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Mixed-Metals Codeposition as a Novel Method for the Preparation of $LiMn_2O_4$ Electrodes with Reduced Capacity Fades

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Mixed-metals codeposition was introduced as an efficient method for the deposition of cathode materials onto substrate surfaces. The approach proposed was typically used for the deposition of $LiMn_2O_4$ with codeposition of mixed gold-cobalt. The results obtained for the system under investigation showed that the method employed is applicable for lithium secondary battery performance. In addition to the efficient deposition of the cathode material which is of interest for battery applications, the approach was used to incorporate cobalt oxide into the cathode material. It was demonstrated that the metal oxide deposited with the cathode material significantly reduces the capacity fade of $LiMn_2O_4$ in both room and elevated temperatures.
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$LiMn_2O_4$ is one of the most promising candidates for cathode materials for lithium secondary batteries due to its advantages such as low cost, nontoxicity, etc. However, the main disadvantage of $LiMn_2O_4$, which made it unsuitable for commercial performances, is its capacity fade during cycling, particularly at elevated temperatures, $T = 55°C$. Several factors have been reported to be responsible for this behavior: manganese dissolution,[1,2] formation of oxygen deficiency,[3] electrolyte decomposition,[4] Jahn-Teller distortion,[5] cation mixing between lithium and manganese,[6] and loss of crystallinity during cycling.[7] Capacity fade of $LiMn_2O_4$ at room temperature can be successfully reduced by cationic substituting the manganese.[8-10] However, the problem of capacity fade at elevated temperatures is still under investigation. Both chemical and physical modification of $LiMn_2O_4$ with $LiCoO_2$ has been reported to improve the capacity fading of $LiMn_2O_4$ at elevated temperatures.[11-13] Other materials have also been recently reported as candidates of modifiers to improve capacity fading of $LiMn_2O_4$.[14-16]

For the practical performance of lithium-secondary batteries, it is needed to prepare thin films of cathode materials. To this end, several methods have been proposed and used for the deposition of cathode materials. These usual methods for the deposition of cathode materials are based on highly technological techniques such as electron-beam evaporation,[17] rf magnetron sputtering,[18] pulsed laser deposition,[19] and chemical vapor deposition (CVD),[20] etc. The main advantage of these methods is the possibility of adding cation dopants to reduce the capacity fade of $LiMn_2O_4$. However, there is great interest in finding novel approaches with some special capabilities or simpler procedures.

In previous works,[21,22] we have successfully used a gold codeposition method[23] for the preparation of $LiMn_2O_4$ cathodes. Here, we extend this method as an efficient and useful approach for the deposition of $LiMn_2O_4$ for lithium battery applications with the possibility of adding modifiers. In addition to the advantages of available methods (with the possibility of adding dopants), the approach proposed here is very simple. Indeed, it is based on a simple electrochemical codeposition process, which is indicative of the powerfulness of electrochemical methods. As a typical investigation, the approach was successfully used for the preparation of a $LiMn_2O_4$ electrode using a typical metal oxide dopant with excellent electrochemical properties for battery purposes.

Experimental

$LiMn_2O_4$ spinel was synthesized in a similar manner to previous work[24] with a nanostructure. Although, $LiMn_2O_4$ particles as large as 1 μm can be prepared by this synthesis method,[25] small particles (smaller than 100 nm) should be used for the present study, as large particles are not suitable for the codeposition method.[26] A platinum electrode was used as the substrate surface. The deposition of $LiMn_2O_4$ was carried out during codeposition of gold-cobalt on the substrate electrode. In this case, the electroactive material is attached to the substrate surface as the result of occlusion between the gold particles deposited. This is an efficient deposition method, as gold does not provide any electrochemical reaction in the potential range of our experiments. This process was performed using a solution containing 15 g/L potassium gold cyanide, 80 g/L monopotassium phosphate, 70 g/L potassium citrate, and 1.5 g/L cobalt chloride with near-neutral pH which was prepared as the deposition electrolyte. At this pH, cobalt is hydrolyzed to cobalt hydroxide during the deposition process. The cobalt hydroxide generated during the deposition process is transformed to cobalt oxide as the result of heating in the final step. Although, it is mainly transformed to the metal oxide, it is hard to claim the absence of any metal hydroxide. Of course, the existence of metal hydroxide does not make any problem, as metal hydroxide can improve capacity fading of $LiMn_2O_4$ as well as metal oxides.[16] Hydrolization and oxidation of cobalt during electrodeposition have been extensively described in the literature.[27] On the other hand, metal hydroxides usually exist in oxide materials; however, we refer the generated cobalt compound as cobalt oxide. The amount of cobalt incorporated was about 4% (w/w).

A small amount of $LiMn_2O_4$ (*ca.* 40 μg) was also added to the deposition solution (with volume of *ca.* 5 mL). 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. Finally, the electrode was heated at 200°C for 1 h to remove water molecules included to the electroactive film. The addition of a small amount of cobalt oxide does not make any noticeable change in the electrochemical behavior and spectroscopic characteristics of $LiMn_2O_4$, and the results were approximately similar to those reported for the $LiMn_2O_4$ prepared by gold codeposition.[22,23] However, the XRD patterns in the discharged state after cycling at 60°C for over 100 cycles displays significant peak broading, indicating structural degradation and a decrease in crystallinity for the $LiMn_2O_4$ electrode prepared by the gold codeposition method, whereas such behavior disappeared for the $LiMn_2O_4$ electrode prepared by the mixed-metals (gold-cobalt) codeposition method.

The amount of the deposits can be simply determined by weighing the electrode before and after the deposition process. However, this amount is related to the mass of the total deposits including the Au (and also cobalt oxide) codeposited. The amount of Au codepos-

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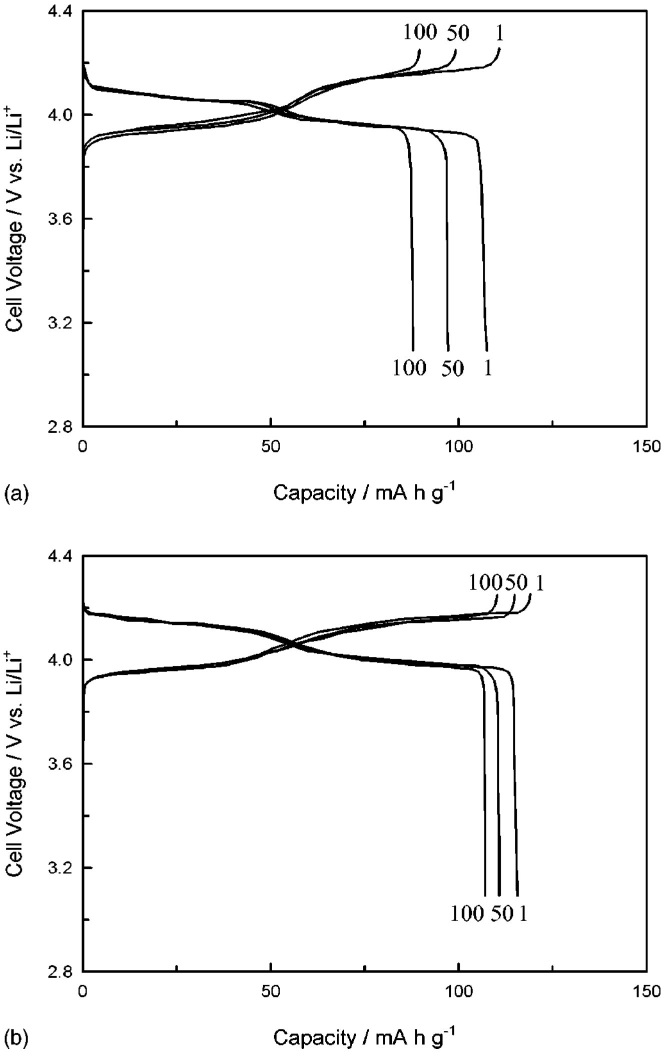

Figure 1. Charge/discharge profiles for the cells with cathodes of (a) the $LiMn_2O_4$ electrode and (b) the cobalt oxide-included $LiMn_2O_4$ electrode recorded with the rate of C/5 at room temperature presented for different cycles (1, 50, and 100).

ited is controlled by the deposition conditions. In our experience, this amount is approximately equal to the amount of $LiMn_2O_4$ attached to the substrate surface. As in the case of the gold-codeposition method in the absence of cobalt, the amount of $LiMn_2O_4$ attached to the substrate surface was 13 μg ± 0.2 and the film thickness estimated by scanning electron microscopy (SEM) was about 2.2 μm.

Results and Discussion

Figure 1 shows typical charge/discharge characteristics of the $LiMn_2O_4$ electrodes prepared based on the gold codeposition and mixed-metals (gold-cobalt) codeposition methods with the rate of C/5. It can be simply concluded from a comparative investigation of the curves that the mixed-metals (*i.e.*, gold-cobalt) codeposition method improves the electrochemical behavior of $LiMn_2O_4$ to gain better battery performance. Interestingly, the first capacity of the cobalt oxide-included $LiMn_2O_4$ electrode is higher than that of the $LiMn_2O_4$ electrode. This is very interesting, as modification of $LiMn_2O_4$ with $LiCoO_2$ decreases the initial capacity of $LiMn_2O_4$.[16]

One may think the capacities reported here for $LiMn_2O_4$ electrodes are lower than usual for $LiMn_2O_4$ electrodes and the theoretical capacity of $LiMn_2O_4$. It is thought that this distinction is related to the existence of gold within the $LiMn_2O_4$ film deposited. As the spinel particles are incorporated within the Au film deposited, some active sites of $LiMn_2O_4$ are covered by the gold codeposit. This means that all of the active sites of $LiMn_2O_4$ are not able to participate in the intercalation/deintercalation processes and the electrode capacity is less than the theoretical capacity of $LiMn_2O_4$. As gold codeposition is a new method for the deposition of $LiMn_2O_4$, further investigations are required to achieve optimum conditions to gain better battery performances. For example, it has been described that the capacity of the $LiMn_2O_4$ electrode prepared based on gold codeposition can be improved by 3D deposition of the electroactive film where more active sites of $LiMn_2O_4$ are available to participate in the intercalation/deintercalation processes.[28]

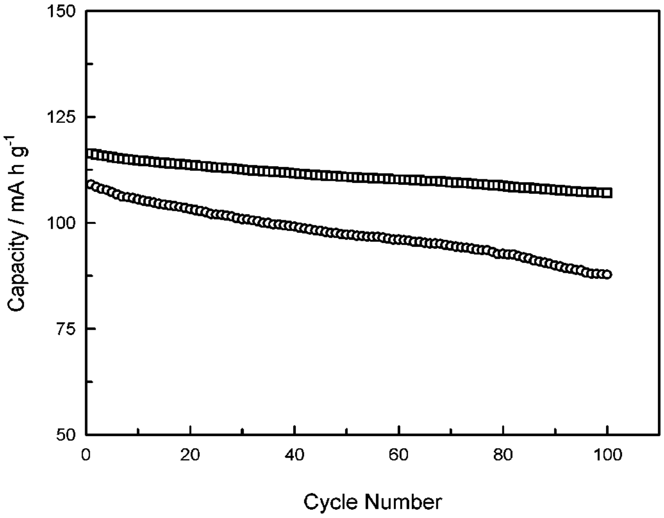

Figure 2. Capacity as a function of cycle number for the cells with cathodes of the $LiMn_2O_4$ electrode (○) and the cobalt oxide-included $LiMn_2O_4$ electrode (□) at room temperature.

Figure 2 illustrates the variation in capacity of the $LiMn_2O_4$ electrodes prepared by the gold codeposition and gold-cobalt codeposition methods during the charge/discharge cycling in the potential range of 3.0-4.3 V with the rate of C/5 at room temperature. As expected, the $LiMn_2O_4$ electrode exhibits a significant loss in the electrode capacity over 100 cycles indicating a significant capacity fade, whereas the cobalt oxide-included $LiMn_2O_4$ electrode has an excellent cycleability over 100 cycles. It is obvious here that the initial capacity of the cobalt oxide-included $LiMn_2O_4$ electrode is higher than that of the $LiMn_2O_4$ electrode.

To investigate the capacity fading phenomenon of the $LiMn_2O_4$ electrode prepared using the mixed-metals (gold-cobalt) codeposition method, the experiments were carried out at an elevated temperature of 60°C (Fig. 3). The results obviously show that capacity fade of the $LiMn_2O_4$ electrode prepared by the gold-cobalt codeposition method is significantly lesser than that of the $LiMn_2O_4$ electrode simply prepared by gold codeposition. Contrary to room temperature, the initial capacity of the cobalt oxide-included $LiMn_2O_4$ electrode at the elevated temperature is lower than that of the $LiMn_2O_4$ electrode. As expected, the initial capacities of both electrodes increases by increasing the temperature. However, this increase is stronger for the conventional (unmodified) $LiMn_2O_4$ electrode in comparison with the cobalt oxide-included $LiMn_2O_4$ electrode. This can be recognized from a comparative investigation of the discharge profiles recorded at room and elevated temperatures, because the initial capacity of the $LiMn_2O_4$ electrode was significantly increases, whereas the initial capacity of the cobalt oxide-included $LiMn_2O_4$ was a little different for the experiments performed at room and elevated temperatures.

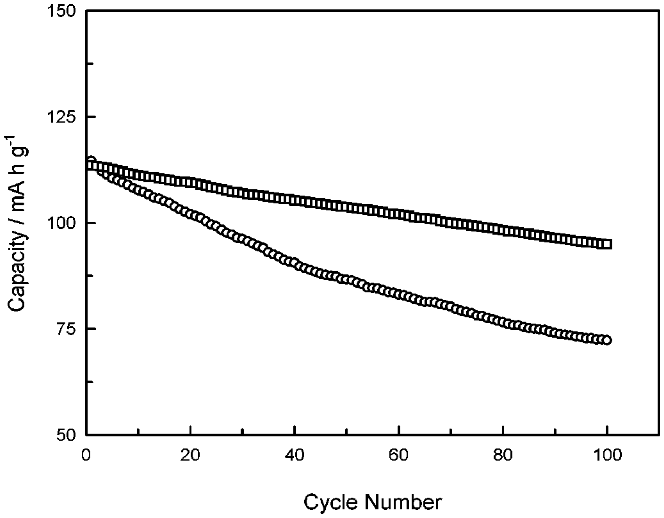

Figure 3. Capacity as a function of cycle number for the cell with cathodes of the $LiMn_2O_4$ electrode (○) and the cobalt oxide-included $LiMn_2O_4$ electrode (☐) at 60°C.

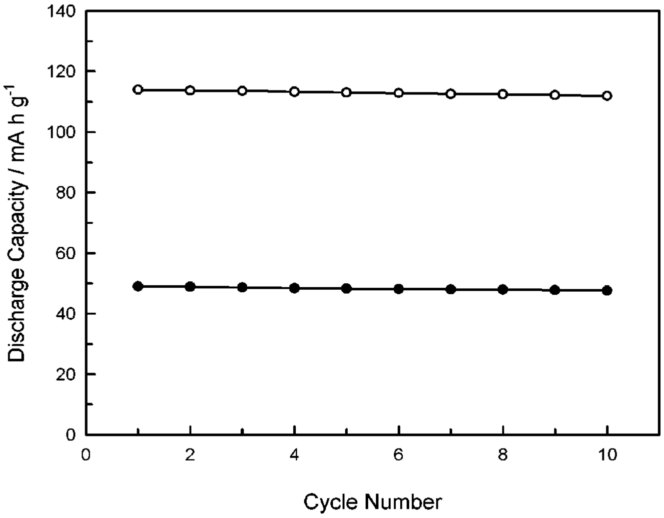

Figure 5. Discharge capacity *vs.* number of cycles for the cobalt oxide-included $LiMn_2O_4$ electrode cycled at room temperature, which was stored in the charged (○) and discharged (●) states for 5 days at 70°C.

Due to the low rate capability of $LiMn_2O_4$ in comparison with $LiCoO_2$, in order to use $LiMn_2O_4$ as a cathode material (an alternative to $LiCoO_2$), it is also necessary to improve its rate capability. To this aim, the rate capabilities of the $LiMn_2O_4$ electrodes prepared by the gold-cobalt codeposition and gold codeposition methods were investigated and compared (Fig. 4). The results are indicative that gold-cobalt codeposition significantly improves the rate capability of $LiMn_2O_4$, which is desirable for its practical performance.

In addition to low cycleability of $LiMn_2O_4$ at elevated temperature, capacity fading during storage at elevated temperature is also an important obstacle in the commercialization of $LiMn_2O_4$ as a cathode material for lithium secondary batteries. Figure 5 presents the capacity loss of the cobalt oxide-included $LiMn_2O_4$ electrode after 5 days storage at the elevated temperature of 70°C. As expected, the gold-cobalt codeposition method also reduces the capacity fading of $LiMn_2O_4$. The electrode stored at the charged and discharged states shows less than 2 and 3% irreversible capacity losses over ten charge/discharge cycles, respectively.

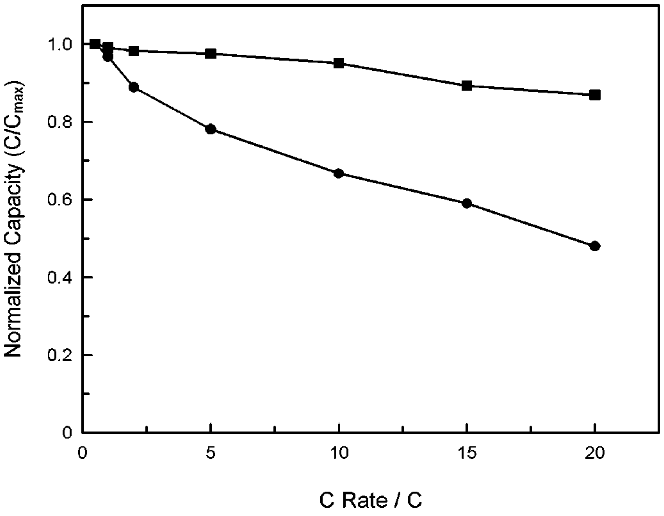

Figure 4. Variations of normalized discharge capacity for the cells with cathodes of the $LiMn_2O_4$ electrode (●) and the cobalt-included $LiMn_2O_4$ electrode (■) as a function of charge-discharge rate recorded at room temperature.

Among different possible reasons for capacity fade of $LiMn_2O_4$, the main reason is Mn dissolution.[29] Indeed, the instability of $LiMn_2O_4$ in the electrolyte solution at elevated temperatures is related to the disproportionation reaction, $2\,Mn^{3+}$ (insoluble) $\rightarrow$ Mn^{4+} (insoluble) + MnO.[30] To overcome this problem, Guyomard and Tarascon[31] have described that reducing the surface area of $LiMn_2O_4$ cathodes is the easiest way to decrease Mn dissolution. However, the best approach is to cover the spinel surface with an insoluble material, which is usually referred to as surface modification. As the cobalt oxide is formed on the depositing $LiMn_2O_4$ particles, surface modification of the spinel with the insoluble oxide is responsible for the reduced capacity fade of the $LiMn_2O_4$ cathode. The improvement in cycling performance of $LiMn_2O_4$ provided by surface modification can be explained within the context of the dissolution mechanism.

We investigated the amount of Mn dissolved during 24 h storage at 70°C in 10 mL of the electrolyte solution for both $LiMn_2O_4$ electrodes. The results showed that 1.87 μg Mn is dissolved from the unmodified $LiMn_2O_4$ electrode, prepared by gold codeposition, where this value is 0.36 μg for the modified $LiMn_2O_4$ electrode, prepared by gold-cobalt codeposition. This provides strong evidence for the fact that surface modification of $LiMn_2O_4$ with cobalt oxide codeposited reduces the Mn dissolution and consequently the capacity fading of the spinel.

Conclusions

A novel method was proposed for the deposition of $LiMn_2O_4$ on substrate surfaces to prepare thin-film cathodes. The method is very simple in comparison with nonelectrochemical methods for the preparation of $LiMn_2O_4$ thin-film cathodes. It is of interest that the approach proposed can also be used for other cathode materials to be deposited on substrate surfaces to fabricate thin-film electrodes. Another important advantage of the method of mixed metals codeposition proposed here is its possibility to incorporate modifiers into the cathode material. The cobalt oxide-included $LiMn_2O_4$ electrode prepared based on this method was suitable for the practical performances, as the electrochemical behavior and cycleability of $LiMn_2O_4$ deposited were significantly enhanced. It was accompanied by high cyclability at elevated temperatures, reduction of capacity fading during storage at elevated temperatures, and enhancement of the rate capability.

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