Int. J. Electrochem. Sci., 10 **(2015)** 3841 - 3847

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

The Properties of $LiMn_2O_4$ Synthesized by Molten Salt Method Using MnO_2 as Manganese Source Recycled from Spent Zn-Mn Batteries

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Received: 24 Janary 2015 / *Accepted:* 27 February 2015 / *Published:* 23 March 2015

The spinel $LiMn_2O_4$ materials were successfully synthesized by Molten Salt method at different temperature using KCl as the molten salt, whose manganese source is γ-MnO_2 recycled from used Zn-Mn batteries with oxalic acid and sodium persulfate as reagents via several redox reactions. The influence of calcination temperature and surface fabrication with ZnO coating upon electrochemical performance has been investigated. The results showed that the spinel $LiMn_2O_4$ materials calcined at 770 °C for 4 hours exhibited good electrochemical performance, that surface modification can improve the good electrochemical performance greatly, especially the cycle performance at high current density. This method to prepare spinel $LiMn_2O_4$ materials provides an alternative way to recycle spent Zn-Mn batteries.

Keywords: Battery recycle; Molten Salt method; $LiMn_2O_4$; Lithium ion batteries; Cathode material

1. INTRODUCTION

In recent years, the number of spent Zn-Mn batteries has been increasing significantly mainly due to its convenience when used in electric equipment like radios, watches. More than 15 billion Zn-Mn batteries were produced annually in China after 2002 [1]. Many batteries still are landfilled or incinerated, instead of being collected and recycled. When corroded by the air and rain, a mass of metal element like Hg, Cu and Zn will infiltrate into water and accumulate in our bodies by food chain, so it is an urgent to recycle the used batteries from the view of environment protecting and resource recycling.

Recently, spinel $LiMn_2O_4$ as cathode materials for lithium-ion battery has attracted more and more investigations because of its low cost, richness in natural sources and low toxicity [2-4]. However, the application of $LiMn_2O_4$ is limited owing to its capacity delay in the charge-discharge cycle process caused by Jahn-Teller distortion, dissolution of manganese into organic electrolyte, and decomposition of electrolyte solution on the electrode [5]. Surface modification is proved to be an important method to reduce the side reaction between the electrode and electrolyte to lower the manganese dissolving in electrolyte. For example, oxides like SiO_2 [6], La_2O_3 [7], and Al_2O_3 [8] were used to minimize the direct contact between $LiMn_2O_4$ and the electrolyte,

In this study, the spinel $LiMn_2O_4$ materials were synthesized by Molten Salt method at different temperature using KCl as the molten salt, whose manganese source is γ-MnO_2 recycled from used Zn-Mn batteries with oxalic acid and sodium persulfate as reagents via several redox reactions. In addition, surface fabrication with ZnO coating upon electrochemical performance has also been investigated.

2. EXPERIMENTAL

2.1 Preparation of MnO_2

Spent Zn-Mn batteries used as raw materials were dismantled into scrap and powders, and then the washing treatment was carried out to separate the plastics, the iron sheet and so on. Residues were calcined with a tube furnace at 750 °C for 4 hours in a constant air flow to collect the Hg and its chemical compound, and then leached in 0.5 mol L^{-1} $H_2C_2O_4$ containing 1mol L^{-1} H_2SO_4 with magnetic stirring at 75 °C for 2 hours. The resulting solution was filtered in time. The filtrate was heated at 90 °C, and then persulfate was added with sufficient magnetic stirring for 4 hours. After having been aged for 3 hours, the solution was filtered. In order to further improve the purity of the MnO_2, the filter residue would be subjected with the following sequence of operations. The product was washed with deionized water until SO_4^{2-} was non-existent, and then dried at 80 °C for 8 h.

2.2 Synthesis the $LiMn_2O_4$

$LiMn_2O_4$ powder was prepared by molten salt method, stoichiometric amount of lithium carbonate and MnO_2 recycled were ground in a mortar, potassium chloride was added as molten salt, the total molar of KCl was four times to that of the Li^+. The mixture was milled with ethanol as dispersant, dried at 100 °C until the ethanol volatilized, and then calcined at 770, 810 and 850 °C for 4 h separately. Amount of product was dissolved into deionized water, after filtration the residues were washed with deionized water, finally dried at 80 °C.

2.3 Synthesis of ZnO-coated $LiMn_2O_4$

The ZnO-coated $LiMn_2O_4$ was synthesized by solid phase method at the calculation of 5 mol% by using zinc acetate as the coating of raw materials. The prepared $LiMn_2O_4$ powder was mixed with zinc acetate thoroughly with deionized water as dispersant. The mixture was dried at 100 °C for 4 hours, and then calcined at 750 °C for 4 hours to form $LiMn_2O_4$ coated with a thin layer of ZnO.

2.4 Characterization

The phase analysis of all materials was carried out by the powder X-ray diffraction, the 2θ angel ranged from 10 to 70°. The surface morphology and particle size were characterized by scanning electron microscope.

2.5 Electrochemical evaluation

The cathode was fabricated with 75 wt% active materials, 20 wt% carbon black and 5 wt% polyvinylilene fluoride binder, then applied onto the aluminum foil. The foil was assembled into a button battery using the lithium wafers as negative pole and 1.0 M $LiPF_6$ as the electrolyte. The galvanostatic charge-discharge measurement was carried out on the LAND CT2001A at room temperature, the cycle experiment was conducted between 3.2 and 4.4 V.

3. RESULTS AND DISCUSSION

3.1 XRD analysis

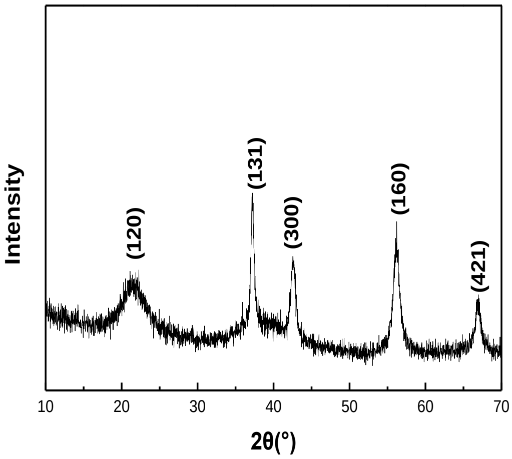

Figure 1. XRD patterns of the obtained MnO_2

Fig. 1 is the XRD pattern of the obtained MnO_2 powders recycled from spent Zn-Mn batteries using redox method. All the diffraction peaks in the XRD pattern can be indexed to the γ-MnO_2 [9]. XRD results in Fig. 2 show the crystal structure, phase and lattice of as-prepared bare $LiMn_2O_4$ synthesized at different temperature (770, 810 and 850 °C), and ZnO-coated $LiMn_2O_4$. All the $LiMn_2O_4$ cathode materials were synthesized by molten salt method with MnO_2 as manganese source recycled from spent Zn-Mn batteries. The strong and sharp peaks indicate that the as-prepared products are highly crystallized. All the diffraction peaks in the XRD pattern agree with those from the JCPDS 35-0782 card corresponding to the cubic spinel structured $LiMn_2O_4$ with a space group of Fd3m [10]. No other detectable peaks from impurities are observed, indicating the high purity of the synthesized products.

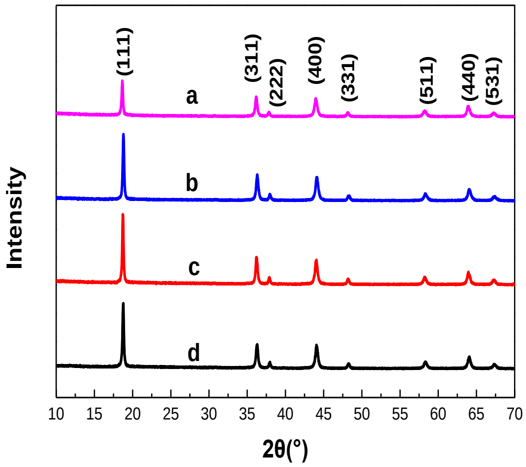

Figure 2. XRD patterns of the materials. (a)ZnO-coated $LiMn_2O_4$ and $LiMn_2O_4$ powders calcinated at (b)810 °C, (c)850 °C and (d)770 °C

3.2 SEM analysis

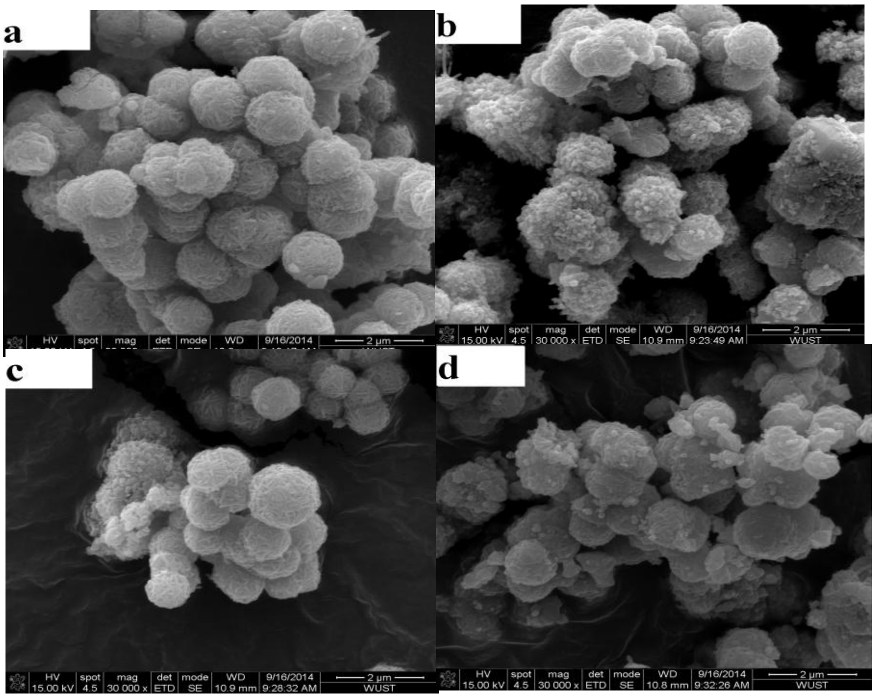

Figure 3. SEM images of $LiMn_2O_4$ synthesized at (a)810 °C, (b)850 °C, (c)770 °C and (d)ZnO-coated $LiMn_2O_4$

Fig. 3 is the SEM images of ZnO-coated $LiMn_2O_4$ and bare $LiMn_2O_4$ powders. The bare $LiMn_2O_4$ synthesized at 770 °C, 810 and 850 °C present spherical morphology and well distributed particle size of about 1-2 μm. The spherical morphology of 850 °C is not so regular. From the bottom right inset of Fig. 3d, we can see that the surface morphology of the ZnO-coated $LiMn_2O_4$ is distinctly different from that of the bare. The agglomeration occurred and particles emerged randomly after surface treatment. It revealed that the loose films made the randomly shaped particles. From the SEM morphology of the ZnO-coated and the fact that no other phases appeared in the XRD pattern, it is concluded that the ZnO layer was amorphous rather than crystalline.

3.3 Electrochemical characterizations

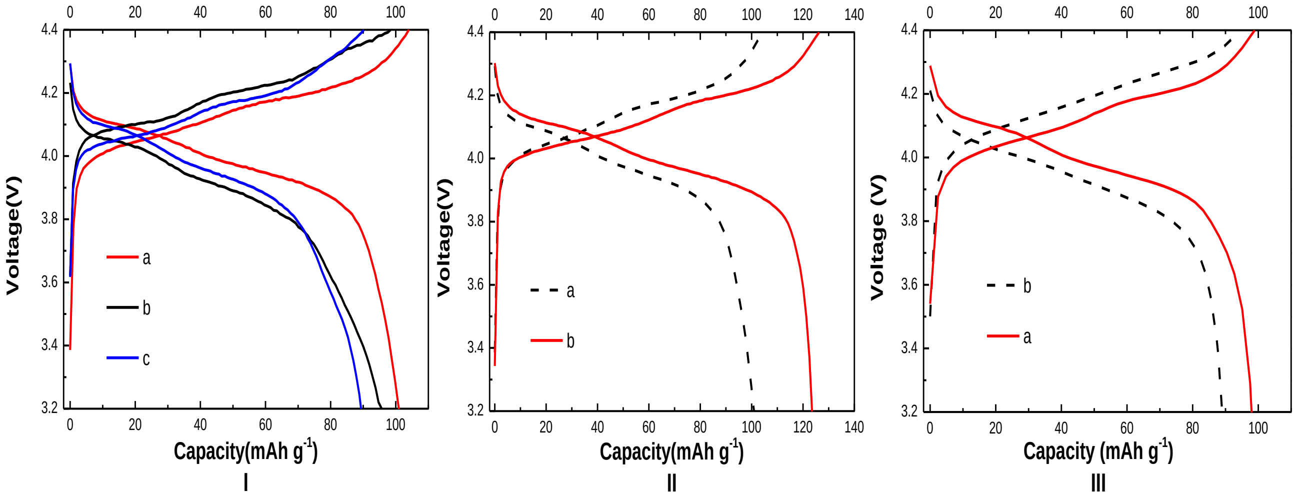

Figure 4. The initial charge-discharge curves of $LiMn_2O_4$ (I)calcined at different temperature (a)770 °C, (b)850 °C and (c)810 °C.(II) (a)bare and (b)ZnO-coated at 0.2 mA cm^{-2}. (III) (a) bare and (b)ZnO-coated at 0.4 mA cm^{-2}

The practical capacity of synthesized spinel were investigated using the Li// $LiMn_2O_4$ cells subjected to constant current cycling. The Li metal acted as both working and reference electrodes, while $LiMn_2O_4$ was treated as counter electrode. Fig. 4(I) shows the initial charge-discharge curves of $LiMn_2O_4$ synthesized at different temperature with a current density of 0.2 mA cm^{-2} between 3.2 and 4.4 V. It is obvious that calcination temperature can make a big difference to the electrochemical performance of the as prepared cathode material, which is consistent with the findings of previous research [11, 12]. In comparison with the sample prepared at 770 °C delivers a large initial discharge capacity of 103.6 mAh g^{-1}, while the samples prepared at 810 °C, 850 °C show a smaller capacity of 91.5 mAh g^{-1}, 95.2 mAh g^{-1}, respectively.

Fig. 4(II) is the first cycle capacity of the bare and ZnO-coated $LiMn_2O_4$ calcined at 770 °C at a current density of 0.2 mA cm^{-2}. In the picture, the charge curve exhibited two plateaus between the voltage 4.05 and 4.25 V, meanwhile, the discharge curve had two plateaus as the voltage varies from 4.15 V to 3.95 V, which represented the two stage intercalation/de-intercalation process of lithium in spinel $LiMn_2O_4$ associated with lithium occupation of tetrahedral sites, in agreement with previous works [13,14], indicating the ZnO-doping didn't change the electrochemical reaction of lithium-ion during charge/discharge process.

In Fig. 4(III), the bare and ZnO-coated $LiMn_2O_4$ were treated at a current density of 0.4 mA cm^{-2}, and had similar charge-discharge profiles in the first cycle charge and discharge curves. Besides, ZnO-coated materials exhibited a higher capacity than the bare at a relative low current density.

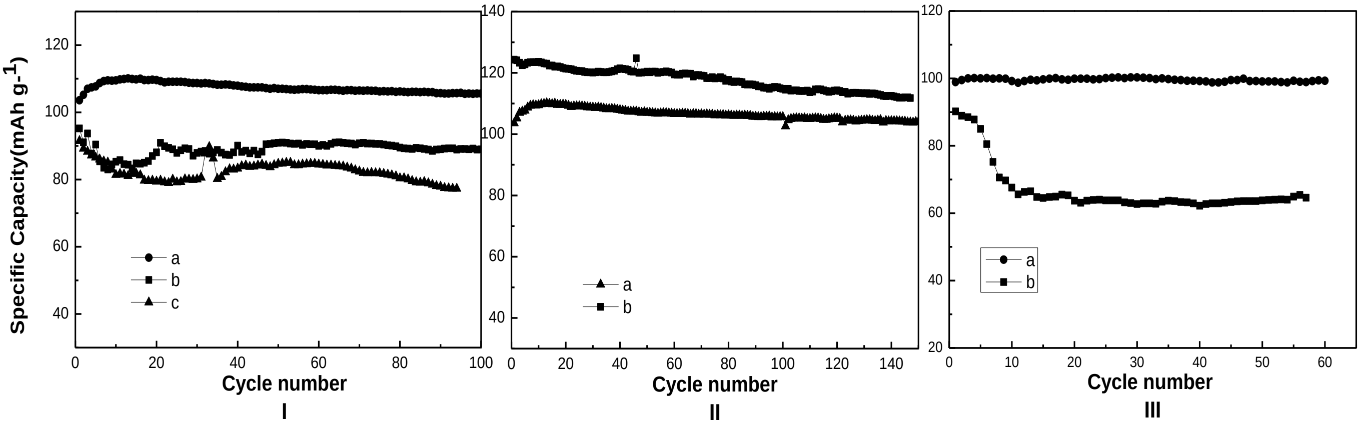

Figure 5. The cycling performance of the powders. (I)Synthesized at (a)770 °C, (b)850 °C and (c)810 °C. (II)The bare(a) and ZnO-coated $LiMn_2O_4$(b) at 0.2 mA cm^{-2}. (III)ZnO-coated $LiMn_2O_4$(a) and bare $LiMn_2O_4$(b) at 0.4 mA cm^{-2}

Fig. 5(I) shows the cyclability of bare $LiMn_2O_4$ calcined at different temperature at 0.2 mA cm^{-2}. It is obvious that $LiMn_2O_4$ calcined at 770 °C has much better cyclability than the others. After 100 cycles, capacity retention for 770 °C, 810 °C, 850 °C, is about 101.9 %, 84.4 % and 93.5 %, respectively. Fig. 5(II) and Fig. 5(III) shows the comparison of cycle performance between the bare and ZnO-coated $LiMn_2O_4$ at two different current densities, 0.2 mA cm^{-2} and 0.4 mA cm^{-2}. As observed, the coated exhibits superior electrochemical performance than the bare, especially the cyclability at high current density. The capacity retention of the bare $LiMn_2O_4$ is only 71.4 % over 60 cycles, while 100 % is obtained for ZnO-coated $LiMn_2O_4$, which is attributed to the reduced contact area between the electrode materials [15]. The specific discharge capacities reduce upon increase of the current density, due to the diffusion-controlled kinetics of the lithium extraction/insertion reactions [16, 17].

4. CONCLUSIONS

The spinel $LiMn_2O_4$ powders with excellent phase-pure particles could be prepared by molten salt method with KCl as the molten salt, whose manganese source is γ-MnO_2 recycled from used Zn-Mn batteries with oxalic acid and sodium persulfate as reagents via several redox reactions, which provided an alternative way to recycle spent Zn-Mn batteries. Calcination temperature can make a big difference to the electrochemical performance of the final cathode material. ZnO coating could improve the electrochemical properties of spinel $LiMn_2O_4$.

ACKNOWLEDGEMENTS
This study was supported by the Nature Science Foundation of Hubei Province (No. 2012FFB04906), and the Nature Science Foundation of Wuhan University of Science and Technology (No. 2011xz012).

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