# UNIVERSITI TEKNOLOGI MARA

# PREPARATION AND CHARACTERIZATION OF NaI-$Na_3PO_4$ SODIUM ION CONDUCTING SOLID ELECTROLYTE WITH PLLTMEDA AS AN ADDITIVE FOR SODIUM BATTERIES

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# ABSTRACT

New binary inorganic salt sodium iodide (NaI)–sodium phosphate ($Na_3PO_4$) prepared by mechanical milling for 3 hours and low sintering temperature method at 50 ºC exhibits maximum ionic conductivity of $(1.02\pm0.19) \times 10^{-4}$ S $cm^{-1}$ at room temperature for the composition 0.50 NaI : 0.50 $Na_3PO_4$. The increase in conductivity is due to the increase in number of mobile $Na^+$ charge carriers through the conducting pathway provided by tetrahedral structures of $Na_3PO_4$. The presence of P–O at wavenumber 580 $cm^{-1}$ and $PO_4^{3-}$ bands at wavenumber 1012 $cm^{-1}$ respectively were detected by the infrared technique. Fourier transform infrared spectroscopy had been shifted indicating changes in polyhedral structure which in turn led to the formation of conducting channel by corner sharing or through edges. The spectra also implies that chelation of iodide anion gave rise to high mobility and elevations of the charge carriers to traverse along the conducting pathway created from tetrahedral phosphate thus giving rise to the conductivity of the sample. However the ionic conductivity value is still not high enough for application in electrochemical devices. Improve conductivity can be achieved by incorporation of an additive to the binary system. Poly(L-Leucine)1,3-diamino propane (PLLTMEDA) has been chosen as an additive due to its unique properties that able to further increase the ionic conductivity. The electrical conductivity of NaI–$Na_3PO_4$ and NaI–$Na_3PO_4$–PLLTMEDA were obtained by employing impedance spectroscopy (IS) technique. It was found the addition of PLLTMEDA resulted in an increase of electrical conductivity. The maximum conductivity of the new system NaI-$Na_3PO_4$ with 4 wt. % of PLLTMEDA shows maximum conductivity of $(1.12\pm0.68) \times 10^{-3}$ S $cm^{-1}$. The temperature dependence conductivity studies show that both systems are Arrhenius in nature and the transport properties can be descript by the hopping mechanism. The activation energy obtained for NaI–$Na_3PO_4$ is 0.34 eV and NaI– $Na_3PO_4$ with PLLTMEDA is 0.26 eV. The collected data from IS studies were analyzed in various complex planes such as impedance, admittance and permittivity for dielectric studies. Ac conductivity is analyzed using the Johscher's universal power law and the hopping mechanism of the charge carriers for both systems follow quantum mechanical tunneling (QMT) model. Ionic transference number was found to be 0.92 and 0.96 for the optimum composition of binary system and binary with additives respectively. This implies that the samples are ionic in nature. The FTIR spectra of NaI–$Na_3PO_4$–PLLTMEDA also verify the chelation of $I^-$ resulted in the immobilization of anion to give rise to high mobility and elevations of the charge carriers to traverse along the conducting pathway created from tetrahedral phosphate thus giving rise to the conductivity of the sample. Result obtained from NMR revealed the narrowing of the line width $^{23}Na$ spectra in the optimum composition of the binary NaI–$Na_3PO_4$–PLLTMEDA system can be assigned to Na population with higher ion mobility. The X-ray diffractogram of the binary with PLLTMEDA shows that the system has become semi-crystalline in nature. Field emission scanning electron microscopy micrographs revealed finer microstructure of the milling samples with grains growth formation and densification upon sintering. The fabricated cell using 50 wt. % of NaI and 4 wt. % of PLLTMEDA showed better performance with discharge time of 173 hours at 1.0 µA current and the value of open circuit voltage is 3.0 V at room temperature.

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# CHAPTER ONE
# INTRODUCTION

## 1.1 BACKGROUND OF STUDY

Handheld electronics from mobile phones to laptops as well as automobiles have transformed the way we live over the past decade. High demands of electronic devices appeal to increase in business route especially in battery development. Vigorous development in batteries has occurred in the last decades even nowadays. It has now become the necessity in the industry especially electronic. Cell phones and laptop chargers are among the examples of products that have increased in demand in the consumer market place.

The science of solid electrolytes is a multidisciplinary field that comprises the discipline of inorganic chemistry, organic chemistry, electrochemistry and polymer science. The unusual high electrical conductivity and low activation energy much below melting point of solid electrolyte materials make them suitable to be a subject of study. In search of high conductive materials, the lattice framework of highly ordered nature in solid electrolyte in which ions or charge carries move have been widely investigated focusing on identification and characterization of crystalline superionic conductors. Solids with high ionic conductivity at room temperature ($10^{-2}$ S $cm^{-1}$ to $10^{-6}$ S $cm^{-1}$) are generally called fast ion conductors or superionic solids. These superionic solids have features of an enormous number of mobile charge carriers and large available sites for migration to take place (Mcgeehin and Hooper, 1977). Each of these mobile charge carriers have approximately similar coordination and same amount of energy as they migrate from one interstitial site to another.

Superionic solid commonly has minimum energy barrier for a chemical reaction to occur as ions jump from one site to another through continuous chain of face sharing octahedral and tetrahedral in three dimensional structures. Monovalent cations ($Li^+$, $Ag^+$, $Cu^+$, $Na^+$, $K^+$ ), monovalent anions ($F^{-1}$, $Cl^{-1}$, $Br^{-1}$, $I^{-1}$) and divalent anion ($O^{2-}$) are among the conducting species that bring forth ionic conduction in solid electrolytes. $Li^+$ and $Na^+$ ion conducting solid electrolytes have been investigated for