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Preparation and Characterization of Cathode Material $Mg_{0.5}Ti_2(PO_4)_3$ for Magnesium Cells

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A cathode material for magnesium cells $Mg_{0.5}Ti_2(PO_4)_3$ was prepared by a solid-state reaction method at 900 °C. Various techniques *i.e.*, TG/DTA, XRD, IR, SEM were used to characterize the reaction and products. The results showed that the product belongs to rhombohedral system with lattice: rhomb-centered, space group R3c and the cell parameters: a = 0.854 nm, b = 0.854 nm, c = 2.070 nm. FTIR spectra studies were carried out and the vibrational bands were assigned. The sample has a spherical morphology that is 10 μm in diameter. Electrochemical magnesium charge/discharge was found possible. The initial discharge capacities for $Mg_{0.5}Ti_2(PO_4)_3$ is 25.16 mAh g^{-1} but the capacities decreased rapidly with the increase in cyclic number and further efforts are needed to improve its electrochemical performances.

Key Words: Magnesium battery, $Mg_{0.5}Ti_2(PO_4)_3$, 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 systems[1-6].

One of the encountered difficulties is the low mobility of Mg^{2+} in the host lattice, since Mg^{2+} has high surface charge density. Consequently, fast Mg^{2+} transport in the intercalation host is required at ambient temperature, which may be realized in a transition metal phosphate $Mg_{0.5}Ti_2(PO_4)_3$. Those have the isostructural lattice with the so-called super ionic conductor of NASICON[7].

In this work, the synthesis of $Mg_{0.5}Ti_2(PO_4)_3$ samples by solid state reaction method and investigated electrochemically as a magnesium host are reported.

EXPERIMENTAL

All the chemicals *viz.*, MgO, TiO_2, $NH_4H_2PO_4$, $NH_4H_2PO_4$ and C_6H_{14} used in the experiment are of analytical grade.

General procedure: $Mg_{0.5}Ti_2(PO_4)_3$ was prepared by solid state reaction. The starting materials were weighed in stoichiometric amounts and homogenized using a mixer. The mixture was put in a tubular furnace and had been heated for 6 h at 600 °C to decompose the oxalate and the phosphate. The powder was cooled down to room temperature and then pressed into Φ 10 mm pellets under 20 MPa. After grinding and homogenization, the mixture was transferred to the furnace and annealed at 900 °C for 20 h.

Detection method: TG/DTA (thermogravimetry/differential thermal analysis) thermal analysis was carried out on Shimadzu TA-60 with the heating temperature from 20 to 900 °C at 5 °C/min in N_2. X-Ray power diffraction (XRD) patterns for all the samples were measured by Rigaku D/max-3B X-ray diffractometer with CuK_α radiation ($\lambda = 0.15406$ 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 (SEM).

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 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 °C.

RESULTS AND DISCUSSION

TG/DTA Analysis: Fig. 1 shows DTA curves of the raw material. There are five endothermic peaks at 97.63, 218.92, 354.21, 372.01 and 490.69 °C in DTA curves. Thermogravimetry (TG) curve revealed the weight loss of 26.4 %, which occurred at 20 to 800 °C. The following reaction can be expected to have weight loss of 25.1 %:

$$MgO + 4TiO_2 + 6NH_4H_2PO_4 \rightarrow 2Mg_{0.5}Ti_2(PO_4)_3 + 9H_2O + 6NH_3$$

Powder X-ray diffraction: Powder XRD data of $Mg_{0.5}Ti_2(PO_4)_3$ are presented in Fig. 2. All observed reflections may be indexed in the rhombohedral system with lattice: rhomb-centered, space group R^{-}_{3c} and the cell parameters: a = 0.854 nm, b = 0.854 nm, c = 2.070 nm, $\alpha = 90°$, $\beta = 90°$, $\gamma = 120°$.

Infrared spectra: Infrared absorption spectra of $Mg_{0.5}Ti_2(PO_4)_3$ are presented in Fig. 3. The spectra are dominated by intense, overlapping intramolecular PO_4^{3-}

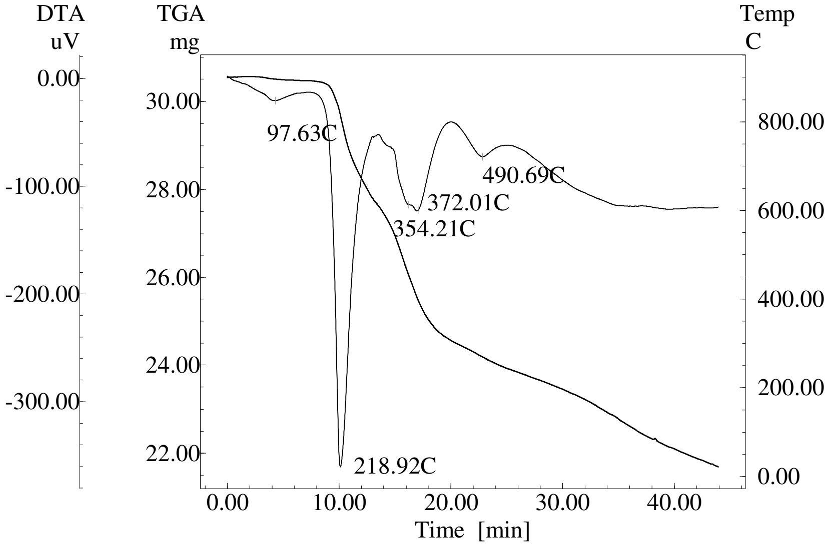

Fig. 1. TG/DTA curves of the raw material

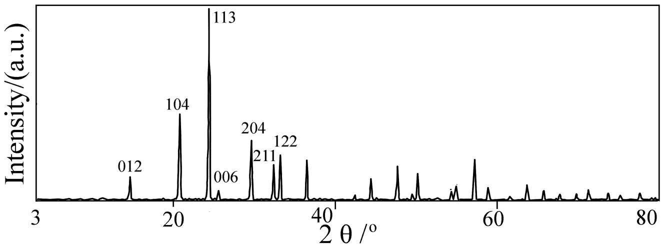

Fig. 2. XRD of $Mg_{0.5}Ti_2(PO_4)_3$

stretching modes that range from 1300 to 700 cm^{-1}. The frequency of the broad features between 700 and 850 cm^{-1} in the spectrum of $Mg_{0.5}Ti_2(PO_4)_3$ are somewhat lower than expected for PO_4^{3-} stretching modes. In fact, bands in this region of the spectrum are often due to condensed phosphate groups such as $P_2O_7^{4-}$ or extended polyphosphate structures. However, there are one bands near 750 cm^{-1} in the infrared spectrum to indicate the presence of bridging P-O-P groups. The spectral activity in this region strongly argues that the $Mg_{0.5}Ti_2(PO_4)_3$ sample contain a significant fraction of condensed phosphate groups[8].

In $Mg_{0.5}Ti_2(PO_4)_2$, ν_4 is expected to yield five IR active vibrational modes at the Brillouin zone center ($2A_{2u} + 3E_u$) and two IR active modes are expected for ν_2 ($2E_u$). Four bands detected at 719, 611 and 511 cm^{-1} of $Mg_{0.5}Ti_2(PO_4)_3$ are assigned to ν_4. The far-IR spectrum of $Mg_{0.5}Ti_2(PO_4)_3$ contains at least one intense bands at 408 cm^{-1}. The ν_2 vibrations probably occur within this spectral range, however, it is difficult to assign these modes with confidence because some of the external modes are also expected to occur at these frequencies[9].

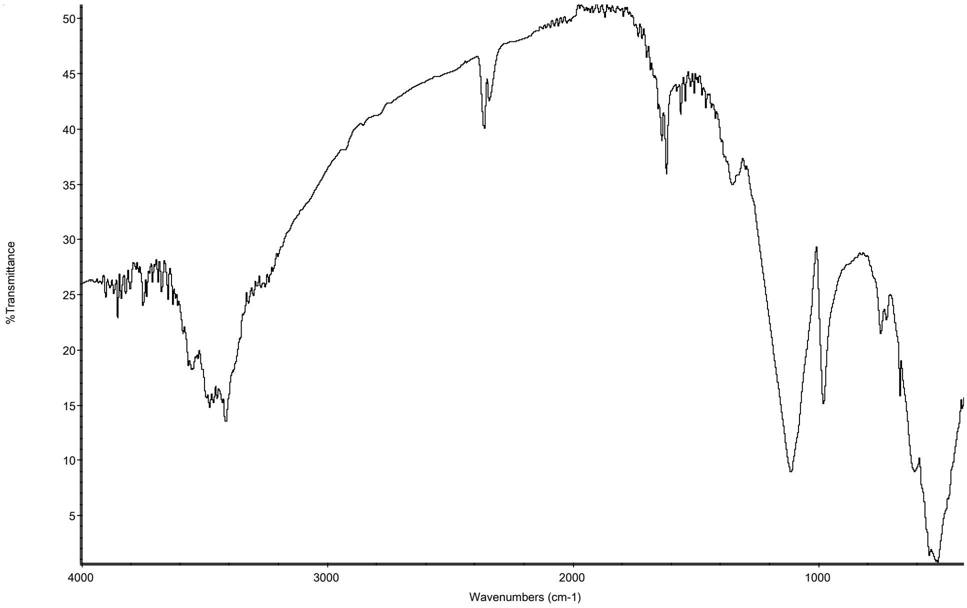

Fig. 3. IR spectrum of $Mg_{0.5}Ti_2(PO_4)_3$

SEM: Fig. 4 showed microstructure of the fracture surfaces of the specimen pellet heat-treated at 1000 °C. The sample has a spherical morphology that is 10 μm in diameter and the small particles show good crystallinity and homogeneity and are connected with each other.

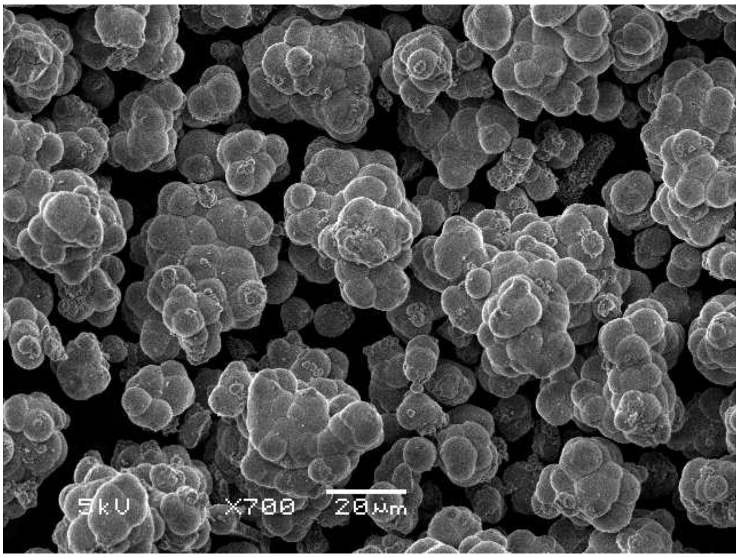

Fig. 4. SEM images of $Mg_{0.5}Ti_2(PO_4)_3$

Electrochemistry: The initial galvanostatic discharge/charge curves for $Mg_{0.5}Ti_2(PO_4)_3$ test cells are measured at a current density of 0.025 mA/cm^2 in the potential range of 0.2-2.0 V at 25 °C. Cell exhibits one charge plateaus around 1.8 V. The initial discharge capacities for $Mg_{0.5}Ti_2(PO_4)_3$ is 25.16 mAh g^{-1} but the capacities decreased rapidly with the increase in cyclic number and further efforts are needed to improve its electrochemical performances.

Conclusion

$Mg_{0.5}Ti_2(PO_4)_3$ could be synthesized by a solid-state reaction method. Electrochemical magnesium charge/discharge was found possible. The initial discharge capacities for $Mg_{0.5}Ti_2(PO_4)_3$ is 25.16 mAh g^{-1} but the capacities decreased rapidly with the increase in cyclic number.

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