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Effects of metal source in metal substitution of lithium manganese oxide spinel

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Abstract

Usefulness of W substitution for improvement of battery performance of $LiMn_2O_4$ cathode was investigated. Small amounts of tungsten were incorporated into $LiMn_2O_4$ spinel instead of available Mn. For this purpose, two sources of tungsten (metallic W or WO_3) were examined. W concentration and source have significant influence on both morphology and electrochemical behavior of W-substituted $LiMn_2O_4$ spinels. W substitution of $LiMn_2O_4$ spinel can lead to the formation of uniform spinel particles and improved battery performance. Cyclic voltammetric behaviors of the samples were examined in an aqueous solution, and Li diffusion process was investigated for different cases. The best case was the $LiW_{0.01}Mn_{1.99}O_4$ spinel prepared from metallic W powder, as exhibits excellent rate capability, but better cycleability was observed for the $LiW_{0.01}Mn_{1.99}O_4$ spinel prepared from WO_3. This means that because of significant influence of the dopant source, this parameter should be chosen in respect with the desire improvement.

Keywords: Lithium battery; Cathode material; $LiMn_2O_4$; Metal substitution; Material morphology; W dopant

1. Introduction

Valuable advantages of $LiMn_2O_4$ as a potential candidate for cathodes of lithium batteries are well-known. However, further advancement is needed to overcome common problems of this cathode material. One of the most efficient approaches in this context is metal substitution of Mn in $LiMn_2O_4$ spinel [1–7]. This can reduce the amount of Mn^{3+}, which is the general goal of Mn substitution, and strengthen the structural stability of the spinel. As it has been found that metal substitution of $LiMn_2O_4$ can lead to the appearance of 5 V redox systems [8–15], this approach has recently reached a considerable attention.

Various transition metals have been employed for this purpose, but less attention had been paid to tungsten, though it is a common transition metal in electrochemical systems. This failure can be attributed to apparent disadvantage of this action, as oxidation state of W is higher than Mn and metal substitution may reduce Mn valence which is unfavorable. However, recent report of Chitrakar et al. [16] regarding usefulness of substitution of Mn in $LiMn_2O_4$ by pentavalent antimony provides a new opportunity. On the other hand, it will be discussed that the problem of reduction of Mn valence is not important for the case of W substitution (as the amount of dopant is low). In the present study, we would like to examine usefulness of W substitution for improvement of electrochemical performance of $LiMn_2O_4$. As we have emphasized before, it is more appropriate to investigate preliminary electrochemical studies of new cathode materials in aqueous media rather than non-aqueous media [17,18]. In fact, aqueous electrolytes contain simple components and the exact electrochemical performance of cathode material can be detected. Whereas, additional process can be occurred in non-aqueous electrolytes, leading to different electrochemical performances. For instance, a considerable attention has been paid to the instability of electrolytes in lithium batteries [19–21]. Thus, it cannot be concluded that the improvements observed are due to better cathode material or better electrolyte stability on the electrode surface. On the other hand, aqueous media are also potential candidates to replace conventional non-aqueous media of lithium batteries and considerable attention has been recently paid to them [22–25].

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2. Experimental

Cathode materials were synthesized by conventional solid-state reaction. Stoichiometric amounts of raw materials were completely mixed by ball milling. Appropriate amounts of tungsten were added from the sources of tungsten oxide or metallic W fine powder. For solid-state synthesis, the furnace temperature was slowly increased with the rate of 1 °C/min to reach the temperature of 800 °C. Slow heating provides an appropriate opportunity for preliminary decomposition of raw materials such as carbonates. The temperature was fixed at 800 °C for 40 h and then the furnace was slowly cooled to room temperature. The composite electrodes for electrochemical studies were prepared from mixture of active material and acetylene black in the ratio of 1:1. For casting the composite, a drop of melted paraffin was added.

Cyclic voltammetric studies were performed using a Metrohm 746 VA potentiostat.

Electrolyte was aqueous solution of saturated lithium nitrate. Potentiostatic experiments were performed using a Princeton Applied Research potentiostat/galvanostat model 173 (PAR 173) equipped with a model 175 universal programmer in conjunction with CorrView software. In the experimental measurements, all potentials were referenced to a saturated calomel electrode (SCE), but the potentials were calculated in reference to conventional Li/Li$^+$. Scanning electron microscopic (SEM) investigations were carried out using a Cambridge scanning electron microscope model Steroscan 360. Powder Xray diffractions (XRD) were recorded using a Phillips PW 1371 diffractometer based on Cu Kα radiation.

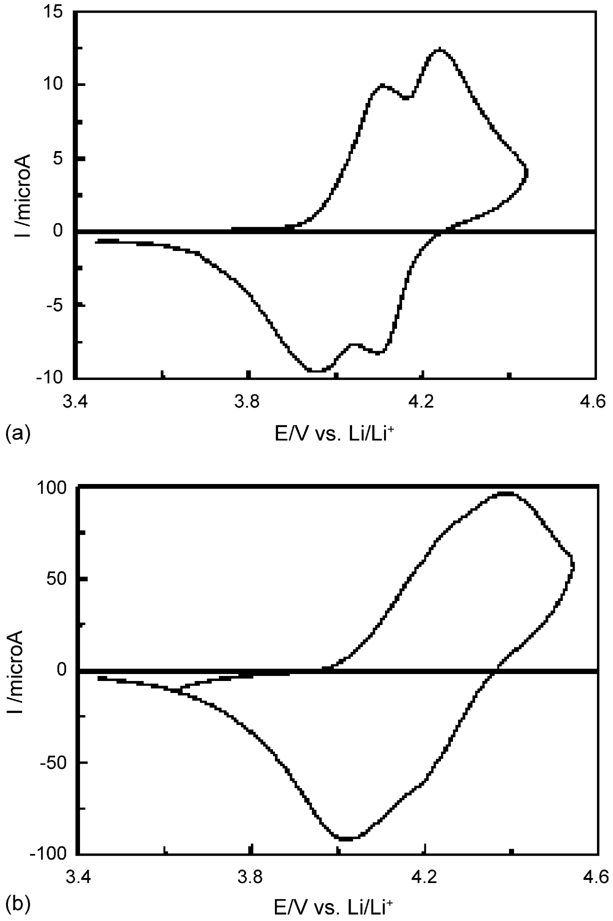

Fig. 1. Typical cyclic voltammograms of $LiMn_2O_4$ spinels synthesized from raw materials of (a) Li_2CO_3, and (b) LiOH. Electrolyte was a saturated solution of $LiNO_3$ and scan rate 0.5 mV/s.

3. Results and discussion

It is known that the source of lithium in solid-state synthesis has a significant influence on the battery performance of $LiMn_2O_4$ spinel [26], as lithium should be extracted and inserted from/into the spinel structure in the course of cycling. The best case is lithium carbonate, which decomposes at smaller temperatures before the occurrence of the main solid-state reaction. Of course, this also depends on manganese raw material, which for the present study was $MnCO_3$. Another alternative is lithium hydroxide, but as its decomposition is not as well as lithium carbonate, $LiMn_2O_4$ spinel prepared from LiOH has not well-defined electrochemical behavior as well as that prepared from Li_2CO_3 (Fig. 1). Of course, this does not mean that $LiMn_2O_4$ prepared from LiOH is not applicable for battery performance. Note that the cyclic voltammetric behaviors presented in Fig. 1 are related to a relatively fast scan (for the case of lithium batteries), and the $LiMn_2O_4$ prepared from LiOH displays a well-defined behavior at slower scans. In fact, we use this critical condition to inspect the difference of two cases. Of course, this is a tricky reason, but the main reason for this choice is that LiOH is a cheaper source for synthesis of $LiMn_2O_4$. In other words, it is of commercial interest to improve synthesis of $LiMn_2O_4$ from LiOH because of cost reason.

In other words, these studies reveal rate capability of the cathode materials, similar to conventional galvanostatic studies of battery performance of cathode materials at different C rates [24,27–29]. Here, we aim to inspect the rate capabilities of the W-substituted $LiMn_2O_4$ cathode materials using cyclic voltammetric studies in aqueous media (this issue will be described further). We will continue this strategy to inspect the influence of W substation on electrochemical behavior of $LiMn_2O_4$. In other words, the W-substituted $LiMn_2O_4$ spinels were synthesized from LiOH and their electrochemical behaviors should be compared with Fig. 1b (of course, W-substituted $LiMn_2O_4$ spinels were also synthesized from Li_2CO_3, but the results were not distinguishable like the present case).

Not only the source of lithium raw material, but also the source of substituting metal has a significant influence on the material properties of $LiMn_2O_4$ spinel. The sources of substituting metals are usually their oxides. However, when the dopant concentration is low (e.g. the case of noble metal substitution), it is possible to use metallic powders [30]. At the condition of high-temperature solid-state synthesis under air atmosphere, the metallic powders will be completely oxidized, and no significant difference is expected. Since the amount of W in $LiMn_2O_4$ is small, we will examine two afore-mentioned sources of tungsten for metal substitution of $LiMn_2O_4$. The results will be reported separately and compared later.