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Short communication

LiMn$_2$O$_4$ electrode prepared by gold–titanium codeposition with improved cyclability

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Abstract

An LiMn$_2$O$_4$ electrode was prepared based on mixed-metals (gold–titanium) codeposition method. By this method, titanium oxide is also incorporated into the electroactive film formed on substrate electrode. Formation of titanium oxide on the spinel surface avoids dissolution of Mn from the spinel at elevated temperatures. TiO$_2$ can act as a bridge between the spinel particles to reduce the interparticle resistance and as a good material for the Li intercalation/deintercalation. Thus, electrochemical performance of the LiMn$_2$O$_4$ spinel can be improved by the surface modification with TiO$_2$. This action improves cyclability for lithium battery performance and reduces capacity fades of LiMn$_2$O$_4$ at elevated temperatures.
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1. Introduction

LiMn$_2$O$_4$ is a promising candidate cathode material for lithium secondary battery applications due to its noticeable advantages such as nontoxicity, inexpensivity, etc. However, its significant capacity fade at elevated temperatures is the greatest obstacle in the commercialization of this valuable cathode material. This phenomenon can be attributed to different reasons such as manganese dissolution [1,2], formation of oxygen deficiencies [3], electrolyte decomposition [4], Jahn-Teller distortion [5], cation mixing between lithium and manganese [6] and loss of crystallinity during cycling [7]. This disadvantage can be reduced by surface modification of LiMn$_2$O$_4$ with LiCoO$_2$ to avoid Mn dissolution and other responsible phenomena [8,9]. More recently, Kannan and Manthiram [10] have reported that metal oxides can also be used for the surface modification of LiMn$_2$O$_4$ as well as LiCoO$_2$ and other modifiers. The surface modification can be carried out by mixing the modifier with LiMn$_2$O$_4$ spinel before the deposition process.

Another important subject of research in studies of LiMn$_2$O$_4$ as cathode material is the investigation of different deposition methods. Various methods such as electron-beam evaporation [11], RF magnetron sputtering [12], pulsed

laser deposition [13], chemical vapor deposition [14], etc. have been proposed for the deposition of thin films of LiMn$_2$O$_4$ suitable for the practical use. The main advantage of these methods is the ability to add doping cations which modifies the capacity fading of LiMn$_2$O$_4$. A low capacity fade is, in fact, the most important requirement for commercial applications. As the above-mentioned methods are based on high-technology, high-energy techniques, proposing simple methods for the deposition of cathode materials is very interesting for the development of lithium secondary batteries. In previous works [15,16], we have successfully used gold-codeposition method [17] for the fabrication of LiMn$_2$O$_4$ cathodes. The simplicity of this method is the interesting advantage in comparison with available high-technology methods. In this work, we show that the unique advantage of the high technology methods, i.e. the addition of the modifiers to LiMn$_2$O$_4$ films, is also achieved by the simple gold-codeposition method. In addition, a new modifier to improve the cyclability of LiMn$_2$O$_4$ particularly at elevated temperature is introduced.

2. Experimental

Nanostructured LiMn$_2$O$_4$ spinel was synthesized similar to the previous work [18]. Detailed characterization of the synthesized LiMn$_2$O$_4$ spinel has been reported in the literature [19]. Small particles (smaller than 100 nm)

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have been used for the present study, as large particles are not suitable for codeposition method. The deposition of $LiMn_2O_4$ was carried out during deposition of gold and codeposition of gold-titanium on a Pt substrate. The electroactive material ($LiMn_2O_4$) is deposited onto the substrate surface as the result of occlusion between the gold particles deposited. The presence of gold in the deposit does not cause any problem in the electrode performance, since gold does not provide any electrochemical reaction in the potential range of our experiments.

The deposition process was performed using a solution containing 15 g/l of potassium gold cyanide, 80 g/l of monopotassium phosphate, 70 g/l of potassium citrate and 1.5 g/l of titanium chloride with near-neutral pH, as the deposition electrolyte. The solution contains Ti hydroxide as a result of the hydrolysis of titanium chloride in water [20].

Due to the small amount of the titanium oxide modifier incorporated into the $LiMn_2O_4$ film, the exact form (whether crystalline or composition) of the electroactive material cannot be determined by XRD to understand if the modification of the $LiMn_2O_4$ spinel was physical (surface covering of the spinel particles) or chemical (e.g. formation of $LiTi_xMn_{2-x}O_4$). As the electroactive material is incorporated within the gold film deposited, it is difficult to inspect the presence of TiO_2 on the spinel particles. Even sequential Ar^+-ion sputtering and XPS analysis, which is a common way for depth analysis of electroactive materials to inspect the distribution of the modifier, was not successful for the present case. Nevertheless, we have found that the dissolution of the deposit in acidic medium for elemental analysis is a reliable way to estimate the Ti content. The results obtained from the elemental analysis of Ti showed that the amount of titanium oxide (or hydroxide) in the electroactive material deposited is about 4 wt.%. The amount of gold deposited is about 50–60 wt.% of the total deposit.

A small amount of $LiMn_2O_4$ (ca. 40 μg) was also added to the deposition electrolyte solution (plating bath). The electrolyte solution was stirred for a few minutes before the deposition process to reach a well-conditioned suspension. The deposition process was carried out by applying a cathodic current of 4.0 mA in a warm bath (50 °C). The electrode was washed thoroughly to remove any potassium ion from its surface, and heated at 200 °C for 1 h to remove water.

The amount of the deposit was determined by weighing the electrode before and after the deposition process. This is related to the overall mass of the deposit including the Au and also the titanium oxide codeposited. The amount of $LiMn_2O_4$ deposited onto the substrate surface was also checked by weighing the insoluble $LiMn_2O_4$ added to the plating bath before and after the deposition process. Indeed, weighing the amount of spinel in the plating bath before and after the deposition process is for one experience the best approach. However, the use of both approaches is desirable to obtain a reliable value for the amount of electroactive material used for the preparation of the cathode and to know the Au/spinel ratio of the deposit.

As the amount of titanium ions in the plating bath (and consequently the amount of titanium oxide incorporated into the deposits) is very small, there is no significant difference in the mass and thickness of the films deposited by gold-codeposition and mixed-metals (gold–titanium) codeposition methods. Indeed, the amount of $LiMn_2O_4$ attached to the substrate surface was 13 μg ± 0.2 and the film thickness estimated by S.E.M. was about 2.2 μm for the cathodes prepared with and without titanium oxide modifier. However, the presence of Ti hydroxide should not make any problem in our investigation, as metal hydroxides are also responsible for the surface modification of $LiMn_2O_4$ [10].

The $LiMn_2O_4$ electrodes prepared using gold-codeposition method are referred to as unmodified electrodes, as $LiMn_2O_4$ was simply attached to the substrate surface. The electrodes prepared using the mixed-metals (gold–titanium) codeposition approach are referred to as modified electrodes, as titanium oxide generated during the Ti electrodeposition can act as a surface modifier of the $LiMn_2O_4$ spinel. The two different types of electrodes were investigated and compared to understand the advantages of the modifier material and the deposition approach proposed. The reproducibility of the results obtained was verified by fabricating several similar electrodes (by gold-codeposition or mixed-metals (gold–titanium) codeposition methods). The electrochemical measurements were performed in a conventional cell containing a lithium metal anode and the prepared cathodes of $LiMn_2O_4$ electrodes as cathodes. The electrolyte solution was 1 M $LiPF_6$ in ethylene carbonate (EC) and diethyl carbonate (DEC).

3. Results and discussion

Addition of a small amount of titanium oxide does not make significant change in the electrochemical behavior and the spectroscopic characteristics of $LiMn_2O_4$, which were approximately similar to those reported for the $LiMn_2O_4$ prepared by the gold-codeposition [16,17].

Fig. 1 shows the discharge characteristics of both unmodified and modified $LiMn_2O_4$ electrodes. While the discharge profiles are similar, it is evident that the modification of $LiMn_2O_4$ by the incorporation of titanium oxide greatly enhances the electrode capacity, as shown by the higher capacity delivered in the first cycle by the modified $LiMn_2O_4$ electrode in comparison with the unmodified $LiMn_2O_4$ electrode. It should be taken into account that the specific capacity is calculated in accordance with the net weight of $LiMn_2O_4$ spinel included into the deposits.

This can be due to the fact that metal oxides can act as Li intercalating materials and most of them have higher theoretical capacity for this process in comparison with $LiMn_2O_4$. For example, $LiCoO_2$-modified $LiMn_2O_4$ has higher capacity than unmodified $LiMn_2O_4$. Of course, intercalation of Li into TiO_2 is not the only possible reason for
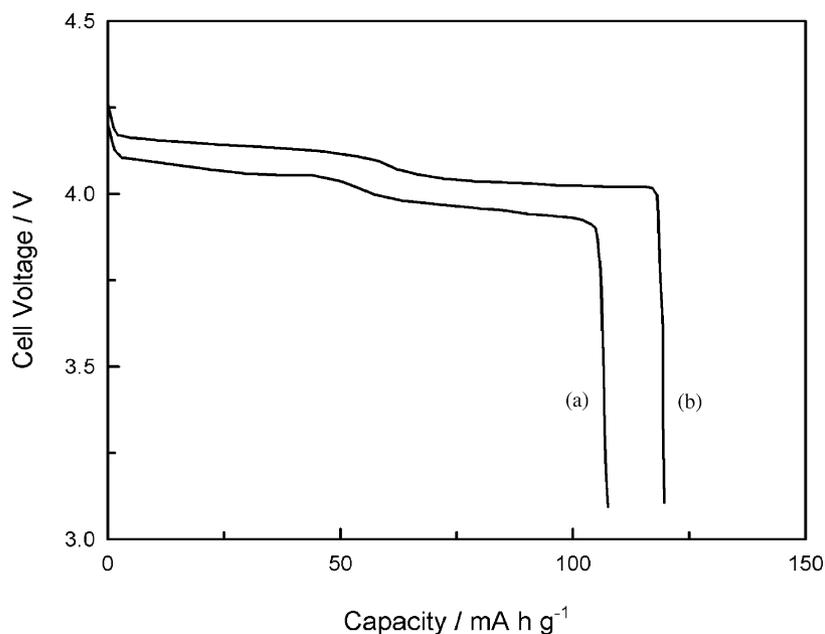
Fig. 1. Discharge characteristic of (a) the unmodified $LiMn_2O_4$ electrode and (b) the modified $LiMn_2O_4$ electrode prepared by the incorporation of titanium oxide recorded at the rate of C/5.

the enhanced capacity of the cathode, as the dispersed particles may provide easier diffusion of Li ions to reach or leave the spinel particles upon insertion and extraction. Also, the TiO_2 particles may act as contact bridges between the spinel particles reducing the interparticle resistance, thus facilitating the insertion–extraction process across the electroactive material mass. Of course, the specific capacity of the modified electrode is still lower than the theoretical capacity of $LiMn_2O_4$.

From Fig. 1, it is obvious that the cell voltage of the TiO_2-modified $LiMn_2O_4$ cathode is higher than the TiO_2-free cathode. This behavior cannot be attributed to the presence of TiO_2, which is known to intercalate Li at significantly lower voltages in comparison with $LiMn_2O_4$ [21–24]. Also, it should not be related to the modification method employed, since it has been reported that the modification of $LiMn_2O_4$ with similar metal oxide (cobalt oxide) by using mixed-metals codeposition had no effect on the cell voltage [16]. Such increase in the intercalating voltage of $LiMn_2O_4$ may be due to the chemical modification of the spinel to form $LiTi_xMn_{2-x}O_4$, though, it is not very probable, since chemical modification of $LiMn_2O_4$ usually occurs at high temperature (e.g. 600 °C) which were not used here. The exact reaction for the observed increased cell voltage of TiO_2-included $LiMn_2O_4$ cathode is not still clear.

The evolution of capacity during cycling in the potential range of 3.0–4.3 V at C/5 rate and room temperature of the modified and unmodified $LiMn_2O_4$ electrodes is compared in Fig. 2. The results indicate that the incorporation of titanium oxide within the $LiMn_2O_4$ film deposited, significantly reduces the capacity fade of $LiMn_2O_4$.

As the main problem for the use of $LiMn_2O_4$ is the capacity fade at elevated temperatures, the experiments were also

carried out at 60 °C. Fig. 3 clearly shows that the capacity fade of $LiMn_2O_4$ at elevated temperatures can be significantly reduced by the incorporation of titanium oxide into the $LiMn_2O_4$ film. Although the influence of temperature to increase the initial capacity is stronger for unmodified $LiMn_2O_4$ [10], the initial capacity of the modified $LiMn_2O_4$ electrode is still higher than that of the unmodified $LiMn_2O_4$ electrode. The XRD pattern in the discharged state after cycling at 60 °C for over 100 cycles displays significant peak broadening, which indicates structural degradation and a decrease of crystallinity of the $LiMn_2O_4$ electrode prepared by the gold codeposition method. Whereas, such behavior is not shown in the $LiMn_2O_4$ electrode prepared by the mixed-metals (gold–titanium) codeposition method.

Similar results were also obtained for storage at elevated temperatures. Table 1 shows the capacity loss of both electrodes stored at 70 °C for 48 h. The values of capacity fading percentage (CFP) of the electrodes indicate the ratio of the difference in discharge capacity before and after the storage divided by the discharge capacity before the storage. The amount of Mn dissolved during the storage was estimated by the measurement of the amount of Mn dissolved in 10 ml of the supporting electrolyte used for the storage. The results obviously suggest that the approach proposed for the surface modification of $LiMn_2O_4$ spinel with TiO_2 is useful to reduce capacity fading of $LiMn_2O_4$ stored at elevated temperatures.

For further investigation of the improvement achieved by the modification approach proposed, effects of both storage temperature and time on the capacity fading and the Mn dissolution at fully charged state were examined in detail. As expected, Mn dissolution and consequently the capacity loss of the cathode material increase by increasing storage
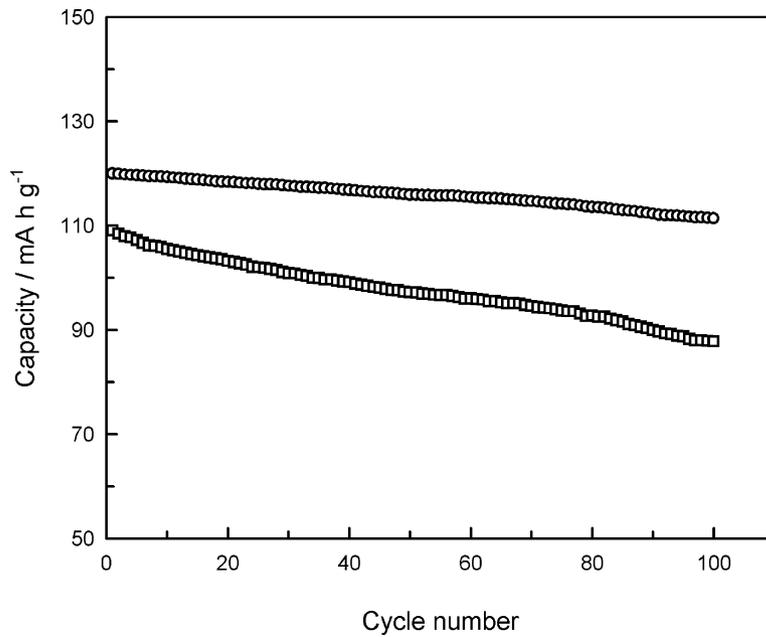
Fig. 2. The variations of the capacity for the cells with the modified $LiMn_2O_4$ (□) and the unmodified $LiMn_2O_4$ cathodes (○) during charge–discharge cycling at room temperature (25 °C).
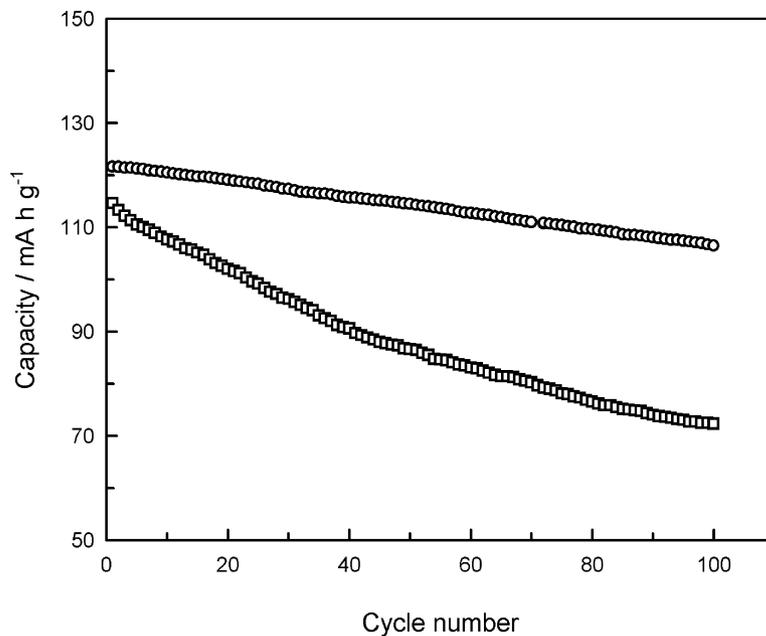

Fig. 3. The variations of the capacity for the cells with the unmodified $LiMn_2O_4$ (□) and the modified $LiMn_2O_4$ (○) cathodes during the charge–discharge cycling at the elevated temperature of 60 °C.

Table 1
Specific capacity and capacity fading of both unmodified $LiMn_2O_4$ electrode and TiO_2-modified $LiMn_2O_4$ electrodes after storage at 70 °C for 48 h

Electrode	Concentration of dissolved Mn (μg)	Specific discharge capacity (mA h/g)		CFP[a] (%)
		Before storage	After storage	
Unmodified $LiMn_2O_4$	2.55	115.3	65.7	43
Modified $LiMn_2O_4$	0.51	121.9	104.8	14

[a] CFP = [(discharge capacity before storage − discharge capacity after storage)/discharge capacity before storage] × 100.

Table 2
Specific discharge capacity performances of the TiO_2-modified $LiMn_2O_4$ electrode after storage at different temperatures for 48 h

Storage temperature (°C)	Concentration of dissolved Mn (µg)	Specific discharge capacity (mA h/g)		CFP[a] (%)
		Before storage	After storage	
25	0.19	119.6	110.4	7.7
40	0.32	120.1	109.0	9.2
50	0.40	121.0	108.1	10.6
60	0.44	121.6	105.6	13.1
70	0.51	121.9	104.8	14.0
80	0.56	122.5	102.2	16.6

[a] CFP = [(discharge capacity before storage − discharge capacity after storage)/discharge capacity before storage] × 100.
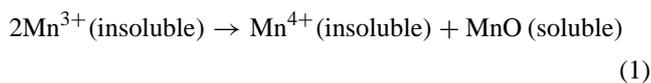
Table 3
Specific discharge capacity performance of the TiO_2-modified $LiMn_2O_4$ electrode stored at 70 °C for different storage times

Storage time (h)	Concentration of dissolved Mn (µg)	Specific discharge capacity (mA h/g)		CFP[a] (%)
		Before storage	After storage	
6	0.31	121.9	119.0	2.4
12	0.37	121.9	116.2	4.7
24	0.39	121.9	113.5	6.9
36	0.45	121.9	109.8	9.9
48	0.51	121.9	104.8	14.0

[a] CFP = [(discharge capacity before storage − discharge capacity after storage)/discharge capacity before storage] × 100.

temperature or time (Tables 2 and 3). The results are indicative of the fact that capacity fading of the $LiMn_2O_4$ cathode is negligible for the TiO_2-modified $LiMn_2O_4$ electrode fabricated with the mixed-metal codeposition method. This suggests that the cathode proposed is suitable for the practical application, as it overcomes the problem of capacity fading of $LiMn_2O_4$. The surface modification of $LiMn_2O_4$ with titanium oxide proposed here can reduce the capacity fade of $LiMn_2O_4$ during both cycling and storage at elevated temperatures. This is also accompanied by the better battery performance at room temperature. The improvement of the $LiMn_2O_4$ cyclability achieved here is comparable with those reported in the literature [8–10]. Furthermore, the present material has another interesting feature due to the simplicity of the fabrication method employed.

To induce the chemically modification of $LiMn_2O_4$, the modifier material is forced to diffuse into the spinel by heating [10], which is not appropriate for the procedure reported here. The metal oxide (TiO_2 is just formed on the surface of the depositing $LiMn_2O_4$ particles, and the present process can be described as surface modification (even rather than physical modification). The surface modification of the spinel can significantly avoid Mn dissolution, which is the main reason for capacity fading of $LiMn_2O_4$. It is described that the instability of spinel in electrolyte solution at elevated temperatures is due to the formation of Mn^{2+} as the result of the following disproportionation reaction [25]:

$$2Mn^{3+} (\text{insoluble}) \rightarrow Mn^{4+} (\text{insoluble}) + MnO (\text{soluble})$$
(1)

According to the values reported in Table 1 for the amount of Mn dissolved for the unmodified and modified $LiMn_2O_4$

electrodes, it is obvious that the surface modification of the spinel with TiO_2 significantly protects the Mn dissolution as a result of reaction (1). In addition, the data presented in Tables 2 and 3 suggest that although the capacity fading of the $LiMn_2O_4$ spinel (as a result of Mn dissolution) is significantly reduced by the approach employed (surface modification), however, Mn dissolution is still responsible for the (slight) capacity fading of the TiO_2-modified $LiMn_2O_4$.

4. Conclusion

The results are indicative of the fact that the incorporation of titanium oxide into the $LiMn_2O_4$ film deposited based on the gold–titanium codeposition method can be applied to improve capacity fade of $LiMn_2O_4$, which is an important need for the practical performances of $LiMn_2O_4$-based lithium battery cathodes. In addition, the simple and efficient approach employed for the $LiMn_2O_4$ deposition can be successfully used for the fabrication of $LiMn_2O_4$ cathodes. Indeed, the advantage of the ability to induce surface modification of $LiMn_2O_4$ makes the method useful as well as usual high-technological methods. Further investigations of different cases may lead to new opportunity for the fabrication of $LiMn_2O_4$ cathodes with improved properties based on the simple method of gold-codeposition.

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