

Short communication

## Surface-modification of $\text{LiMn}_2\text{O}_4$ with a silver-metal coating

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### Abstract

Spinel lithium manganese oxides with a nominal composition of  $\text{LiMn}_2\text{O}_4$  are prepared by using a conventional ceramic synthesis method and are coated by a chemical deposition of silver particles. The silver-coated nano-particle  $\text{LiMn}_2\text{O}_4$  shows excellent cycleability at 2 C galvanostatic conditions. The high surface electronic conductivity caused by the metal coating reduces cell polarization. The results indicate that such surface treatment of cathode powders should be an effective way to improve cycle-life with high current retention.

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### 1. Introduction

The demand for compact rechargeable batteries of high specific energy is continuously increasing in concept with advances in portable devices and power sources for automobile electrical systems. Among various candidate power systems, lithium batteries offer the greatest promise for high specific energy and power [1]. Although various positive electrode materials have been studied for lithium-ion batteries,  $\text{LiMn}_2\text{O}_4$  is more attractive than other materials (such as  $\text{LiCoO}_2$  and  $\text{LiNiO}_2$ ) because of its low cost and environmental compatibility [2].

High lithium-ion conductivity and high electron conductivity are essential for the good performance of  $\text{LiMn}_2\text{O}_4$  electrodes in lithium-ion secondary batteries. Guan et al. [1] and Pistoia et al. [3] have reported that the electrical conductivity of the  $\text{LiMn}_2\text{O}_4$  electrode is about  $2 \times 10^{-6} \Omega \text{ cm}^{-1}$ ; while the ionic conductivity is approximately  $10^{-4} \Omega \text{ cm}^{-1}$ . These results suggest that  $\text{LiMn}_2\text{O}_4$  is a mixed ionic-electronic conductor with dominating lithium-ion conduction. Thus, an electronically conductive phase, such as carbon, may be necessary in order to form composite electrode with adequate electronic conductivity [4].  $\text{LiMn}_2\text{O}_4$  electrodes require, however, considerably more carbon than  $\text{LiCoO}_2$  electrodes, which have electrical conductivities of about  $10^{-4}$  to  $10^{-5} \Omega \text{ cm}^{-1}$  [1]. Thus, the

added carbon will reduce the energy efficiency of  $\text{LiMn}_2\text{O}_4$  electrodes.

This study examines the effect on the electrochemical performance of  $\text{LiMn}_2\text{O}_4$  by coating the surface with silver metal. The treatment is expected to affect both the charge–discharge capacity and the cycleability.

### 2. Experimental

$\text{LiMn}_2\text{O}_4$  was synthesized by a solid-state reaction from reagent grade carbonates which were fired repeatedly for 24 h at 800 °C. Reagents of  $\text{MnCO}_3$  (Junsei Chemicals; 99%) and  $\text{Li}_2\text{CO}_3$  (Junsei Chemicals; 99%) were used as starting materials. The product was characterized by X-ray power diffraction analysis.

The flow chart of the synthesis procedure for metal coating is shown in Fig. 1. Water and ethanol were mixed in a beaker and heated to 80 °C on a hot plate. The weight ratio of  $\text{AgNO}_3$  and  $\text{LiMn}_2\text{O}_4$  was 5[ $\text{AgNO}_3$ ]/95[ $\text{LiMn}_2\text{O}_4$ ]. The powder was suspended in the solution which was stirred vigorously with a magnetic stirrer. Then, a reducing agent such as  $\text{NH}_4\text{OH}$ ,  $\text{HCHO}$  was added to the solution to reduce  $\text{Ag}^+$  ions and thereby deposit nano-scale, ultra-fine, silver particles on the  $\text{LiMn}_2\text{O}_4$  powder. The residual substances were separated by filtration with a vacuum pump rinse machine and water. After drying the powder in vacuum, it was used for the preparation of a silver-coated  $\text{LiMn}_2\text{O}_4$  cathode. Scanning electron microscopy (SEM) was employed to examine the morphology of the powder, and energy dispersed

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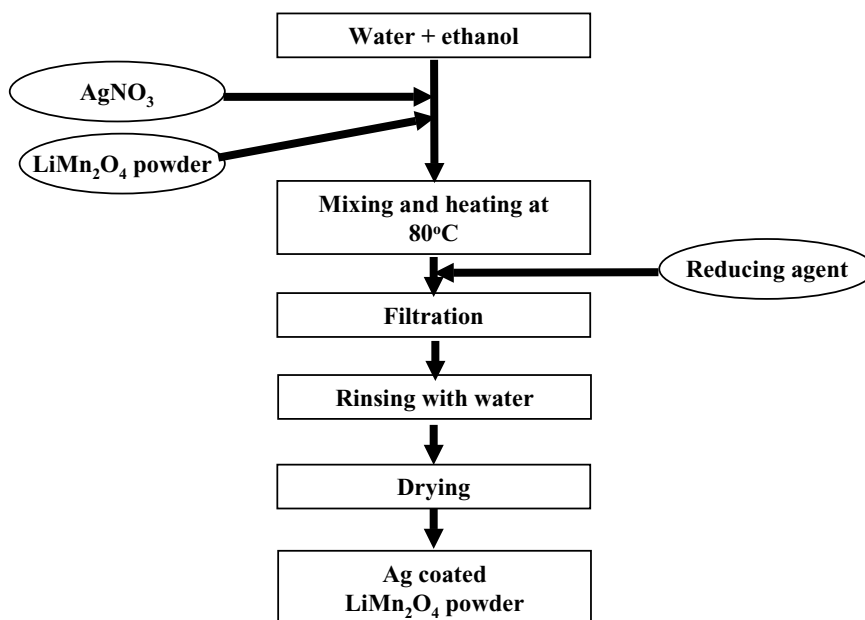


Fig. 1. Flow chart of synthesis of silver-coated  $\text{LiMn}_2\text{O}_4$ .

X-ray analysis (EDAX) was used to examine the uniformity and thickness of the metal coating.

A cathode electrode was prepared by mixing  $\text{LiMn}_2\text{O}_4$  powder with 10 wt.% carbon black (Vulcan, XC-72) and 5 wt.% PVDF (poly-vinylidene fluoride) in NMP (*N*-methyl pyrrolidinone) solution. The stirred mixture was spread onto a 316 stainless-steel ex-met.

The electrode specimens were dried under a vacuum at  $120^\circ\text{C}$ .

A three-electrode cell was constructed for charge–discharge experiments. Lithium foil (Foote Mineral, 99.9%) was used for both the reference and the counter-electrodes. The electrolyte was 1 M  $\text{LiClO}_4$  in propylene carbonate (pre-mixed at Mitsubishi Chemicals). Galvanostatic charge–discharge experiments were performed using a potentiostat/galvanostat (EG&G PARC Model 263). The cut-off voltage was set at 4.3 and 3.0 V for charge and discharge, respectively, at a current rate of 2 C.

### 3. Results and discussion

The surface morphology of the silver-coated  $\text{LiMn}_2\text{O}_4$  powder, in which the silver content was 3.2 wt.%, is presented in Fig. 2(a). Very small white spots were found to be highly dispersed on the  $\text{LiMn}_2\text{O}_4$  powders. The spots were identified as silver metal by energy dispersed X-ray analysis (Fig. 2(b)). The diameters of the silver particles are in the range of 10–100 nm. Uniformly coated  $\text{LiMn}_2\text{O}_4$  has an extremely low resistance and can therefore enhance the surface intercalation reaction. Under 2 C current conditions (Fig. 3), the silver-coated  $\text{LiMn}_2\text{O}_4$  has a high discharge voltage and a capacity that is mainly the result of a reduction in cell polarization through a decrease in electronic conductivity.

If the silver content is too high, the coated layer forms a barrier to the movement of Li ions, which results in a poor initial specific capacity [5]. In the present study, however, a  $\text{LiMn}_2\text{O}_4$  electrode coated with 3.2 wt.% Ag exhibits no

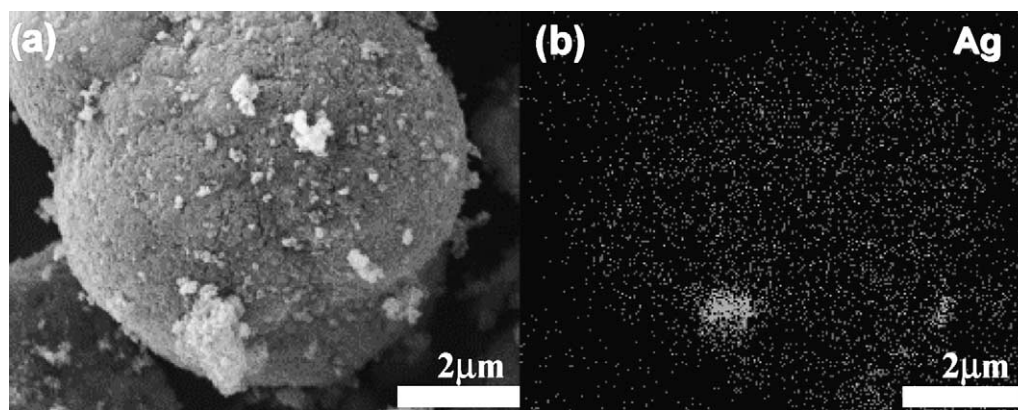


Fig. 2. (a) Scanning electron micrograph of silver-coated  $\text{LiMn}_2\text{O}_4$  and (b) corresponding silver-distribution map obtained by energy dispersed X-ray analysis.

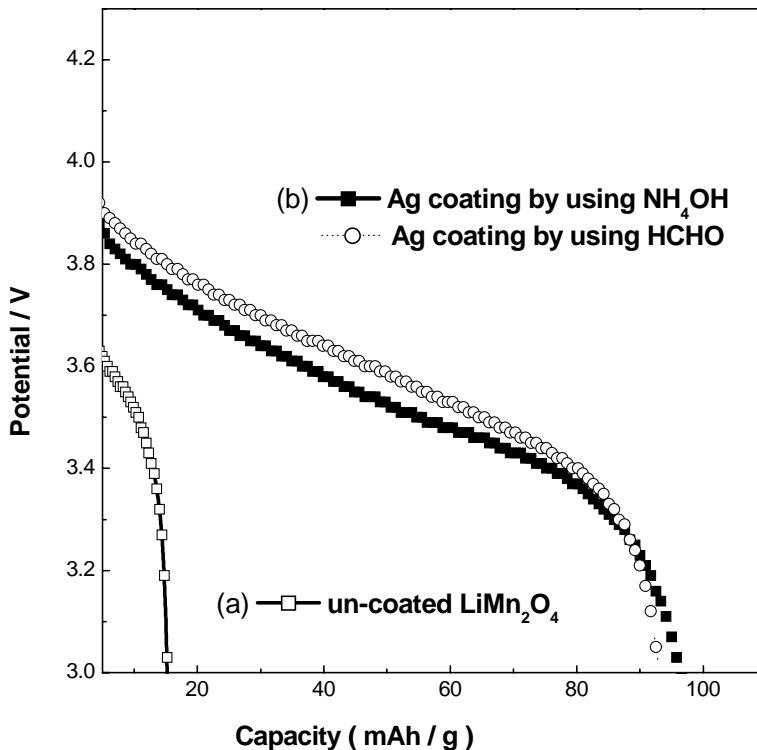


Fig. 3. Initial discharge curve of LiMn<sub>2</sub>O<sub>4</sub> under 2C galvanostatic conditions: (a) uncoated LiMn<sub>2</sub>O<sub>4</sub> and (b) silver-coated LiMn<sub>2</sub>O<sub>4</sub>.

lowering of initial capacity. This indicates that the porous coating does not hinder Li ion movement on the electrode surface.

The electrochemical cycling behavior of uncoated and silver-coated LiMn<sub>2</sub>O<sub>4</sub> electrodes is presented in Fig. 4. The

data show that the silver-coated electrode has superior cycling performance and higher capacity. The improved cycleability may be attributed to enhanced electron conduction between LiMn<sub>2</sub>O<sub>4</sub> particles, because of the low resistance of silver.

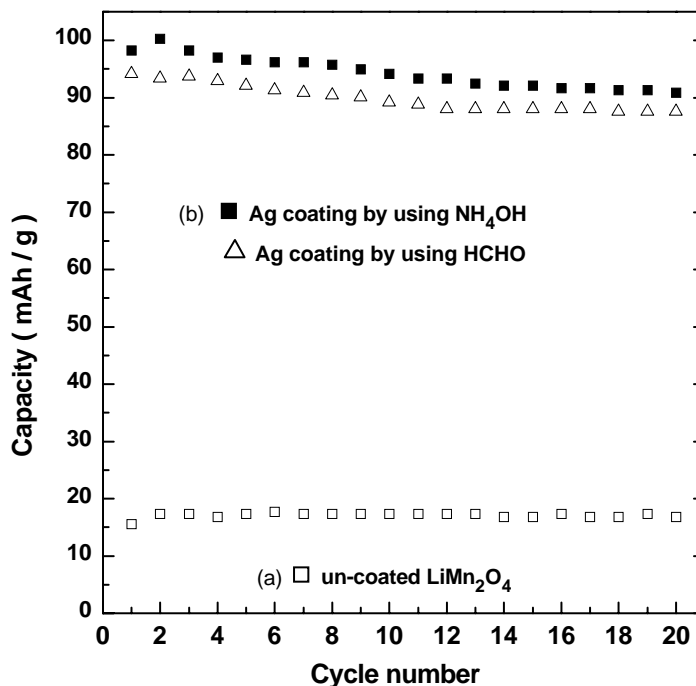


Fig. 4. Cycle efficiency of LiMn<sub>2</sub>O<sub>4</sub> under 2C galvanostatic conditions: (a) uncoated LiMn<sub>2</sub>O<sub>4</sub> and (b) silver-coated LiMn<sub>2</sub>O<sub>4</sub>.

#### 4. Conclusions

The electrochemical performance of  $\text{LiMn}_2\text{O}_4$  as a cathode in Li-ion batteries has been investigated.  $\text{LiMn}_2\text{O}_4$  treated with a silver coating (3.2 wt.% Ag) gives higher charge-discharge capacity and lower cell polarization than an untreated electrode. The improved cycleability is attributed to enhanced electron conduction between  $\text{LiMn}_2\text{O}_4$  particles, because of the low resistance of silver.

Surface treatment of  $\text{LiMn}_2\text{O}_4$  powder suggests a new approach to the development of alternative commercial cathodes to  $\text{LiCoO}_2$  for application in lithium-ion batteries.

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