Characterization of Mg$_{0.5}$Zr$_2$(PO$_4$)$_3$ for potential use as electrolyte in solid state magnesium batteries

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Received 1 April 2014; received in revised form 5 May 2014; accepted 5 May 2014
Available online 14 May 2014

Abstract

Samples of Mg$_{0.5}$Zr$_2$(PO$_4$)$_3$ compound with pure NASICON-phase were prepared by sol gel method and characterized by X-ray diffraction, Fourier transform infrared analysis, differential scanning calorimetry, scanning electron microscopy, energy dispersive X-ray, impedance spectroscopy, magnesium transference number measurement and linear sweep voltammetry technique. The compound consisted of the monoclinic crystalline phase with a space group of $P2_1/n$ ($Z=4$). The sample sintered at 750 °C showed the highest total conductivity of $1.0\times10^{-6}$ S cm$^{-1}$ at ambient temperature and $7.1\times10^{-5}$ S cm$^{-1}$ at 500 °C. Ionic transference number corresponding to Mg$^{2+}$ ion transport determined by means of Bruce and Vincent technique was found to be 0.69. Linear sweep voltammetry result showed that the Mg$_{0.5}$Zr$_2$(PO$_4$)$_3$ compound was electrochemically stable up to 2.50 V versus Mg/Mg$^{2+}$ electrode. These results indicated suitability of the compound to be used for development of solid state electrolytes for magnesium batteries.

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Keywords: Magnesium electrolyte; Ceramic electrolyte; Solid electrolyte; NASICON structured

1. Introduction

Extensive research on secondary batteries has been undertaken in order to improve their electrochemical performance, especially for lithium ion battery. Researchers found that all-solid-state lithium ion batteries have several advantages; high cell voltage, high power, high energy density and long cycle life [1,2]. However, the main disadvantage of Li-ion batteries is that they require careful attention in aspect of safety. Overcharging, overheating or short-circuiting may result in fire or explosion [3,4]. Therefore, it is urgent to find new types of batteries with greater safety and lower cost to meet the demand of gradually expanding market.

Magnesium batteries have been considered as one such potential alternative to lithium batteries. In fact, magnesium is in the diagonal position of lithium in the periodic table of the elements. As such, it has similar physical and chemical properties as lithium. It is a low cost, light and abundant element, environmentally benign and relatively easy to handle [5]. Electrochemically, magnesium has a high theoretical specific charge capacity (2205 A h kg$^{-1}$) and high theoretical energy density (3.8 A h cm$^{-3}$) making it possible candidate for battery application [6].

NASICON (Natrium Super Ionic Conductor) compound is one of potential candidates to be used for development of solid electrolytes in magnesium batteries. This is because NASICON structure has large enough interstitial void to uptake guest species, high structural stability based on 3D framework and is a promising host for Mg$^{2+}$ transport. The capability of charge carrier transport in the compound is the main criteria to be an electrolyte in the battery systems. NASICON structure was discovered in 1976 by Hong and Goodenough [7]. The crystal structure of NASICON is based on the covalent skeleton $[Zr_2(PO_4)_3]^{-}$ constituted of ZrO$_6$ octahedra which share all their corners with PO$_4$ polyhedra to form 3-dimension network structure, space group $R3c$ [8,9]. There are two types of cation sites, $M_1$ and $M_2$, in the structure. The size of
2.1. Synthesis of Mg0.5Zr2(PO4)3

For sample preparation, magnesium acetate tetrahydrate ((CH3COO)2Mg - 4H2O), zirconium (IV) acetate hydroxide (C6H18O4Zr) and ammonium phosphate monobasic (NH4H2PO4) were used as the starting materials. The molar ratio of Mg/2Zr/P was fixed according stoichiometric ratio 0.5:2:3. Magnesium acetate and ammonium phosphate were first dissolved in deionized water and then mixed under magnetic stirring. The solution was continuously stirred until a homogeneous solution was obtained. C6H18O4Zr, which was earlier dissolved in nitric acid, was added to this homogeneous solution. After stirring for one hour the solution was vaporized for about 4 h under magnetic stirring at 75 °C. The resulting wet gel was dried in an oven at 150 °C for 24 h to give a powder phase. The obtained powder was heated at 400 °C for 4 h to remove ammonium and acetate groups and later sintered at different temperatures (700 °C, 750 °C, 800 °C, 850 °C) for 3 h.

2.2. Characterization techniques

XRD patterns of the powder samples were recorded using X-ray Diffraction spectrometer (PANalytical-X’pert™) with Cu-Kα radiation of wavelength of 1.5406 Å in 2θ range from 10 to 70° at the rate of 0.01°/step width. The patterns were analyzed using High score plus software. FTIR was carried out to confirm the structure of the studied ceramic samples. FTIR spectra were recorded at room temperature using a Perkin Elmer Frontier Spectrometer with resolution 2 cm⁻¹. Thermal behavior of the precursor and sintered samples was analyzed by differential scanning calorimetry using Setaram Evo Lab³ thermal analyser in argon atmosphere at a constant heating rate 10 K min⁻¹ in the temperature range from 25 to 1400 °C. The morphology of the sample powders was analyzed by SEM and EDX which were carried out using Zeiss Evo MA10 scanning electron microscope attached with Oxford Aztec X-Act EDX spectrometer. The particle size information was obtained using FRITCH-Analysette 22 NanoTec laser particle sizer. The conductivities were determined by ac impedance spectroscopy using Solatron 1260 impedance analyzer over a frequency range from 1 to 10⁶ Hz with applied voltage of 200 mV. All measurements were done in temperature range 25–500 °C.

Mg⁰.⁵Zr²(PO₄)₃ transference number measurement was done using Bruce and Vincent method in order to determine the actual type of charge carriers. This method requires characterization of cell before and after polarization (after reaching the steady state) by using combination of EIS and DC polarization technique. For this measurement, the sample was sandwiched between magnesium metal electrodes which were used as non-blocking electrodes that only allow Mg²⁺ ions to transfer. The magnesium transference number (τMg²⁺) was calculated using the equation [12,14,15]:

\[ \tau_{\text{Mg}^{2+}} = \frac{I_{\text{ss}}(\Delta V - I_{\text{ss}}R_{\text{ss}})}{I_{\text{ss}}(\Delta V - I_{\text{ss}}R_{\text{ss}})} \]

In this equation, \( I_{\text{ss}} \) is initial current (\( t=0 \)), \( I_{\text{ss}} \) is the steady state current, \( R_{\text{ss}} \) and \( R_{\text{ss}} \) are the initial resistances of the passive layer before polarization and resistance of the passive layer after polarization respectively, and \( \Delta V \) is the applied voltage bias (\( \Delta V=0.22 \) V). The electrochemical stability was evaluated by linear sweep voltammetry using Wonatech ZIVE MP2 multichannel electrochemical workstation.

3. Result and discussion

3.1. Differential scanning analysis and thermo gravimetric analysis

Coupled DSC-TGA was carried out in order to determine suitable calcination temperature of the Mg0.5Zr2(PO4)3
precursor. This enables the authors to optimize the calcination's condition of the compound. DSC and TGA curves for the \( \text{Mg}_{0.5}\text{Zr}_2(\text{PO}_4)_3 \) precursor are shown in Fig. 1(a). From the figure, it is noticed that there are three main weight losses in the TGA curve. The first loss is between 70 °C and 120 °C, with a total weight loss of 3.4%, due to the evaporation of water. This is supported by the DSC curve which shows an endothermic peak in this temperature range. The second weight loss is of about 11.1% in the range from 210 to 292 °C which is attributed to the decomposition of ammonium and acetate groups [13]. This phenomenon is confirmed by the disappearance of sharp exothermic curve at temperature range between 200 °C to 300 °C in the DSC curve for sample heated at 400 °C illustrated in Fig. 1(b).

The third weight loss is of about 4.6% in the temperature range from 294 to 650 °C. This loss is attributed of the chemical reaction during the formation of \( \text{Mg}_{0.5}\text{Zr}_2(\text{PO}_4)_3 \). This is supported by the DSC curve which shows a weak and broad exothermic peak in this temperature range. The plateau at temperature range 650 to 1000 °C suggests that all chemical reactions in the sample have completed.

### 3.2. Structural properties

Presented in Fig. 2 are X-ray diffractograms of \( \text{Mg}_{0.5}\text{Zr}_2(\text{PO}_4)_3 \) precursor samples sintered at different temperatures. As can be observed in the figure, sintering of sample at 600 °C did not successfully produce pure \( \text{Mg}_{0.5}\text{Zr}_2(\text{PO}_4)_3 \) due to incomplete chemical reaction which is in agreement with the result in Fig. 1(a). However, the diffractograms for the samples sintered at 700, 750 and 800 °C show peaks attributed only to \( \text{Mg}_{0.5}\text{Zr}_2(\text{PO}_4)_3 \) [16]. This demonstrates that pure \( \text{Mg}_{0.5}\text{Zr}_2(\text{PO}_4)_3 \) has been obtained. Higher sintering temperature of 850 °C resulted in the diffraction peaks at \( 2\theta = 26.50^\circ \) and \( 37.83^\circ \) suggesting the existence of \( \text{ZrP}_2\text{O}_7 \) impurity.

All pure \( \text{Mg}_{0.5}\text{Zr}_2(\text{PO}_4)_3 \) peaks are sharp and well defined, indicating that the compound is generally well crystallized. The pure \( \text{Mg}_{0.5}\text{Zr}_2(\text{PO}_4)_3 \) compound produced is found to be single phase in nature, crystallizing in monoclinic structure with a space group of: \( P2_1/n \) (\( Z=4 \)). The lattice constants are \( a = 12.427 \, \text{Å} \), \( b = 8.945 \, \text{Å} \), \( c = 8.8405 \, \text{Å} \) and \( \beta = 90.47^\circ \). Those values are consistent with those reported in [16].

![Fig. 1. DSC and TGA curves for (a) precursor and (b) the sample heated at temperature 400 °C.](image1)

![Fig. 2. XRD patterns of \( \text{Mg}_{0.5}\text{Zr}_2(\text{PO}_4)_3 \) sample sintered at different temperatures.](image2)

![Fig. 3. FTIR spectra for pure \( \text{Mg}_{0.5}\text{Zr}_2(\text{PO}_4)_3 \) sintered at temperatures of 700, 750 and 800 °C in the spectral region from 550 cm\(^{-1}\) to 1400 cm\(^{-1}\).](image3)
3.3. FTIR analysis

FTIR spectra for pure \(\text{Mg}_{0.5}\text{Zr}_2(\text{PO}_4)_3\) samples sintered at temperature 700, 750 and 800 °C in the spectral region from 550 to 1400 cm\(^{-1}\) are depicted in Fig. 3. The three different sintering temperatures did not produce any considerable change in transmission peak positions. The vibrational and stretching modes are the same in all samples. The bands associated with vibrational or stretching of \(\text{PO}_4^{3-}\) anions are found to be active in this compound. The absorption bands in the region of 1280–1020 cm\(^{-1}\) are assigned to the asymmetric stretching vibrations and bands in the region of 980–915 cm\(^{-1}\) correspond to the symmetric stretching vibrations of the \(\text{PO}_4^{3-}\) ions. Stretching vibration of P–O–P can be seen in the region 700–758 cm\(^{-1}\). Meanwhile, bands in the 670–550 cm\(^{-1}\) range are assigned to the bending vibrations of the ion \([17–22]\).

In the present study, all the characteristic bands for PO\(_4\) vibration are in agreement with those observed for Li-based NASICON (Li\((\text{Zr,Ti})_2(\text{PO}_4)_3\)). This indicates that the anion ring has not been distorted upon switching Li\(^+\) with Mg\(^{2+}\) in the NASICON structure.

3.4. SEM, EDX and particle size distribution analysis

The cross-sectional SEM micrographs of pure \(\text{Mg}_{0.5}\text{Zr}_2(\text{PO}_4)_3\) pellets sintered at temperatures of 700, 750 and 800 °C are displayed in Fig. 4. The pellet sintered at 800 °C showed good grain contact. This can be correlated to the result of particle size analyses, Fig. 5. From the results, it can be inferred that the formation of good grain contact in the pellet sintered at 800 °C is due to the presence of small sized particles which can form contacts easily. The average particle size of \(\text{Mg}_{0.5}\text{Zr}_2(\text{PO}_4)_3\) sintered at 700 and 750 °C are 120 and 92.5 μm, respectively. Meanwhile, the average particle size decreases in the sample sintered at 800 °C at 89.1 μm.

The EDX analyses of the \(\text{Mg}_{0.5}\text{Zr}_2(\text{PO}_4)_3\) samples sintered at different sintering temperatures are shown in Fig. 6. All samples showed the presence of Mg, Zr, P, and O\(_2\). From the
atomic percentage data in Fig. 6, the atomic ratios of all samples have been calculated and listed in Table 1. The chemical compositions of the prepared samples are very close to the designed compositions confirming the formation of Mg$_{0.5}$Zr$_2$(PO$_4$)$_3$ compounds.

### 3.5. Thermal analysis

Fig. 7 depicts the DSC curve of the Mg$_{0.5}$Zr$_2$(PO$_4$)$_3$ compound heated from 30 to 1400 °C and cooled back to 800 °C. There are two dominant peaks in the DSC curve during the process. The first endothermic peak at temperature of 1165 °C represents the melting temperature of the Mg$_{0.5}$Zr$_2$(PO$_4$)$_3$ compound. The second sharp exothermic peak during the cooling process observed at temperature of 1101 °C is due to crystallization process of the melted compound confirming that the melting temperature is 1165 °C. It is also clearly seen that there are no phase transitions occurred in the compound up to 850 °C.

### 3.6. Impedance measurement

The D.C. conductivity of Mg$_{0.5}$Zr$_2$(PO$_4$)$_3$ compound has been determined from the total conductivity, ($\sigma_t$) (bulk conductivity, $\sigma_b$ + grain boundary conductivity, $\sigma_{gb}$) calculated from equation [15]:

$$\frac{1}{\sigma_t} = \frac{1}{\sigma_b} + \frac{1}{\sigma_{gb}}$$

where $\sigma_b = d/AR_b$ and $\sigma_{gb} = d/AR_{gb}$. In this equation, $d$ is the sample thickness, $A$ is the cross-sectional area of sample, $R_b$ is the bulk resistance and $R_{gb}$ is the grain boundary resistance. The Cole–Cole plots of the pure sample at room temperature and 500 °C are shown in Fig. 8. The figure shows that when temperature increases, the total resistance ($R_t$) shifts towards lower value indicating increase in conductivity. The D.C. conductivity for pure samples sintered at 700, 750 and 800 °C are shown in Fig. 9. The sample sintered at 750 °C showed the highest conductivity at all temperatures ($1 \times 10^{-6}$ S cm$^{-1}$) followed by samples...
sintered at 800 °C and 700 °C. The conductivity of the compound obtained in this study is still low. To obtain higher conductivities, modifications on this compound need to be done. The modifications may enhance conductivity values up to two orders of magnitude as reported earlier by the authors [15,23].

The plots of temperature dependence of total conductivity for all samples are depicted in Fig. 10. The conductivity plots of the three samples are linear and fit the Arrhenius equation as expressed by:

$$\sigma(T) = A(T)\exp\left(-\frac{E_\alpha}{kT}\right)$$  \hspace{1cm} (3)

where $A$ is the pre-exponential factor, $E_\alpha$ is the activation energy for conduction and $k$ is the Boltzmann constant. The conductivity of all samples increases with temperature. However, the log $\sigma - 1000/T$ plots show a discontinuity at $\sim180$ °C ($1000/T = 2.20$ K$^{-1}$) which is in agreement with the results reported by Ivanovic and Bykov [24]. The change in slope $\sigma - 1000/T$ plots may due to the transition of ion from $M_1$ site to $M_2$ site that influenced the conductivity at even the
slightest change in ion arrangement. The activation energy for the highest conducting sample extracted from the Arrhenius plot is 0.0977 eV. The low value of activation energy indicates high mobility of ions in the sample.

3.7. Magnesium transference number

Fig. 11(a) and (b) presents the plot of current versus time and impedance plots before and after polarization, respectively for the Mg/electrolyte/Mg cell fabricated using the Mg0.5 Zr2(PO4)3 sample sintered at 750 °C. Under a dc polarization of 0.27 V, the current in the cell exhibited only a small decay with time. The initial, $I_o$ and final steady, $I_{ss}$ currents and the impedance responses of the cells prior, $R_o$, and after, $R_{ss}$, polarization for the cell are listed in Table 2. Using the data, the Mg$^{2+}$ transference number was calculated and the value is
found to be 0.69. This value shows that the majority charge carriers in the electrolyte sample are $\text{Mg}^{2+}$ ions.

### 3.8. Linear sweep voltammetry

The electrochemical stability window of the ceramic electrolyte was evaluated by linear sweep voltammetry. Fig. 12 illustrates linear sweep voltammogram of the $\text{Mg}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ sample sintered at 750 °C. From the figure, the magnitude of current is fairly low below 2.50 V and the current starts to increase at potentials beyond this limit due to decomposition of the electrolyte. This suggests a voltage stability window in the $\text{Mg}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ compound at ambient temperature is up to 2.5 V.

### 4. Conclusions

Pure $\text{Mg}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ samples were successfully prepared by sol–gel method followed by sintering at 700–800 °C. The XRD, FTIR, and EDX analyses confirmed the formation of the compound. The DSC/TGA analyses predicted the chemical reaction in the sample completed at 650 °C and no phase transitions were observed up to 850 °C. The melting temperature of the $\text{Mg}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ compound was found to be 1165 °C. The SEM showed that the grain size decreased with increase of sintering temperature and was in agreement with the particle size distribution data. The highest conductivity values obtained for this compound were in the order of $10^{-6} \text{ S cm}^{-1}$ at room temperature and $10^{-2} \text{ S cm}^{-1}$ at 500 °C, respectively. The value of magnesium transference number was 0.69 confirming that it was $\text{Mg}^{2+}$ conducting compound. The compound showed reasonably wide stable voltage window; up to 2.5 V vs. $\text{Mg}/\text{Mg}^{2+}$ at ambient temperature. These suggest that $\text{Mg}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ could be further explored as electrolytes by enhancing the conductivity and ion transport in the structure. It can be done by partial (single or multiple) elemental substitutions.

### Acknowledgment

Financial support from the University of Malaya (research grant RP031A-13AFR) is gratefully acknowledged.

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