OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 9, No. 9-10, September – October 2015, p. 1204 - 1207

Synthesis and characterization of cathode material for rechargeable magnesium battery technology

M. F. RAHMAN*, D. GEROSA
Dipartimento di Chimica, Materiali e Ingegneria Chimica Giulio Natta, Politecnico di Milano, Via Mancinelli, 7 - 20131, Milan, Italy

Synthesis and characterization of magnesium manganese spinel ($MgMn_2O_4$) as cathode material for magnesium (Mg) secondary battery were reported in this paper. Wet chemical (coprecipitation) method was employed where graphite was used with precipitate for one sample. X-ray diffraction (XRD) analysis revealed formation of crystalline $MgMn_2O_4$ for both samples. Scanning electron microscopy (SEM) micrographs demonstrated that flake shape $MgMn_2O_4$ was formed by simple coprecipitation method, while nano spheroids of spinel were formed from precipitate having graphite. Carbon powder (μm) and carbon nano tube (CNT) were added to the cathode material as conductive additive separately. Electrochemical characterization exhibited promising results as cathode material for nano structured spinel for Mg secondary battery where carbon nanotube was added as conductive additive.

(Received October 23, 2014; accepted September 9, 2015)

Keywords: Manganese spinel, Magnesium, Rechargeable battery, Cathode material

1. Introduction

The world has been emphasizing on green energy technology over the last few decades. Consequently, renewable energy sources such as solar, hydropower, wind have become popular day by day. However, efficient electrical energy storage (EES) devices are needed in order to utilize efficiently these energy sources [1-7]. Rechargeable batteries are among the major EES devices. Furthermore, they have become very popular in electric vehicles (EVs), plug in hybrid vehicles (PHVs), and portable electronic devices [8-12]. Considering large scale applications in smart grid and automotive industry, existing battery technology is not viable both economically and environmentally. Costs, safety, cell capacity, rate of charge-discharge cycling, long term stability are the key factors for developing a new secondary battery system [1]. Considering these factors it is a big challenge to develop suitable rechargeable battery technology.

Divalent battery system such as Mg rechargeable battery can be a potential rechargeable battery system. Mg being eighth abundant material in earth's crust is cheap and nontoxic. It has higher volumetric energy density (3833 mAh/cm^3) than Lithium (Li) (2061 mAh/cm^3) [9]. In addition; Mg battery shows its potential for working at room temperature compared to other large scale battery systems which work at high temperature [1]. Extensive research is being carried out by several groups since its first introduction in 2000 [13]. However, to date it is found that due to cathode materials the energy density of this system is constrained. So far, different materials have been suggested such as molybdenum chalcogenides, V_2O_5, TiS_2 nanotubes, graphene-like MoS_2, todorokite-type/hollandite-type MnO_2, and sulfur. Still, these materials do not exhibit high capacity, high voltage, and excellent cyclability concurrently [14-17]. It is essential to develop suitable cathode material where Mg can reversibly cycle for longer periods. Besides, electrolyte having suitable electrochemical window is yet to be discovered. These limitations have restricted commercialization of Mg secondary battery [8]. In this study suitability of $MgMn_2O_4$ as cathode material for rechargeable Mg battery application has been studied. Coprecipitation method was employed to synthesize $MgMn_2O_4$ which is low cost method.

2. Experimental

2.1 Synthesis method

The cathode material $MgMn_2O_4$ was prepared by coprecipitation method. The material was prepared from solution containing anhydrous magnesium sulfate ($MgSO_4$) (Sigma-Aldrich), manganese sulfate monohydrate ($MnSO_4.H_2O$) (Sigma-Aldrich) and sodium hydroxide (NaOH) (Sigma-Aldrich). The solution was stirred for 20 hours before filtration. The precipitate was washed three times to remove sodium and sulfate ions and then heated to 750°C for 6 hours to form the spinel. Another method was also employed in this study which was addition of graphite. The precipitate containing graphite was heated to 750°C under nitrogen atmosphere to reduce manganese. Then it was heated at the same temperature in air to eliminate carbon and oxidize manganese to form spinel. This procedure was applied to synthesize nano spinel spheroids.

2.2 Characterization of the samples

X-ray diffraction (XRD) of the samples was performed by Philips PW 1830, in conventional Bragg–Brentano configuration with Cu Kα radiation of 1.5418 Å wavelength X-ray diffractometer. The surface morphology of the samples was examined by scanning electron microscopy (SEM, Zeiss EVO50).

2.3 Electrochemical tests

Coin cell structure was employed in this study. Magnesium was used as anode. $MgMn_2O_4$ synthesized and treated in different conditions was used as cathode separately. Propylene carbonate containing magnesium acetate 0.2M and aluminum chloride 0.1M (PC) was used as electrolyte. A porous polymeric film was used as separator. Carbon powder (µm) and carbon nanotube (CNT) (10%wt.) were added to the cathode material as conductive additive. Electrochemical properties were investigated by AMEL Model 2549 Potentiostat-Galvanostat installed with AMELSCOPE software.

3. Results and discussion

TGA was performed in order to investigate the changes occurred in precipitate during heating in the range 100°C-900°C. The first pick just above 100°C represents loss of unbounded water, while the peaks at 250°C and 650°C represent formation of MgO and Mn_2O_3 respectively (Fig. 1). The weight loss is 6.988% at just above 100°C, 10.485% at 250°C followed by 3.984% at 650°C.

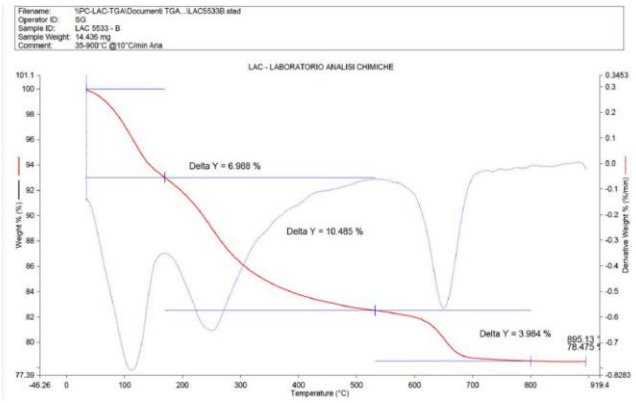

Fig. 1. TGA curve of the coprecipitated sample.

After heating the precipitate at 750°C for 6 hours, XRD and morphological analyses were executed. Fig. 2(a) demonstrates formation of crystalline $MgMn_2O_4$ of the sample obtained by coprecipitation method. The micrograph of the sample shows flake shape of the spinel having length around 2-3 µm and thickness around 200-250nm (Fig. 2(b)).

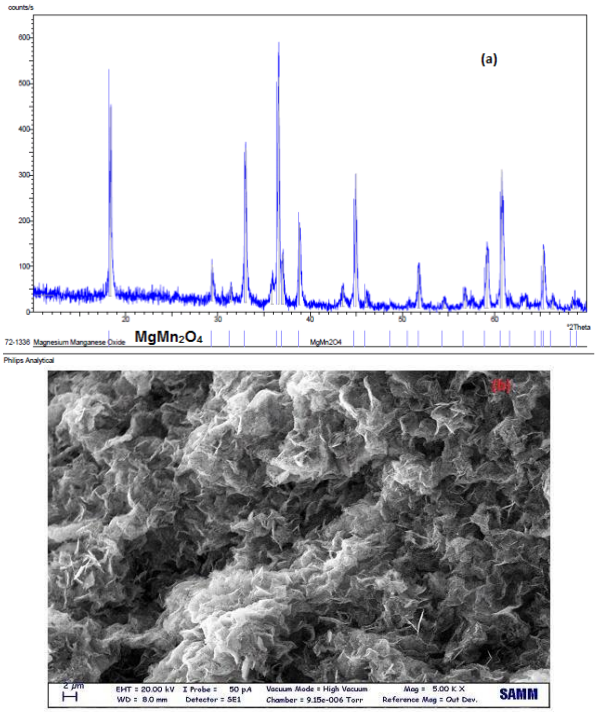

Fig. 2. (a) XRD analysis and (b) SEM micrograph of the sample obtained by coprecipitation method.

On the other hand, another sample was synthesized where graphite was added to the precipitate. The sample was first heated to 750°C in nitrogen and then at same temperature in air. After heating, the sample was characterized by XRD and SEM analyses. Fig. 3 (a) exhibits presence of crystalline $MgMn_2O_4$. Presence of small amount of Mg_2MnO_4 is also evident. SEM image of the sample is shown in Fig. 3(b). The micrograph shows nano spheroids of $MgMn_2O_4$.

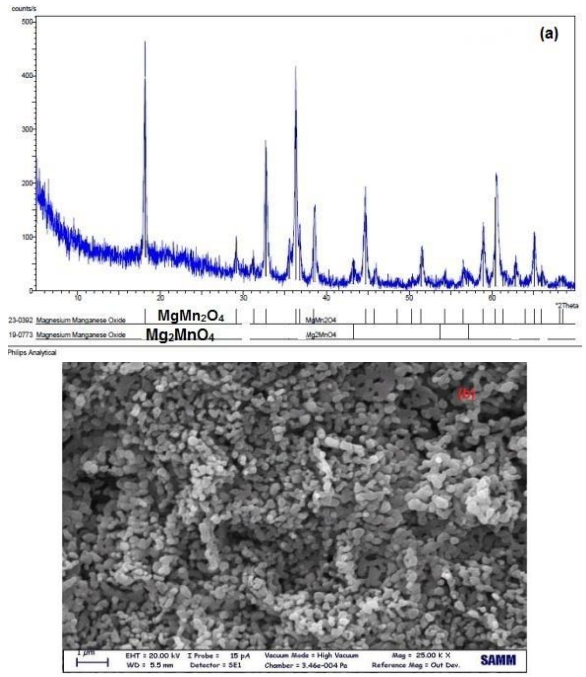

Fig. 3. (a) XRD and (b) SEM image of the sample where graphite was added.

The addition of graphite reduces manganese and at the same time breaks the flakes formed by simple coprecipitation process. Further heating in air eliminates carbon and oxidizes manganese to form spinel spheroids at nano scale. In this process small amount of Mg_2MnO_4 is also formed.

Carbon powder (µm) (10%wt.) was added to the cathode materials. Single discharge test was performed with both samples. Sample having spheroidal structure exhibited slightly better result than sample having flake shape (Fig. 4 (a), 4 (b)). Specific energy capacity of sample having spheroidal structure and flake shape were 20 mAh/g and 15 mAh/g respectively.

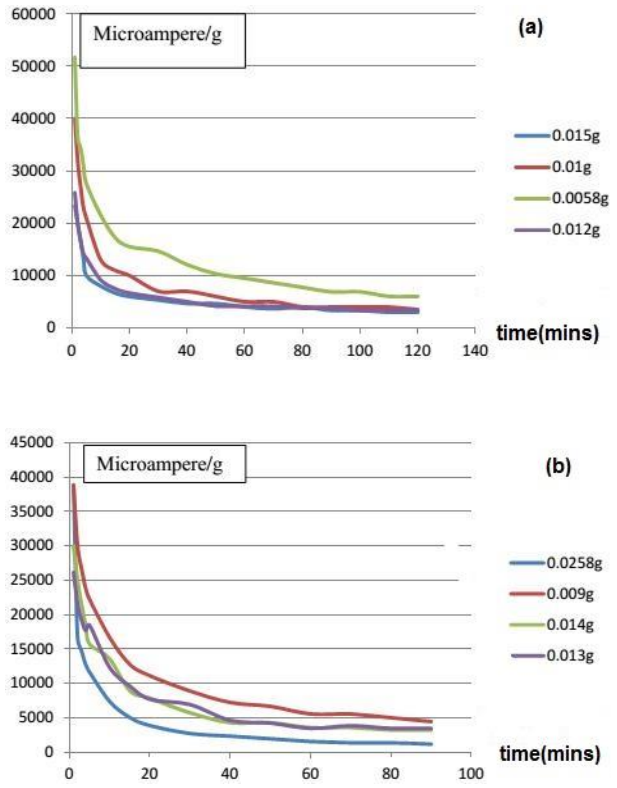

Fig. 4. Single discharge test values (a) spinel having flake shape, (b) spinel having nano spheroidal structure (carbon powder additive).

On the other hand, another conductive additive carbon nanotube (CNT) was added (10%wt) to $MgMn_2O_4$. The single discharge test values are shown in Fig. 5. Sample having nano spheroid crystal structure demonstrated better performance.

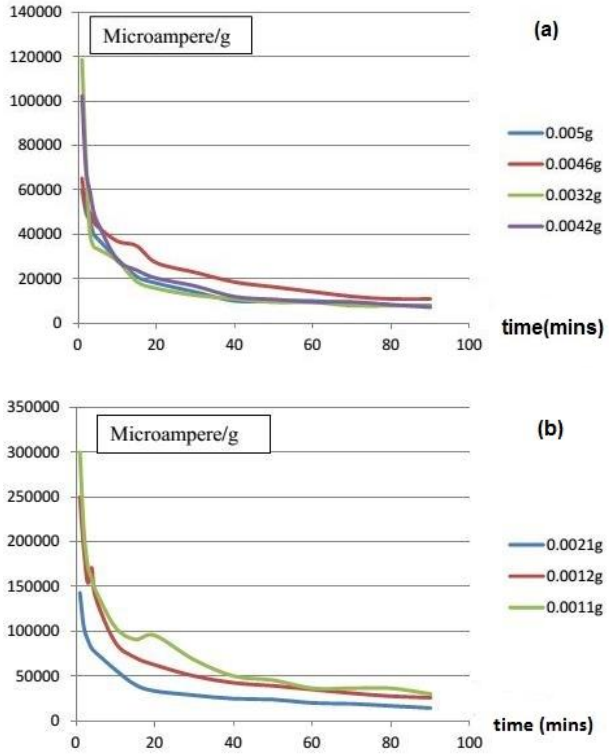

Fig. 5. Single discharge test values (a) spinel having flake shape, (b) spinel having nano spheroidal structure (CNT additive).

The specific energy capacity of the spinel having flake shape was 35.3 mAh/g, while spinel having nano spheroidal structure was 102 mAh/g. The specific area of CNT is greater than carbon powder. Consequently, CNT showed higher conductivity than carbon powder. In addition, the specific surface area of spheroids is greater than flakes. It is supported from the above data that sample having spheroidal structure milled with carbon nanotube demonstrates best result. Besides, the lighter samples exhibited better performance in all cases. When thickness of the sample increases, the resistance of the cathode material increases. This effect can be minimized by improving milling process.

4. Conclusions

Pure $MgMn_2O_4$ was successfully prepared by coprecipitaton method. $MgMn_2O_4$ made from simple coprecipitation method produced flake shape, while adding graphite as reducing agent showed spheroid structure at nano scale. Carbon powder and CNT were added as conductive additive with the cathode materials. CNT exhibited better conductivity over carbon powder. Furthermore, cathode made from nano spheroids showed better performance over flake shape during single discharge experiment. The specific energy capacity for spinel having flake shape and spheroidal structure were 35.3 mAh/g and 102 mAh/g respectively.

References

[1] P. Saha, M. K. Datta, O. I. Velikokhatnyi , A. Manivannan, D. Alman, P. N. Kumta Prog. in Mat. Sci. **66,** (2014).

[2] U.S. DOE. Smart grid research and development multi-year program plan (MYPP) 2010–2014. <http://www.oe.energy.gov>.

[3] U.S. DOE. Barriers to achieving the modern grid; July 2007. <http://www.netl.doe.gov/smartgrid>.

[4] U.S. DOE, Energy Storage – A key enabler of the smart grid; September 2009. <http://www.netl.doe.gov/smartgrid>.

[5] U.S. DOE. Technology and applied R&D needs for electrical energy storage, resource document for the workshop on basic research needs for electrical energy storage; March 2007. <http://www.energy.gov>.

[6] EPRI-DOE handbook of energy storage for transmission & distribution applications, EPRI, Palo Alto, CA, and the U.S.

[7] Department of Energy, Washington, DC; 2003. p. 1001834. Basic Research Needs for Electrical Energy Storage, Office of Basic Energy Sciences, U.S. DOE; July 2007.

[8] Y. Orikasa et al. Sci. Reports (2014), in print, **4**: 5622 | DOI: 10.1038/srep05622.

[9] N. Singh et al. Chem. Commun. **49**, 149 (2013).

[10] J. M. Tarascon, M. Armand, Nature **414**, 359 (2001).

[11] P. Novak, R. Imhof and O. Haas, Electrochim. Acta **45**, 351 (1999).

[12] T. S. Arthur, N. Singh, M. Matsui, Electrochem. Commun. **16**, 103 (2012).

[13] D. Aurbach et al. Nature **407**, 724 (2000).

[14] E. Levi., Y. Gofer, & D. Aurbach, Chem. Mater. **22**, 860 (2010).

[15] D. B. Le, et al. Chem. Mater. **10**, 682 (1998).

[16] Z. L. Tao, et al. Chem. Commun. 2080 (2004).

[17] Y. L. Liang, et al. Adv. Mater **.23**, 640 (2011).

*Corresponding author: md.farabi@mail.polimi.it