n$H$_2$O, Co(OAc)$_{2.5}$H$_2$O, and Al$_2$(OAc)$_3.4$H$_2$O in a total acid/metals molar ratio of 1:1 were dissolved in distilled water at boiling temperature. While the solution was kept a boiling, the pink solid mixture was obtained after evaporation of the water. This solid mixture can produce final mass product of