Characterization of the T#2-$Li_{2/3}Co_{2/3}Mn_{1/3}O_2$ system obtained by lithium ion-exchange

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Layered $LiMO_2$ materials obtained by lithium ion exchange in P2 sodium containing phases demonstrated interesting properties as positive electrode materials for Li-ion batteries.

Recently, the crystal structure analysis and battery performance of T#2-$Li_{2/3}Co_{2/3}Mn_{1/3}O_2$ obtained by Li/Na ionic exchange in molten salts were studied [1, 2]. As shown in Fig. 1, three tetrahedral surroundings are available for lithium in the interslab space of the T#2 stacking; but for T#2-$Li_{2/3}Co_{2/3}Mn_{1/3}O_2$ it was determined from nuclear density Fourier difference map calculations that lithium ions are only distributed among the 8e and $8f_{edges}$ sites, with a larger occupancy of the latter. T#2-$Li_{2/3}Co_{2/3}Mn_{1/3}O_2$ shows good electrochemical performances, with several phase transitions and an irreversible transition towards an O6-type phase at the end of the 1st cycle (Fig. 2).

The redox processes were characterized from electrical properties as well as XANES and ^{7}Li MAS NMR. Upon lithium deintercalation, cobalt oxidation is observed, whereas upon lithium intercalation manganese and cobalt reduction seems to occur even if for the latter it was not expected.

The phase transition from T#2 to O6 stacking observed for $Li_{2/3}Co_{2/3}Mn_{1/3}O_2$ upon increasing temperature (above 300°C) was studied using *in situ* X-ray diffraction (Fig. 3). The kinetics study of this phase transformation is still in progress. This $O6_{HT}$-$Li_{2/3}Co_{2/3}Mn_{1/3}O_2$ phase is stable up to 480ºC before a decomposition into Li_2MnO_3 and Co_3O_4 at higher temperature. Note that $O6_{HT}$-$Li_{2/3}Co_{2/3}Mn_{1/3}O_2$ exhibits comparable battery performances with the T#2 ones.

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References

[1] F. Tournadre et al., *Chem. Mater.* 16, 1411 (2004)
[2] F. Tournadre et al., *Chem. Mater.* 16, 1418 (2004)

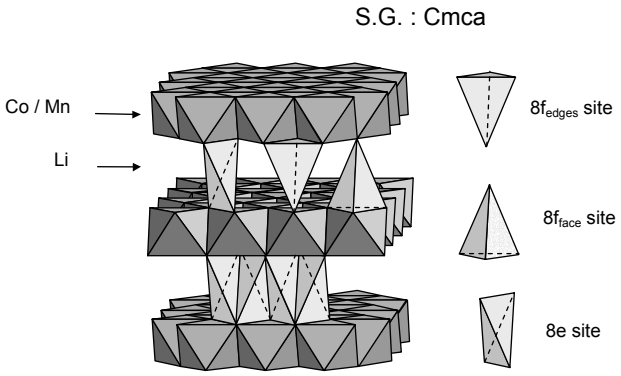

Figure 1: Schematic structure of T#2-$Li_{2/3}Co_{2/3}Mn_{1/3}O_2$. Lithium ions are only distributed in the 8e and $8f_{edges}$ tetrahedral sites.

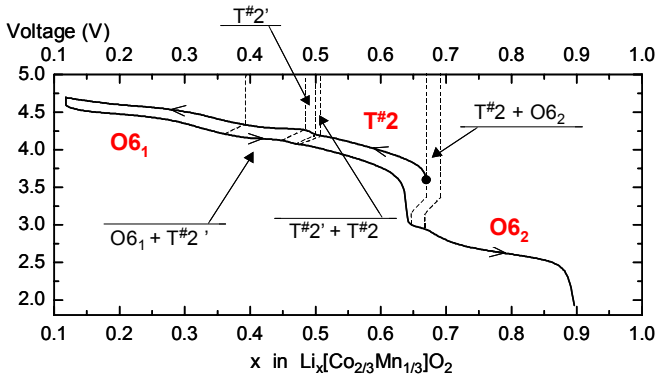

Figure 2: Phase diagram of the $Li_xCo_{2/3}Mn_{1/3}O_2$ system reported on the galvanostatic curve (1st charge and discharge) of an Li//T#2-$Li_{2/3}Co_{2/3}Mn_{1/3}O_2$ cell.

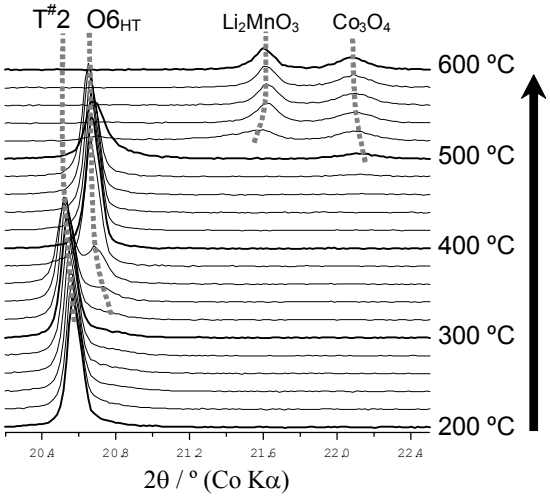

Figure 3: Thermal (in-situ) powder XRD patterns measured during heating process of T#2-$Li_{2/3}Co_{2/3}Mn_{1/3}O_2$ up to 600 ºC in air. Each pattern has been recorded at a stabilized temperature.