Self-discharge Study of $LiCoO_2$ and $LiMn_2O_4$ Cathodes

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Introduction

The self-discharge of lithium half-cells based on $LiCoO_2$ and $LiMn_2O_4$ cathodes was carried out by monitoring the OCV vs. time and the total capacity loss Q_{tl} at different storage temperatures in order to compare these cathode materials in terms of activation energy and phase transformations.

Experimental

The half-cells consisted of Li/PC-$LiClO_4$/ $LiCoO_2$ and $LiMn_2O_4$ cells. After 5 cycles at ambient temperature up to 4.2V and 4.4V for $LiCoO_2$ and $LiMn_2O_4$ respectively, the cells were aged in their initial charged state at different temperatures ($60<T<75^oC$). The crystal structure of cathodes after aging were studied ex-situ by XRD and TEM.

Results and Discussion

Figure 1 shows the OCV vs. time traces at 60 and 75^oC for $LiCoO_2$ and $LiMn_2O_4$ based cells. At 60^oC, after 10 days aging, the OCV with $LiMn_2O_4$ remained higher than with $LiCoO_2$. The result is different at 75^oC as the OCV of $Li_xMn_2O_4$ decreased more rapidly than in $LiCoO_2$. The OCV of $Li_xMn_2O_4$ shows two plateaus similar to the ones observed during low-rate galvanostatic discharge before thermal storage, suggesting lithium re-intercalation.

The comparison of total capacity loss Q_{tl} at 60 and 75^oC between $LiCoO_2$ and $LiMn_2O_4$ is shown in figure 2. For each temperature, the total capacity loss Q_{tl} is higher in $LiMn_2O_4$ than Li_xCoO_2. The analysis of the OCV(t, T) and Q_{tl}(t, T) traces by fitting with semi-empirical kinetics laws allowed the activation energy of both processes to be determined. The activation energy E_a of $LiMn_2O_4$ and $LiCoO_2$ calculated from OCV(t, T) and Q_{tl}(t, T) curves are shown in table I.

The capacity loss has two components; a reversible and an irreversible loss. The reversible part is attributed to the Li^+ re-intercalation in delithiated cathodes. This may take place as result of electrolyte oxidation (PC oxidation or $ClO_4^{\bullet}$ radical formation). The irreversible loss may due to phase transformation taking place on the surface of the crystallites. In a recent work we showed the formation of the spinel lithium cobalt oxide after thermal aging[1]. In $LiMn_2O_4$, XRD revealed a new phase after 6 days aging at 60^oC, which is attributed to orthorhombic Li_2MnO_3[2]. After 30 days, another phase is present that corresponds to the monoclinic $LiMnO_2$[2]. Concomitantly, the relative intensity of the Li_2MnO_3 peaks decreased. Therefore we believe that $LiMnO_2$ results from Li_2MnO_3 decomposition. This may involve the Mn dissolution and migration across the cell.

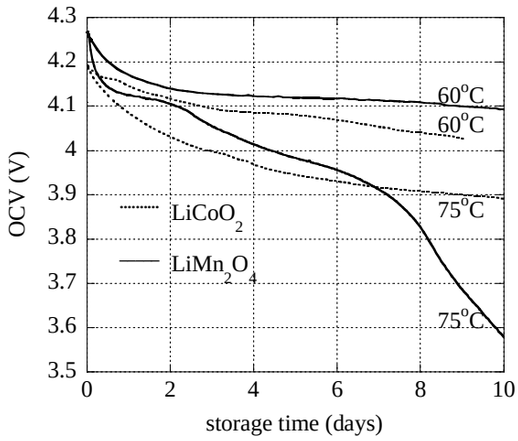

Figure 1: Comparison of OCVvs. time at 60 and 75^oC in Li_xCoO_2 and $Li_xMn_2O_4$ based half cells

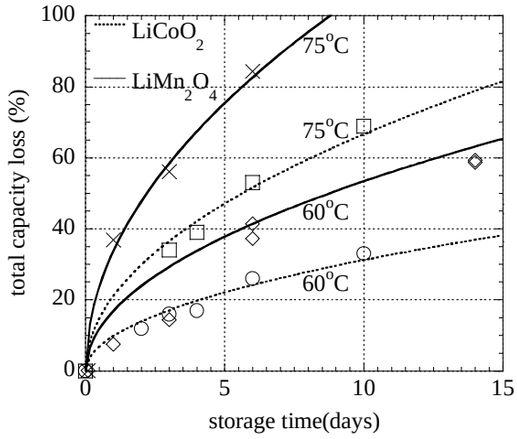

Figure 2: Comparison of total capacity losses Q_{tl} at 60 and 75^oC in Li_xCoO_2 and $Li_xMn_2O_4$ half-cells

E_a (kJ/mole/K)	OCV	Q_{tl}
$LiCoO_2$	41.3	81.2
$LiMn_2O_4$	92.0	83.2

Table 1: activation energy of self discharge from the OCV and capacity loss measurements

References

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