Capacity Fading Mechanisms of LiMnO$_2$ at Elevated Temperature Investigated by In Situ Synchrotron X-Ray Diffraction Studies

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Lithium manganese oxide with spinel structure has been considered as a promising cathode material for lithium secondary batteries. It has been studied extensively due to its advantages such as low cost, high cell voltage, and environmental benignity. However, capacity fading during cycling especially at elevated temperatures limited its use in commercial lithium secondary batteries. Manganese dissolution[1] and a Jahn-Teller distortion[2,3] have been proposed to be responsible for the capacity fading. And, manganese dissolution is reported to play a major role at elevated temperature. Although it is one of the important factors in capacity fading, the material loss due to manganese dissolution can account for only 10–60% of the capacity fading. Therefore, other factors should also be investigated.

In the present study, we propose another mechanism for capacity fading of LiMnO$_2$ at elevated temperature. Recently, Sloop et al. reported LiPF$_6$ decomposes thermally to produce LiF and PF$_6$. Moreover, LiPF$_6$ can also decompose into HF, LiF, and POF$_3$, by reacting with trace amount of moisture during cycling at high potential region, especially at elevated temperature.[4] Therefore, if the electrolyte containing LiPF$_6$ is cycled at elevated temperature, LiF can be produced by both thermal decomposition and hydrolysis reaction, which reduces both conductivity and numbers of free Li$^+$ ions. LiF precipitation was also found at the surface of electrode and in the pores of the separator membrane, which may block the transportation of Li$^+$ ions.[5,6] Thus, the formation of LiF at the surface of electrode may contribute to the capacity fading by blocking Li$^+$ insertion/extraction into/out of spinel matrix. In our previous report, we proposed tris(pentafluorophenyl) borane (TFFPB) as a additive to improve the thermal stability of LiPF$_6$-based electrolyte and compared the cycle performance of LiMnO$_2$ at elevated temperature in LiPF$_6$/EC-DMC(1:1) electrolyte with and without TFFPB.[7] In that study, it was shown that the cycling performances was greatly improved by adding 0.1M TFFPB into the electrolyte. This effect was attributed to the enhancement of LiPF$_6$ ion-pair dissociation. In addition to stabilization effect, TFFPB works very well in helping the dissolution LiF in organic solvents. Therefore, in the presence of TFFPB in electrolyte, LiF formed at the surface of electrode materials can be dissolved back into electrolyte, which means the blocked Li$^+$ insertion/extraction channels were reopened, and the electrochemical activity was restored.

Fig. 1(a) and (b) show in situ XRD patterns of LiMnO$_2$ during the second discharge in LiPF$_6$/EC-DMC without and with TFFPB, respectively. In Fig. 1(a), when no TFFPB were added in the electrolyte, the precipitation of LiF was presumably formed at the surface of the electrode, which would in turn block the Li$^+$ path and made significant portion of the electrode inactive. As a result, the structural changes from cubic III to cubic II, and then to cubic I could not be completed at the end of discharge. These unreacted parts, which we call residues, at various charge-discharge states, are detectable by XRD and marked in Fig. 1(a) with arrows. The intensities of the peaks representing the residues are quite large, almost equal to those representing the structure at equilibrium (the cubic I phase). In contrast, as can be seen in Fig. 1(b), the intensities of the peaks representing the residues reduced significantly. This can be interpreted as the LiF removal effects of TFFPB. Since significant portion of the LiF formed at the surface of electrode during cycling might be removed, the electrochemical activity of the inactive parts was restored. These results provide clear evidence about the importance of the electrolyte decomposition effects on capacity fading for LiMnO$_2$ cycling at elevated temperature.

Figure 1. In situ XRD patterns of LiMnO$_2$ during the second discharge from 4.5 to 3.5V in LiPF$_6$/EC-DMC (1:1) (a) without and (b) with TFFPB.

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References