



Asian Journal of Chemistry; Vol. 24, No. 5 (2012), 1909-1911

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in



Sol-Gel Synthesis of Cathode Material MgCoSiO₄ for Magnesium Cells

JIAN-ZHI SUN

Department of Chemistry, Dezhou University, Shandong, Dezhou, P.R. China

Corresponding author: Fax: +86 534 8982229; Tel: +86 534 8987866; E-mail: jianzhisun@163.com

(Received: 14 January 2011;

Accepted: 1 December 2011)

AJC-10789

In present studies, the rechargeable magnesium batteries. MgCoSiO₄ was synthesized *via* sol-gel method and evaluated by TG/DTA, XRD, IR, SEM. The results showed that the product is well-crystalline and gets uniform particle size. Simulation cells were assembled employing the product as positive electrode. Charge/discharge cycle test show that the product present good electrochemical behaviours with discharge capacities 60.5 mAh g⁻¹ after 20 cycles.

Key Words: Magnesium battery, MgCoSiO₄, Infrared spectroscopy, Positive electrode.

INTRODUCTION

Lithium-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 systems, 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 per Faraday) is higher than that of lithium (7 g per 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 systems¹⁻⁵.

Magnesium rechargeable batteries had not been paid much attention because of mainly two problems. One is passivating surface film grown on Mg, which obstructs reversible electrochemical reaction. Another is difficulty of insertion and diffusion in cathode material for divalent magnesium ion⁶. It is well known that Mg²⁺ insertion into ion transfer hosts proceeds slowly owing to the strong polarization effect of small and divalent Mg²⁺ ion compared with Li⁺ or Na⁺ and only a small discharge capacity has been reported for magnesium insertion cathode. As a result, it is necessary to realize fast Mg²⁺ transport in the host in addition to other requirements as practical cathode materials for magnesium battery.

Recently, it has been suggested that MgMnSiO₄ can store large amounts of charge per unit mass as cathode materials

for rechargeable magnesium batteries *via* a highly reversible redox reaction. The similar ion sizes of monovalent lithium and divalent magnesium cations may lead, from a steric point of view, to an analogous insertion electrochemistry. Here, we propose that MgCoSiO₄ is feasible as potential cathode materials for magnesium batteries. In this work, we report the synthesis of MgCoSiO₄ samples by sol-gel method and investigated electrochemically as a magnesium host⁷.

EXPERIMENTAL

All the chemicals *viz.*, magnesium acetate tetrahydrate, copper acetate tetrahydrate, ethyl silicate and alcohol used in the experiment are of analytical grade.

General procedure: MgCoSiO₄ was synthesized *via* sol-gel method. First, magnesium acetate tetrahydrate and copper acetate tetrahydrate 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 °C and keep stirring 18-24 h. The gel was decomposed at 100 °C in vacuum drying oven for 12 h and the obtained product was ground and sintered at 800 °C for 24 h under conditions of argon shield.

Detection method: Thermo gravimetry/differential thermal analysis (TG/DTA) was carried out on SHIMADZU TA-60 with the heating temperature from 20 to 900 °C at 20 °C/min in N₂. XRD (X-ray Power Diffraction) patterns for all the samples were measured by Rigaku D/max-3B X-ray Diffractometer with Cu K_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).

Electrochemical Mg-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 polytetrafluoroethylene (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 °C for 10 h. Magnesium metal was used as an anode. The electrolyte was composed of 0.25 M $\text{Mg}(\text{AlBu}_2\text{Cl}_2)_2/\text{THF}$ 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 °C.

RESULTS AND DISCUSSION

Thermogravimetry/differential thermal analysis: Fig. 1 shows DSC-TGA curves of the precursor for MgCoSiO_4 . The endothermic peak at 85 °C with slight weight loss can be ascribed to the desorption of absorbed water. Endothermic peaks at 299 °C with a significant weight loss respectively can be ascribed to the decomposition of ester. Following the endothermic peak, an acute exothermic peak around 331 °C, which can be attributed to the decomposition of acetate.

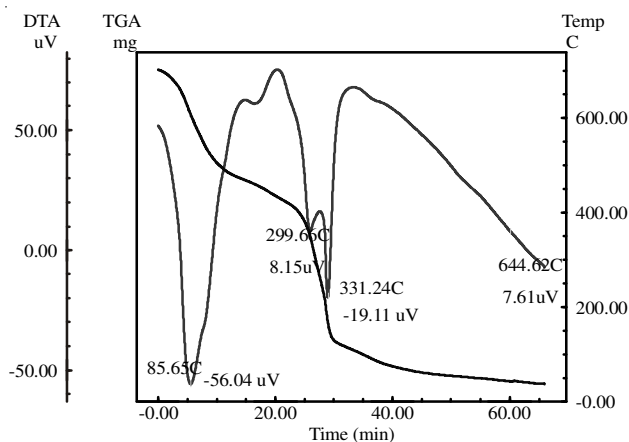


Fig. 1. Thermogravimetry-differential scanning calorimetry curves of precursors

Powder X-ray diffraction: The results of the X-ray diffraction study have shown that MgCoSiO_4 powder is mainly a single phase material. The corresponding X-ray powder diffraction pattern obtained at room temperature is presented in Fig. 2.

FTIR: The IR spectra of diffraction patterns MgCoSiO_4 are shown in Fig. 3. The spectra are dominated by intense, overlapping intramolecular SiO_4^{4-} stretching modes that range from 1100 to 400 cm^{-1} . The characteristic absorption peak of MgCoSiO_4 is divided into four main parts. The first part between 1100-1000 cm^{-1} is great intensity and due to Si-O-Si asymmetric stretching vibration, The second part with moderate strength absorption bands between 900-550 cm^{-1} is due to

Si-O stretching vibration, The third part 512 cm^{-1} is expected for Co-O vibration mode. The fourth part 420 cm^{-1} belongs to Si-O bending vibration.

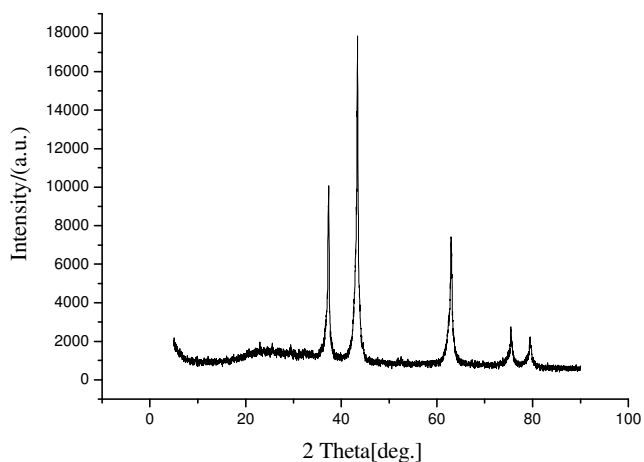


Fig. 2. The XRD patterns of MgCoSiO_4 samples

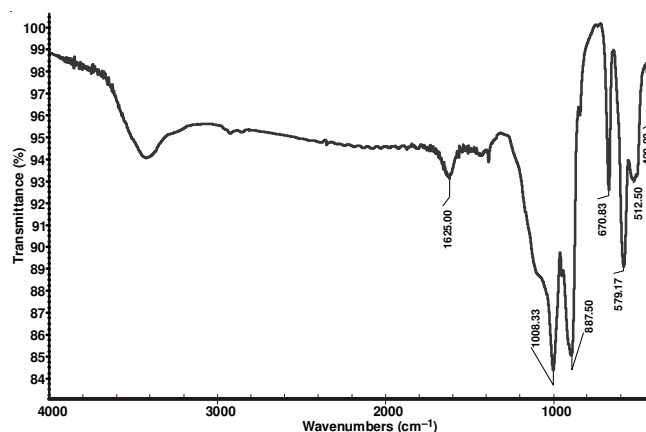


Fig. 3. FTIR spectra of MgCoSiO_4

SEM: Fig. 4, showed microstructure of the fracture surfaces of the specimen pellet heat-treated at 750 °C. This material has a uniform small particle size.

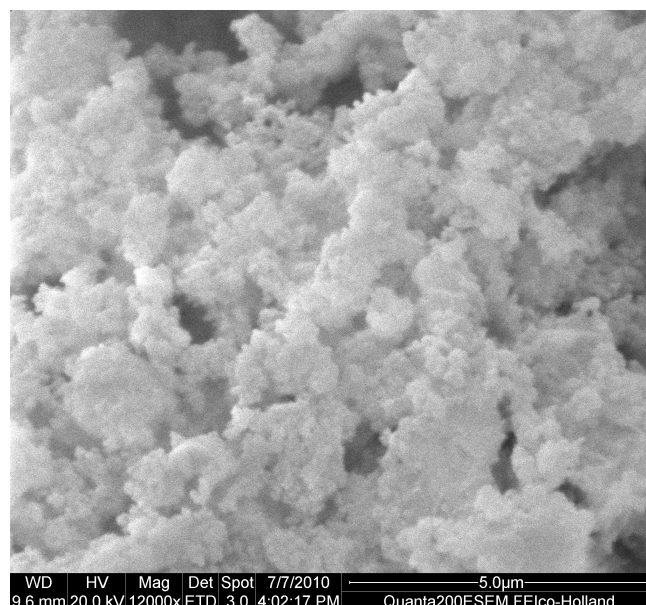


Fig. 4. SEM images of MgCoSiO_4

Electrochemistry: The initial galvanostatic discharge/charge curves for MgCoSiO₄ test cells are measured at a current density of 0.02mA/cm² in the potential range of 0.5-2.0 V at 25 °C. Cell exhibits one charge plateaus around 1.5 V. The discharge capacities for MgCoSiO₄ is 60.5 mAh·g⁻¹ after 20 cycles.

Conclusion

A new cathode material MgCoSiO₄ was synthesized *via* sol-gel method. It was found to electrochemically absorb and desorb magnesium. The discharge capacities for MgCoSiO₄ is 60.5 mAh·g⁻¹ after 20 cycles. The use of MgCoSiO₄ as active cathode materials for magnesium batteries in general shows great promise for secondary batteries.

ACKNOWLEDGEMENTS

This work was supported by a grant from the Natural Science Foundation of Shandong (No. ZR2009FQ027) and the Technology Program of Shangdong Institution of Higher Education (J09LB52).

REFERENCES

1. D. Aurbach, Z. Lu, A. Schechter, Y. Gofer, H. Gizbar, R. Turgeman, Y. Cohen, M. Moskovich and E. Levi, *Nature*, **407**, 724 (2000).
2. J. Giraudet, D. Claves and K. Guérin, *J. Power Source*, **173**, 592 (2007).
3. J.-Z. Sun, *Asian J. Chem.*, **22**, 260 (2010).
4. E. Sheha and M.K. El-Mansy, *J. Power Source*, **185**, 1509 (2008).
5. Y.N. Li, Z.P. Guo and H.K. Liu, *Electrochem. Commun.*, **9**, 1913 (2007).
6. J.Z. Sun, *Asian J. Chem.*, **23**, 1397 (2011).
7. N. Amir, Y. Vestfrid, O. Chusid, Y. Gofer and D. Aurbach, *J. Power Source*, **174**, 1234 (2007).