Surface modification of LiMn$_2$O$_4$ thin films at elevated temperature

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Abstract

In order to improve the cycle stability of spinel LiMn$_2$O$_4$ electrode at elevated temperature, the LiCoO$_2$-coated and Co-doped LiMn$_2$O$_4$ film were prepared by an electrostatic spray deposition (ESD) technique. LiCoO$_2$-coated LiMn$_2$O$_4$ film shows excellent cycling stability at 55°C compared to pristine and Co-doped LiMn$_2$O$_4$ films. The samples were studied by X-ray diffraction, scanning electron microscopy, Auger electron spectroscopy, cyclic voltammetry and electrochemical impedance spectroscopy. The excellent performance of LiCoO$_2$-coated LiMn$_2$O$_4$ film can be explained by suppression of Mn dissolution. On the other hand, the LiCoO$_2$-layer on the LiMn$_2$O$_4$ surface allows a homogenous Li$^+$ insertion/extraction during electrochemical cycles and improves its structure stability.

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1. Introduction

Spinel LiMn$_2$O$_4$ is of great interest for use in lithium ion battery due to its high voltage, low cost and low toxicity. Unfortunately, fast capacity fading at elevated temperature limits its application in commercial cells. The major factors responsible for the capacity fading at the elevated temperature are ascribed as follows: (i) Jahn-Teller distortion caused by presence of Mn$^{3+}$ ions [1]; (ii) Mn dissolution induced by HF acid [2–4]; (iii) the transformation of the unstable two-phase structure to a more stable one-phase structure [5,6]. All the above-proposed factors are mainly associated with the morphology and crystal structure. Therefore, many studies have been reported in these directions. In order to improve the performance of LiMn$_2$O$_4$ related with surface morphology, many research works have been performed including directly preparing spinel with small surface area [7] and also by coating spinel with Li$_2$O–B$_2$O$_3$ [8]. On the other hand, many efforts have been devoted to stabilize its structure by partial substitution of other transition metals into Mn sites [9,10]. However, all these attempts were effective to a certain extent for overcoming the capacity fading at elevated temperature. Recently, significant improvement on the performance of LiMn$_2$O$_4$ cathode material at elevated temperature has been achieved by sol–gel coating on its particle surface with LiCoO$_2$ [11,12], these attempts have opened up new avenues.

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Thus, the progress in the microelectronics industry has reduced the current and power requirements of electronic devices to an extremely low level, making the use of thin-film rechargeable micro-batteries as power sources for these devices possible [13]. Hence, the thin film electrodes show great commercial potential. Further, the thin film electrode has simple geometric form without additives such as a polymer binder and conducting materials and therefore makes the theoretical analysis of their electrochemical performance easier.

In this study, we report the results of a new approach to improve the cycle stability of the LiMn$_2$O$_4$ electrostatic spray deposition (ESD) thin film electrode at elevated temperature by means of coating of LiCoO$_2$ onto its surface. LiCoO$_2$-coated LiMn$_2$O$_4$ film shows excellent cycle stability at elevated temperature compared to pristine and Co-doped LiMn$_2$O$_4$ film. The suppression of Mn dissolution and the improvement of its structure stability can explain the excellent performance of LiCoO$_2$-coated LiMn$_2$O$_4$ film.

2. Experimental

LiCoO$_2$-coated LiMn$_2$O$_4$ films were prepared by ESD technique and its working principles have been described in the literature [14–16]. The precursor solution consisted of 25 mM LiNO$_3$ + 50 mM Mn(NO$_3$)$_2$ in EtOH for LiMn$_2$O$_4$ layer and 25 mM LiNO$_3$ + 25 mM Co(NO$_3$)$_3$ for LiCoO$_2$ layer was pumped at 2 ml h$^{-1}$ through a stainless steel nozzle respectively, a distance of 3 cm was kept and a voltage of 10 kV was applied between the nozzle and substrate, all ESD films were deposited on Pt foils. The substrate temperature was maintained at 400 °C during the deposition and then the deposited film was annealed further for 1 h at 600 °C in an air oven. Stoichiometric mixtures of LiNO$_3$, Co(NO$_3$)$_3$ and Mn(NO$_3$)$_2$ in EtOH were used for preparation of Co-doped LiMn$_2$O$_4$. The concentration of Co in both LiCoO$_2$-coated and Co-doped LiMn$_2$O$_4$ was controlled in 6%.

Scanning electron microscope (SEM, HITACHI S2700) was used for evaluating the surface morphology. The crystal structure of ESD films were characterized by X-ray diffraction (XRD) patterns using Cu Kα radiation in a Rigaku diffractometer.

All electrochemical measurements were carried out using three-electrode cells assembled under argon atmosphere in a glove box. The studies were carried out with the ESD film as the working electrode in nonaqueous electrolyte (1 M LiPF$_6$ + EC + DMC) using lithium foil as reference and counter electrodes. Electrochemical impedance spectroscopy (EIS) measurements were performed using a Solartron 1287 electrochemical interface and 1260 impedance/gain-phase analyzer driven by the Zplot software in the frequency range $10^{-2}$–$10^5$ Hz.

3. Results and discussion

The XRD patterns of LiMn$_2$O$_4$ thin film obtained by using ESD technique on a Pt foil substrate are presented in Fig. 1. In order to minimize interference from the diffraction peaks of the substrate, near grazing angle scans, were made in which the angle of the incident radiation with respect to the plane of the substrate was fixed at 5° while the detector with a parallel-beam thin-film attachment placed in front of it was moved through 2θ angle. It can be seen clearly that all the hkl peaks could be indexed to the spinel structure of LiMn$_2$O$_4$ representing the space group, Fd3m. The two peaks of the substrate due to Pt are also marked in Fig. 1. Thus, we can assign the position of Li and Mn ions to the 8a tetrahedral and 16d octahedral sites, respectively [17]. However, due

![Fig. 1. XRD spectra of LiMn$_2$O$_4$ film prepared onto Pt substrate by ESD.](image-url)
to almost similar diffraction pattern between LiMn$_2$O$_4$ and LiCoO$_2$ [12], no extra diffraction peak was detected in LiCoO$_2$-coated and Co-doped LiMn$_2$O$_4$.

The surface morphology of pristine and LiCoO$_2$-coated LiMn$_2$O$_4$ film observed by scanning electron microscopy is shown in Figs. 2 and 3, respectively. The surface morphology of pristine LiMn$_2$O$_4$ is smooth (Fig. 2) but it becomes coarse after a layer of LiCoO$_2$ is coated on the surface of the LiMn$_2$O$_4$ (Fig. 3). In order to identify the spatial distribution of Co within the surface of LiMn$_2$O$_4$ thin film, the element concentration profiles were obtained by Auger electron spectroscopy (AES) and shown in Fig. 4. It can be seen that the Co atoms are only distributed on the surface of film. The decrease of the Co content accompanies simultaneously the increase of Mn content toward the bulk of film indicating that LiCoO$_2$ is coated on the LiMn$_2$O$_4$ surface.

Fig. 5 shows the cyclic voltammogram (CV) of LiMn$_2$O$_4$ ESD film at room temperature, the pair of oxidation and reduction peaks appear around 4.0 and 4.15 V which is in agreement with the results reported by several researchers [18,19]. The two pairs of redox peaks indicate that spinel LiMn$_2$O$_4$ experiences a two-
step reaction during extraction/insertion of Li\textsuperscript{+} ions in the 4 V region, and the electrochemistry clearly suggests the existence of an intermediate phase between initial LiMn\textsubscript{2}O\textsubscript{4} and Li\textsubscript{2}MnO\textsubscript{2} \cite{20}. Symmetric current peaks observed in Fig. 5 imply good kinetic response due to short diffusion distance of Li\textsuperscript{+} ions in ESD film. The result also shows only 12% capacity loss after 100 cycles and demonstrates the good reversible cycling behavior of LiMn\textsubscript{2}O\textsubscript{4} ESD film at room temperature. However, fast capacity fading of LiMn\textsubscript{2}O\textsubscript{4} ESD film is observed in Fig. 6 when the CV experiment was performed at 55 °C. The fast capacity fading of LiMn\textsubscript{2}O\textsubscript{4} is a main obstacle for its commercial application. It is well known that the reversibility of spinel LiMn\textsubscript{2}O\textsubscript{4} can be improved by doping of various metal ions such as Li\textsuperscript{+}, Co\textsuperscript{2+}, Ni\textsuperscript{2+}, Zn\textsuperscript{2+}, Mg\textsuperscript{2+}, Ga\textsuperscript{3+}, Al\textsuperscript{3+} and Cr\textsuperscript{3+}. These doping ions substitute for Mn\textsuperscript{3+} occupying the 16d octahedral sites in the spinel phase. As seen from CV of Co-doped LiMn\textsubscript{2}O\textsubscript{4} at 55 °C (Fig. 7), the introduction of Co\textsuperscript{3+} into 16d octahedral sites in the spinel phase improves the reversibility of LiMn\textsubscript{2}O\textsubscript{4}. However, it is seen from Fig. 9, that the capacity fading of Co-doped LiMn\textsubscript{2}O\textsubscript{4} after 50 cycles remains at 26%, so the improvement of reversibility by doping Co is limited to some extent at 55 °C. Fig. 8 shows the CV of LiCoO\textsubscript{2}-coated LiMn\textsubscript{2}O\textsubscript{4} at 55 °C and indeed the LiCoO\textsubscript{2}-coated LiMn\textsubscript{2}O\textsubscript{4} shows excellent reversibility, the capacity fading after 50 cycles is seen to be only 11% (Fig. 9). Further, it is observed in Figs. 5–8 that broad redox peaks (Figs. 5 and 7) can be related with good reversibility.


It is well known the main factors contributing to the capacity fading of spinel LiMn\textsubscript{2}O\textsubscript{4} electrode are ascribed as follows:

1. **Jahn-Teller distortion**: Jahn-Teller distortion takes place when Li\textsuperscript{+} ions insert into LiMn\textsubscript{2}O\textsubscript{4} in 3 V region, it results a phase transformation from a cubic to tetragonal symmetry. However in the present case, the CV experiments were performed in 4 V region (3.5–4.4 V), so Jahn-Teller distortion could be ruled out as a major contributor to capacity fading.
Mn dissolution: Mn dissolution is induced by HF acid generated by temperature-enhanced electrolyte decomposition. Excellent reversibility of LiCoO$_2$-coated LiMn$_2$O$_4$ ESD film implies that the Mn dissolution is blocked by a layer of LiCoO$_2$ on LiMn$_2$O$_4$ film surface. It is well known that LiCoO$_2$ exhibits excellent performance at elevated temperature, so the layer of LiCoO$_2$ on the surface of LiMn$_2$O$_4$ prevents direct contact between the spinel and the electrolyte thereby suppressing the Mn dissolution which is responsible for the capacity fading.

Structure instability: Xia et al. [5,7] pointed out that the transformation of an unstable two-phase to a more stable one-phase structure takes place during the extraction/insertion of Li$^+$ ions and is accompanied by the loss of MnO. The structural instability results in the capacity fading of the spinel LiMn$_2$O$_4$. The two pairs of redox peaks in Figs. 5–8 indicate phase change during the extraction/insertion of Li$^+$ ions. At elevated temperature, the sharp redox peaks in the CVs of pristine and Co-doped LiMn$_2$O$_4$ suggest that phase change is focused on a narrow potential region, and the sudden phase change results in the poor reversibility due to its structural instability. The CVs of LiMn$_2$O$_4$ film at room temperature and LiCoO$_2$-coated LiMn$_2$O$_4$ at 55 °C reveal that the phase change take place in a large potential region, so this process is relatively smooth and the structure is more stable thereby exhibiting excellent reversibility. Further, at elevated temperature, a layer of LiCoO$_2$ on LiMn$_2$O$_4$ surface allow a homogenous Li$^+$ insertion/extraction in the entire 4 V intercalated region, thereby stabilizing the structure of spinel phase and improving the reversibility of LiCoO$_2$-coated LiMn$_2$O$_4$. Recently, Hwang et al. [21] confirmed by XRD that the structure stability of spinel LiMn$_2$O$_4$ improved after LiMn$_2$O$_4$ core was surrounded by LiCo$_x$Mn$_{2-x}$O$_4$ shell material.

Electrochemical impedance spectroscopy is one of the most powerful techniques for investigating the nature of an electrode during an electrochemical process. Fig. 10 shows the Nyquist plots measured from the LiMn$_2$O$_4$ ESD film before CV cycle at the different potential as indicated. Fig. 11 displays the Nyquist plots measured from the LiMn$_2$O$_4$ ESD film after 40th CV cycle at the different potential as indicated.
process. Structural change of LiMn$_2$O$_4$ ESD film should therefore affect the impedance behavior. Hence, the EIS measurements of LiMn$_2$O$_4$ ESD film were performed in different potentials and cycles.

The Nyquist plots of fresh LiMn$_2$O$_4$ ESD film are shown in Fig. 10. The measurements were performed at 55 °C. The EIS profiles at certain potential consist of a semicycle and a straight line. The semicycle is related to charge transfer resistance ($R_{CT}$) and double layer capacitance. The straight line ascribes to Warburg impedance due to diffusion process. Fig. 10 shows that a minimum value of $R_{CT}$ appears at 4.14 V with the increase of potential from 3.8 to 4.3 V and is in accordance with the observation of several other researches [22–24].

Fig. 11 shows the EIS profiles of LiMn$_2$O$_4$ ESD film after 40 cycles. Similar tendency could be observed but $R_{CT}$ becomes larger. The increase in $R_{CT}$ value could be ascribed to the structural changes. The EIS measurements were also carried out using LiCoO$_2$-coated LiMn$_2$O$_4$ (6%) ESD film. In order to compare the difference between the pristine and LiCoO$_2$-coated LiMn$_2$O$_4$ film, a peak potential of 4.08 V was selected, the developments of impedance vs. cycle number are shown in Figs. 12 and 13. The $R_{CT}$ increases with the increase of cycle number in both the electrodes. Fig. 14 shows the $R_{CT}$ change vs. cycle number deduced from EIS data of pristine and LiCoO$_2$-coated LiMn$_2$O$_4$ ESD film at 4.08 V.

4. Conclusion

The surface of LiMn$_2$O$_4$ film was coated with a layer of LiCoO$_2$ using ESD method. LiCoO$_2$-coated LiMn$_2$O$_4$ (6%) ESD film showed an excellent reversibility than pristine one at elevated temperature (55 °C). The reason for the improvement at elevated temperature is that the layer of LiCoO$_2$ preserves the
surface of LiMn$_2$O$_4$ from the electrolyte, which results in the suppression of Mn dissolution. Further, the LiCoO$_2$ layer on the LiMn$_2$O$_4$ surface allows a homogenous Li$^+$ insertion/extraction and improves its structure stability during the electrochemical cycling.

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References