

Electrochemical Performance of Modified LiMn_2O_4 Used as Cathode Material for an Aqueous Rechargeable Lithium Battery

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ABSTRACT: To improve the electrochemical performance of cathode material in aqueous LiNO_3 solution, modified spinel LiMn_2O_4 materials prepared with different amounts of sucrose additive are synthesized using a two-step sintering method. The phase structure and morphologies of as-prepared samples are characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. Electrochemical performances of modified LiMn_2O_4 used as the cathode material of the aqueous rechargeable lithium battery (ARLB) are investigated by galvanostatic charge/discharge testing. The effects of the carbon, which decomposed from the additive sucrose, on the electrochemical performances of the modified spinel LiMn_2O_4 cathode for the ARLBs are discussed. In comparison to pristine LiMn_2O_4 , the optimum quantity of sucrose addition improves the electrochemical performance of spinel LiMn_2O_4 material in an aqueous LiNO_3 solution, especially for the addition of 20 wt % sucrose, and its initial discharge specific capacity is 118.3 mAh g^{-1} ; moreover, it still has 102.8 mAh g^{-1} after 40 cycles.

1. INTRODUCTION

An aqueous rechargeable lithium battery (ARLB) is a new rechargeable lithium battery using an inorganic aqueous solution electrolyte instead of an organic electrolyte, which is advantageous with respect to safety, manufacturing simplicity, and no pollution. It has competitive potential for the large-scale energy storage compared to a lead–acid battery, a nickel–cadmium battery, and some other low-voltage batteries.^{1–7}

It is possible for the lithium compounds to extract/insert lithium ion from/into the hosts in an aqueous solution, as well as in the organic electrolyte.⁸ In addition, the oxidation/reduction potential of water is varied with the pH value in aqueous solution. However, an important criterion of the cathode candidate for ARLB is that its intercalation potential range locates within the stable electrochemical potential window for the aqueous solution electrolyte.² Therefore, the voltage of ARLB is dependent upon the pH value of the aqueous electrolyte. Figure 1 shows the intercalation potentials of some electrode materials used for the ARLB. The left part represents O_2/H_2 potential versus the normal hydrogen electrode (NHE) [i.e., standard hydrogen electrode (SHE) in Pt, H_2 (100 kPa)/ H^+ (1 mol L^{-1})] for different pH values in 1 M aqueous solution. The right part illustrates Li^+ intercalation potential of various electrode materials versus the NHE and Li/Li^+ .⁹ LiMn_2O_4 and LiV_3O_8 could exist partly in the stable region of water. Practically, many researchers^{1–9} composed the ARLB with a LiMn_2O_4 cathode and LiV_3O_8 anode in an aqueous solution electrolyte.

Researchers have studied the LiMn_2O_4 positive electrode in an aqueous solution electrolyte. Wang et al.¹⁰ fabricated ARLB, such as (–) $\text{Zn}|\text{5 M LiNO}_3|\text{LiMn}_{2-x}\text{Mn}_x\text{O}_4$ (+), and its initial discharge capacity was $70\text{--}80 \text{ mAh g}^{-1}$. Wang et al.¹¹ composed the (–) $\text{Li}_2\text{Mn}_4\text{O}_8|\text{5 M LiNO}_3 + 0.001 \text{ M LiOH}|\text{LiMn}_2\text{O}_4$ (+) cell, and the initial discharge capacity of this ARLB was 100 mAh g^{-1} . Wang et al.⁶ also constructed the (–) $\text{LiV}_3\text{O}_8|2 \text{ M Li}_2\text{SO}_4|\text{LiMn}_2\text{O}_4$ (+) cell, and its initial discharge capacity was 61.8 mAh g^{-1} .^{12,13} Lei et al.¹⁴ assembled the ARLB in 9 M LiNO_3 aqueous solution, and

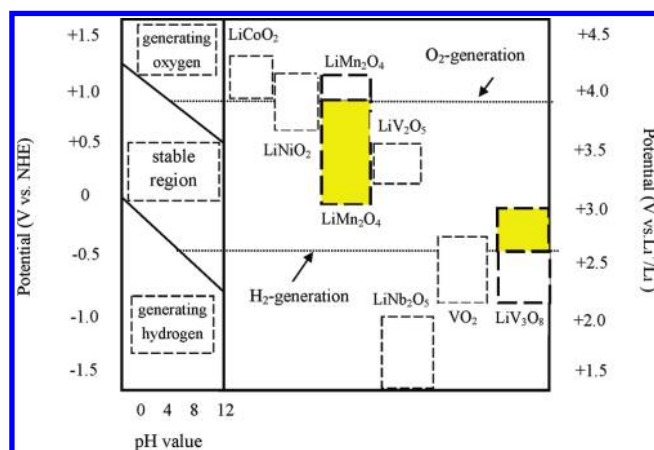


Figure 1. Intercalation potential of some electrode materials in 1 M lithium ion aqueous solution versus different pH values.

then the electrochemical performance of this ARLB was better. Schlijrb et al.¹⁵ synthesized LiMn_2O_4 with a vacuum-freeze-dry method and manufactured it in 9 M KOH aqueous solution, and its initial discharge capacity was 75 mAh g^{-1} . Wang et al.¹⁶ prepared LiMn_2O_4 by an ultrasonic spray decomposition method and made an ARLB as (–) $\text{LiV}_3\text{O}_8|2 \text{ M Li}_2\text{SO}_4|\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{-O}_2$ (+), and its second discharge capacity was 46.9 mAh g^{-1} . Cvjeticanin et al.¹⁷ used a rapid glycine–nitrate method (GNM) to synthesize $\text{LiCr}_{0.15}\text{Mn}_{1.85}\text{O}_4$ and dipped it in the saturated LiNO_3 solution, which had symmetric redox peaks and good Li^+ reversibility. Besides, other experiments were also performed and improved the electrochemical performance of LiMn_2O_4 in an

Received: October 11, 2011

Revised: November 10, 2011

Published: November 22, 2011

aqueous solution electrolyte, such as decreasing the particle size of the active material^{14,18} or synthesizing cation-doped $\text{LiMn}_{2-x}\text{M}_x\text{O}_4$ ($\text{M} = \text{Cr}, \text{Ni}, \text{Co}, \text{and Al}$) materials.^{10,16,17,19}

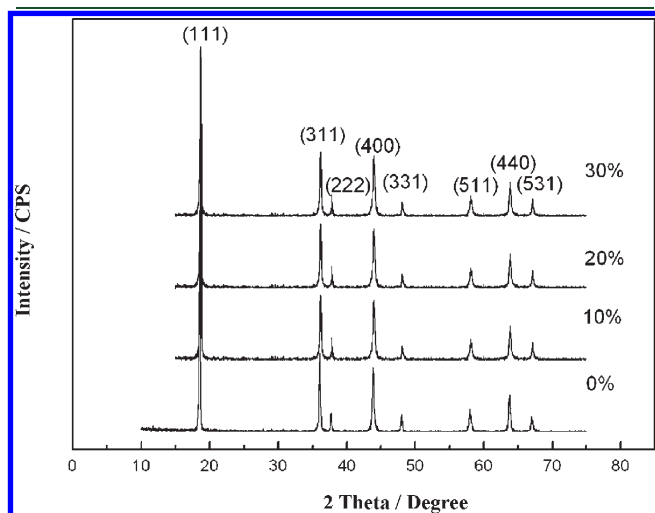


Figure 2. XRD patterns of LiMn_2O_4 samples prepared with different amounts of sucrose additive.

In this paper, to improve the electrochemical performance of spinel LiMn_2O_4 in an aqueous solution, the modified spinel LiMn_2O_4 materials were synthesized by a two-step sintering method added with different amounts of sucrose. Also, the discharge capacity and cycling performance of modified spinel LiMn_2O_4 were tested in LiNO_3 aqueous solution with cyclic galvanostatic charge/discharge measurements. Moreover, the effect of different amounts of sucrose additive on the electrochemical performance of the $(-)\text{LiV}_3\text{O}_8|\text{LiNO}_3$ aqueous electrolyte/ LiMn_2O_4 $(+)$ cell was sketched.

2. EXPERIMENTAL SECTION

2.1. LiMn_2O_4 Preparation and Characterization. Li_2CO_3 (analytical reagent 98%, Sinopharm Chemical Reagent Co., Ltd. product) and MnO_2 (analytical reagent 85%, Tian Jin Bodi Chemical Holding Co., Ltd. product) with a stoichiometric molar ratio of 0.51:2 were mixed, and a given amount (10, 20, and 30 wt %) of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) was added to the above mixture, then milled 4 h using a high-energy mill, and pressed into the pellet. The pellet was heated at 350°C for 12 h and 800°C for 24 h in air in a horizontal-tube furnace. After cooling to room temperature, the black crystalline LiMn_2O_4 samples prepared with/without sucrose additive were obtained. The X-ray diffraction (XRD) experiments were performed using a Bruker D8

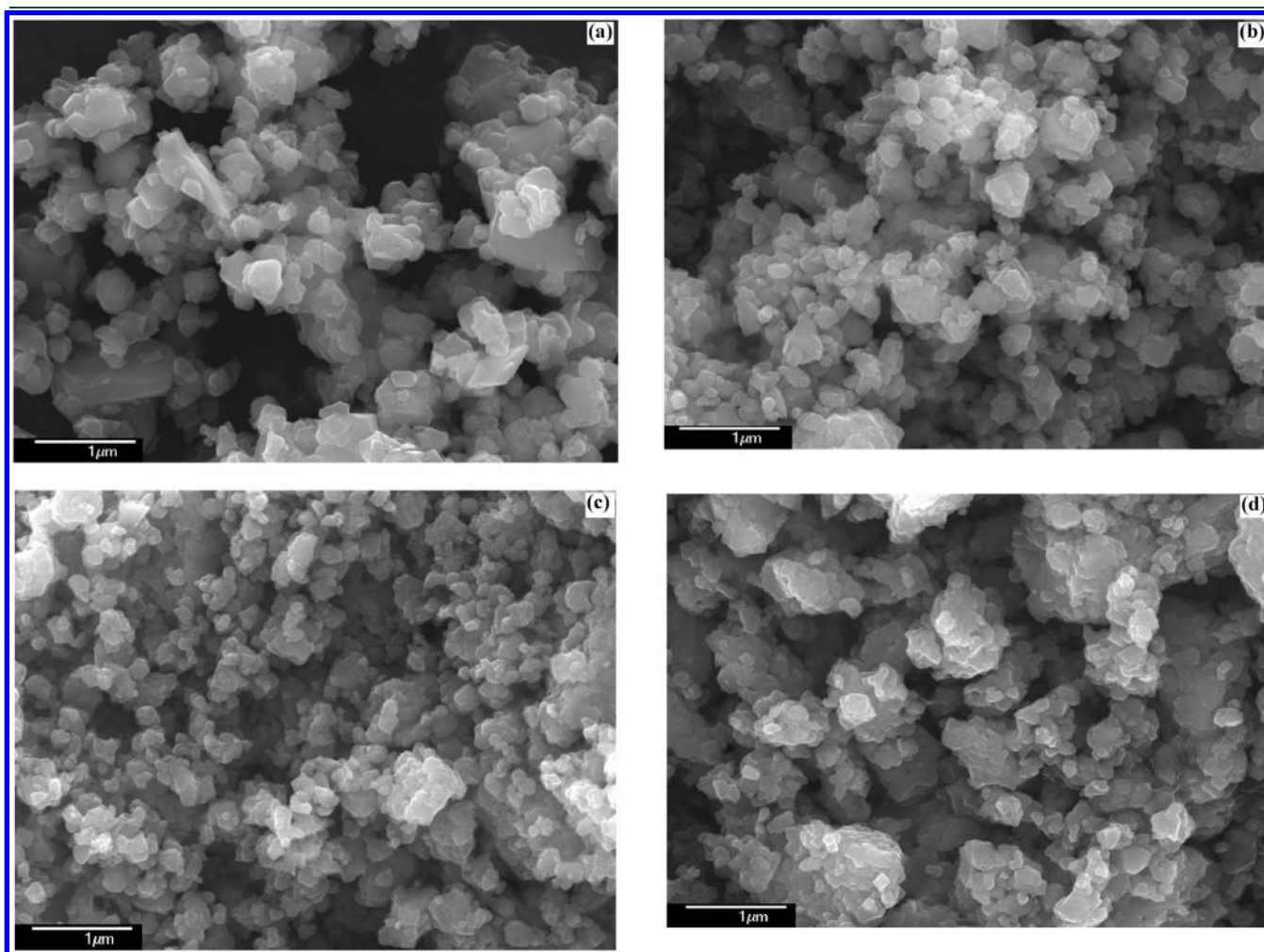


Figure 3. SEM photos of LiMn_2O_4 samples prepared with different amounts of sucrose additive: (a) pristine LiMn_2O_4 , (b) 10 wt % sucrose, (c) 20 wt % sucrose, and (d) 30 wt % sucrose.

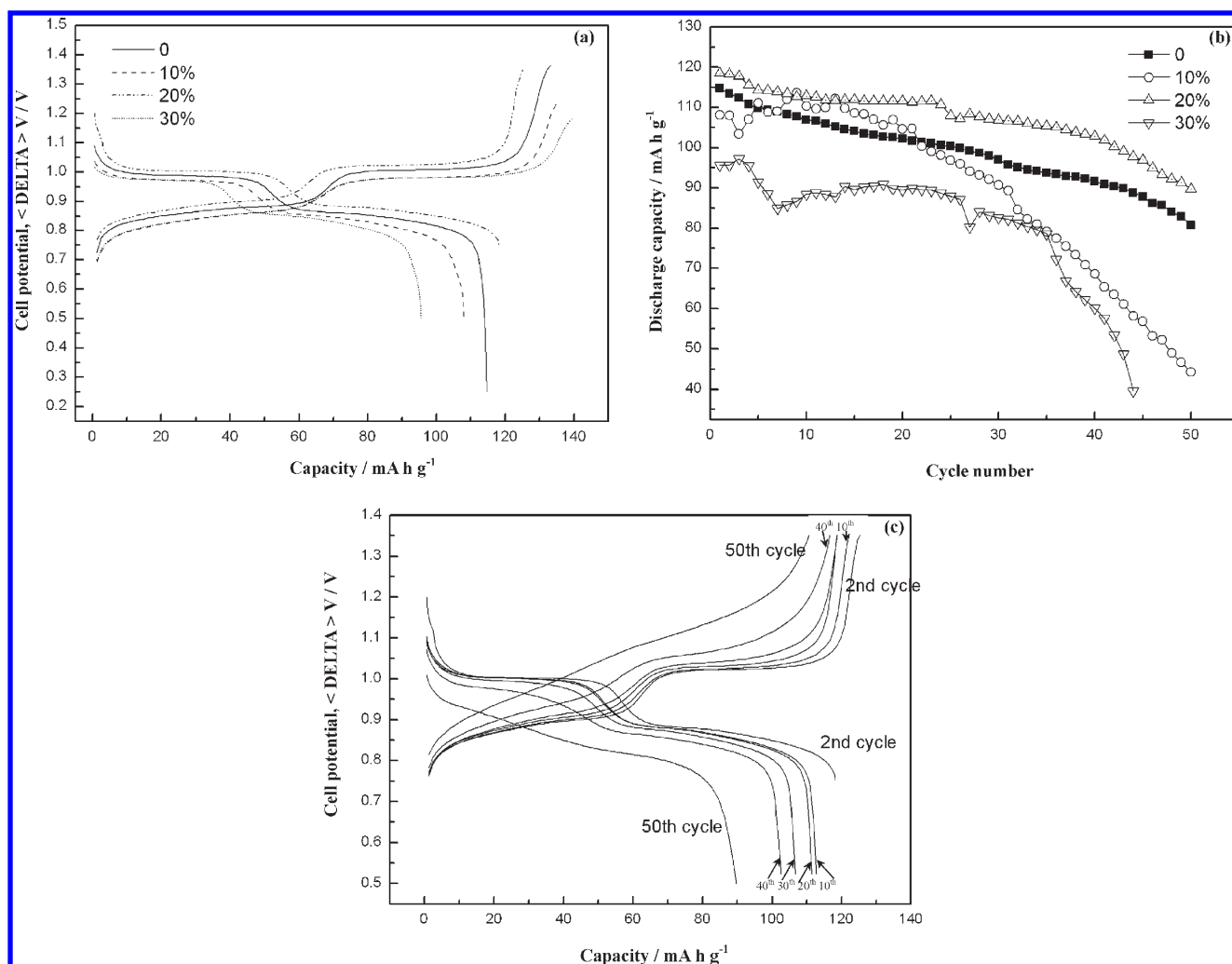


Figure 4. Electrochemical performances of modified LiMn₂O₄ samples used for ARLB: (a) first charge–discharge curves of ARLB, (b) cycle performance of ARLB, and (c) charge–discharge curves of modified LiMn₂O₄ material prepared with 20 wt % sucrose at the 2nd, 10th, 20th, 30th, 40th, and 50th cycles.

Advance diffractometer with Cu K α radiation. The particles morphologies were observed with a JEOL JSM-7000F instrument.

2.2. Electrochemical Setup and Testing. The preparation of working electrode (WE) paste involved as-prepared LiMn₂O₄ samples,²¹ acetylene black, and polyvinylidene fluoride (PVDF) binder dissolved in 1-methyl-2-pyrrolidone (NMP), which were in a weight ratio of 80:10:10, and the suspension was coated onto a nickel mesh and then dried under vacuum at 100 °C for 10 h. The counter electrode (CE) active material was LiV₃O₈ (which was synthesized with Li₂CO₃ and V₂O₅, mixed at a molar ratio of 1.02:3, pressed, and then sintered at 680 °C for 12 h and 350 °C for 8 h), and the CEs were also manufactured using the above-mentioned method. The reference electrode (RE) was a saturated calomel electrode (SCE). We assembled an ARLB in 5 M LiNO₃ solution.

Galvanostatic charge/discharge experiments were performed at room temperature using a software-controlled Arbin BT-2000 instrument. The charge–discharge voltage range of ARLB was between 0.2 and 1.4 V.

3. RESULTS AND DISCUSSION

3.1. Particle Characterization. Figure 2 shows the XRD patterns of pristine LiMn₂O₄ and modified samples. It can be

seen that the diffractions at $2\theta = 18.7^\circ, 36.2^\circ, 37.9^\circ, 44.0^\circ, 48.2^\circ, 58.2^\circ, 64.1^\circ$, and 67.0° are the characteristic diffractions of the cubic spinel LiMn₂O₄ with *Fd3m* space group [powder diffraction file (PDF) 35-0782]. When the XRD patterns of modified spinel LiMn₂O₄ samples are compared to those of pristine LiMn₂O₄,^{20,21} we can see no obvious difference between these LiMn₂O₄ samples. Figure 3 presents the scanning electron microscopy (SEM) micrographs of as-prepared LiMn₂O₄ samples. It can be seen from panels a–d of Figure 3 that the particle size of the modified LiMn₂O₄ sample prepared with 20 wt % sucrose is smaller than that of the others, including pristine LiMn₂O₄ and LiMn₂O₄ samples prepared with 10 or 30 wt % sucrose. Besides, the agglomerations of crystallites for these samples are evident, except for the LiMn₂O₄ sample prepared with 20 wt % sucrose.

3.2. Electrochemical Performance. Figure 4a shows the typical charge–discharge curves of ARLB with modified LiMn₂O₄ samples and pristine LiMn₂O₄ between 0.2 and 1.4 V at 0.2 C. In Figure 4a, the initial discharge-specific capacities of pristine LiMn₂O₄ and LiMn₂O₄ prepared with 10, 20, and 30 wt % sucrose additive are 113.5, 108.1, 118.3, and 95.6 mA h g⁻¹, respectively.

Figure 4b displays the cycling performance of modified LiMn₂O₄ in the ARLB. In comparison to the electrochemical

Table 1. Electrochemical Properties of Different Lithium Compounds Used as the Cathode of the ARLB in Various Aqueous Solution Electrolytes

material	electrolyte solution	theoretical capacity (mAh g ⁻¹)	capacity in the first cycle (mAh g ⁻¹)	capacity in <i>n</i> cycles (mAh g ⁻¹)	current density, <i>C</i> _{rate}	reference
LiMn ₂ O ₄	saturated LiNO ₃	148	120.28	100.16 (42)	0.2 C	21
LiMn ₂ O ₄ (single crystalline nanoline)	5 M LiNO ₃	148	110	100 (56)	10 C	23
LiMn ₂ O ₄	1 M Li ₂ SO ₄	148	84.6	50.1 (1000)	0.1 A g ⁻¹	24
LiMn ₂ O ₄ /MWCNTs		140	117	112.8 (1000)	0.1 A g ⁻¹	24
sub-micrometer-sized LiMn ₂ O ₄	5 M LiNO ₃	148	73		1.5 C	18
LiMn ₂ O ₄	1 M Li ₂ SO ₄	148	62	50 (150)	4.6 A g ⁻¹	25
LiAl _{0.1} Mn _{1.9} O ₄	5 M LiNO ₃	148	100	70 (5000)		19
γ-MnO ₂	saturated LiNO ₃ + 1 M ZnSO ₄	148	120		0.5 mA cm ⁻²	26
LiCoO ₂	saturated Li ₂ SO ₄	140	50	30 (120)	0.1 C	27
LiCoO ₂	5 M LiNO ₃	140	112	105 (90)	1 C	8
LiFePO ₄	Li ₂ SO ₄	170	130	80 (10)	5 C	28
LiMnPO ₄	LiOH + ZnSO ₄	170	75	26 (20)	0.25 mA cm ⁻²	29
LiMnPO ₄	LiOH	170	88	70 (25)	0.5 mA cm ⁻²	30
LiMn _{0.05} Ni _{0.05} Fe _{0.05} PO ₄	Li ₂ SO ₄	170	87	55 (50)	0.2 mA cm ⁻²	31
LiCoPO ₄	LiOH	167	82	70 (20)	0.5 mA cm ⁻²	32

behavior of pristine LiMn₂O₄ and the other modified LiMn₂O₄ samples, the LiMn₂O₄ sample prepared with 20 wt % sucrose additive exhibits higher reversible capacity and better cycling performance in 5 M LiNO₃ aqueous solution. LiMn₂O₄ prepared with 20 wt % sucrose additive provides a discharge capacity of 118.3 mAh g⁻¹ and still has 102.8 mAh g⁻¹ after 40 cycles. Thus far, many studies on the improvement of the electrochemical performance of cathode active materials in the ARLB have been reported. Table 1 summarizes the behavior of various cathode materials in different aqueous solution electrolytes. The following materials have been studied: LiMn₂O₄,^{18,21–25} MnO₂,²⁶ LiCoO₂,^{8,27} LiFePO₄,²⁸ LiMnPO₄,^{29,30} LiMn_{0.05}Ni_{0.05}Fe_{0.05}PO₄,³¹ and LiCoPO₄.³² In this paper, the LiMn₂O₄ sample prepared with 20 wt % sucrose additive shows that its capacity decreased only 13.1% after 40 cycles in LiNO₃ aqueous solution, which is better than the reported results in refs 16, 18, 19, and 25.

In combination with Figure 4a, it can be seen that the capacity and cycling stability of the ARLB are improved by adding an optimum amount of sucrose to prepare modified LiMn₂O₄. The irreversible capacity loss of the first cycle is also reduced. The cycling performance is improved as well. Moreover, this electrochemical testing showed that the capacity and the cycling performances are related to the composition and morphology of the electrode active materials, especially for the different amounts of sucrose added to prepare modified LiMn₂O₄ samples. This may be ascribed to the effect of sucrose. Figure 3c shows that the average particle diameter is below 300 nm, the particle distribution is closely packed, and no agglomeration texture is evident. However, SEM images of the others (i.e., panels a, b, and d of Figure 3) show that most of the spinel particles with particle sizes around 500 nm are agglomerates. Therefore, LiMn₂O₄ prepared with 20 wt % sucrose additive has better reversible storage capacity and better electron transport, which may be ascribed to the physical features of modified LiMn₂O₄.

The other samples, such as LiMn₂O₄ prepared with 10 or 30 wt % sucrose additive, show inferior capacity and cycling performance compared to pristine LiMn₂O₄ during the electrochemical

cycles. The electrode reaction is not simple and is composed of several reaction steps, such as a phase transition of the electrode active material, electron conduction and ion diffusion, and charge-transfer reaction.³³ The interfacial reactions and mechanisms have a direct effect on the electrochemical performance of the materials used for energy storage.³⁴ The charge-transfer process is kinetically more favorable, leading to a mass transport controlling mechanism. In addition, other factors, such as the crystallinity and kinetics of aqueous electrolyte penetration in the first cycle, should also be important for the difference of capacities.³⁵ Among these, an interesting point is that this charge-transfer reaction is recognized as an interfacial lithium ion transfer reaction and not a general electron transfer reaction. These results suggest that the interactions between the lithium ions, electrode surface, and aqueous solution electrolyte are the key factor in the kinetics of the charge-transfer reaction. The active mass transfer is influenced by the distribution of the carbon decomposing from the additive sucrose in preparing modified LiMn₂O₄ samples in the inorganic aqueous electrolyte.³⁵ The modified LiMn₂O₄ sample, which is used as the cathode material of the ARLB, exhibits higher capacity and better cycling performance than those of pristine LiMn₂O₄.

Figure 4c shows 2nd, 10th, 20th, 30th, 40th, and 50th charge–discharge curves of the modified LiMn₂O₄ material, which was prepared with 20 wt % sucrose additive. In combination with Figure 4a, one can distinguish that the voltage of the ARLB changes gradually during the charge–discharge processes and two plateaus can be observed: one at the mean potential of 1.00 V and the other at the mean potential of 0.86 V. This is consistent with the electrochemical behavior of spinel LiMn₂O₄ materials in organic electrolyte.^{36–38} However, in the application of the battery, a more flat charge–discharge curve is necessary, and fortunately, for this ARLB with modified LiMn₂O₄ prepared with 20 wt % sucrose additive, the high-voltage plateau disappears after 50 cycles. The carbon, which is decomposed from the adding sucrose, serves as not only an electric conductor but also a conductive network. A total discharge capacity of 118.3 mAh g⁻¹ can be observed if modified LiMn₂O₄ is prepared with 20 wt %

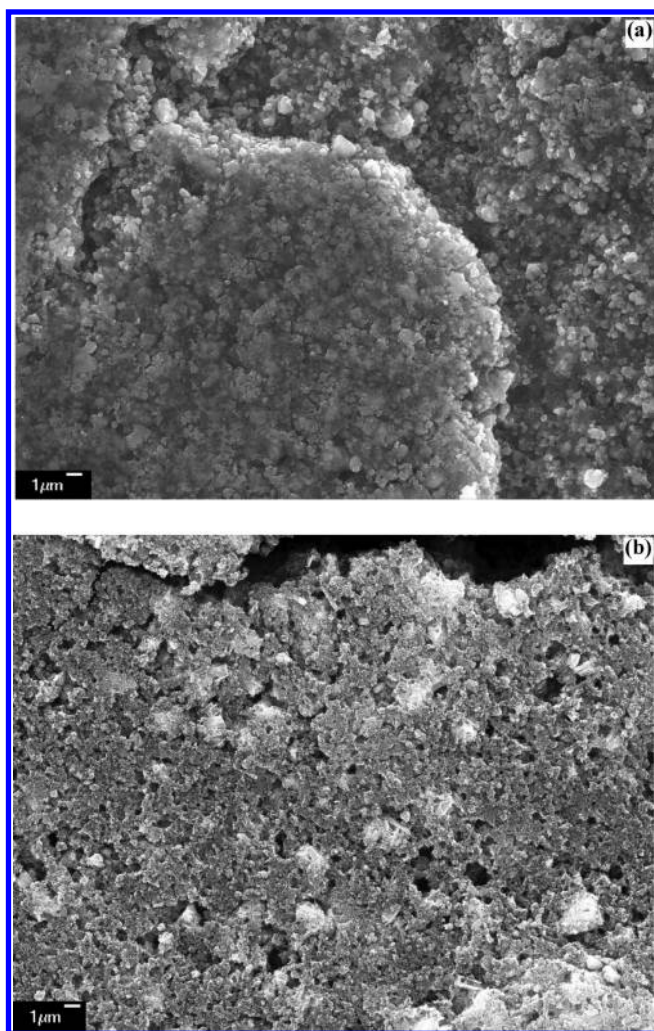


Figure 5. SEM images of the electrode after 1 and 50 charge–discharge cycles: (a) after the first cycle and (b) after the 50th cycle.

sucrose additive, which is about 4.8 mAh g^{-1} larger than that of ARLB with pristine LiMn_2O_4 electrode. These results indicate that it is necessary for modified LiMn_2O_4 to have the well-organized conductive path, and then it will have a better electrochemical performance.

According to the above discussion, the electrochemical performance of modified LiMn_2O_4 prepared with 20 wt % sucrose additives is significantly superior. The main reason is optimum amounts of sucrose added in the preparation of modified LiMn_2O_4 material, which decomposed into the carbon along with gas, thus avoiding particles to aggregate, and it also provides the conductive net for the modified LiMn_2O_4 material to increase its electron conductivity and then improves the electrochemical properties of (–) $\text{LiV}_3\text{O}_8|\text{LiNO}_3 \text{ aqueous}|\text{LiMn}_2\text{O}_4$ (+) ARLB. In this experiment, the discharge capacity of the ARLB remains about 120 mAh g^{-1} , which shows great potential for the application in the large-scale devices, where it could replace lead–acid rechargeable batteries with safety and no pollution.

To further understand the effect of optimum amounts of sucrose added in the preparation of modified LiMn_2O_4 cathode material, the positive electrodes after 1 and 50 cycles were both observed with SEM, and the results are shown in Figure 5. Figure 5a shows that the cathode is clearly in the form of integrity

after the first cycle. However, after 50 cycles, some microholes are obviously observed on the surface of this electrode presented in Figure 5b. In addition, the lithium ion insertion/extraction mechanism of modified LiMn_2O_4 used in an aqueous solution is being explored.

4. CONCLUSION

We have fabricated the ARLB composed of a LiMn_2O_4 cathode and LiV_3O_8 anode in an aqueous LiNO_3 solution. The electrochemical performance of the ARLB was studied. The ARLB, which used modified LiMn_2O_4 prepared with the addition of 20 wt % sucrose, displays an improved Li intercalation behavior in 5 M aqueous LiNO_3 solution, which is evidenced by the galvanostatic charge–discharge testing. It shows great potential in the application of a large-scale device, where it could replace lead–acid rechargeable cells.

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ACKNOWLEDGMENT

The authors acknowledge the Xi'an Science and Technology Plan Project (CX1124), the Province Natural Science Foundation of Shaan Xi (2010JM6018), and the Fundamental Research Funds for the Central University (0109-08140020). Mingshu Zhao is an International Society of Electrochemistry (ISE) member.

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