

Electrochemical Performance of $\text{LiMn}_{0.9}\text{Fe}_{0.09}\text{Mg}_{0.01}\text{PO}_4/\text{C}$ Synthesized Under Vacuum Condition

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Pure $\text{LiMn}_{0.9}\text{Fe}_{0.09}\text{Mg}_{0.01}\text{PO}_4/\text{C}$ composites are successfully synthesized by a new solid-state reaction under vacuum condition. The prepared materials are characterized by XRD, SEM and charge/discharge test, and effects of heating temperature and time on the properties of $\text{LiMn}_{0.9}\text{Fe}_{0.09}\text{Mg}_{0.01}\text{PO}_4/\text{C}$ are investigated. All samples synthesized under vacuum condition have a porous characteristic. Among all samples, the sample synthesized at 700 °C for 5 h shows optimum electrochemical performance with the smallest polarization and the best rate performance. The results suggest that synthesis of $\text{LiMn}_{0.9}\text{Fe}_{0.09}\text{Mg}_{0.01}\text{PO}_4/\text{C}$ composite under vacuum condition is a viable way.

Keywords: Lithium ion batteries; cathode; LiMnPO_4 ; Vacuum; Porous

1. INTRODUCTION

Olivine structured LiMnPO_4 has recently attracted increasing interest as a promising cathode material for lithium ion batteries due to its high operating voltage (4.1 V) and high energy density (697 Wh kg^{-1}) [1-5]. Though first principle calculation revealed that LiMnPO_4 is an insulator with extremely poor electronic conductivity [6], its performance has been significantly improved by carbon coating [7-10], particle size reduction [11-14] and cation doping or substitution [15-22]. These approaches could be easily achieved, but their effects are highly dependent on the synthesis method and condition.

So far, various synthesis methods have been developed to prepare LiMnPO_4 based materials, such as solid-state reaction [2, 23], sol-gel process [12, 24-26], hydrothermal synthesis [27-29], polyol

process [13], precipitation route [3], electrostatic spray deposition [30] and spray pyrolysis [31]. Most of these methods undergo a process of heat-treatment under an inert atmosphere. The role of using inert atmosphere is to prevent the oxidation of LiMnPO_4 based materials and/or to form carbon coating on the surface of materials. From a technical point of view, we think that a vacuum condition can also achieve these roles and meanwhile, may reduce production cost, but its effect on properties of LiMnPO_4 based materials is still unknown at present. In our previous study, we reported that carbon coated $\text{LiMn}_{0.9}\text{Fe}_{0.09}\text{Mg}_{0.01}\text{PO}_4$ synthesized by a simple solid-state reaction under an Ar atmosphere had good performance [32]. In the present study, a vacuum condition is adopted to prepare $\text{LiMn}_{0.9}\text{Fe}_{0.09}\text{Mg}_{0.01}\text{PO}_4/\text{C}$ composite, and effects of heating temperature and time on the properties of $\text{LiMn}_{0.9}\text{Fe}_{0.09}\text{Mg}_{0.01}\text{PO}_4/\text{C}$ are investigated.

2. EXPERIMENTAL

$\text{LiMn}_{0.9}\text{Fe}_{0.09}\text{Mg}_{0.01}\text{PO}_4/\text{C}$ was synthesized by a solid-state method under vacuum condition. A stoichiometric amounts of LiH_2PO_4 , $\text{MnC}_4\text{H}_6\text{O}_4 \cdot 4\text{H}_2\text{O}$, $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $\text{MgC}_4\text{H}_6\text{O}_4 \cdot 4\text{H}_2\text{O}$ and $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ was mixed with 14 wt.% of sucrose by ball-milling for 6h. The milled mixture was heated at various temperatures (600, 700 and 800 °C) for different reaction times (1, 5 and 10 h) in vacuum furnace. The samples were identified by X-ray diffraction (XRD) utilizing Cu Ka radiation and the diffraction patterns were measured in the range from 10° to 80°. The morphology of the samples was observed by scanning electron microscopy (SEM). The cathode was obtained from mixing powders of the samples, carbon conductive additive (Super P) and polyvinylidene fluoride (PVDF) in an 8:1:1 weight ratio. The mixture was cast as a slurry in 1-methyl-2-pyrrolidinone (NMP) onto aluminum current collectors and dried 12 h at 80°C under vacuum. Electrochemical properties were measured using 2025 coin-type cells which were assembled in an Ar-filled glove box containing lithium foils as negative electrodes, separators and the electrolyte (1 M LiPF_6 in EC/DMC (1/1) solution). The electrochemical behavior of prepared materials was measured in a voltage range from 2.0 to 4.5 V. Cells were charged at a constant current-constant voltage (CC-CV) mode and then discharged at a constant current at 25 °C.

3. RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of the samples synthesized at different temperatures for 5 h under vacuum condition. All diffraction peaks of the three patterns could be fully indexed into an orthorhombic structure with a space group of $Pnma$, and no impurities were detected. The three samples have narrow diffraction peaks indicating a good crystallinity. The absence of carbon peaks in the XRD patterns of these samples indicates the amorphous nature of the residual carbon pyrolyzed from the sucrose. The results indicated that pure $\text{LiMn}_{0.9}\text{Fe}_{0.09}\text{Mg}_{0.01}\text{PO}_4/\text{C}$ phase could be prepared by heating the precursor under vacuum condition.

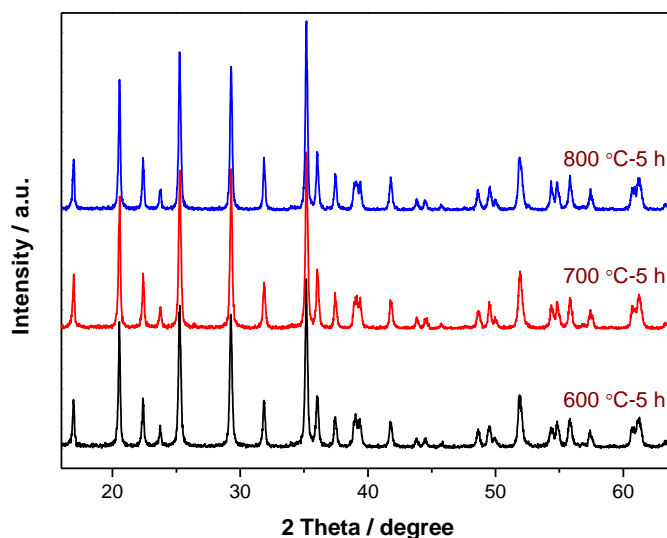


Figure 1. XRD patterns of $\text{LiMn}_{0.9}\text{Fe}_{0.09}\text{Mg}_{0.01}\text{PO}_4/\text{C}$ synthesized at various temperatures for 5 h under vacuum condition.

Figure 2 shows SEM images of $\text{LiMn}_{0.9}\text{Fe}_{0.09}\text{Mg}_{0.01}\text{PO}_4/\text{C}$ synthesized at different temperatures for 5 h under vacuum condition. It is seen that all samples consist of irregular particles with a wide size distribution from 0.1 to 1 μm and show a porous morphology. A small difference is observed on the particles synthesized at 800 $^\circ\text{C}$ which show a relatively smooth surface with a slight shrinkage of pores due to high temperature sintering. Our previous report showed that this porous structure was not observed when the samples were prepared under an Ar atmosphere using the same precursor [22, 32]. These observations indicate that the morphology of the $\text{LiMn}_{0.9}\text{Fe}_{0.09}\text{Mg}_{0.01}\text{PO}_4/\text{C}$ is highly determined by the synthesis atmosphere. The pores formation is probably related to the quick release of gas pyrolyzed from the precursor under vacuum condition.

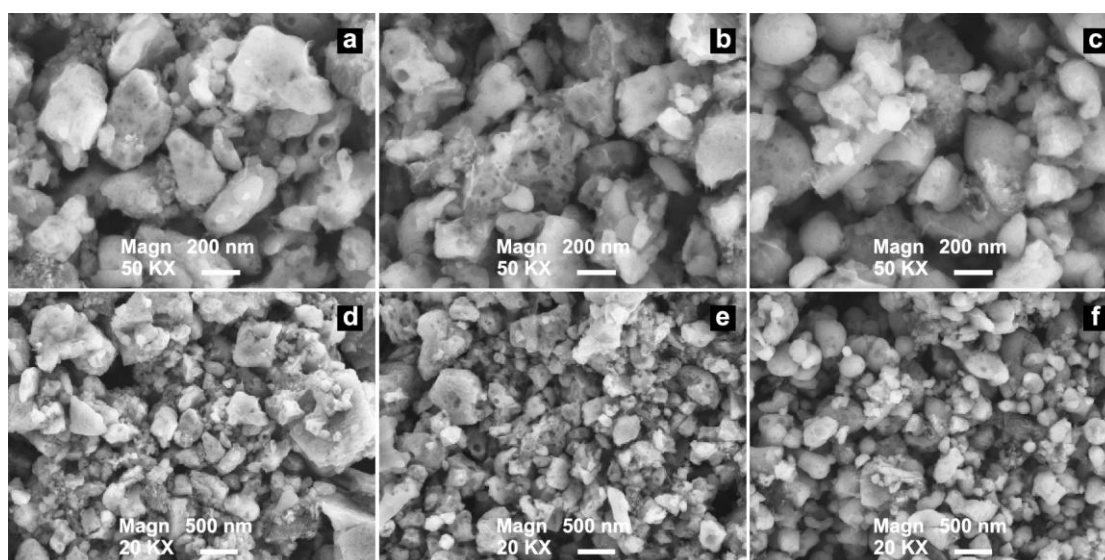
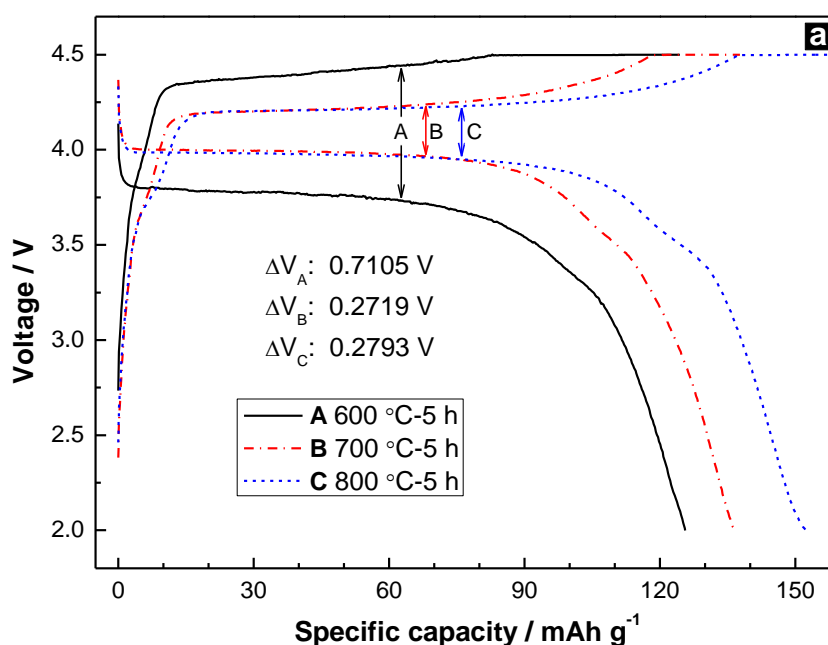


Figure 2. SEM images of $\text{LiMn}_{0.9}\text{Fe}_{0.09}\text{Mg}_{0.01}\text{PO}_4/\text{C}$ synthesized at (a, d) 600 $^\circ\text{C}$, (b, e) 700 $^\circ\text{C}$, (c, f) 800 $^\circ\text{C}$ for 5 h under vacuum condition.

Our previous work shows that heating temperature is very important for preparing carbon coated LiMnPO_4 due to the effects on the electronic conductivity of pyrolytic carbon and the crystallinity of materials[32], and the $\text{LiMn}_{0.9}\text{Fe}_{0.09}\text{Mg}_{0.01}\text{PO}_4/\text{C}$ synthesized at $800\text{ }^\circ\text{C}$ under an Ar atmosphere had the best rate performance. Herein porous characteristic is another factor that may affect the electrochemical performance, and thus the effect of heating temperature on electrochemical performance of $\text{LiMn}_{0.9}\text{Fe}_{0.09}\text{Mg}_{0.01}\text{PO}_4/\text{C}$ synthesized under vacuum condition may be different. Figure 3 shows the electrochemical performance of $\text{LiMn}_{0.9}\text{Fe}_{0.09}\text{Mg}_{0.01}\text{PO}_4/\text{C}$ synthesized under vacuum condition. Cells were charged at 0.1 C (15 mA g^{-1}) 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 3a shows charge and discharge curves of $\text{LiMn}_{0.9}\text{Fe}_{0.09}\text{Mg}_{0.01}\text{PO}_4/\text{C}$ at 0.1 C . All samples exhibit typical charge/discharge plateaus around 4.1 V which is related to $\text{Mn}^{2+}/\text{Mn}^{3+}$ redox couple. The sample synthesized at $600\text{ }^\circ\text{C}$ has the lowest specific capacity and the biggest polarization. As the temperature increased to $700\text{ }^\circ\text{C}$ and $800\text{ }^\circ\text{C}$, both samples show an increased capacity and a significantly reduced polarization. Figure 3b shows rate performance of $\text{LiMn}_{0.9}\text{Fe}_{0.09}\text{Mg}_{0.01}\text{PO}_4/\text{C}$. The sample synthesized at $600\text{ }^\circ\text{C}$ had a poor rate performance. When the discharge rate increased from 0.5 to 1 C , the capacity decreased rapidly to less than 10 mAh g^{-1} . For samples synthesized at 700 and $800\text{ }^\circ\text{C}$, enhanced rate performance was observed. The sample synthesized at $800\text{ }^\circ\text{C}$ showed higher capacities than the sample synthesized at $700\text{ }^\circ\text{C}$ when the discharge rate was smaller than 2 C . However, the sample synthesized at $700\text{ }^\circ\text{C}$ had a slight higher capacity at 2 C . The degraded rate performance of the sample synthesized at $800\text{ }^\circ\text{C}$ may be resulted from the slight change of morphology of $\text{LiMn}_{0.9}\text{Fe}_{0.09}\text{Mg}_{0.01}\text{PO}_4/\text{C}$ as observed by SEM in Figure 2. The samples synthesized at 700 and $800\text{ }^\circ\text{C}$ delivered a specific capacity of 135.1 and 150.1 mAh g^{-1} at 0.1 C , 95.8 and 99.6 mAh g^{-1} at 2 C , respectively, which are better than many of those prepared by other methods. [5, 8, 33]. In general, these results indicate that the sample synthesized at $700\text{ }^\circ\text{C}$ under vacuum condition has the best rate capability, which is different from that obtained under an Ar atmosphere.



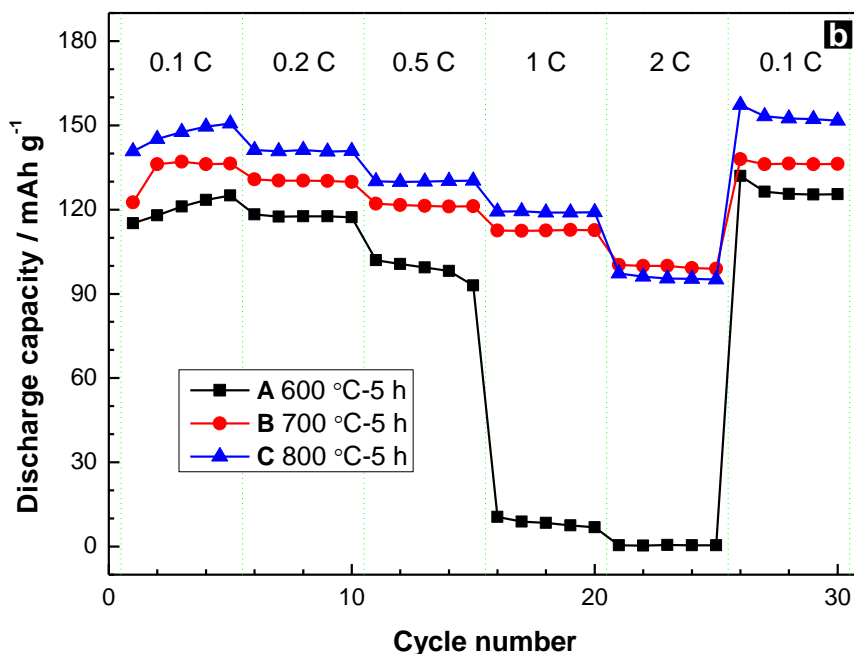


Figure 3. (a) Charge/discharge curves and (b) rate performance of $\text{LiMn}_{0.9}\text{Fe}_{0.09}\text{Mg}_{0.01}\text{PO}_4/\text{C}$ synthesized at various temperatures for 5 h under vacuum condition. Cells were charged at 0.1 C (15 mA g^{-1}) to 4.5 V, held at 4.5 V until the current decreased to 0.01 C, and then discharged at various rates to 2.0 V.

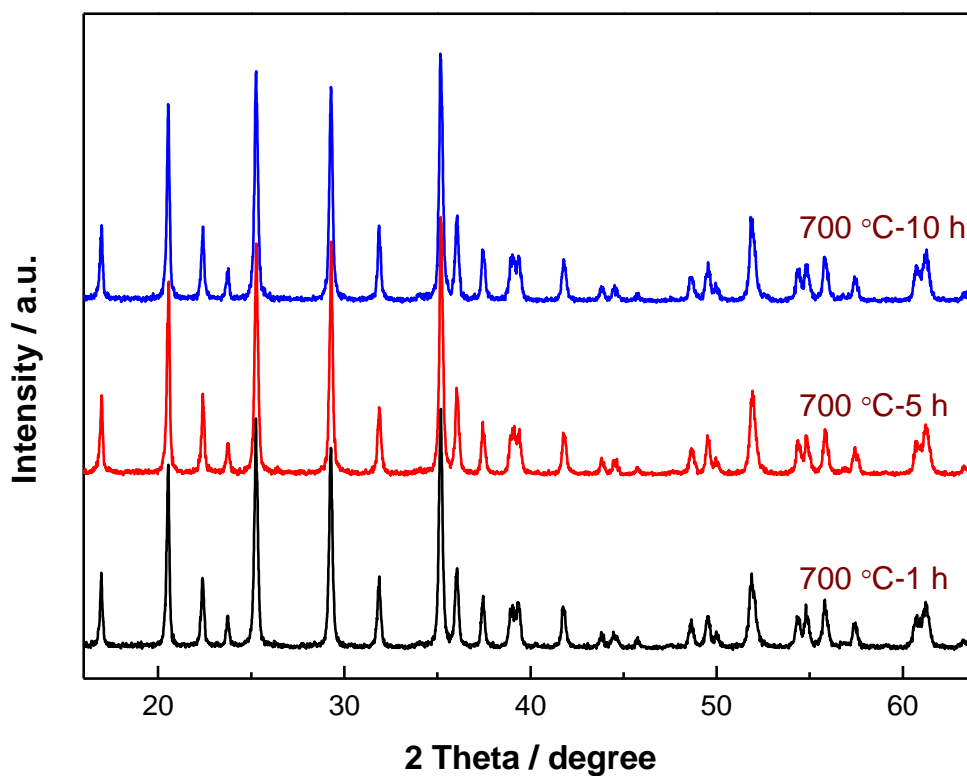


Figure 4. XRD patterns of $\text{LiMn}_{0.9}\text{Fe}_{0.09}\text{Mg}_{0.01}\text{PO}_4/\text{C}$ synthesized at 700 °C for various times under vacuum condition.

Besides heating temperature, heating time will also affect the property of LiMnPO_4 , and hence we also synthesized $\text{LiMn}_{0.9}\text{Fe}_{0.09}\text{Mg}_{0.01}\text{PO}_4/\text{C}$ at $700\text{ }^\circ\text{C}$ for various times. Figure 4. shows XRD patterns of $\text{LiMn}_{0.9}\text{Fe}_{0.09}\text{Mg}_{0.01}\text{PO}_4/\text{C}$ synthesized at $700\text{ }^\circ\text{C}$ for 1, 5 and 10 h. All samples are pure phase and no obvious changes are observed. Figure 5. shows SEM images of $\text{LiMn}_{0.9}\text{Fe}_{0.09}\text{Mg}_{0.01}\text{PO}_4/\text{C}$ synthesized at $700\text{ }^\circ\text{C}$ for various times. The sample heated for 1 h displays the smallest particle size and a little amount of pores. With increasing heating time, big particles and more pores are observed.

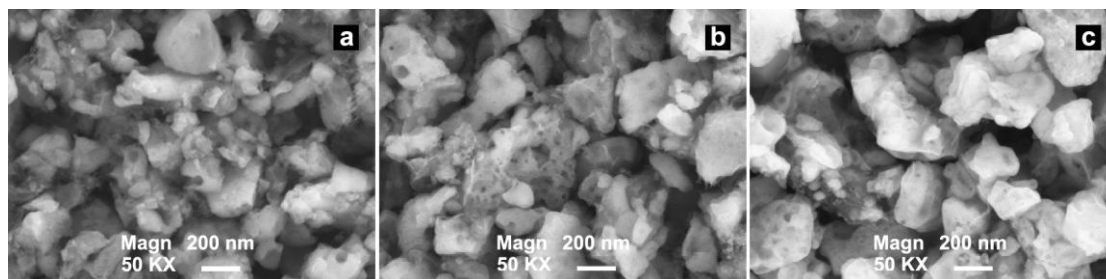
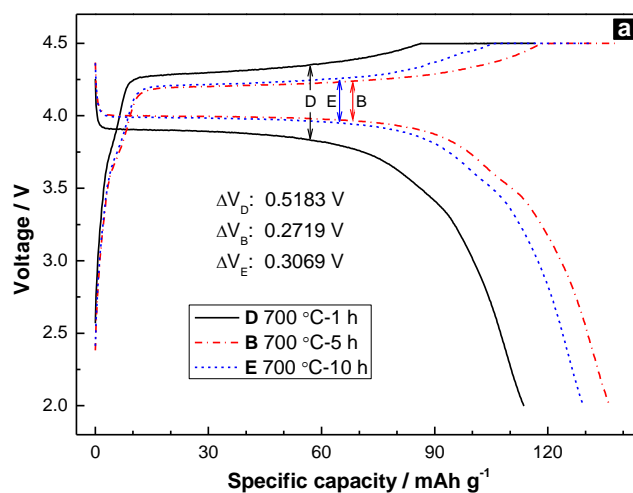


Figure 5. SEM images of $\text{LiMn}_{0.9}\text{Fe}_{0.09}\text{Mg}_{0.01}\text{PO}_4/\text{C}$ synthesized at $700\text{ }^\circ\text{C}$ for (a) 1 h, (b) 5 h and (c) 10 h under vacuum condition

Figure 6.a shows charge/discharge curves of $\text{LiMn}_{0.9}\text{Fe}_{0.09}\text{Mg}_{0.01}\text{PO}_4/\text{C}$ synthesized at $700\text{ }^\circ\text{C}$ for 1, 5 and 10 h at 0.1 C . It is evident that increasing heating time from 1 to 5 h gave rise to a remarkably reduced polarization, and further increasing heating time to 10 h had less influence on the polarization. The polarization of samples synthesized at $700\text{ }^\circ\text{C}$ for 1, 5 and 10 h is 0.5183 , 0.2719 and 0.3069 V , respectively. The sample synthesized at $700\text{ }^\circ\text{C}$ for 5 h exhibited not only the smallest polarization but also the highest discharge capacity, which implies that heating at $700\text{ }^\circ\text{C}$ for 5 h is an optimum synthesis condition under vacuum condition.



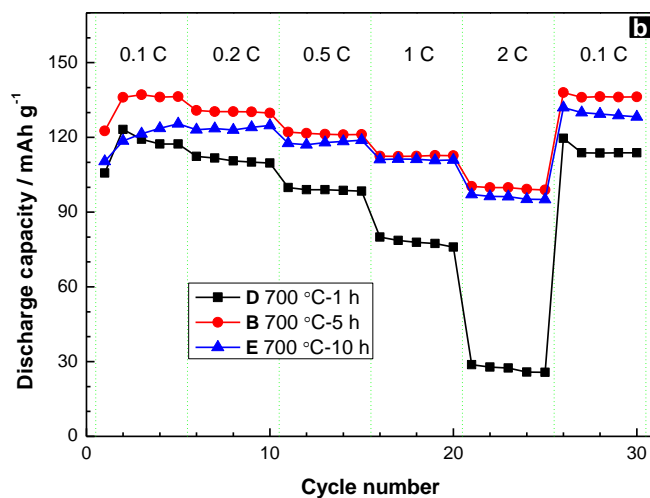


Figure 6. (a) Charge/discharge curves and (b) rate performance of $\text{LiMn}_{0.9}\text{Fe}_{0.09}\text{Mg}_{0.01}\text{PO}_4/\text{C}$ synthesized at $700\text{ }^\circ\text{C}$ for various times under vacuum condition. Cells were charged at 0.1 C (15 mA g^{-1}) to 4.5 V , held at 4.5 V until the current decreased to 0.01 C , and then discharged at various rates to 2.0 V .

This is confirmed by the rate test as shown in Figure 6.b. The average discharge capacity of samples synthesized at $700\text{ }^\circ\text{C}$ for 1, 5 and 10 h over the initial five cycles at 0.1 C is 116.6 , 133.7 and 119.9 mAh g^{-1} , respectively. As the discharge rate increased to 2 C , the sample synthesized at $700\text{ }^\circ\text{C}$ for 5 h still remained the highest capacity of 99.6 mAh g^{-1} . From the above results, it can be concluded that the sample synthesized at $700\text{ }^\circ\text{C}$ for 5 h has the best electrochemical performance.

4. CONCLUSIONS

Carbon coated $\text{LiMn}_{0.9}\text{Fe}_{0.09}\text{Mg}_{0.01}\text{PO}_4$ can be successfully synthesized under vacuum condition. All $\text{LiMn}_{0.9}\text{Fe}_{0.09}\text{Mg}_{0.01}\text{PO}_4/\text{C}$ samples are pure phase and have porous structure. The sample synthesized at $700\text{ }^\circ\text{C}$ for 5 h shows the smallest electrode polarization and the best rate performance.

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