

Local Structure and Electrochemistry of Doped Lithium-Cobalt Oxides as Positive Electrode for Li-ion Batteries

C. Julien

Laboratoire des Milieux Désordonnés et Hétérogènes
UMR7603, Université Pierre et Marie Curie
4 place Jussieu, case 86, 75252 Paris cedex 05, France

INTRODUCTION

Lithium transition-metal oxides are functional intercalation compounds for their applications in rechargeable lithium-ion batteries. They are widely studied in search of structural stability and improved electrochemical performance. Compounds of α - NaFeO_2 -type structure (space group $R\bar{3}m$) are layered frameworks, which belong to the 4-volt class cathodes. LiCoO_2 with a theoretical gravimetric capacity of 273 mAh/g can deliver high electric energy and has adequately high reversibility in the range 3.5-4.5 volts.

In this work, we wish to show the relationship between local cationic environment and electrochemical characteristics of 4-volt cathodes. Various oxides of the cobaltate family grown by solid-state reaction, wet chemistry and film deposition techniques are investigated. It is shown that synthesis greatly affects the compound morphology, its electrochemical properties and consequently its cycle life characteristics.

LOCAL STRUCTURE

LiCoO_2 and $\text{LiCo}_{1-y}\text{M}_y\text{O}_2$ materials doped with various M^{3+} cations, i.e. nickel, aluminum, magnesium or boron, were investigated by x-ray diffraction and vibrational spectroscopies to investigate their low-temperature (LT) and high-temperature (HT) form. As an example, Fig. 1 shows the Raman spectra of LT- and HT- LiCoO_2 materials. It is clearly shown that HT- LiCoO_2 has the layered structure, while LT- LiCoO_2 exhibits a modified-spinel structure.

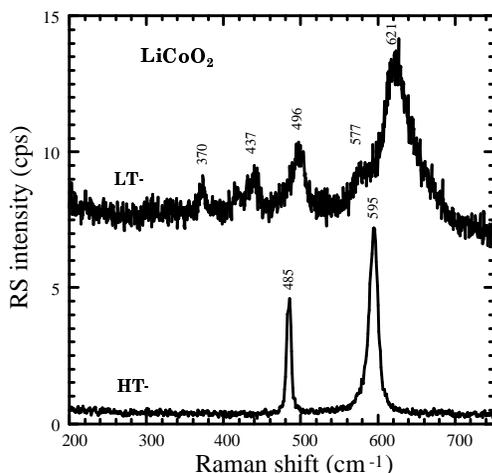


FIG. 1. Raman spectra of LT- and HT- LiCoO_2 materials showing the structure as a function of the synthesis temperature.

Structural data show that substituted $\text{LiCo}_{1-y}\text{Ni}_y\text{O}_2$ oxides display a solid solution in the whole range $0 \leq y \leq 1$, while the solubility limit of $\text{LiCo}_{1-y}\text{Al}_y\text{O}_2$ and $\text{LiCo}_{1-y}\text{B}_y\text{O}_2$ is about $y=0.35$. Similar results are obtained for the $\text{LiCo}_{1-y}\text{Mg}_y\text{O}_2$ system.

Extensive damage including local strain variation, nano-domain formation, and change in cation ordering has been observed by local probes such as Raman scattering and FTIR spectroscopies, which are complementary tools for x-ray diffraction. Analysis of vibrational spectra in terms of localized vibrations, considering the layered structure built of CoO_6 and LiO_6 octahedra shows the degree of disorder of LiCoO_2 [1-2].

ELECTROCHEMICAL PROPERTIES

These studies allowed to establish a relationship between crystallinity and electrochemical features for materials prepared by various techniques such as solid-state reaction, wet chemistry and laser ablation. Electrochemical features of $\text{LiCo}_{1-y}\text{Ni}_y\text{O}_2$ electrode materials show remarkable stability in their charge-discharge profiles. The overall capacity of the $\text{LiCo}_{1-y}\text{B}_y\text{O}_2$ oxides has been reduced due to the sp metal substitution, however, a more stable charge-discharge cycling

performances have been observed when electrodes are charged up to 4.4 volts as compared to the performances of the native oxides. Electrochemical features profiles of $\text{Li}/\text{LiCo}_{1-y}\text{Mg}_y\text{O}_2$ cells show also that the charge-discharge occur without the appearance of voltage plateau. However, we observed a slight decrease of the average cell potential with the increasing amount of magnesium as shown in Fig. 2.

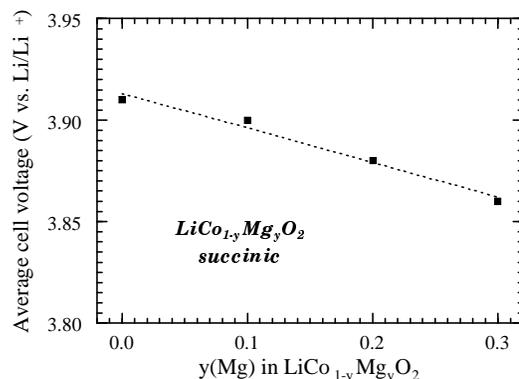


FIG. 2. Variation of the average cell voltage as a function of the Mg content in $\text{LiCo}_{1-y}\text{Mg}_y\text{O}_2$ electrode.

REFERENCES

1. C. Julien, *Solid State Ionics* **136-137** (2000) 877.
2. C. Julien, *Ionic* **6** (2000) 30.