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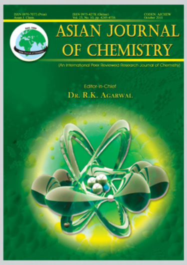

Synthesis and Characterization of Cathode Material for Secondary Magnesium Batteries

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In this work, a cathode material for secondary magnesium batteries $MgMnSiO_4$ was synthesized *via* sol-gel method. TG-DTA, XRD, IR, SEM were used to characterize the reaction and product. The results showed that the product is well-crystalline and gets small particle size. Simulation cells were assembled employing the product as positive electrode. The initial discharge capacity for $MgMnSiO_4$ is 95 mAh g^{-1} and it shows great promise for secondary batteries.

Key Words: Secondary magnesium batteries, $MgMnSiO_4$, Cathode material, Synthesis.

INTRODUCTION

Li-ion battery has become the main source for the portable devices, replacing older nickel-cadmium and nickel-metal-hydride batteries. It has higher energy density than conventional system; however, its cost is also higher. Following the achievements in the field of lithium-ion batteries, there have been more and more attempts over the years to develop rechargeable magnesium batteries, due to its natural abundance, relatively low price and higher expected safety, although the equivalent weight of magnesium (12 g/Faraday) is higher than that of lithium (7 g/Faraday) and its electrode potential is less negative than that of lithium. Magnesium batteries are not competitive with lithium batteries in terms of energy density and high operation voltage for small-scale applications. However, magnesium battery systems may be a cheap, safe and environmentally friendly substitute for heavy load, dangerous battery systems[1-3].

Magnesium rechargeable batteries had not been paid much attention because of mainly two problems. One is passivity surface film grown on magnesium, which obstructs reversible electrochemical reaction. Another difficulty is of insertion and diffusion in cathode material for divalent magnesium ion[4,5].

Recently, it has been suggested that Li_2MnSiO_4 can store large amounts of charge per unit mass as cathode materials for rechargeable lithium batteries *via* a highly reversible redox reaction[6]. The similar ion sizes of monovalent lithium and divalent magnesium cation may lead, from a steric point of view, to an analogous insertion electrochemistry. Here, we propose that $MgMnSiO_4$ is feasible as potential cathode materials for magnesium batteries. In this work, we report the synthesis of $MgMnSiO_4$ samples by sol-gel method and investigated electrochemically as a magnesium host.

EXPERIMENTAL

All the chemicals *viz*., ethyl silicate, $Mg(CH_3COO)_2{\cdot}4H_2O$, $Mn(CH_3COO)_2{\cdot}4H_2O$ and alcohol used in the experiment are of analytical grade.

General procedure: $MgMnSiO_4$ was synthesized *via* sol-gel method. First, $Mg(CH_3COO)_2{\cdot}4H_2O$ and $Mn(CH_3COO)_2{\cdot}4H_2O$ in a stoichiometric ratio were dissolved in alcohol with magnetic stirring. After a clear solution formed and then the ethyl silicate is added dropwise into the resulting solution while increasing the temperature to 60-90 ºC and keep stirring 18-24 h. The gel was decomposed at 100 ºC in vacuum drying oven for 12 h and the obtained product was ground and sintered at 800 ºC for 24 h under conditions of argon shield.

TG-DTA thermal analysis was carried out on Shimadzu TA-60 with the heating temperature from 20-900 ºC at 20 ºC/min in N_2. XRD (X-ray power diffraction) patterns for all the samples were measured by Rigaku D/max-3B X-ray diffractometer with CuK_α radiation (λ = 0.15406 nm). The Fourier transform infrared (FTIR) spectra were recorded on a Thermo Nicolet Nexus in the wave number range of 4000-400 cm^{-1}. Care was taken to press all the KBr pellets under the same conditions to minimize any effect of pressure on peak frequencies for the power samples. The morphology of the samples was observed by JEOL JSM-5600LV SEM (scanning electron microscope).

Magnesium ion intercalation performances of the samples were evaluated in Mg test cells. The cathode materials were prepared by mixing the samples with acetylene black and polytetrafluoro ethylene (PTFE) with a weight ratio of 85:10:5 in ethanol to ensure homogeneity. After the ethanol was evaporated, the mixture was rolled into a sheet and the sheet was cut into circular strips of 8 mm in diameter. The strips were then dried at 100 ºC for 10 h. Magnesium metal was used as an anode. The electrolyte was composed of 0.25M $Mg(AlBu_2Cl_2)_2$ /THF solution was performed in a cylindrical glass cell. 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 25 ºC.

RESULTS AND DISCUSSION

Fig. 1 shows TG-DTA curves of the precursor for $MgMnSiO_4$. The endothermic peak at 87 ºC with slight weight loss can be ascribed to desorption of absorbed water. Endothermic peaks at 163 ºC with a significant weight loss, respectively can be ascribed to the decomposition of ester. Following the endothermic peak, an acute exothermic peak around 357 ºC can be attributed to the decomposition of acetate.

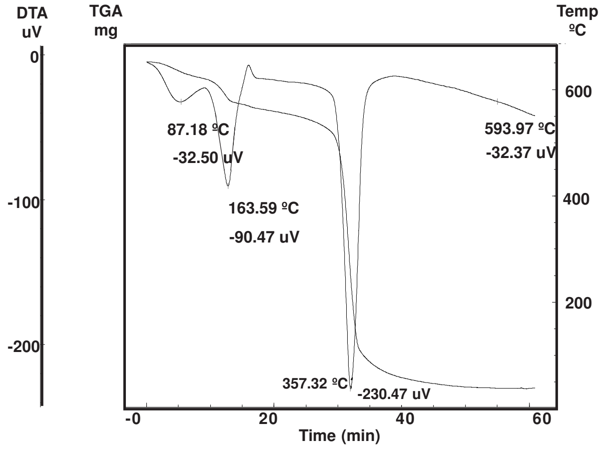

Fig. 1. TG-DTA curve of the precursor

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. 2. 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.

The FT-IR spectra of diffraction patterns $MgMnSiO_4$ are shown in Fig. 3. The spectra are dominated by intense, overlapping intramolecular SiO_4^{4-} stretching modes that range from 1100-400 cm^{-1}. Characteristic absorption peaks of $MgMnSiO_4$ are divided into four main parts. The first part between 1100-1000 cm^{-1} is great intensity and due to Si-O-Si antisymmetric stretching vibration, the second part with moderate strength absorption bands between 800-550 cm^{-1} is due to Si-O stretching vibration, The third part within a range around 550 cm^{-1} is expected for Mn-O vibration mode. The fourth part between 460-420 cm^{-1} belongs to Si-O bending vibration.

Fig. 4 showed microstructure of the fracture surfaces of the specimen pellet heat-treated at 900 ºC. This material has a small particle size.

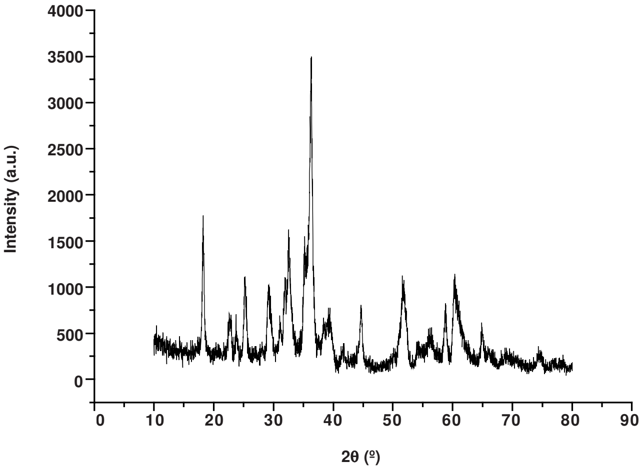

Fig. 2. X-ray diffraction pattern of $MgMnSiO_4$ sample

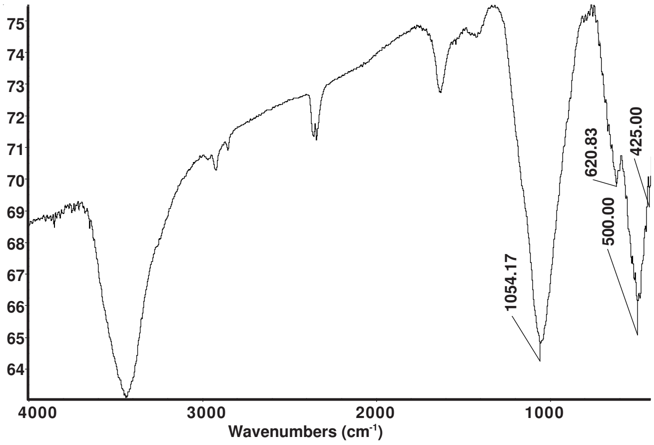

Fig. 3. FTIR spectrum of $MgMnSiO_4$

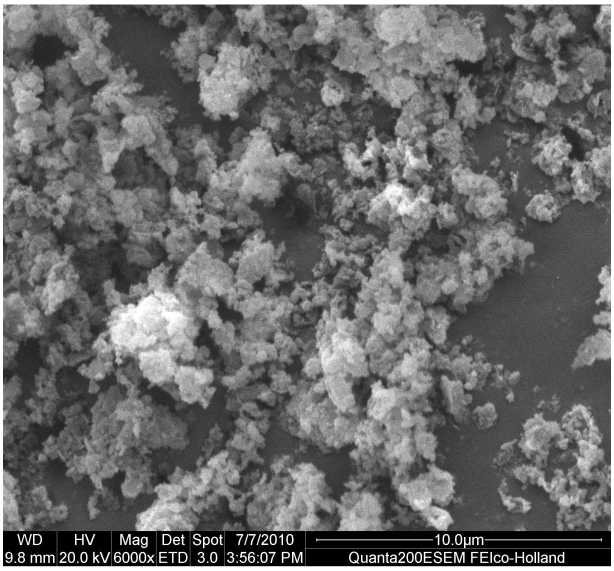

Fig. 4. SEM image of $MgMnSiO_4$

Electrochemistry: The initial galvanostatic discharge/ charge curves for $MgMnSiO_4$ test cells are measured at a current density of 0.02 mA/cm^2 in the potential range of 0.5-2.0 V at 25 ºC. Cell exhibits one charge plateaus around 1.5 V. The initial discharge capacities for $MgMnSiO_4$ is 95 mAh g^{-1}, the discharge capacities is 63 mAh g^{-1} after 10 cycles.

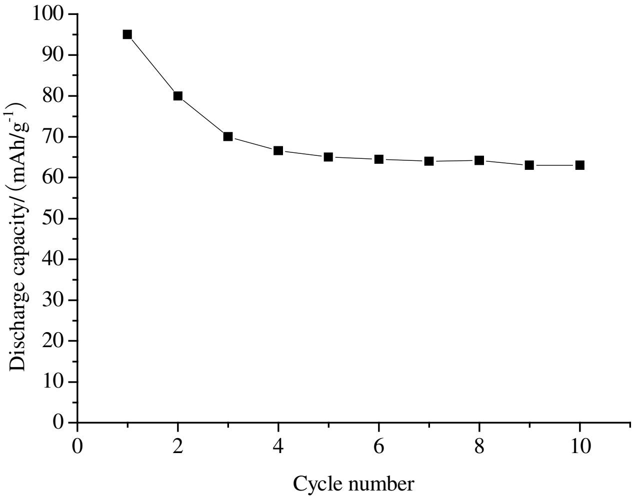

Fig. 5. Cyclic performance of $MgMnSiO_4$

Conclusion

A new cathode material $MgMnSiO_4$ was synthesized *via* sol-gel method. It was found to electrochemically absorb and desorbs magnesium. The discharge capacities for $MgMnSiO_4$ is 63 mAh g^{-1} after 10 cycles. The use of $MgMnSiO_4$ as active cathode materials for magnesium batteries in general shows great promise for secondary batteries.

ACKNOWLEDGEMENTS

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