MgFeSiO₄ prepared via a molten salt method as a new cathode material for rechargeable magnesium batteries

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Well-crystallized MgFeSiO₄ microparticles were synthesized at different temperatures by a simple molten salt method using KCl flux. As a new cathode for rechargeable magnesium batteries, the material shows a reversible Mg²⁺ intercalation-deintercalation process. In 0.25 mol/L Mg(AlCl₂EtBu)₂/THF electrolyte, MgFeSiO₄ synthesized at 900°C can deliver a 125.1 mAh/g initial discharge capacity and a 91.4% capacity retention on the 20th cycle at a rate of 0.1C (about 15.6 mA/g). The results show that MgFeSiO₄ could be a good host for Mg²⁺ intercalation, and a potential cathode material for high-energy rechargeable magnesium batteries.

rechargeable magnesium batteries, cathode materials, molten salt method

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Following the development of electrolyte solutions based on Mg(AlCl₃R)₂ and Mg(AlCl₂RR')₂ (R, R'=alkyl or aryl groups) in tetrahydrofuran (THF) for electrochemically reversible deposition-dissolution of magnesium [1,2], rechargeable magnesium batteries have received increasing attention because of their low cost, safety, environmentally friendly nature, low electrode potential and high charge density of metallic magnesium [3]. It is said that rechargeable magnesium batteries, which are not designed to compete with lithium batteries in terms of energy density for small scale application, may eventually replace the standard batteries used in large-scale energy conversion [4,5]. However, the strong polarization of small and divalent Mg²⁺ makes it difficult to achieve reversible magnesium intercalation-deintercalation in many hosts [6]. So far, most effective magnesium insertion cathodes, such as transition metal sulfides or oxides, exhibit either a small discharge capacity or a low discharge voltage [7–9]. Therefore, it is necessary to develop new types of competitive insertion materials for the

development of high-energy rechargeable magnesium batteries.

As magnesium intercalation hosts, the materials should possess voids of suitable dimensions to uptake Mg²⁺ and maintain good structural stability. Polyanionic compounds (XO₄ⁿ⁻; X=P, Si, Ge etc.) have been successfully used as the hosts of Li⁺ insertion/extraction and as promising cathodes for lithium-ion batteries [10]. Recently, we reported the electrochemical performance of magnesium manganese silicate as a novel cathode material for rechargeable magnesium [11–13]. It was clearly shown that the electrode could be cycled, although the kinetic performance and cycling stability remain unsatisfactory. Orthosilicate Mg_xM_ySiO₄ (M=Mn, Fe, Ni, x+y=1) has a compact tetrahedral “anion” structure (SiO₄)⁴⁻, which can afford intrinsic lattice stabilization through the presence of strong Si–O bonds. Furthermore, the strong inductive effect of (SiO₄)⁴⁻ can moderate the transition metal redox couple to generate a relatively high operating voltage. Herein, MgFeSiO₄ was prepared by a simple molten salt method, and the Mg²⁺ intercalation-deintercalation process was investigated as a new cathode material for rechargeable magnesium batteries.

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1 Experimental

1.1 Preparation and characterization of materials

KCl (melting point is 780°C) was used as flux after drying overnight at 120°C under vacuum. Magnesium oxide (MgO), Iron (II) oxalate dihydrate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) and silicon dioxide (SiO_2 , 15–20 nm) powder were analytically pure and used without further purification. The stoichiometric amount for the precursors was accurately controlled with the molar ratio of $\text{Mg}:\text{Fe}:\text{Si}=1:1:1$. The mixture (flux/reactants = 4:1 by molar ratio) was mixed using a mortar and pestle for a few minutes and poured into a corundum crucible. It was then dried at 120°C for 5 h under vacuum to remove the water content from the mixture. After that, the mixture was immediately transferred to a tube furnace and heated in an Ar atmosphere at 350°C for 2 h to remove oxalate groups, followed by final firing at different temperatures (800, 900 and 1000°C) at a rate of 2°C/min for 6 h, then cooling to room temperature naturally. At last, the products were washed three times with deionized water to dissolve any remaining salt, separated by centrifugation, and dried under vacuum at 100°C for 2 h.

X-ray diffraction (XRD) analyses were carried out using a Rigaku diffractometer D/MAX-2200/PC equipped with $\text{Cu K}\alpha$ radiation ($\lambda=0.15418$ nm) with 2θ ranging from 15° to 75° at a rate of 4°/min to analyze the structure of the obtained powder. The particle morphology was observed using scanning electron microscopy (SEM) with a JEOL field-emission microscope (JSM-7401F).

1.2 Electrochemical measurements

Electrodes were prepared by stirring the mixture of active material, super-P carbon powder (Timcal) and poly (vinylidene fluoride) (PVDF) dissolved in N-methyl-2-pyrrolidinone with a weight-ratio of 78:12:10, loading the mixture on a copper foil current collector with a scraper, drying at 80°C for 2 h, cutting into circular slices with 12.5 mm diameter, pressing at 2 MPa, and then further drying at 100°C for 3 h under vacuum. The active material loading was about 0.3 mg and the typical thickness of the active layer was 50 μm . The electrochemical performance of the materials was tested via CR2016 coin cells with a magnesium ribbon counter electrode, Enter PE membrane separator and 0.25 mol/L $\text{Mg}(\text{AlCl}_2\text{EtBu})_2/\text{THF}$ electrolyte [14]. The cells were assembled in an Ar-filled glove box (Mbraun, Unilab, Germany). Galvanostatic charge-discharge measurements were conducted at ambient temperature on a Land battery measurement system (Wuhan, China) with a cut-off voltage of 2.1/0.5 V vs. Mg/Mg^{2+} . Cyclic voltammetry (CV) and electrochemical impedance measurements were carried out using a CHI650C Electrochemical Workstation (Shanghai, China). The scanning rate for CV was 0.1 mV/s and the amplitude of the alternating voltage signal in impedance

measurements was 5 mV over the frequency range between 10^5 and 1 Hz. The electrochemical impedance measurements were performed at the open-circuit voltage (OCV) after the CV experiments.

The thermal stability of material at a charged state was examined by differential scanning calorimetry (DSC, Netzsch STA 449 F3 Jupiter, Germany). The material in the coin cell was galvanostatically charged to 2.1 V with a 0.2 C rate (1 C means the rate charged or discharged of the theoretical capacity of MgFeSiO_4 in 1 h, 155.6 mA/g), followed by potentiostatically charging at constant voltage of 2.1 V for 40 h. Then, the cell was disassembled in the Ar-filled glove box. The cathode powders with residual electrolyte were removed from the Cu substrate using a doctor blade, and 5–10 mg samples were immediately sealed in Al crucibles. The DSC experiments were carried out at a rate of 20°C/min under a N_2 atmosphere in the range 100–400°C.

2 Results and discussion

The XRD patterns of the as-prepared powders, which were fired respectively at 800, 900 and 1000°C are shown in Figure 1. All the diffraction peaks for the 3 samples can be well indexed to orthorhombic MgFeSiO_4 (standard database JCPDS card No: 76-0853), and no other peaks for impurities were detected. The peaks sharpen with increasing temperature, indicating the growth of the particles. In natural olivine MgFeSiO_4 (space group $Pbnm$), Fe and Mg occupy two non-equivalent octahedral structural sites, denoting M1 (the more distorted) with point symmetry $\bar{1}$ and M2 (the larger) with point symmetry m [15]. The crystal structure in the polyhedral representation with coordinate system is presented in Figure 2 [16]. Typical octahedral and tetrahedral patterns can be recognized. Mg^{2+} and Fe^{2+} are located in the center of the MO_6 units. Alternate sites of Mg1Fe1 (sphere marked as 1) and Mg2Fe2 (spheres marked as 2) are within the octahedra and Si sites within the tetrahedra, while oxygen atoms are at the corners. The high-temperature partitioning of Fe and Mg between the M1 and M2 sites occurs in synthetic olivine, and Fe segregates progressively into the M1 sites, with Mg, which increases continuously with rising temperature, preferring the M2 sites [17].

Figure 3 shows SEM photographs of MgFeSiO_4 synthesized at 1000, 900 and 800°C. The materials are composed of well-shaped microparticles. The particle size increases with increasing temperatures due to better growth of particles at a higher temperature. The less-aggregated crystalline powder derives from the medium action of KCl flux during the calcination process.

Cyclic voltammetry (CV) measurements were carried out to characterize the process of electrochemical magnesium de-intercalation and intercalation. Figure 4 shows a typical steady state (after 5–6 preliminary cycles) voltammetric

Figure 1 X-ray powder diffraction patterns of as-prepared powders, which were fired at different temperatures, and the standard pattern of JCPDS 76-0853.

Figure 2 Ordered crystal structure of natural olivine MgFeSiO_4 in polyhedral representation. Alternate Mg1Fe1 and Mg2Fe2 are shown as spheres marked 1 and 2, respectively.

curve of MgFeSiO_4 synthesized at 900°C at a scan rate of 0.1 mV/s . A strong anodic peak and two cathodic peaks (a' and b') can be distinguished, attributed to the expected feature of magnesium de-intercalation and intercalation, respectively. The result means that Mg^{2+} intercalation into the magnesium-deficient electrode proceeds via two stages, although only one de-intercalation process can be observed.

The insert in Figure 4 presents the Nyquist plots obtained after CV experiments for the samples synthesized at different temperatures. The plots are similar to each other in shape, with a semicircle appearing in the high frequency domain and a straight line in the low frequency region. The semicircle is the smallest for the sample synthesized at 900°C , suggesting that the electrode possesses an easier charge transfer process than others.

Figure 3 SEM images of MgFeSiO_4 synthesized at (a) 1000°C , (b) 900°C and (c) 800°C .

Figure 4 A typical steady state (after 5–6 preliminary cycles) voltammogram of MgFeSiO_4 synthesized at 900°C at 0.1 mV/s . The insert shows the Nyquist plots obtained after the CV experiments for the samples synthesized at different temperatures.

Figure 5 shows typical steady state charge-discharge curves for MgFeSiO_4 synthesized at different temperatures at a rate of 0.1 C (about 15.6 mA/g) and MgFeSiO_4 synthesized at 900°C at 0.2 C . For the material synthesized at 900°C , 139.2 mAh/g (0.89 Mg^{2+} per unit formula), that is, 89.5% of the theoretical value of 155.6 mAh/g , is extracted from the pristine sample during charging, and 113.7 mAh/g (0.73 Mg^{2+} per unit formula) is intercalated back over the following discharge at 0.1 C . For those obtained at 1000 and 800°C , the charge and discharge capacity are 83.1 and 79.4 , 119.2 and 109.1 mAh/g , respectively. Two discharge voltage plateaus can be distinguished at about $1.5\text{--}1.6 \text{ V}$ and $1.05\text{--}1.15 \text{ V}$, related to the peaks a' and b' in Figure 4, respectively.

As mentioned above, Mg prefers more M2 sites in high-temperature samples. It is obvious that the plateau at $1.05\text{--}1.15 \text{ V}$ becomes longer for the samples heat-treated at higher temperature, especially for the sample obtained at

Figure 5 Typical steady state charge-discharge curves of MgFeSiO_4 synthesized at different temperatures at 0.1 C (about 15.6 mA/g) and MgFeSiO_4 synthesized at 900°C at 0.2 C.

1000°C. It can be suggested that 1.05–1.15 V plateau is related to the intercalation of Mg at the M2 sites, and 1.5–1.6 V plateau to Mg intercalation at the M1 sites. Furthermore, the capacity fraction of the 1.05–1.15 V plateau for the material obtained at 900°C increases with an increase in the rate to 0.2 C. This result means that Mg^{2+} intercalation in the M2 sites is kinetically superior to that in the M1 sites, although the occupation of Mg^{2+} in the M1 sites is thermodynamically superior to that in the M2 sites.

Figure 6 shows the cycling performance of MgFeSiO_4 obtained at different temperatures at 0.1 C and that of the 900°C-material at 0.3 C. The capacity for the material synthesized at 800°C increases during the initial cycles, indicating an activation process due to the slow penetration of electrolyte between the smaller particles. Compared with other samples, the 900°C-material shows a higher discharge capacity and better cycling stability. The initial discharge capacity is 125.1 mAh/g and the capacity retention is 91.4% at the 20th cycle, against the 28.5 mAh/g initial capacity for the material synthesized at 800°C and the 87.0% capacity retention for the material synthesized at 1000°C. The difference in intercalation energy at the M1 or M2 sites results in a different electrochemical performance and the 900°C-

Figure 6 Discharge capacity versus cyclic number curves of MgFeSiO_4 synthesized at different temperatures at 0.1 C (about 15.6 mA/g) and that of the 900°C-material at 0.3 C.

material probably undergoes an easier intercalation process, which has been shown in electrochemical impedance experiments. The material still maintains good cycling performance at 0.3 C, as shown in Figure 6.

Differential scanning calorimetry (DSC) experiments were carried out to investigate the thermal stability of the MgFeSiO_4 cathode material at a charged state in contact with the electrolyte solution. Figure 7 shows the results of the thermal analyses of the 900°C-material. A sharp exothermic peak at 136.3°C was observed and the total heat flow value was 93.38 J/g. The peak may be due either to evaporation of the electrolyte solvent or the decomposition of the surface film. The three small exothermic peaks with low heat flow that appeared at 150–270°C may be caused by thermal decomposition of the products of the electrochemical deintercalation reaction. The DSC result indicates that the thermal stability of MgFeSiO_4 is good.

Figure 7 DSC curve of the 90°C- MgFeSiO_4 cathode material after being charged galvanostatically with a 0.1 C rate to 2.1 V and potentiostatically at 2.1 V for 40 h.

3 Conclusions

We describe here a one-pot mass production process for MgFeSiO_4 cathode material of rechargeable magnesium batteries through a simple molten salt route heat-treated at 800, 900 and 1000°C. The material synthesized at 900°C shows a 125.1 mAh/g initial discharge capacity and a 91.4% capacity retention on the 20th cycle at 0.1 C. For the sake of improving the capacity and cycling stability of the process, the materials doped with other transition elements (such as Mn and Ni) can be further attempted.

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