STRUCTURAL AND PHYSICAL PROPERTIES OF $T^{\#}2\text{-}Li_{2/3}[Co_{2/3}Mn_{1/3}]O_2$ UPON CYCLING.

F. Tournadre [a], L. Croguennec [a], I. Saadoune [b],
M. Ménétrier [a], M. Morcrette [c], P. Willmann [d] and
C. Delmas [a]

[a] *Institut de Chimie de la Matière Condensée de Bordeaux-CNRS and Ecole Nationale Supérieure de Chimie et Physique de Bordeaux, Université Bordeaux I, 87 Av. du Dr A. Schweitzer, 33608 Pessac cedex, France*

[b] *Département de Chimie, Faculté des Sciences et Techniques, Av. Abdelkrim El Khattabi, B.P. 618, 40000 Marrakech, Morocco*

[c] *Laboratoire de Réactivité et Chimie des Solides, Université Picardie Jules Verne, 33 Rue Saint Leu, 80000 Amiens, France*

[d] *Centre National d'Etudes Spatiales, 18 Av. Edouard Belin, 31401 Toulouse cedex 4, France*

In the last few years, the layered $LiMO_2$ materials obtained by Li-ion exchange in P2 sodium phases, such as $T^{\#}2\text{-}Li_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ and $O2\text{-}LiCoO_2$, were shown to be interesting as positive electrodes materials for Li-ion batteries[1-2]. The behavior of the metastable phase $T^{\#}2\text{-}Li_{2/3}[Co_{2/3}Mn_{1/3}]O_2$ recently prepared[3] by Li/Na ionic exchange in molten salts is presented in this paper.

The galvanostatic curve of the $Li//Li_x[Co_{2/3}Mn_{1/3}]O_2$ cell given in **Fig. 1** exhibits two domains: the first one (around 4.3 V) corresponds to the lithium composition range $0 < x \leq 0.67$ and to the Co^{4+}/Co^{3+} redox couple; the second one (around 2.6 V) corresponds to the lithium composition range $0.67 < x \leq 1$ and to the Mn^{4+}/Mn^{3+} redox couple. The first cycle capacity is 150 mAhg^{-1} between 3.5 V and 4.7 V, it corresponds to deintercalation of almost all lithium ions. During the first cycle, several phase transitions occur. The different phases have been characterized *ex-situ* and *in-situ* by XRD. **Fig. 2** presents a part of the *in-situ* diffraction patterns (enlargement of the first (00*l*) peaks). Upon charge (i.e. for $0 < x \leq 0.67$), the evolution of the phase diagram is very close to that obtained for the $O2\text{-}LiCoO_2$ system[4], the different domains are:

- $T^{\#}2\text{-}Li_xCo_{2/3}Mn_{1/3}O_2$ single phase domain for $0.46 < x \leq 0.67$,
- 4.3 V voltage plateau resulting from the existence of a biphased domain assigned to the $T^{\#}2 \rightarrow O6_1$ transformation for $0.39 < x \leq 0.46$,
- $O6_1\text{-}Li_xCo_{2/3}Mn_{1/3}O_2$ single phase domain for $0.22 < x \leq 0.39$,
- 4.6 V voltage plateau resulting from the existence of a biphased domain assigned to the $O6_1 \rightarrow O2$ transformation for $0.18 < x \leq 0.22$,
- $O2\text{-}Li_xCo_{2/3}Mn_{1/3}O_2$ single phase domain for $x \leq 0.18$.

Upon discharge a small $T^{\#}2 \rightarrow O6_2$ biphased domain is observed for $0.67 < x \leq 0.71$ and then, an $O6_2\text{-}Li_xCo_{2/3}Mn_{1/3}O_2$ single phase domain for $0.71 < x$. Cycling in the $3.5\text{ V} < V \leq 2.5\text{ V}$ potential domain, which is corresponding to the presence of trivalent manganese ions in the structure, induces an irreversible phase transition: the $T^{\#}2$ domain disappears and $Li_x[Co_{2/3}Mn_{1/3}]O_2$ exhibits an O6-type structure for $0.21 < x \leq 1$.

Combination of XRD, conductivity and NMR measurements are in progress in order to investigate the evolution of the structural and physical properties upon lithium deintercalation.

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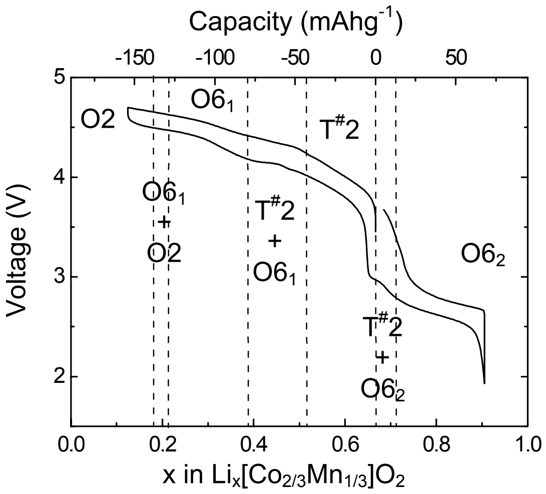

Fig. 1: *First galvanostatic curve of $Li//Li_x[Co_{2/3}Mn_{1/3}]O_2$ cell obtained at C/20 current density rate.*

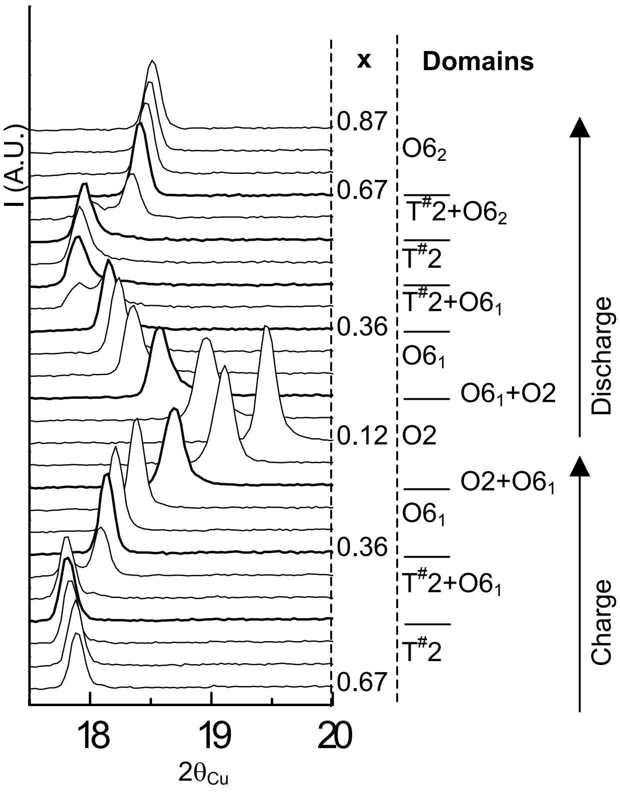

Fig. 2: *First Bragg reflections recorded during the first cycle of $Li//Li_x[Co_{2/3}Mn_{1/3}]O_2$ cells. An XRD pattern is recorded every $\Delta x = 0.05$*