# UNIVERSITI TEKNOLOGI MARA

# EFFECTS OF TRIVALENT ION ($Al^{3+}$) SUBSTITUTION ON THE STRUCTURAL, ELECTRICAL AND ELECTROCHEMICAL PROPERTIES OF MAGNESIUM TITANIUM PHOSPHATE CERAMIC ELECTROLYTES

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# ABSTRACT

Research related to Magnesium-Ion Batteries for application in energy storage devices focusing on developing all solid-state batteries becomes subject of interest in achieving a safe and environmentally energy storage device. However, Magnesium-Ion Batteries are facing lower ionic conductivity compared to Lithium-ion Batteries. Hence, this research is presented to investigate the effects of $Al^{3+}$ substitution on the structural, electrical and electrochemical properties of the $Mg_{0.5}Ti_2(PO_4)_3$ compound in enhancing the conductivity of the compound. Herein, NASICON-based framework structure, $Mg_{0.5}Ti_2(PO_4)_3$ was developed as a potential material electrolyte focusing on the solid electrolytes. This research is divided into two (2) parts. The first part is to study the effects of heat treatment at different sintering temperatures (650, 700, 750, 800, 850, 900 and 950 $^oC$) on the parent compound $Mg_{0.5}Ti_2(PO_4)_3$ while the second part is to study the effects of trivalent ion, $Al^{3+}$ at different composition ($x$ = 0.1, 0.3, 0.5, 0.7 and 0.9) in $Mg_{0.5+0.5x}Al_xTi_{2-x}(PO_4)_3$ compound. The sample of $Mg_{0.5}Ti_2(PO_4)_3$ parent compound was successfully synthesized via sol-gel method at different sintering temperatures with the same sintering duration (24 hours). Then, the structural, electrical and electrochemical properties of the compound were determined. The X-ray diffraction and Rietveld analysis showed $Mg_{0.5}Ti_2(PO_4)_3$ compounds can be indexed to rhombohedral structure with space group (R3c) for all the samples sintered with the same duration. However, all $Mg_{0.5}Ti_2(PO_4)_3$ compounds showed trace amount of impurity of $TiP_2O_7$. The characterization of impedance for the best sample, 850 $^oC$ is done at 30 $^oC$ and 500 $^oC$. The $Mg_{0.5}Ti_2(PO_4)_3$ compound sintered at temperature 850 $^oC$ showed average bulk, grain boundary and total conductivity of $2.88 \times 10^{-8}$ S $cm^{-1}$, $7.20 \times 10^{-10}$ S $cm^{-1}$ and $7.02 \times 10^{-10}$ S $cm^{-1}$ at 30 $^oC$. The total conductivity of sample sintered at temperature 850 $^oC$ increased to $2.63 \times 10^{-7}$ S $cm^{-1}$ when the temperature was 500 $^oC$. The frequency dependence of conductivity followed Jonscher's universal power law. The plot of pre-exponent, $s$ versus temperature suggested that Correlated Barrier Hopping Model as the conduction mechanism of the compound. The highest conducting sample sintered at 850 $^oC$ was electrochemically stable up to 1.5 V. Next, the effects of partial substitution using trivalent $Al^{3+}$ is further investigated in $Mg_{0.5+0.5x}Al_xTi_{2-x}(PO_4)_3$ ($x$ = 0.1, 0.3, 0.5, 0.7 and 0.9) and the structural, electrical and the electrochemical properties is determined. There is a lattice contraction once a substitution of $Al^{3+}$ take place based on Rietveld analysis. This revealed that the substitution of $Al^{3+}$ has changes the lattice volume of the $Mg_{0.5}Ti_2(PO_4)_3$. The impedance analysis showed that the conductivity of the parent compound increases with increasing compositions of substitution ions. The substitution of smaller ionic radius of trivalent ion, $Al^{3+}$ at $x$=0.5 enhanced the conductivity of substituted compound at 30 $^oC$. The value of bulk, grain boundary and total conductivity of $x$=0.5 were $7.85 \times 10^{-8}$ S $cm^{-1}$, $3.91 \times 10^{-8}$ S $cm^{-1}$ and $2.61 \times 10^{-8}$ S $cm^{-1}$ respectively. The total conductivity of $x$=0.5 increased to 5.41 x $10^{-6}$ S $cm^{-1}$ when temperature was 500 $^oC$. Linear sweep voltammetry analysis indicated that $x$=0.5 sample improved the electrolyte decomposition from 1.5 V in the parent compound to 1.8 V. The transference number value of parent compound and $x$=0.5 sample were 0.99 and 0.98 suggesting that the majority of mobile charge carriers were ions and anticipated to be $Mg^{2+}$. Thus, the results of this study indicated that $Al^{3+}$ substitution significantly enhanced the electrical and electrochemical properties of the $Mg_{0.5}Ti_2(PO_4)_3$ ceramic electrolytes.

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# CHAPTER ONE
# INTRODUCTION

## 1.1 Research Background

The increment in the consumption of fossil fuels is parallel with the economic growth. The growth of energy storage devices urges the metal to be produced more with the consumptions of different types of metal. For the past few centuries, our technologies revolution was mainly been fuelled by various of combustion reaction. However, the usage of fossil fuels such as coal, oil and gas surge the potential effects of global warming. Due to that concern, a cheap and sustainable energy supply has to be obtained for the sake of future generations. Batteries can provide a solution as they can be used as an alternative to store intermittent, renewable and clean energy from sustainable sources such as wind, sun, water and others. Inherently, batteries are simple in concept but it progresses slower than other areas of electronics due to the lack of suitable electrode materials and electrolytes other than difficulties in mastering the interfaces between them (Wu et al., 2022; Chong et al., 2022; Asif et al., 2021; Zhang et al., 2020; Yang et al., 2021;Armand & Tarascon, 2008).

Among various storage technologies, secondary storage devices developed faster in the field of the renewable clean energy because of the effectiveness and stability in the conversion of electrical energy into chemical energy. Secondary batteries also proposed good application prospects in electronic equipment because of their advantages such as light weight, high energy density, clean and pollution free (Zhang et al., 2020; Kou et al., 2019). In the past decades, Lithium-ion batteries (LIBs) have achieved commercial success and become a common power source in the portable electronics market. LIBs also are getting more attention from researchers because of their wide working voltage range, long cycle life and no memory effect (Kou et al., 2019; Wu et al., 2022). Figure 1.1 shows various shapes and components of LIBs.