

A Modification of LiMn_2O_4 by Ionic Conductive Agent and Electronic Conductive Agent Coating

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Keywords: Electronic Conduction, Ionic Conduction, LMO/LSO/C

Received: December 11, 2023

Accepted: January 20, 2024

Published: January 23, 2024

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ABSTRACT

Carbon was used as electronic conductive agent, and metasilicic acid lithium (Li_2SiO_3) as ionic conductive agent, the two factors were investigated cooperatively. We evaluated their effect by using spherical spinel LiMn_2O_4 which prepared ourselves as cathode material. Then Li_2SiO_3 /carbon surface coating on LiMn_2O_4 (LMO/C/LSO) which Li_2SiO_3 inside and carbon/ Li_2SiO_3 coated LiMn_2O_4 (LMO/LSO/C) were prepared, All of materials were characterized by X-ray diffraction (XRD) and electrochemical test; spherical LiMn_2O_4 was characterized by scanning electron microscopy (SEM); and coated materials were characterized by transmission electron microscopy (TEM). While uncoated spinel LiMn_2O_4 maintained 72% of capacity in 60 cycles by the rate of 0.2C, and LMO/LSO/C showed the best electrochemical performance, 89% of the initial capacity remained after 75 cycles at 0.2C. Furthermore, the rate performance of LMO/LSO/C also improved obviously, about $30 \text{ mAh}\cdot\text{g}^{-1}$ of capacity attained at the rate of 5C, higher than LMO/C/LSO and bare LiMn_2O_4 .

1. INTRODUCTION

Spinel LiMn_2O_4 has become one of the most expected cathode materials for lithium ion battery due to its high power density, low cost, environmental friendliness, and high abundance [1-3]. The fatal shortcoming of LiMn_2O_4 can be seen in previous literatures [4, 5].

Most surface modification of LiMn_2O_4 just considered enhancing the cycle performance by restraining Jahn-Teller distortion of Mn^{3+} , reducing the dissolution of Mn^{2+} and decreasing the electrolyte solution to decompose on the electrode [6, 7]. D. Arumugam *et al.* [8] coated LiMn_2O_4 cathode materials with various wt.% SiO_2 by a polymeric process, the SiO_2 surface coating on LiMn_2O_4 controlled the formation of a passive layer film during electrochemical cycling; Dongqiang Liu *et al.* [5] used AlPO_4 -coated LiMn_2O_4 to increase cycling stability.

Electronic conduction was always considered as the crucial factor on cathode materials, Sanghan Lee *et al.* [9] got LiMn_2O_4 micrometer-sized particles that consist of aggregated nanoparticles, but exhibit a

large electric resistance, so they coated spinel LiMn_2O_4 nanoclusters with a thin carbon layer using sucrose as the carbon source. But Byoungwoo Kang and Gerbrand Ceder [10] gave us a new concept: creating a fast ion-conducting surface phase on the surface of LiFePO_4 to improve ionic conductivity, the rate capability enhanced significantly. Lu-Lu Zhang *et al.* [11] prepared SiO_2 -modified $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composites significantly improved electrochemical performance of materials. SiO_2 modification significantly improved materials' structural stability, Li-ion conductivity, and capacity retention. The ionic conduction of Li_2SiO_3 had been researched by Hirotsuchi Yamada, Shin-ichi Furusawa [12, 13]. In our work, we consider using coating layer to restrain Jahn-Teller distortion without performance reducing. The sucrose as source of carbon and metasilicic acid lithium (Li_2SiO_4) were used as electronic conductive agent and ionic conductive agent respectively. The synergistic effect of them coated on micrometer-sized spherical spinel LiMn_2O_4 consisted of aggregated nanoparticles was investigated.

2. EXPERIMENTAL

2.1. Spherical LiMn_2O_4 Preparation

Spherical MnCO_3 was synthesized by liquid phase precipitation method as the precursor of spherical spinel LiMn_2O_4 . $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (A. R. 99%) and NH_4HCO_3 (A. R. 99%) were dissolved in distilled water to get 0.3 mol/L and 0.1 mol/L solution respectively, NH_4HCO_3 solution were dropped into MnSO_4 solution slowly and kept stirring at 30°C with sodium dodecyl sulfate (SDS) as grain size control agent. Spherical MnCO_3 then mixed with Li_2CO_3 by Stoichiometric ratio 4:1.03, and the mixture was calcined to produce LiMn_2O_4 by heat-treatment as follow [14]: 1) heating from room temperature to 560°C by heating rate $5^\circ\text{C}/\text{min}$ and holding for 4 h; 2) heating from 560°C to 750°C by rate $5^\circ\text{C}/\text{min}$ and holding for 10 h; 3) cooling to room temperature spontaneously.

2.2. Coated LiMn_2O_4 Preparation

1 w% Li_2SiO_3 dissolved in 10 mL distilled water, 5 g bare LiMn_2O_4 added into and ultrasonic dispersed 30 min, then magnetic stirred until dry, and subsequently annealed at 600°C under air for 2 h in a furnace, Li_2SiO_3 coated LiMn_2O_4 (LMO/LSO) obtained. Herein, we referenced a very special characteristic of Li_2SiO_3 : After dried and formed a thin film, cannot dissolved in water again. LMO/LSO (2 g) was dispersed in water and ethanol (1:3 v/v; 12 mL), and then sucrose solution (0.1 g sucrose/10 mL distilled water) was added. The mixed solution was dispersed by ultrasonication for 10 min and then concentrated to dryness, fired at 600°C for 10 min and cooled quickly to room temperature [10], LMO/LSO/C obtained. LMO/C/LSO was prepared by similar methods, just exchanged coating order. But the step of Li_2SiO_3 coating was in tube furnace full of nitrogen and kept 600°C for 2 h, in order to avoid carbon oxy-generated.

2.3. Samples Detection

Phase analysis of prepared samples was carried out by X-ray diffraction (XRD, Rigaku D/max 2500 PC). The morphology of bare LiMn_2O_4 was observed by scanning electron microscope (SEM, JSM-6360LA) and high resolution projection electron microscopy (HRTEM). Images of coated samples were obtained by a JEOL-JEM 2100 Electron Microscope equipped with an X-EDS analysis system.

For the fabrication of the cathode, a slurry with 80 wt.% synthesized materials, 10 wt.% acetylene black and 10 wt.% Polyvinylidene fluoride (PVDF) was prepared and rolled onto aluminum foil, then dried at 40°C for 4 h, moved into vacuum drying oven and dried at 80°C under vacuum overnight. The size of cathode pole piece was $0.5 \times 0.5 \text{ cm}^2$. The experimental model batteries were assembled in an argon-filled glove box using Lithium foil as counter electrode and the electrolyte ethylene carbonate (EC): dimethylcarbonate (DMC) 1:1-1 M LiPF_6 . The cycling tests and ratio tests were performed using Neware Battery Testing System, the cyclic voltammogram were tested by Electrochemical workstation (Chenhua Chi 660D).

3. RESULTS AND DISCUSSION

3.1. XRD Analysis

Figure 1 shows that the carbon and Li_2SiO_3 coating did not damage the crystal structure of LiMn_2O_4 . All the diffraction peaks are indexed to a cubic spinel structure with a space group $\text{Fd}\bar{3}\text{m}$. However, impurities founded in LMO/C/LSO, this may because a small part of LiMn_2O_4 had been deoxidated by carbon, Mn_2O_3 and Mn_3O_4 generated.

3.2. Morphology Characterization

Spherical particles could increase the tap density of material. **Figure 2(a)** shows the SEM image of prepared spherical LiMn_2O_4 , the particles dispersed uniformly and the partial size about $1\ \mu\text{m}$. From **Figure 2(b)**, we could see the particle is compactly made up of a large number of sheet crystalline grains of spinel LiMn_2O_4 .

Figure 2(b) and **Figure 2(c)** show the TEM images of LMO/C/LSO and LMO/LSO/C. We chose two areas analyzed with X-EDS in each image, the results shown in **Figure 3** and confirmed that we have coated two layers.

3.3. Electrochemical Investigation

Figure 4(1) summarizes cycling performances of bare LiMn_2O_4 , LMO/C/LSO and LMO/LSO/C as cathode cycled at a current density of $22\ \text{mAh}\cdot\text{g}^{-1}$ (0.2C , $1\text{C} = 110\ \text{mAh}\cdot\text{g}^{-1}$) in a potential range of $3 - 4.3\ \text{V}$ (vs. Li/Li^+). The initial discharged capacity was $105.987\ \text{mAh}\cdot\text{g}^{-1}$, $100.733\ \text{mAh}\cdot\text{g}^{-1}$, and LMO/LSO/C is $107.321\ \text{mAh}\cdot\text{g}^{-1}$ respectively. LMO/C/LSO delivers the lowest initial discharged capacity and the worst cycling capacity could be expected by XRD analysis, In the LMO/C/LSO phase a part of Mn^{4+} was reduction into Mn^{3+} by carbon, which lead to a much more obvious Jahn-Teller distortion and the decrease of active materials. The excellent performance of LMO/LSO/C is attributed to the electron conduction ability and the inhibition of the reduction of Mn^{4+} to Mn^{3+} provided by the Li_2SiO_4 coating layer. At the same time, the carbon coating layer improves the electron conduction ability of LMO/LSO. Part (2) of **Figure 4** shows the rate capabilities of three samples. It is obvious that LMO/LSO/C exhibits better rate capability than the other two samples. At a 1C rate, LMO/LSO/C gives a discharge capacity of $80\ \text{mAh}\cdot\text{g}^{-1}$, which is higher than those of LMO/C/LSO (about $75\ \text{mAh}\cdot\text{g}^{-1}$) and bare LiMn_2O_4 (about $69\ \text{mAh}\cdot\text{g}^{-1}$). It should be noted that when the current rate is decreased from 5C to 1C rate, the discharge capacity of LMO/LSO/C can be recovered to $105\ \text{mAh}\cdot\text{g}^{-1}$, indicating a good reversibility upon cycling. Herein, LMO/C/LSO shows better rate capability than bare LiMn_2O_4 , this may because the protection of Li_2SiO_3 dominant.

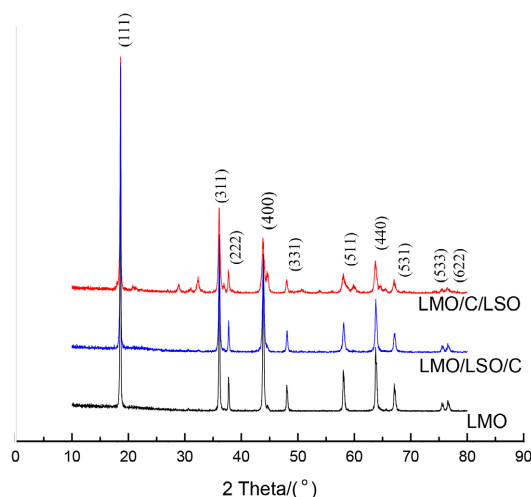


Figure 1. XRD patterns of prepared samples.

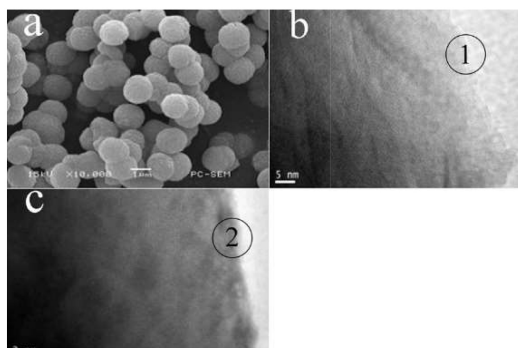


Figure 2. SEM images of (a) spherical spinel LiMn_2O_4 ; TEM images of (b) LMO/C/LSO and (c) LMO/LSO/C.

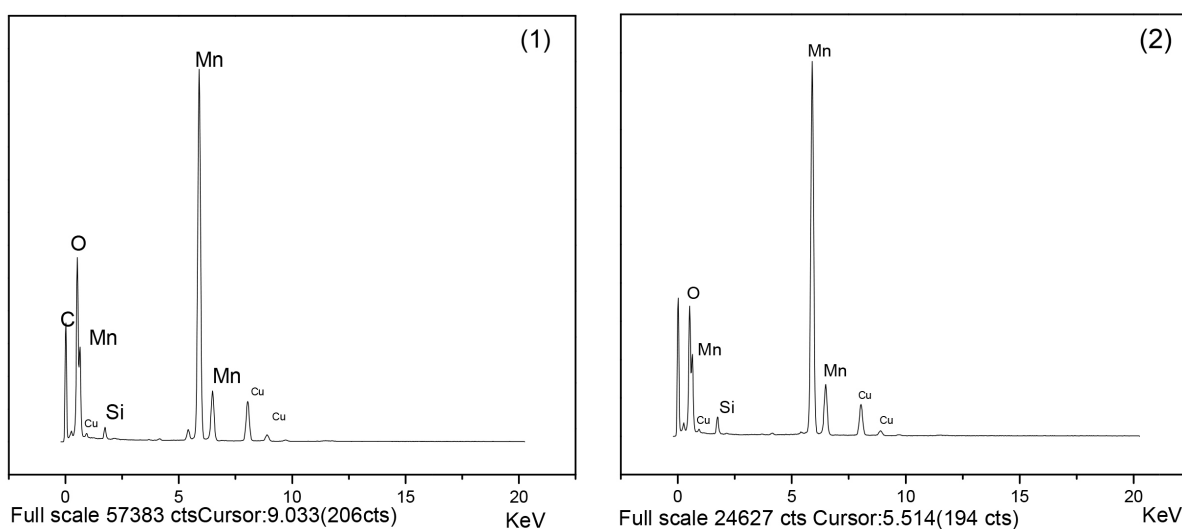


Figure 3. Two areas of images of Figure 2(b) LMO/C/LSO and Figure 2(c) LMO/LSO/C analyzed by X-EDS respectively.

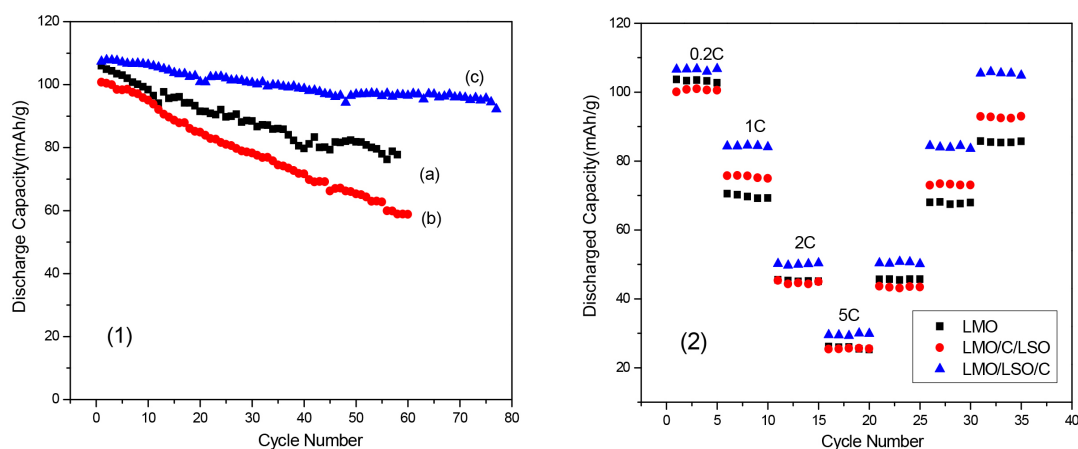


Figure 4. (1) Cycling performances of (a) bare LiMn_2O_4 cathode, (b) LMO/C/LSO cathodes and (c) LMO/LSO/C cathodes. (2) Discharge capacity with cycling number at different current rates of LMO, LOM/C/LSO, LMO/LSO/C.

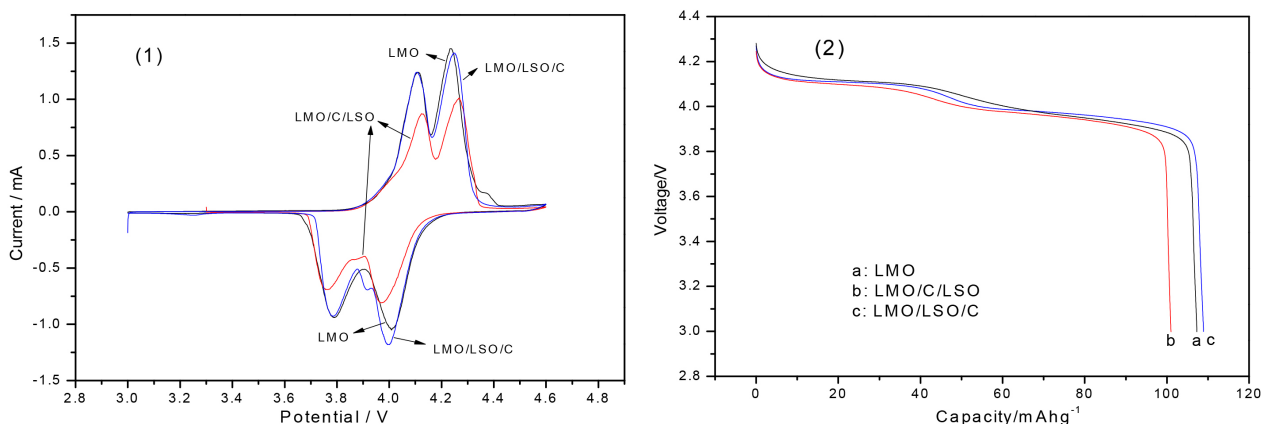


Figure 5. (1) Initial cyclic voltammogram curves for LMO, LMO/C/LSO, LMO/LSO/C at the scan rate was 0.1 mV/s and (2) initial discharged capacity of three materials.

Figure 5(1) show all of samples have two reversible redox peaks based on $\text{Mn}^{4+}/\text{Mn}^{3+}$. It is obvious that the samples which coated have more sharp peaks and even more symmetrical, at least indicate that the coated samples still keep spinel structure very well, and LMO/LSO/C shows the most stable structure. **Figure 5(2)** gives us informations of discharged voltage plats and initial discharged capacity. The two discharged voltage plats corresponding to the two reduction peaks of cyclic voltammogram curve.

4. CONCLUSIONS

1) Spherical spinel LiMn_2O_4 was synthesized by solid-state reaction combined with liquid phase precipitation.

2) Li_2SiO_3 and carbon were both coated on the surface of LiMn_2O_4 by different orders and obtained LMO/LSO/C and LMO/C/LSO.

3) Compared with LMO/C/LSO and bare LiMn_2O_4 , LMO/LSO/C exhibited the best capacity retention and rate performance due to the inside Li_2SiO_4 provided a certain degree of ionic conductivity and inhibited the direct contact between LiMn_2O_4 and electrolyte. At the mean time, the outside carbon insured the electronic conductivity.

CONFLICTS OF INTEREST

The authors declare no conflicts of interest regarding the publication of this paper.

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