In Situ Assessment of LiMn_2O_4 Degradation During Prolonged Exposure in Carbonate-Based Electrolytes

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The degradations of thin-film LiMn_2O_4 electrodes during prolonged exposure to 1 M $\text{LiPF}_6/\text{EC-DMC}$ at room temperature and 55°C , were assessed by *in situ* Raman spectroscopy. Our results demonstrate that different deterioration mechanisms of the spinel were found depending on the temperature. Exposure of a thin-film spinel LiMn_2O_4 electrode to $\text{LiPF}_6/\text{EC-DMC}$ electrolyte at room temperature and 55°C led to spontaneous formation of a thin insulating surface layer. This process is accompanied by the transformation of the LiMn_2O_4 electrode surface into $\lambda\text{-MnO}_2$ and Mn_2O_3 at room temperature and 55°C , respectively.

Key Words : Lithium Manganese Oxide, Elevated Temperatures, Degradation, Carbonate-Based Electrolytes

1 Introduction

Among all the systems having practical relevance to the field of rechargeable batteries, the spinel LiMn_2O_4 remains the most promising candidates. The most popular electrolyte used in the Li-ion battery by manufacturers and researchers is LiPF_6 salt dissolved in a binary or ternary solvent mixture of ethylene carbonate (EC) and linear carbonates like dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC).

The stability of the interface between LiMn_2O_4 and LiPF_6 -containing electrolyte, particularly at elevated temperature, is crucial towards commercial application. Cell performance degrades at unacceptably high rates when LiMn_2O_4 electrodes are cycled at temperatures of $50\text{--}60^\circ\text{C}$. The mechanisms proposed for the deterioration vary widely and are discussed in depth in the recent paper by Amatucci *et al.*¹⁾

In our previous report,²⁾ by means of electrochemical quartz crystal microbalance (EQCM) technique, it was shown that when the LiMn_2O_4 electrode was immersed in the $\text{LiPF}_6/\text{EC-PC}$ solution at 50°C , the mass of the electrode decreased steadily, leading eventually to a complete dissolution of the manganese film. Such manganese dissolution was attended by a shift of the open circuit potential (OCP) from 3.8 to 4.3 V vs. Li. The observed increase in the OCP was attributed to a lithium extraction process and the possible formation of a protonated form of $\lambda\text{-MnO}_2$ according to the mechanism described by Hunter.³⁾ In addition, experiment conducted at in $\text{LiClO}_4/\text{EC-PC}$ and $\text{LiBF}_4/\text{EC-PC}$ did not show any significant change both in the OCP and the mass. This led us to propose that the manganese dissolution is peculiar to LiPF_6 -containing electrolyte at elevated temperatures. However, recent studies showed that the solvent might

contribute to LiMn_2O_4 degradation even at room temperature, especially in DMC containing electrolyte.^{4–5)}

The $\text{LiPF}_6/\text{EC-DMC}$ electrolyte solution has been reported to be stable up to 4.9 V (vs. Li/Li^+) at a LiMn_2O_4 electrode at room temperature, its stability remains in question during prolonged storage to the electrolyte. We have been using thin dense films of LiMn_2O_4 , produced with electrostatic spray deposition (ESD),^{6–7)} as a model system for the study of the electrochemical properties of this important cathode material, in the absence of conductive diluents or binders. In the present work, we endeavor to investigate the degradation mechanism of LiMn_2O_4 thin film electrodes in $\text{LiPF}_6/\text{EC-DMC}$ by means of Raman measurements carried out *in situ* during storage at room temperature and at 55°C . Special emphasis was placed on characterizing electrode dissolution /phase transformation processes upon storage without potential control. The locations, shapes, and sizes of Raman vibration peaks can signal the appearance or disappearance of chemical species, and the formation or destruction of distinct phases. These informations can be used to identify new strategies to increase electrode performance and lifetime.

2 Experimental

Thin films of LiMn_2O_4 (ca. $0.5\ \mu\text{m}$ thick) were deposited at 400°C on both sides of a gold flag substrate with an electrostatic spray deposition (ESD) technique.^{6–7)}

For the simultaneous use of *in situ* Raman and open-circuit potential (OCP) measurements, an airtight cell equipped with a random orientation sapphire window (35 mm diameter, $300\ \mu\text{m}$ thick) was used.⁸⁾ A radiation of an argon ion laser (Coherent, Innova 70, 514.5 nm, 40 mW) was focused on a $0.1\ \text{mm} \times 1.0\ \text{mm}$ spot on the

electrode surface at an incident angle of *ca.* 60°. Two lithium foils pressed on nickel meshes were used as the counter and the reference electrodes. The electrolyte was 1 M LiPF₆-ethylene carbonate (EC)/dimethyl carbonate (DMC) 1 : 1 by volume mixture. All potentials reported in this work are versus the Li/Li⁺ reference electrode. Time zero corresponds when the open circuit potential measurements started.

The electrochemical measurements were performed with a Solartron 1267 potentiostat driven by Corrware for Windows (Scribner Associates).

3 Results and Discussion

3.1 *Ex-situ* characterization of the thin films

Figure 1 shows ordinary (*ex situ*) Raman spectra of fresh LiMn₂O₄ thin film electrodes. The ordinary Raman spectrum of the LiMn₂O₄ electrode consists of a series of broad bands between 450 and 700 cm⁻¹. The peaks at 620 (symmetric Mn-O stretching vibration of MnO₆ groups), 597, 480, 430 and 350 are assigned to A_{1g}, T_{2g}(3), T_{2g}(2), E_g, T_{2g}(1) mode, respectively, as predicted by group theory for the cubic compound.⁹⁾

3.2 *In-situ* Measurements in LiPF₆/EC-DMC

Figure 2 shows the open-circuit potential versus time profile of LiMn₂O₄ film electrode in 1 M LiPF₆/EC-DMC at room temperature. Initially, the OCP of the electrode decreased to about 3.5 V vs. Li/Li⁺ at which it sustained for about 60 hours. Afterwards, the OCP increased to reach a potential around 4.3 V, which suggests that complete delithiation occurred. *In situ* Raman spectra recorded during the course of OCP are reported in Fig. 3. The spectra show a new band at 596 cm⁻¹, which is attributed to the formation of the λ-MnO₂ phase,⁹⁾ and is similar to that of λ-MnO₂ reported by Kanoh *et al.*¹⁰⁾ for the fully delithiated spinel manganese oxide.

Figure 4 shows cyclic voltammograms of the thin-film LiMn₂O₄ electrode recorded after 100 hours storage in LiPF₆/EC-DMC electrolyte. Two anodic peaks 4.0 and 4.17 V and two corresponding cathodic peaks characteris-

Fig. 1 Ordinary Raman (*ex situ*) spectrum of a fresh thin-film LiMn₂O₄ electrode fabricated by electrostatic spray deposition (ESD) technique.

Fig. 2 The time-courses of variation of open circuit voltage of LiMn₂O₄ thin film conducted at room temperature in LiPF₆/EC-DMC electrolyte.

Fig. 3 *In situ* Raman spectra recorded during storage up to 92 hrs of a LiMn₂O₄ thin-film electrode in LiPF₆/EC-DMC at room temperature.

Fig. 4 Cyclic voltammograms at room temperature and 0.3 mV/s for a thin-film LiMn₂O₄ electrode exposed for 100 hrs in LiPF₆/EC-DMC electrolyte.

Fig. 5 The time-courses of variation of open circuit voltage of LiMn_2O_4 thin film conducted at 55°C in $\text{LiPF}_6/\text{EC-DMC}$ electrolyte.

Fig. 6 *In situ* Raman spectra recorded during storage up to 90 hrs of a LiMn_2O_4 thin-film electrode in $\text{LiPF}_6/\text{EC-DMC}$ at 55°C .

tic for the LiMn_2O_4 spinel are clearly observed. Thus, the remaining active part of the electrode still exhibited good cyclability and showed moderate capacity fading.

Accordingly, after prolonged exposure in $\text{LiPF}_6/\text{EC-DMC}$ even at room temperature, the LiMn_2O_4 decomposed to $\lambda\text{-MnO}_2$ without disruption of the original structure as observed by CV (Fig. 4) recorded after the OCP experiment.

Figure 5 shows the open-circuit potential versus time profile of LiMn_2O_4 film electrodes in 1 M $\text{LiPF}_6/\text{EC-DMC}$ at 55°C . Contrarily to room temperature observations, the OCP of the electrode decreased and reached 3 V vs. Li/Li^+ and sustained at this value.

The *in situ* Raman spectra shown in Fig. 6 displayed only a strong peak at about 660 cm^{-1} , which is characteristic of Mn_2O_3 .¹¹ Taking into account that the absence of evidence for a Mn_2O_3 in our *ex-situ* Raman and XRD patterns, we confirm that the electrode surface was enriched with Mn_2O_3 during storage in $\text{LiPF}_6/\text{EC-DMC}$ at 55°C .

The data obtained in this study indicate that exposure of a thin-film spinel LiMn_2O_4 electrode to $\text{LiPF}_6/\text{EC-DMC}$ electrolyte at room temperature and 55°C led to spontaneous formation of a thin insulating surface layer. This

process is accompanied by the transformation of the LiMn_2O_4 electrode surface into $\lambda\text{-MnO}_2$ and Mn_2O_3 at room temperature and 55°C respectively. We have to emphasize that result of Fig. 2 were not observed in $\text{LiPF}_6/\text{EC-PC}$ electrolyte at room temperature. In this electrolyte, the OCP of the thin-film electrode did not change upon 100 hrs of storage. This is another indication that DMC is playing a part in the degradation of LiMn_2O_4 in DMC containing electrolyte.

Indeed, McLarnon *et al.*⁴⁾, and Striebel *et al.*⁵⁾ observed that LiMn_2O_4 degrades at room temperature in $\text{LiPF}_6/\text{EC-DMC}$ electrolyte. The reaction mechanism for the deterioration proposed by these groups differ each other. McLarnon *et al.* proposed that LiMn_2O_4 decomposes to $\lambda\text{-MnO}_2$ accompanied by the formation thin passive electrode surface layer most likely Li_2O .⁴⁾ The formation of $\lambda\text{-MnO}_2$ is evidenced by our *in situ* Raman spectra (Fig. 3). With regard to Li_2O , we cannot provide confirmation for that compound. Probably, measurements of the surface conductivity would be helpful. Striebel *et al.*⁵⁾ proposed part of the LiMn_2O_4 reversibly disproportionates into $\text{Li}_2\text{Mn}_2\text{O}_4$ at the surface and a lithium-deficient material, $\text{Li}_{1-\delta}\text{Mn}_2\text{O}_4$ in the rest of the film. With extended current cycling part of the $\text{Li}_2\text{Mn}_2\text{O}_4$ degrades to the Mn_2O_3 and the process is no longer reversible. $\text{Li}_2\text{Mn}_2\text{O}_4$ is known to be an insulator and possesses poor kinetics for lithium exchange. The lithium deficient portion of the film would cause an increase in the OCP of the film, which might explain the results of Fig. 2. However, our *in situ* Raman spectra did not show the presence of such compound. In addition, $\text{Li}_2\text{Mn}_2\text{O}_4$ is not expected to be present at potentials above 3 V vs. Li/Li^+ .

Accordingly, we ascribe the observed increase of the electrode open circuit potential to 4.3 V (Fig. 2) to a disproportionation ($2\text{Mn}^{3+} \rightarrow \text{Mn}^{2+} + \text{Mn}^{4+}$) followed by Mn^{2+} dissolution in $\text{LiPF}_6/\text{EC-DMC}$ electrolyte leaving the higher voltage to $\lambda\text{-MnO}_2$.

At 55°C , the OCP behavior of the LiMn_2O_4 was completely different from that at room temperature. We believe that we are seeing a different mechanism for the deterioration of this material at elevated temperature in DMC-containing electrolyte. *In situ* Raman spectra of Fig. 6 suggest that degradation of LiMn_2O_4 electrode proceeds rapidly to the formation of Mn_2O_3 and the process is no longer reversible. In a study of Li-Mn-O spinel electrodes that had been stored at 55°C in a 1 M $\text{LiPF}_6/\text{EC-DMC}$ electrolyte, Blyr *et al.*¹²⁾ reported that manganese dissolution changes the spinel composition with the concomitant formation of rock salt Li_2MnO_3 at the particle surface. These results were later supported by Cho and Thackeray,¹³⁾ who proposed that the presence of Li_2MnO_3 is attributed to the dissolution of MnO from $\text{Li}_2\text{Mn}_2\text{O}_4$ that is generated as an over-discharged product at the surface of the LiMn_2O_4 spinel electrode. However, the rock salt phase Li_2MnO_3 was not observed in our Raman spectra. SEI layers containing Li_2O or lithium alkoxides have been observed *ex-situ* Raman spectroscopy of LiMn_2O_4 films held at elevated temperatures in the $\text{LiPF}_6/\text{EC-DMC}$.¹⁴⁾ The surface layer must be either nonuniform or permeable to the electrolyte (lithium ions) be-

Fig. 7 Cyclic voltammograms at room temperature and 0.3 mV/s for a thin-film LiMn_2O_4 electrode exposed for 100 hrs at 55°C in $\text{LiPF}_6/\text{EC-DMC}$ electrolyte.

cause the electrode still shows some electrochemical activity judging from CVs recorded after storage (Fig. 7). In addition, the broadening peak suggests the presence of such a surface layer.

For flat surfaces containing a thin adsorbed film, it is obvious that yet with an optimized system, the Raman signal from the surface species would be very problematical to detect without enhancement. Surface enhanced Raman spectroscopy (SERS) may provide useful information about SEI layer structure and composition.

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