



# 3D Deposition of $\text{LiMn}_2\text{O}_4$ : enhancement of lithium battery performance

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## Abstract

A film of  $\text{LiMn}_2\text{O}_4$  with 3D macroporous structure was deposited on a substrate surface during gold codeposition. Fractal analysis of the  $\text{LiMn}_2\text{O}_4$  suggested a 3D structure for the film deposited with a fractal dimension approaching 3. Battery performance of a lithium secondary cell employing the 3D  $\text{LiMn}_2\text{O}_4$  cathode was investigated and compared with that of using a conventional  $\text{LiMn}_2\text{O}_4$  cathode. The results indicated that the 3D cathode fabricated has higher capacity in comparison with the conventional cathode. It is due to the existence of higher surface area for lithium intercalation/deintercalation processes. Indeed, 3D structure of the electrode provides chance for the Li deintercalation in three directions.

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## 1. Introduction

$\text{LiMn}_2\text{O}_4$  is one of the promising cathode materials for lithium secondary batteries. Studies of electrochemical behavior and properties of  $\text{LiMn}_2\text{O}_4$  are an active area of research. It is well known that electrochemical behaviors of  $\text{LiMn}_2\text{O}_4$  and other cathode materials for lithium battery applications are strongly dependent on their physical structures.  $\text{LiMn}_2\text{O}_4$  powders with different morphology have been synthesized, displaying different electrochemical behaviors in lithium secondary batteries [1–5].

One of the important factors in the performance of electrochemical systems involving particle-based elec-

trodes is particle size effects. The effects of particle sizes on the electrochemical behavior of  $\text{LiMn}_2\text{O}_4$  in Li intercalation/deintercalation processes have been studied in the literature [6,7]. Fabrication of nanostructured  $\text{LiMn}_2\text{O}_4$  electrodes consisting  $\text{LiMn}_2\text{O}_4$  nanotubes with different sizes has been reported and the influence of particle sizes on their rate capabilities has been described [8]. The influence of pressure applied during the preparation of cathodes on their electrochemical properties for lithium battery performances has also been studied [9]. More recently, we have proposed an efficient method for the fabrication of thin-film  $\text{LiMn}_2\text{O}_4$  cathodes deposited on substrate electrode under centrifugal force with higher capacity [10]. Deposition under centrifugal force provides denser films with ordered structures as the result of preferred directional deposition [11]. In addition, this action increases electrochemical stability

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of the film deposited under centrifugal force [12]. This is due to stronger connection (adhesion) of the electroactive film attached to the substrate surface in the presence of an external (mechanical) force. The ordered structure provided as the result of centrifugal forces causes easier transfer of lithium ions involved in the intercalation/deintercalation processes, which is accompanied by better battery performance.

## 2. Experimental

LiMn<sub>2</sub>O<sub>4</sub> was prepared by a solid-state reaction according to the method proposed previously [13] and was used in our previous works [14,15]. According to the literature, a platinum electrode was used as substrate to deposit the cathode material. The deposition of LiMn<sub>2</sub>O<sub>4</sub> was carried out during deposition of gold on the electrode surface. In this case, the electroactive material will be attached onto 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. Detailed studies of LiMn<sub>2</sub>O<sub>4</sub> spinel deposited by this method have been reported in the literature [16]. This approach has also been used for incorporation of modifier material within LiMn<sub>2</sub>O<sub>4</sub> films to improve cyclability of the cathodes [17,18]. This process was performed using an aqueous solution containing 15 g/l potassium gold cyanide, 80 g/l monopotassium phosphate and 70 g/l potassium citrate with near-neutral pH was prepared as the plating bath. A small amount of LiMn<sub>2</sub>O<sub>4</sub> (ca. 40 µg) was also added to the plating bath. Although the synthesis method proposed in Ref. [13] is able to prepare LiMn<sub>2</sub>O<sub>4</sub> particle as large as 1 µm, only small particles (smaller than 100 nm) can be used, as codeposition is not suitable for the deposition of large particles. On the other hand, as the electroactive material should be deposited within small pores generated on the substrate surface, it is of importance to use small particles, which can be easily incorporated into such pores. 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 10 mA cm<sup>-2</sup> in a warm bath (50 °C). The electrode was washed

thoroughly to remove any potassium ion from its surface.

To obtain a 3D structure, empty pores were generated on the film deposited. For this purpose, polystyrene latex spheres (with size of ca. 400 nm) were also added to the plating bath. Interestingly, the polystyrene latex spheres are self-assembled to both the substrate electrode surface and the gold particles deposited. Then, electrode was thoroughly washed by toluene to remove the polystyrene spheres. The powerfulness of this method for the formation of macroporous substrates has been described in the literature [19]. To cover the bare surfaces beneath the polystyrene latex spheres removed, we repeated the deposition process to form a thin layer of LiMn<sub>2</sub>O<sub>4</sub> without use of polystyrene latex spheres in the plating bath.

This process (the approach proposed for the preparation of 3D electrode) just generates empty pores across the solid film attached to the substrate surface and does not make any change to electrochemical behavior of the cathode material. Indeed, no evidence was observed showing partly reduction of the electroactive material. On the other hand, formation of a solid solution containing Au at the spinel particle is improbable, as this action is usually occurred as the result of thermal treatment. Even for smaller dopants (such as cobalt and aluminum oxides), chemical modifications of the spinel is occurred only by heating at high temperature (e.g., 800 °C) [20], which was not performed in the present research. The properties of the cathode material attached with the 3D deposition method are similar to those reported for the conventional LiMn<sub>2</sub>O<sub>4</sub> electrode prepared with the Au codeposition method [16].

The amount of the deposits can be simply determined by weighing the electrode before and after the deposition process. However, this is related to the mass of total deposits including the Au film deposited. The amount of the deposited Au is controlled by the deposition conditions. In our experience, this amount is approximately equal to the amount of LiMn<sub>2</sub>O<sub>4</sub> attached to the substrate surface. The amount of LiMn<sub>2</sub>O<sub>4</sub> attached to the substrate surface was 13 ± 0.2 µg. This value was also checked by weighing the LiMn<sub>2</sub>O<sub>4</sub> spinel in the deposition bath before and after the deposition process, which is the most reliable method for the estimation of the mass of such

electroactive materials attached to the substrate surface due to the existence of codeposits. Indeed, it is of importance to determine the exact mass of the electroactive material codeposited with Au for the estimation of specific capacity of the cathode. The film thickness estimated by SEM was about 2.2  $\mu\text{m}$ .

A conventional  $\text{LiMn}_2\text{O}_4$  electrode was also fabricated by the Au codeposition method in the absence of polystyrene latex spheres. The mass of  $\text{LiMn}_2\text{O}_4$  deposited for the conventional electrode is approximately double in comparison with the 3D  $\text{LiMn}_2\text{O}_4$  electrode fabricated, as the 3D electrode contains many empty pores during 3D deposition (due to remove of polystyrene latex spheres), but such empty pores are absent in the conventional electrode. These two electrodes (3D and conventional) were compared throughout the research by normalizing the mass of the electroactive film; thus, both electrodes were prepared and investigated at the same conditions. For example, the second deposition process was also done for the conventional  $\text{LiMn}_2\text{O}_4$  electrode to reach the same film thickness. A solution of 1 M  $\text{LiClO}_4$ /propylene carbonate (PC) was used as the electrolyte. The electrochemical measurements were performed using a low-noise homemade potentiostat connected to a computer running Corr-View software.

### 3. Results and discussion

Fig. 1 shows cyclic voltammetric characteristics of the 3D  $\text{LiMn}_2\text{O}_4$  electrode and the conventional  $\text{LiMn}_2\text{O}_4$  electrode with respect to the lithium intercalation/deintercalation processes. Although, the shapes of the CVs are similar, the 3D  $\text{LiMn}_2\text{O}_4$  electrode is accompanied by a stronger electrochemical behavior showing higher peak currents. In addition, the reversible charge is higher for the 3D  $\text{LiMn}_2\text{O}_4$  electrode in accordance with the mass of  $\text{LiMn}_2\text{O}_4$  attached to the substrate electrodes.

Another interesting feature observable in the CVs is related to the peak potentials. Although, the cathodic peaks of different electrodes are approximately occurred at the same potentials, the anodic peaks of the conventional  $\text{LiMn}_2\text{O}_4$  electrode are occurred at more positive potentials in comparison with the 3D  $\text{LiMn}_2\text{O}_4$  electrode. This distinction is indicative of

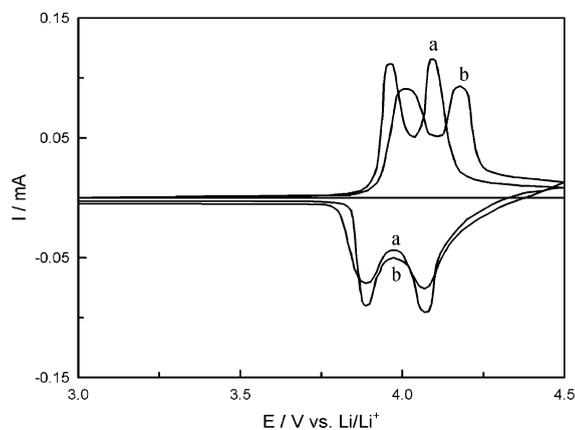


Fig. 1. Typical cyclic voltammetric characteristics of (a) the 3D  $\text{LiMn}_2\text{O}_4$  electrode and (b) the conventional  $\text{LiMn}_2\text{O}_4$  electrode for the  $\text{Li}^+$  intercalation/deintercalation processes in 1 M  $\text{LiClO}_4$ /PC. Scan rate 5  $\text{mV s}^{-1}$ .

the fact that more driving force is needed to instigate the lithium ions to leave the host structure of the cathode to move towards the anode. Indeed, there is a higher mass transfer resistance for the latter case.

Physical reason for this behavior is due to the surface structure and its porosity. In the electrochemical cell, empty spaces and pores of the cathode are filled with the electrolyte. Thus, whatever the size of these pores and spaces be larger, the ion transfer is easier and the mass transfer resistance of the lithium ions is lesser. It is accompanied by less potential needed for the deintercalation process. For the 3D  $\text{LiMn}_2\text{O}_4$  electrode, which has more active sites to participate in the intercalation/deintercalation processes with more empty spaces and pores in its structure, mass transfer resistance is lesser and the lithium ions are easier to transfer across the solid film to joint the electrolyte solution.

In fact, the 3D structure of the  $\text{LiMn}_2\text{O}_4$  electrode fabricated provides 3D diffusion of  $\text{Li}^+$  at the electrode surface. This distinction is illustrated in Fig. 2 (a simple scheme). The pores generated within the solid film provide more empty spaces for easier transport of lithium ions and reduce the mass transfer resistance of  $\text{Li}^+$ .

To shed light on the physical significance of the 3D structure of the  $\text{LiMn}_2\text{O}_4$  electrode, fractal analysis of the electrodes was performed. Fractal dimension of surfaces can be used as a factor for their porosity.

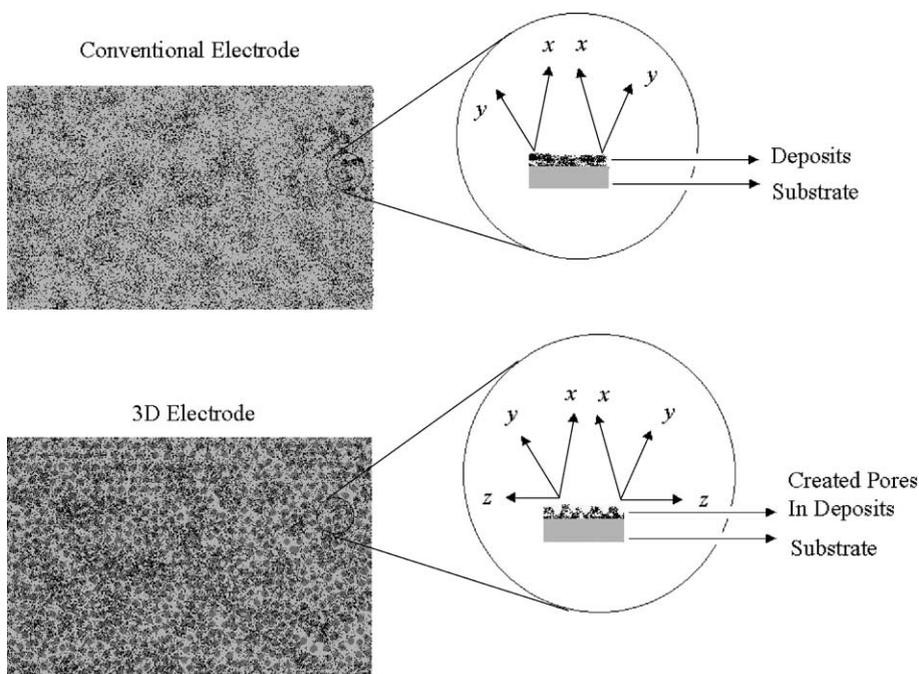


Fig. 2. Schematic of the surface structures of the  $\text{LiMn}_2\text{O}_4$  electrodes. The insets display the possible directions involving in the Li deintercalation process. The gray color was used to show the substrate surface, deep gray for the pores created and black for the deposits.

Although the electrode surface is porous with a macroporous structure, it has a degree of fractality. This fractal structure appears on the walls of the pores, which were covered with the  $\text{LiMn}_2\text{O}_4$  films. Indeed, the generation of macroporous structure does not change surface fractality of deposited  $\text{LiMn}_2\text{O}_4$  films in comparison of conventional  $\text{LiMn}_2\text{O}_4$  film deposited onto a smooth substrate surface. The macroporous structure can be considered as a source of the formation of “ups and downs” on the electrode surface allowing the spinel to be deposited in three directions.

More recently, we have reported the possibility of available electrochemical methods for the determination of fractal dimension of electrode surfaces in lithium battery media [15]. According to Stromme et al. [21], the cathodic peak currents are dependent on scan rate as follows:

$$I_{pc} = \sigma'_F v^\alpha \text{ or } I_{pc} \propto v^\alpha \quad (1)$$

where  $\alpha$  is the fractal parameter. Thus, fractal parameter can be obtained by plotting the peak current against scan rate in a log–log scale. On the other

hand, fractal parameter is related to the fractal dimension of the electrode surface as [22]:

$$\alpha = (D_f - 1)/2 \quad (2)$$

Although this equation has been proposed by de Gennes [23] in somewhat different context, it is also applicable for electrochemical methods as it has been successfully used for calculating the fractal dimension of electrode surfaces based on various diffusion-limited electrochemical techniques.

Fig. 3 illustrates the scan rate dependencies of the cathodic peak currents for different electrodes. According to Eq. (2), the values calculated for the fractal parameter suggest fractal dimensions of  $2.84 \pm 0.02$  and  $2.54 \pm 0.02$  for the 3D  $\text{LiMn}_2\text{O}_4$  electrode and the conventional  $\text{LiMn}_2\text{O}_4$  electrode, respectively. As the fractal dimension of the 3D  $\text{LiMn}_2\text{O}_4$  electrode approaches the value of 3 (theoretical value for space, a 3D object), it is warrant to be called as a 3D electrode. The appearance of such 3D structure is due to the existence of such pores within the solid film operating the third direction actively. Similarly, 3D structure of silica gel with a fractal dimension

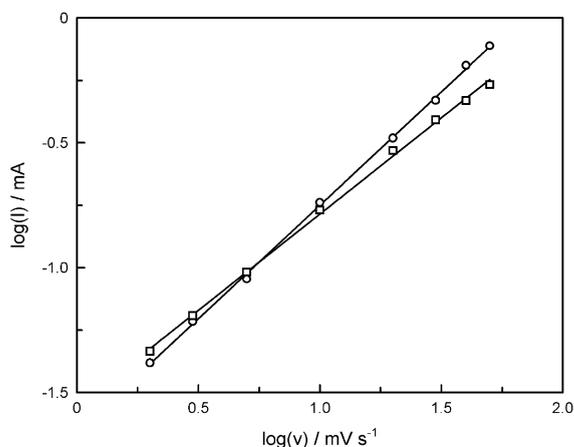


Fig. 3. Scan rate dependencies of the cathodic peak currents for the 3D  $\text{LiMn}_2\text{O}_4$  electrode (○) and the conventional  $\text{LiMn}_2\text{O}_4$  electrode (□). The slopes indicate the values of fractal parameters of electrode surfaces.

close to 3 can be attributed to the existence of pores within the material [24]. It should also be emphasized that the value reported for 3D  $\text{LiMn}_2\text{O}_4$  electrode cannot be claimed to be the exact fractal dimension of the electrode (as report of this value is not the aim of the present study), as for very complex surfaces with significant degrees of roughness, the ideal diffusion towards electrode surfaces cannot be expected. However, the results reported are satisfactory for comparative study. The limitations of electrochemical techniques for the determination of fractal dimension of real electrode surfaces has been recently debated (interestingly, for the system under investigation) [25].

It should also be noted that all conventional cathodes have significant porosity as well as other electroactive film-deposited electrodes. The fractal dimensions of such electrodes are around 2.5, and they are referred to as film electrodes. However, for the system under investigation, a significantly high fractal dimension approaching 3 was determined. Therefore, using 3D term to show this significant different is not inappropriate. Similar nomenclature has been used for highly ordered macroporous materials.

Thus, the results obtained are indicative of the fact that although the electrode proposed has a complex 3D structure; its complexity is closer to the fractal patterns. It can be referred to as an ordered complexity

[26]. It comes from the fact that although, the  $\text{LiMn}_2\text{O}_4$  attached to the substrate surface is complex from microscopic point of view (and even is more complicated than the conventional electrode due to the operation of the third direction), the electrode surface has a factor of order from macroscopic point of view due to the existence of the pores generated within the solid film. It is thought that the intercalation/deintercalation processes are easier to proceed through ordered surfaces, as it has been shown for the ordered electrodes prepared under centrifugal forces [10]. It is also in agreement with fundamentals of diffusion due to less self-interaction of ions. On the other hand, the pores generated in the present research are not very regular (as patterned in Fig. 2), however, highly ordered macroporous surfaces with 3D structures have been widely prepared for different materials using different methods [27].

Discharge curves of both electrodes are presented in Fig. 4. It should be taken into account that specific capacities must be estimated by using the mass of the electroactive material attached to the substrate surface (not total mass of the deposits including Au). The curves obtained for both electrodes are similar to the typical electrochemical characteristics of  $\text{LiMn}_2\text{O}_4$  accompanying with two plateaus. It is obvious that the discharge capacity of the 3D  $\text{LiMn}_2\text{O}_4$  electrode is significantly higher than that of the conventional  $\text{LiMn}_2\text{O}_4$  electrode. One may think that the capacity

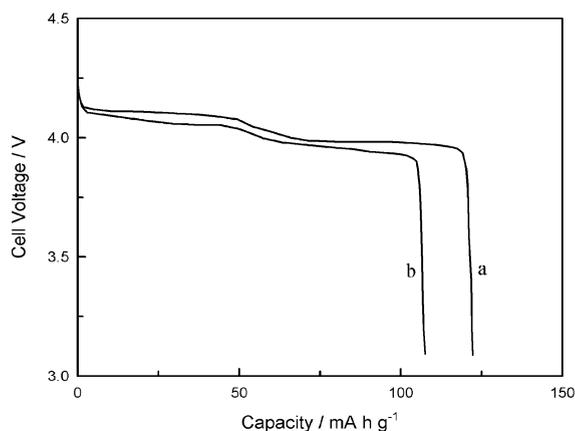


Fig. 4. Discharge characteristics of (a) the 3D  $\text{LiMn}_2\text{O}_4$  electrode and (b) the conventional  $\text{LiMn}_2\text{O}_4$  electrode recorded by cycling between 3.0 and 4.3 V with the rate of  $C/5$ .

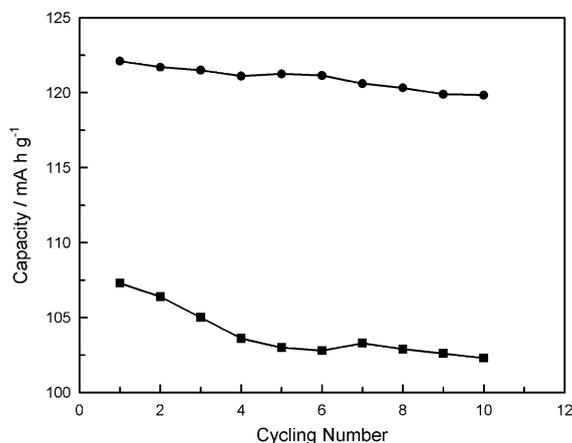


Fig. 5. Plot of the specific discharge capacity versus number of cycles for the 3D LiMn<sub>2</sub>O<sub>4</sub> electrode (●) and the conventional LiMn<sub>2</sub>O<sub>4</sub> electrode (■). The test condition was a current density of 0.2 mA cm<sup>-2</sup> in the potential range between 3.0 and 4.3 V at room temperature.

reported is lower than the usual LiMn<sub>2</sub>O<sub>4</sub> electrodes approaching the theoretical capacity of LiMn<sub>2</sub>O<sub>4</sub>. It is thought that this distinction is related to the existence of gold within the LiMn<sub>2</sub>O<sub>4</sub> film deposited, as may take some active sites of LiMn<sub>2</sub>O<sub>4</sub> participating in the intercalation/deintercalation processes. Our recent works have suggested several approaches to improve battery performance of this newly proposed method of deposition [17,18]. However, as deposition of LiMn<sub>2</sub>O<sub>4</sub> using gold codeposition is a new method, further investigations are required to achieve optimum condition to gain better battery performances. Nevertheless, as this method is simple and electrochemically stable, optimizing to reach an acceptable situation for the practical applications is desirable.

The variations in the specific discharge capacities of both electrodes with the number of cycles are illustrated in Fig. 5. In addition to higher capacity of the 3D LiMn<sub>2</sub>O<sub>4</sub> electrode, the capacity curve of this electrode has higher stability showing a very excellent cycling performance, and, indeed, the changes of the capacity during potential cycling is negligible. Indeed, 3D deposition of the cathode materials significantly improves capacity fades appearing during usage time.

Finally, it is worth noting that the present work was a preliminary investigation to show usefulness of 3D

electrodes for the preparation of cathodes. It is known that electrodes with low porosity are desirable for the commercial performances in order to increase the loading density and hence the energy density. Interestingly, the porosity provided as the result of 3D deposition can be adjusted by other approaches such as the deposition under centrifugal forces. As this is the subject of our future research, in preliminary investigations, we found that 3D deposition under centrifugal forces can provide a porosity similar to conventional LiMn<sub>2</sub>O<sub>4</sub> electrode with doubly improved battery performance.

#### 4. Conclusion

It was demonstrated that by the generation of empty pores within the solid film of the cathode materials deposited onto substrate surfaces, 3D electrodes could be obtained. For the typical 3D LiMn<sub>2</sub>O<sub>4</sub> electrode, it was shown that the electrode has better properties as a cathode material of lithium secondary battery. Due to simplicity of the method proposed, it can be easily used for the fabrication of different cathodes for the battery applications. Generally, the approach can be used for similar purposes such as fabrication of anodes, electrocatalysts and other systems using electrodes with attached materials.

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