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Short Communication

Synthesis of $MgMnSiO_4$ and Its Application as Cathode Material for Magnesium Battery

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Abstract: *Orthosilicate $MgMnSiO_4$ was prepared by sol-gel route and a subsequent heating procedure as a cathode material for rechargeable magnesium batteries. XRD patterns showed that $MgMnSiO_4$ has a orthorhombic system with space group Pbnm(62). $MgMnSiO_4$ presents good electrochemical behaviors at 10 mAg^{-1} discharge current density with specific capacity 130.1 $mAhg^{-1}$ after 20 cycles. The results show that $MgMnSiO_4$ could be a potential cathode material for high-energy magnesium secondary battery.*

Keywords: Magnesium battery; $MgMnSiO_4$; positive electrode

1. INTRODUCTION

The growing demand for portable batteries with high energy density is exerting pressure for the development of advanced new batteries. Magnesium cells may be a candidate of high energy density cells compatible with Li-ion cells, because the raw material costs may be lower than those in Li-ion cells and magnesium is less dangerous than lithium [1-4]. Metallic magnesium is a good candidate of negative electrode material because of its high theoretical specific capacity (2250 $mAh\cdot g^{-1}$), rather low electrode potential (2.37V), high safety and abundance in nature. However, it is difficult to realize reversible magnesium insertion/extraction in this material due to the strong polarization of small and divalent magnesium ion.

For large-scale applications such as hybridvehicle and electric systems, the vital issue is the availability of advanced new materials [5-6]. In 1990s, Aurbach et al. reported an attempt to construct a rechargeable magnesium battery based on an Mg_xCoO_y intercalation cathode. They developed a structure for a Mg-ion battery, which comprises a magnesium metal anode, an $Mg_xMo_3S_4$ cathode and an Mg organohaloaluminate salts electrolyte solution. This structure demonstrated good performance during thousands of charge–discharge cycles and the capacity faded by less than 15%. All of these show prospects for development and promise for applications.

Polyanion-type Cathode Materials (XO_4^{n-}; X=Si, P etc.) have been successfully used as the hosts of Li^+ insertion/extraction and as promising cathodes for Mg-ion batteries[7-9]. Polyanion-type Cathode Materials Orthosilicate $Mg_xM_ySiO_4$ (M=Mn, Co, Ni etc.) has a compact tetrahedral “anion” structure SiO_4^{4-}, which can afford intrinsic lattice stabilization through the presence of strong Si-O bonds. In addition, the strong inductive effect of SiO_4^{4-} can moderate the transition metal redox couple to generate a relatively high operating voltage. In this study, $MgMnSiO_4$ was prepared by sol-gel method and its electrochemical behavior in 0.25 $mol\cdot L^{-1}$ $Mg(AlBu_2Cl_2)_2$/THF electrolytes is discussed.

2. EXPERIMENTAL

2.1. Preparation of $MgNiSiO_4$

$MgMnSiO_4$ was synthesized via sol-gel method and a subsequent heating procedure. First, the starting materials of magnesium acetate ($MgAc_2\cdot 4H_2O$) and manganese acetate ($MnAc_2\cdot 4H_2O$) in a stoichiometric ratio were dissolved in a beaker with alcohol and the mixture was magnetically stirring. After a clear solution formed, the Ethyl silicate ($C_8H_{20}O_4Si$) is added by drop wise into the resulting solution while increasing the temperature to 60 ~ 90 °C and keep stirring 18-24h. The gel was decomposed at 100 °C in vacuum drying oven for 12h, and the obtained product was ground, and sintered at 800 °C for 24 h under conditions of argon shield. The final product was $MgNiSiO_4$.

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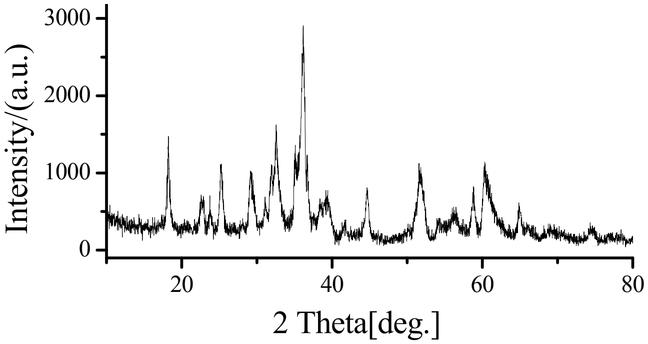

Figure 1. The XRD patterns of $MgMnSiO_4$ sample

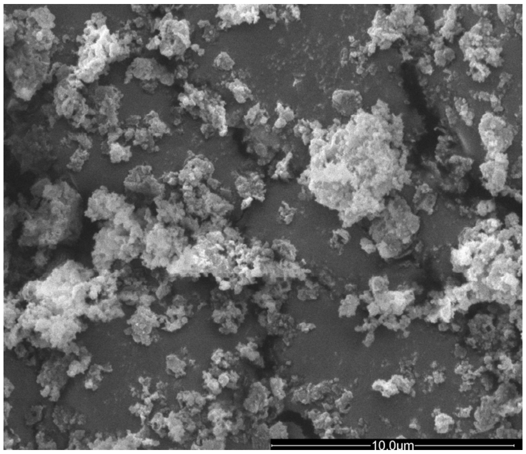

Figure 2. SEM image of $MgMnSiO_4$

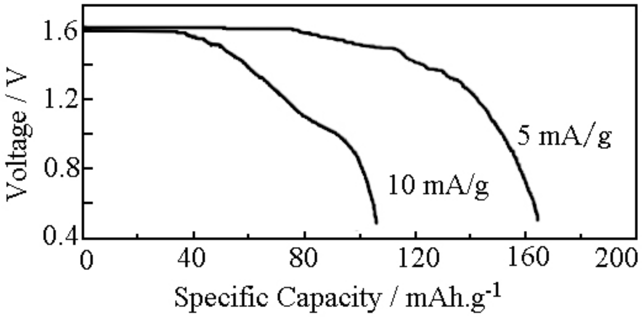

Figure 3. The voltage profiles of $MgMnSiO_4$ at 5 and 10 $mA{\cdot}g^{-1}$ at 25 °C

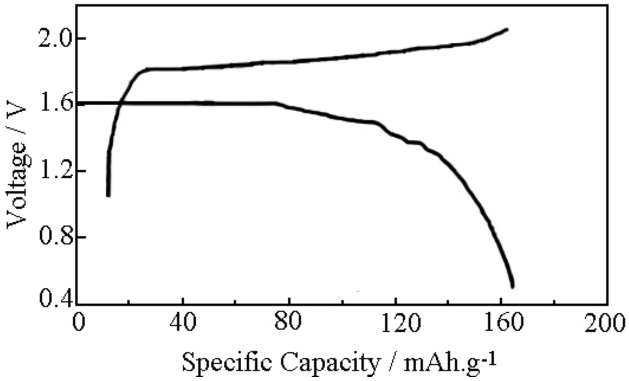

Figure 4. Typical charge/discharge curves of $MgMnSiO_4$ electrodes.

2.2. Characterization and Electrochemical Measurements

2.2.1. XRD and SEM

X-ray diffraction(XRD) was performed on a Rigaku D/max-3B X-Ray diffractometer, the X-ray beam was nickel-filtered Cu *Ka* (λ=0.15406 nm) radiation operated at 40 kV and 30 mA; and the data were collected from 5 ° to 80 °(2θ) at a scanning rate of 5 °/min.

The morphology of the samples was observed by JEOL JSM-5600LV SEM.

2.2.2. Electrochemical measurements

Electrochemical magnesium insertion from 0.25 M $Mg(AlBu_2Cl_2)_2$/THF solution prepared according to the method used by Aurbach et al. was performed in cell [5]. The sample electrode pellet was prepared by pressing the 80:10:10 (in wt.) mixture of $MgMnSiO_4$, acetylene black and PTFE. Magnesium ribbon was used as the counter electrode. Test cells were assembled in an argon-filled dry glove box. The galvanostatic charge/discharge tests were performed with a Land CT2001 battery tester at different current densities in a voltage range of 0.5-2.0 V at 25 °C. The cell assembly was carried out in a controlled environment using a glove box under an argon atmosphere. Then, the cell was maintained at 20 °C for 24 h in order to establish the equilibrium state of the electrodes with the electrolyte. Galvanostatic charge/discharge was recorded with a Land battery measurement system (Wuhan, China) with the cutoff voltage of 2.1/0.5 V, at room temperature.

3. RESULTS AND DISCUSSION

3.1. Characterization of sample

The results of the X-ray diffraction study have shown that $MgMnSiO_4$ power is mainly a single phase material. The corresponding X-ray power diffraction pattern obtained at room temperature is presented in Fig. 1. The $MgMnSiO_4$ compounds belong to the orthorhombic system with space group Pbnm(62) and the cell parameters: a=0.4794 nm, b=1.0491 nm, c=0.6123 nm.

In natural olivine $MgMnSiO_4$, the Mn and Mg ions were located in the center of the MO6 units, while the alternating sites of Mn1Mg1 and Mg2Mn2 were located within the octahedrons. Silicon sites were located within the tetrahedrons, while oxygen atoms were located in the corners[10]. The crystal structure revealed mixed site occupation of the same octahedral sites by Mg and Mn atoms with different atomic site occupied fractions. In other words, there were two positions for the Mg atoms to occupy in the crystal structure with different geometrical circumstances.

SEM: Fig. 2 shows the microspheres for $MgMnSiO_4$ of heat-treated at 900°C. The results show they are highly dispersive particles with diameters ranged at 1~4µm.

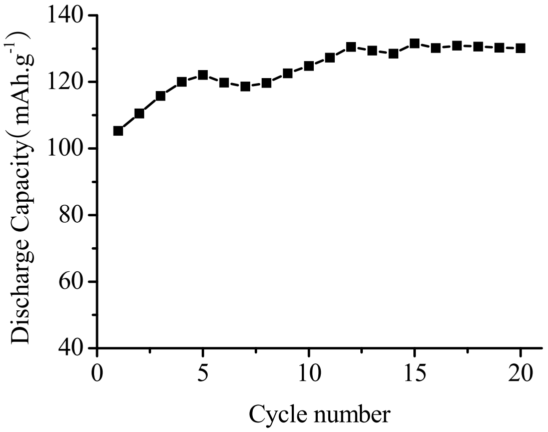

Figure 5. Cyclic performance of $MgMnSiO_4$ tested at 10 mA·g^{-1} at 25 °C

3.2. Electrochemical properties

Fig. 3 presents the first discharge of $MgMnSiO_4$ curves at different discharge current densities. It can be seen from Fig. 4 that the $MgMnSiO_4$ present good electrochemical behaviors at 10 mA·g^{-1} discharge current density with initial specific capacity 105.3 mAh·g^{-1}. However, it gave the best result with initial specific capacity 164.1 mAh·g^{-1} at lower discharge current density 5 mA·g^{-1}. These results suggest that the kinetic properties have important impacts on the electrochemical performance of this material.

The initial galvanostatic discharge/charge curves for $MgMnSiO_4$ test cells are shown in Figure 4, measured at a current density of 5 mA·g^{-1} in the potential range of 0.5-2.0 V at 25 °C. The cell exhibits one charge plateaus around 1.6V and correspondingly one discharge plateaus around 1.8V.

Fig. 5 shows the variation of the discharge capacity with the cycling number. This is the result of prototype Mg batteries obtained with coin-type cells comprising Mg anodes and $MgMnSiO_4$ cathodes. The discharge capacity of $MgMnSiO_4$ is 130.1 mAhg^{-1} after 20 cycles at a current density of 10 mAg^{-1}, Thereby, this material seems to be a good cathode material proposed for rechargeable Mg batteries.

4. CONCLUSION

$MgMnSiO_4$ materials prepared by sol-gel approach exhibited distinct and reversible electrochemical intercalation behavior. Preliminary electrochemical data demonstrated that $MgMnSiO_4$ as a novel cathode material for rechargeable magnesium battery. The characteristics of this battery show important advantages in terms of environmental considerations, safety and relative high capacity. Further work on their applications and intercalation mechanism is in progress.

5. ACKNOWLEDGMENTS

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