Full Length Article

Effects of Mg$^{2+}$ interstitial ion on the properties of Mg$_{0.5+x/2}$Si$_{2-x}$Al$_x$(PO$_4$)$_3$ ceramic electrolytes

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Abstract

Nasicon type, Mg$_{0.5+x/2}$Si$_{2-x}$Al$_x$(PO$_4$)$_3$, was synthesized using citric acid assisted sol-gel method. The X-ray diffraction was applied to investigate the effect of extra Mg$^{2+}$ interstitial ion on the phase, unit cell parameters and structure of the samples. The Mg$_{0.5+x/2}$Si$_{2-x}$Al$_x$(PO$_4$)$_3$ sample exhibited highest bulk conductivity value of $1.34 \times 10^{-4}$ S cm$^{-1}$ at ambient temperature. The frequency dependence of the $\sigma_{dc}$ of these ceramic electrolytes follows the universal power law variation, $\sigma_{dc}(\omega) = \sigma_{dc} + Aω^n$. The conductivity parameters such as hopping frequencies, charge carrier concentration and mobile ion concentration proved that the increase in conductivity with x was due to the existence of Mg$^{2+}$ interstitial ions. The experiment results also revealed that the dielectric constant and dielectric loss decreased with frequency: The Mg$_{0.5+x/2}$Si$_{2-x}$Al$_x$(PO$_4$)$_3$ was found to be electrochemically stable up to 2.51 V at ambient temperature.

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1. Introduction

Magnesium batteries have recently attracted great interest due to their high energy density and environmentally friendly components [1]. Theoretically, these Mg batteries can offer high volumetric specific capacity compared to lithium (3833 mAh/cm$^3$ for Mg vs. 2046 mAh/cm$^3$ for Li) [1]. Considering all these aspects, it is clear that magnesium battery systems could offer a significantly cheaper, safer and better-performing battery option in contrast to lithium [1]. Despite these attractive attributes of Mg batteries, there are several challenges pertaining to the use of cathodes, electrolytes and anodes. With respect to electrolytes, the magnesium electrolytes' compound has to show high ionic conductivity, large enough interstitial void and high structural stability based on 3D framework [2].

There are only a limited number of works on the use of magnesium as an electrolyte in magnesium batteries. This is due to the (i) difficulty for the divalent Mg-ion to diffuse in solid electrolytes compared to the monovalent Li-ion, (ii) narrow electrical window of electrolytes used for Mg-ion electrochemical activity and finally (iii) relatively low specific energy of magnesium ion batteries compared to its lithium counterpart [3]. Anuar et al started to synthesize magnesium electrolytes based on Nasicon type, Mg$_{0.5}$Zr$_2$(PO$_4$)$_3$ [2]. However, the Nasicon’s lattice size was too large making the structure unstable. To overcome this problem, the authors replaced Zr$^{4+}$ with Si$^{4+}$ as reported in an early paper [4] in order to reduce the lattice size of the Nasicon’s structure. The conductivity of Mg$_{0.5}$Si$_2$(PO$_4$)$_3$ solid electrolytes is an order of magnitude higher than the Mg$_{0.5}$Zr$_2$(PO$_4$)$_3$ solid electrolytes.

The conductivity of the Nasicon materials can also be improved by modifying their unit cell dimension and ion concentration (interstitial ion and vacant site) [5–7]. Therefore, in the effort to enhance the conductivity of previous Mg$_{0.5}$Si$_2$(PO$_4$)$_3$ compound, the authors substituted Al$^{3+}$ at the Si$^{4+}$ site (Si$^{4+}$$\leftrightarrow$ Al$^{3+}$ + 1/2Mg$^{2+}$) in order to create Mg$^{2+}$ interstitial ions in the lattice site to obtain compounds with formula Mg$_{0.5+x}$Si$_{2-x}$Al$_x$(PO$_4$)$_3$. To the best of our knowledge, no studies on the use of Al$^{3+}$ as conductivity enhancing agent in the Mg$_{0.5}$Si$_2$(PO$_4$)$_3$ compound have been reported in the literature.

In this paper, the effects of Mg$^{2+}$ interstitial ion on the structural, electrical and electrochemical properties of the Mg$_{0.5+x}$Si$_{2-x}$Al$_x$(PO$_4$)$_3$ compound prepared by the sol-gel method were investigated. For this purpose, the Mg$_{0.5+x}$Si$_{2-x}$Al$_x$(PO$_4$)$_3$