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Short Communication

Rate Performance of $LiMnPO_4$ Based Materials from Different Carbon Source Addition Process

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In the present work, two types of cation doped $LiMnPO_4$ based materials, $LiMn_{0.9}Fe_{0.09}Mg_{0.01}PO_4/C$ and $LiMn_{0.98}Mg_{0.02}PO_4/C$, are synthesized by a solid-state reaction method with different carbon source addition process and characterized to investigate the effect of carbon source addition process on the quality of carbon coating and rate performance. The result shows that the $LiMnPO_4$ based cathode materials synthesized by adding carbon source via one-step process have better carbon coating than those synthesized by adding carbon source via two-step process, which leads to faster electron transport across the surface and thus better rate performance. This observation on $LiMnPO_4$ based materials is different from that previously reported for $LiFePO_4$.

Keywords: Lithium ion batteries; Cathode; $LiMnPO_4$; Carbon coating

1. INTRODUCTION

There has been an increasing interest in olivine structured $LiMnPO_4$ as a promising cathode material for lithium ion batteries because of its high redox potential of 4.1 V versus Li/Li^+, low-cost and good safety, but its low electronic conductivity and slow ionic diffusion lead to a poor electrochemical performance [1-3]. Strategies including surface modification, particle size reduction and cation doping have been integrated to improve the performance of $LiMnPO_4$ [4-19]. From the reported results, it is known that carbon coating is essential to achieve high rate $LiMnPO_4$ based materials [8,10,12,20], and the quality of carbon coating has a great effect on the performance of $LiMnPO_4$ based cathode [5,7,8,21,22]. In the previous report [23], Dahn et al. reported that the quality of carbon coating on $LiFePO_4$ was highly influenced by carbon-coating method, and their available data indicated that the $LiFePO_4$/C composite synthesized by adding carbon source via two-step process had better carbon coating and rate capability as compared to that synthesized by adding carbon source via one-step process. However, whether this experience is applicable to $LiMnPO_4$ still remains unknown and needs further study.

To address the effect of carbon source addition process on the quality of carbon coating and rate performance, $LiMnPO_4$ based materials synthesized with different carbon source addition process were investigated in the present work. The result revealed that the $LiMnPO_4$ based cathode materials synthesized by adding carbon source via one-step process showed better carbon coating and rate performance, which is different from that observed for $LiFePO_4$.

2. EXPERIMENTAL

Two types of cation doped $LiMnPO_4$ based materials, $LiMn_{0.9}Fe_{0.09}Mg_{0.01}PO_4$/C and $LiMn_{0.98}Mg_{0.02}PO_4$/C, were synthesized by a solid-state reaction method with different carbon source addition process. $LiMn_{0.9}Fe_{0.09}Mg_{0.01}PO_4$/C composites: (1) one-step process: Chemicals of LiH_2PO_4, $MnC_4H_6O_4\cdot4H_2O$, $MgC_4H_6O_4\cdot4H_2O$, $H_2C_2O_4\cdot2H_2O$ and $FeC_2O_4\cdot2H_2O$ were mixed with sucrose (14 wt.%) by ball-milling for 6h. The milled mixture was dried and then heated at 800 °C for 10 h under an Ar atmosphere; (2) two-step process: Chemicals of LiH_2PO_4, $MnC_4H_6O_4\cdot4H_2O$, $MgC_4H_6O_4\cdot4H_2O$, $H_2C_2O_4\cdot2H_2O$ and $FeC_2O_4\cdot2H_2O$ were mixed with sucrose (7 wt.%) by ball-milling for 6h. The milled mixture was dried and then heated at 800 °C for 5 h under an Ar atmosphere. Subsequently, the cooled powders were added into the aqueous solution of sucrose (7 wt.%) and fully mixed by magnetic stirring. Finally, the obtained mixture was dried and heated at 800 °C for 5 h under an Ar atmosphere. The same procedures used for $LiMn_{0.9}Fe_{0.09}Mg_{0.01}PO_4$/C were adopted to prepare $LiMn_{0.98}Mg_{0.02}PO_4$/C composites.

The crystalline phase was identified by powder X-ray diffraction (XRD). The morphology and particle size were observed by scanning electron microscopy (SEM). Raman spectroscopy was measured using a Reinshaw inVia Raman microscope at room temperature with an Ar 514.5 nm laser as excitation source. The carbon content was measured by the VarioEL III (elementar, Germany).

Electrochemical measurement was conducted by assembly of 2025 coin-type cell with a lithium metal anode. The cathode was made by mixing active material, Super P and polyvinylidene fluoride (PVDF) in a weight ratio of 8: 1: 1. The electrolyte was 1 M $LiPF_6$ in EC/DMC (1/1) solution. All cells were assembled in an Ar-filled glove box. For rate test, cells were charged at 0.1 C to 4.5 V, held at 4.5 V until the current decreased to 0.01 C, and then discharged at various rates to 2.0 V. at 25 ^{o}C. Electrochemical impedance spectroscopy (EIS) was carried out in a frequency range from 0.1 Hz to 100 kHz with an AC signal of 5 mV.

3. RESULTS AND DISSCUSSION

Figure 1 shows XRD patterns of the $LiMn_{0.9}Fe_{0.09}Mg_{0.01}PO_4$/C with different carbon source addition process. Both samples have a similar pattern which can be fully indexed into an orthorhombic structure with a space group of *Pmnb*, and the carbon source addition process did not influence lattice parameters and bulk structure of the $LiMn_{0.9}Fe_{0.09}Mg_{0.01}PO_4$. Moreover, no carbon peak is observed in the XRD patterns, indicating the amorphous nature of the carbon pyrolyzed from sucrose in the samples, but the presence of carbon could be easily observed by Raman spectroscopy.

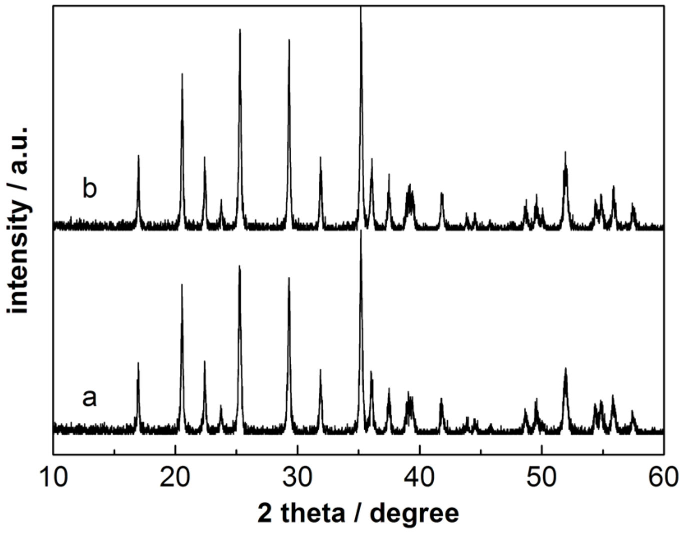

Figure 1. XRD patterns of $LiMn_{0.9}Fe_{0.09}Mg_{0.01}PO_4/C$ with different carbon source addition process: (a) one-step, (b) two-step.

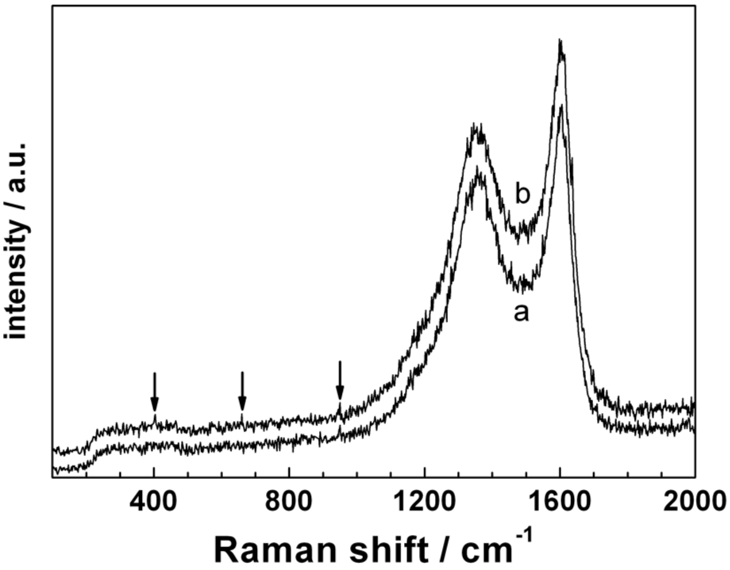

Figure 2. Raman spectra of $LiMn_{0.9}Fe_{0.09}Mg_{0.01}PO_4/C$ with different carbon source addition process: (a) one-step, (b) two-step.

Figure 2 shows Raman spectra of the $LiMn_{0.9}Fe_{0.09}Mg_{0.01}PO_4/C$ with different carbon source addition process. Both spectra have a similar profile and mainly consist of two broad bands around at 1350 and 1600 cm^{-1}, which are generally assigned to the D and G bands of carbon [24], respectively. It is seen that there is negligible difference in shape and intensity of the carbon bands of the two samples, indicating that the carbon source addition process did not affect the structure of the pyrolyzed carbon. Moreover, due to the screening effect of carbon [24], only few bands of $LiMn_{0.9}Fe_{0.05}Mg_{0.05}PO_4$ (indicated by arrows) faintly appear, but these extremely weak bands are more visible in the spectrum for the two-step sample, suggesting a more uniform carbon coating on the surface of $LiMn_{0.9}Fe_{0.05}Mg_{0.05}PO_4$ synthesized by adding carbon source via one-step process. In addition, the carbon content is 6.78 wt.% for the one-step $LiMn_{0.9}Fe_{0.09}Mg_{0.01}PO_4/C$ sample and 7.61 wt.% for the two-step one.

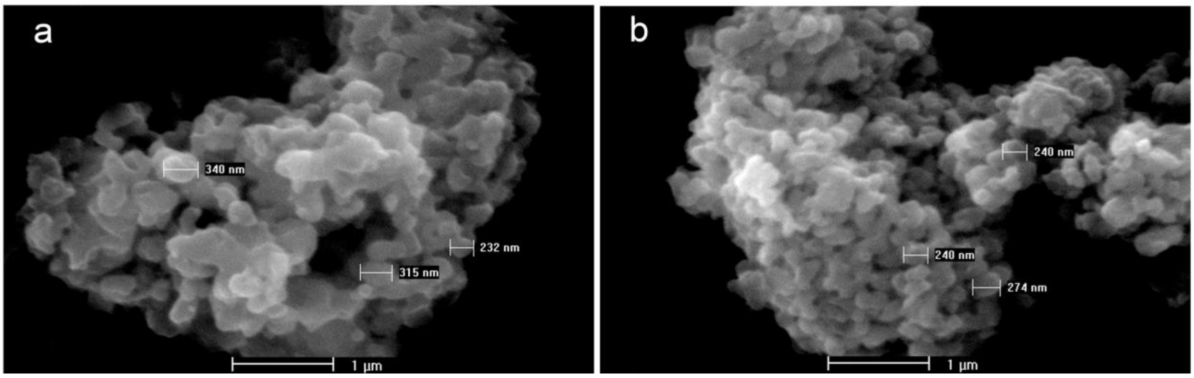

Figure 3. SEM images of $LiMn_{0.9}Fe_{0.09}Mg_{0.01}PO_4/C$ with different carbon source addition process: (a) one-step, (b) two-step.

Figure 3 shows SEM images of the $LiMn_{0.9}Fe_{0.09}Mg_{0.01}PO_4/C$ with different carbon source addition process. In general, the two samples have a similar morphology, and the micron particles are the aggregate of a large number of submicron primary crystals. However, it is noted that the primary crystals for the one-step sample is slightly larger than those for the two-step one.

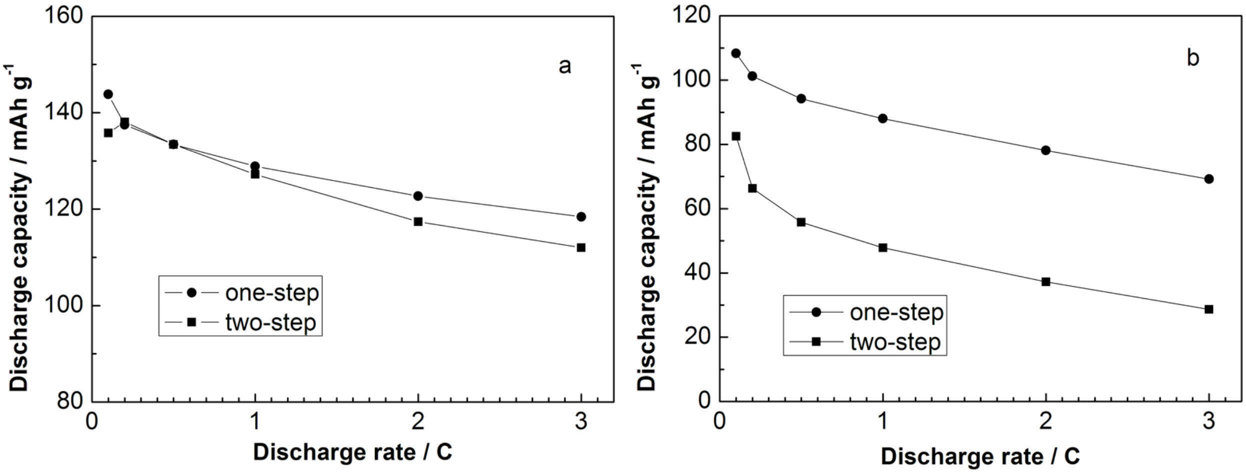

Figure 4. (a) Rate capability of $LiMn_{0.9}Fe_{0.09}Mg_{0.01}PO_4/C$ with different carbon source addition process. (b) Rate capability of $LiMn_{0.98}Mg_{0.02}PO_4/C$ with different carbon source addition process. For rate test, cells were charged at 0.1 C to 4.5 V, held at 4.5 V until the current decreased to 0.01 C, and then discharged at various rates to 2.0 V.

Figure 4a shows rate capability of the $LiMn_{0.9}Fe_{0.09}Mg_{0.01}PO_4/C$ with different carbon source addition process. It is seen that the one-step $LiMn_{0.9}Fe_{0.09}Mg_{0.01}PO_4/C$ sample has a better rate performance, though the two-step sample has relatively higher carbon content and smaller crystal size. We thought that the quality of carbon coating should be responsible for this result. As indicated in Figure 2, better carbon coating could be achieved on the surface of $LiMn_{0.9}Fe_{0.09}Mg_{0.01}PO_4$ by adding carbon source via one-step process, which would lead to faster electron conduction across the surface. This was demonstrated by EIS test as shown in Figure 5. The spectra of the two samples have a similar profile, but smaller semicircle was observed for the one-step sample, which means a smaller charge transfer resistance. Since the bulk property of the two $LiMn_{0.8}Fe_{0.19}Mg_{0.01}PO_4$ samples is unaffected by carbon source addition process and the components except the active material of the cathode for cells are the same, this charge transfer resistance difference should mainly arise from the different surface resistance. Hence, the one-step sample has a smaller surface resistance than the two-step one because of the better carbon coating, which results in better rate performance.

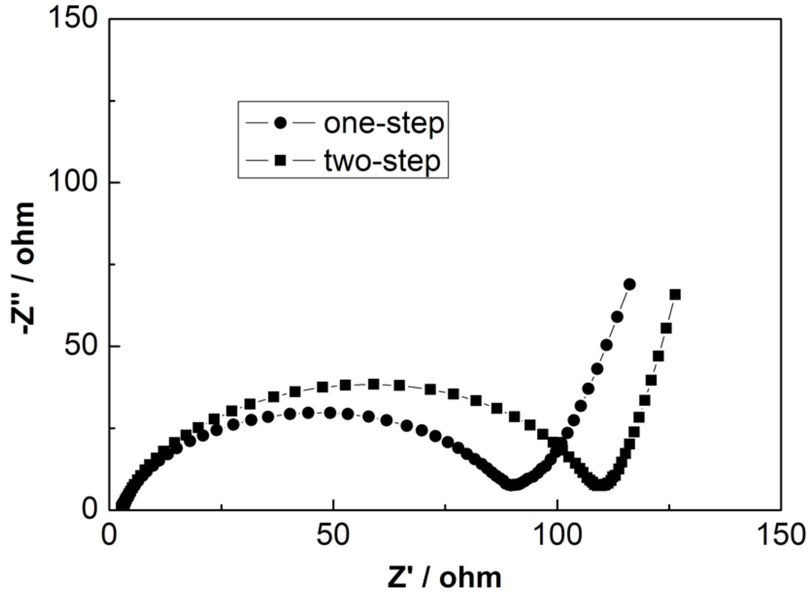

Figure 5. EIS plots of $LiMn_{0.9}Fe_{0.09}Mg_{0.01}PO_4/C$ with different carbon source addition process recorded in a discharged state after 5 cycles. Cells were charged at 0.1 C to 4.5 V, held at 4.5 V until the current decreased to 0.01 C, and then discharged at 0.1 C to 2.5 V.

To see whether such an effect of carbon source addition process is applicable to other $LiMnPO_4$ based materials, $LiMn_{0.98}Mg_{0.02}PO_4/C$ samples with different carbon source addition process were also prepared and their rate performance was shown in Figure 4b. It is evident that the one-step $LiMn_{0.98}Mg_{0.02}PO_4/C$ sample also has a better rate capability. Therefore, our results suggest that the carbon source added in one step is more effective for creating better carbon coating on the surface of the $LiMnPO_4$ based material, which results in accelerated electron transport across the surface and improved rate performance. This behavior is different from that observed for $LiFePO_4$ [23].

4. CONCLUSIONS

$LiMnPO_4$ based materials with different carbon source addition process were prepared and the effect of carbon source addition process on the properties was investigated. The result demonstrates that the carbon source added in one step is more effective for creating better carbon coating on the surface of the $LiMnPO_4$ based material, which leads to accelerated electron transport across the surface and improved rate performance.

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