

**Direct Synthesis of LT-LiMn<sub>x</sub>Co<sub>1-x</sub>O<sub>2</sub> (x =0; 0.2; 0.4) by a Sol-Gel Method: Characterization and Electrochemical Properties in Lithium Cells**

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The layered mixed oxide LiCoO<sub>2</sub> is the basic product used for the positive electrode in commercial secondary lithium batteries. However, different limitations – high toxicity and cost of Co, narrow range of lithium extraction – have resulted in the search of alternative layered materials. Substitution of Co by Mn has been proposed as an attractive option. The synthesis of these layered compounds is usually carried out either by high temperature methods (1) or by ion-exchange reactions from Na-based compounds (2).

In this communication we report the synthesis, characterization and electrochemical properties of LiMn<sub>x</sub>Co<sub>1-x</sub>O<sub>2</sub> (0 ≤ x ≤ 0.4) layered solid solutions acting as cathodes in lithium cells. The synthesis was achieved by a sol-gel method using propionic acid as the resin framework (3). The most outstanding feature of the phases formed when the gel is calcined at 400 °C is their ability to display the same structure of the LT-LiCoO<sub>2</sub> (4). The XRD patterns of the three studied samples (x = 0; 0.2; 0.4) were indexed in a hexagonal system. No extra peaks belonging to impurities were found. On substitution of Mn in LiCoO<sub>2</sub>, a slight expansion of the unit cell parameters was observed, in agreement with differences in size between Co<sup>3+</sup> and Mn<sup>3+</sup> (Table 1).

Sample	a	c
LiCoO <sub>2</sub>	2.818	13.871
LiCo <sub>0.8</sub> Mn <sub>0.2</sub> O <sub>2</sub>	2.830	13.896
LiCo <sub>0.6</sub> Mn <sub>0.4</sub> O <sub>2</sub>	2.844	13.962

XPS spectra confirmed the presence of Co<sup>3+</sup>, probably in a low-spin state. More uncertainty was created by Mn because of the binding energy of the 2p<sub>3/2</sub> photoemission peak, 642.3eV, which is closer to that of MnO<sub>2</sub>. Nevertheless, a limitation of this spectroscopic method is the fact that it only analyses few nanometers in depth, and Mn<sup>3+</sup> is an unstable oxidation state that can be easily oxidized to Mn<sup>4+</sup> when in contact with air. It seems rather plausible that Mn atoms close to the particle's surface could be found as Mn<sup>4+</sup>.

The insertion and de-insertion of Li were followed by cyclic voltammetry. The anodic scan of LT-LiCoO<sub>2</sub> gave rise to a large signal formed by two peaks, one more intense at 3.80 and a second one at 3.95 V. This two-stepped process should be in agreement with the different structural modifications that this compound undergoes on lithium de-insertion (5). The subsequent cathodic scan was characterized by a single peak at 3.40 V. The high voltage peak acquires importance with the presence of Mn. Both anodic and cathodic scans of the LiMn<sub>0.4</sub>Co<sub>0.6</sub>O<sub>2</sub>-based cell was characterized by a single peak at 3.95 and 3.86 V, respectively, indicative that the lithium extraction and insertion take place in an one-stepped process. Moreover, the presence of Mn has also a beneficial effect consisting in a significative reduction of the anodic and cathodic polarization. Different structural models are used to explain the alterations induced on Co substitution. Cycling properties of these phases studied under galvanostatic conditions are also discussed.

## References

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