Asian Journal of Chemistry; Vol. 23, No. 3 (2011), 1399-1400

ASIAN JOURNAL OF CHEMISTRY

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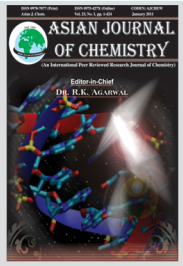

NOTE

Study of MgV_2O_6 as Cathode Material for Secondary Magnesium Batteries

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*: 2 April 2010; *Accepted*: 19 November 2010) AJC-9317

MgV_2O_6 was prepared *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-crystalled and gets uniform particle size. The electrochemical performance of MgV_2O_6 has been studied in propylene carbonate-containing magnesium perchlorate electrolytes in view of their application as positive electrode in the rechargeable magnesium batteries. Charge/discharge cycle test show that the product has good reversibility.

Key Words: Magnesium battery, MgV_2O_6, Positive electrode.

Magnesium has attracted much attention as the active material of high energy density batteries, because rechargeable magnesium battery may be a candidate of high energy density battery due to its natural abundance, a relatively low price of its raw materials and an expected higher safety of batteries based on metallic magnesium compared to lithium[1,2]. Despite of the practical use of primary and reserve batteries, development of rechargeable Mg batteries has been retarded due to two problems: (1) difficulties in the reversibility of an Mg negative electrode concerning its passivating characteristics and (2) a lack of appropriate non-aqueous media that conduct Mg^{2+} species[3].

Recently, there has been a considerable interest in seeking vanadium oxide compounds as anode materials of rechargeable magnesium batteries, because they have large enough interstitial voids to uptake guest species. Therefore, fast Mg^{2+} transport may be expected in such compound and between layers, which seems as promising host for magnesium[4-6].

In this paper, MgV_2O_6 is prepared by sol-gel method. The charge and discharge characteristics of the cell were briefly examined to evaluate the applicability of the MgV_2O_6 rechargeable Mg batteries.

All the chemicals *viz.*, $Mg(CH_3COO)_2$, NH_4VO_3 and citric acid used in the experiment are of analytical grade.

General procedure: MgV_2O_6 was synthesized *via* sol-gel method. First, citric acid and $Mg(CH_3COO)_2$ in a stoichiometric ratio were dissolved in deionized water with magnetic stirring at 60 ºC. After a clear solution formed, NH_4VO_3 was added to the solution while stirring for 4 h and then a gel formed in an air oven at 100 ºC. The gel was decomposed at 350 ºC in an air for 4 h and the obtained product was ground, pressed into pellets and sintered at 600 ºC for 12 h in an air.

Detection method: Thermogravimetry/differential thermal analysis was carried out on Shimadzu TA-60 with the heating temperature from 20-900 ºC at 20 ºC/min in N_2. 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). Infrared absorption spectra are measured with a Thermo Nicolet Nexus spectrometer equipped and samples are prepared using standard KBr pellet techniques. The morphology of the samples was observed by Jeol JSM-5600LV 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 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 1 M $Mg(ClO_4)_2$/acetonitrile 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.

TG/DTA analysis: Fig. 1 shows DTA curves of the gel. There are four endothermic peaks at 106.20, 169.84, 274.28 and 342.10 ºC and one exothermic peak at 399.98 ºC in DTA

curves. Firstly, the gel loses crystal water at 106. 20 ºC. At the temperature range from 150-350 ºC, the gel further decomposes and releases ammonia, acetic acid and citric acid at above 399.98 ºC, the gel produces a pure MgV_2O_6, whose structure is characterized by X-ray diffraction. the third stage was to be exothermic.

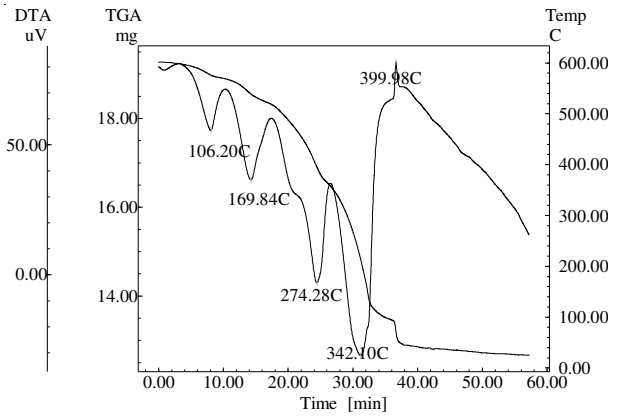

Fig. 1. TG/DTA curves of the gel

Powder X-ray diffraction: The XRD pattern of sample (Fig. 2) revealed that the crystal structure of the sample was pure MgV_2O_6 crystal, which belonged to monoclinic crystal system compared with the standard PDF cards (#34-0013). The lattice is monoclinic lattice and the cell parameters: a = 0.9279 nm, b = 0.3502 nm, c = 0.6731 nm.

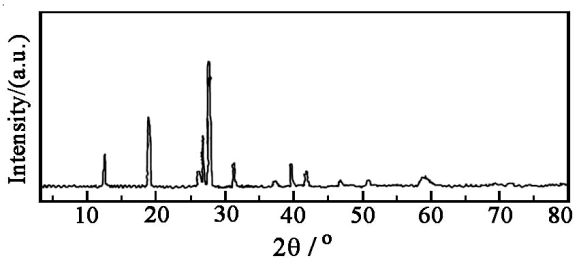

Fig. 2. XRD of MgV_2O_6

Infrared spectra: Infrared absorption spectra of MgV_2O_6 are presented in Fig. 3. The spectra are dominated by intense, overlapping intramolecular $V_2O_6^{2-}$ stretching modes[7] that range from 1000-400 cm^{-1}. Two bands detected at 877 and 557 cm^{-1} of MgV_2O_6 are ascribed to the symmetric stretching mode ν(V-O-V) of $V_2O_6^{2-}$ and 424 cm^{-1} to the absymmetric stretching mode ν(V-O-V). The Mg-O vibrations occur at 690 cm^{-1}.

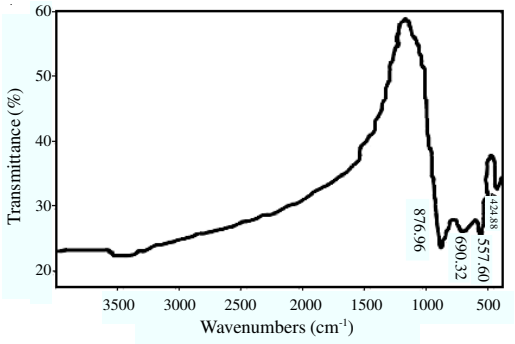

Fig. 3. IR spectrum of MgV_2O_6

SEM: Fig. 4 showed microstructure of the fracture surfaces of the specimen pellet heat-treated at 600 ºC. The sample has a spherical morphology that is 2 μm in diameter and the small particles show good crystallinity and homogeneity.

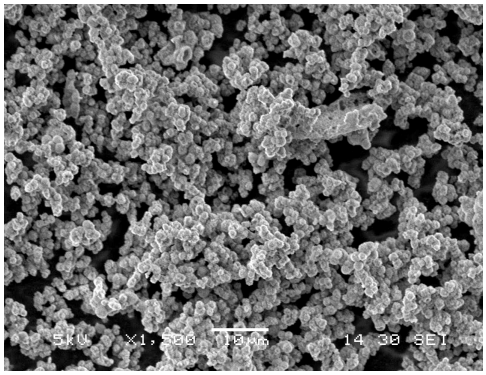

Fig. 4. SEM images of MgV_2O_6

Electrochemistry: The initial galvanostatic discharge/charge curves for MgV_2O_6 test cells are measured at a current density of 0.02 mA/cm^2 in the potential range of 0.0-2.0 V at 25 ºC. Cell exhibits one charge plateaus around 1.3 V. The fist discharge capacity is about 120 mAh/g, The discharge capacities for MgV_2O_6 is 40 mAh g^{-1} after 10 cycles.

Conclusion

A new cathode material MgV_2O_6 was synthesized *via* sol-gel method. The fist discharge capacity is about 120 mAh/g. Accordingly, the composite of MgV_2O_6 was found to be a promising cathode material for Mg rechargeable batteries, though anode and electrolyte materials have to be developed and optimized together.

ACKNOWLEDGEMENTS

This work was supported by a grant from the Natural Science Foundation of Shandong (No. 2009ZRA14010),the Technology Program of Shangdong Institution of Higher Education (J09LB52) and the Technology Research and Development Program of Dezhou (No. 20080153).

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