

PHYSICAL AND ELECTRICAL PROPERTIES OF $\text{Li}_{1+x}\text{Ti}_{2-x}\text{Al}_x(\text{PO}_4)_3$ AND
 $\text{Li}_{1+2x}\text{Ta}_{1-x}\text{Al}_{x+1}(\text{PO}_4)_3$ ELECTROLYTES

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DEDICATION

To my loving and caring Mother Hajiya Maryam Aliyu Lemu
(May her magnanimous gentle soul continues to rest in perfect peace, amen)



PTTA UTHM
PERPUSTAKAAN TUNKU TUN AMINAH

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ABSTRACT

Sodium superionic conducting materials (NASICON) are promising solid electrolytes for Li-ion rechargeable batteries. In this study, two compositions; lithium titanium aluminium phosphate (LTAP), $\text{Li}_{1+x}\text{Ti}_{2-x}\text{Al}_x(\text{PO}_4)_3$ ($x = 0.0, 0.2, 0.6, 1.0$) and lithium tantalum aluminium phosphate (LTaAP), $\text{Li}_{1+2x}\text{Ta}_{1-x}\text{Al}_{x+1}(\text{PO}_4)_3$ ($0 \sim 0.5$) solid electrolyte were synthesized via solid state reaction techniques at various sintering temperature ranging from 700 to 1000 °C for 8 and 12 h respectively. Lithium carbonate (Li_2CO_3), titanium dioxide (TiO_2), aluminium dioxide (Al_2O_3), tantalum oxide (Ta_2O_5) and ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) of high purity grade were used as the starting material. Physical properties of LTAP and LTaAP electrolyte show bulk density of 2.83 and 3.63 g/cm³ at 900 and 800 °C sintering temperature. XRD revealed major phase of $\text{LiTi}_2(\text{PO}_4)_3$ NASICON structure and secondary phases ($\text{Ti}_4(\text{PO}_5)_3$, TiO_2 and AlPO_4) co-exist in LTAP and LTaAP samples. FTIR shows presence of NASICON phosphate peaks which were dominated with vibration of PO_4 ion in all prepared LTAP and LTaAP electrolytes. This also confirms the presence of $\text{LiTi}_2(\text{PO}_4)_3$ in all of the samples. The ionic conductivity of solid electrolytes was analyzed with IS at room temperature. The highest conductivity was 1.06×10^{-4} and 9.854×10^{-6} S/cm for $\text{Li}_{1.2}\text{Ti}_{1.8}\text{Al}_{0.2}(\text{PO}_4)_3$ and $\text{Li}_{1.2}\text{Ta}_{0.9}\text{Al}_{1.1}(\text{PO}_4)_3$ electrolytes at room temperature. Conductivity behavior is enhanced when the sample was doped with aluminium, $x = 0.2$ for LTAP and $x = 0.1$ for LTaAP composition. The high ionic conductivity of LTAP-0.2 was supported by density data and lower impurity peaks, as reported in XRD. LTAP had better conductivity behavior compared to LTaAP composition which could be due to hard nature of tantalum in the stoichiometry ratio of LTaAP compound resulted into wide grain boundary and lower its conductivity. However, from ac conductivity analysis, the conductivity values for LTAP-0.2 and LTaAP-0.1 are within the range of $0 < s < 1$.

ABSTRAK

Bahan pengaliran natrium superionik (NASICON) berpotensi sebagai elektrolit pepejal untuk bateri Li-ion yang boleh dicas semula. Dalam kajian ini, dua komposisi elektrolit pepejal: litium titanium aluminium fosfat (LTAP), $\text{Li}_{1+x}\text{Ti}_{2-x}\text{Al}_x(\text{PO}_4)_3$ ($x = 0, 0.2, 0.6, 1.0$) dan litium tantalum aluminium fosfat (LTaAP), $\text{Li}_{1+2x}\text{Ta}_{1-x}\text{Al}_{x+1}(\text{PO}_4)_3$ ($0 \leq x \leq 0.5$) telah disintesis menggunakan teknik tindak balas keadaan pepejal pada suhu pensiteran berbeza iaitu daripada 700 hingga 1000 °C selama 8 dan 12 jam masing-masing. Litium karbonat (Li_2CO_3), titanium dioksida (TiO_2), aluminium dioksida (Al_2O_3), tantalum oksida (Ta_2O_5), dan ammonium dihidrogen fosfat ($\text{NH}_4\text{H}_2\text{PO}_4$) yang bergred tinggi digunakan sebagai bahan permulaan. Sifat-sifat fizikal elektrolit LTAP dan LTaAP menunjukkan ketumpatan pukal sebanyak 2.83 dan 3.63 g/cm³ pada suhu pensiteran 900 dan 800 °C. XRD mengesahkan fasa utama struktur $\text{LiTi}_2(\text{PO}_4)_3$ NASICON dan fasa kedua ($\text{Ti}_4(\text{PO}_5)_3$, TiO_2 , dan AlPO_4 wujud di dalam sampel LTAP dan LTaAP. FTIR pula mendedahkan kewujudan puncak fosfat NASICON yang didominasi dengan getaran ion PO_4 di dalam semua elektrolit LTAP dan LTaAP yang disediakan. Ini juga membuktikan kewujudan $\text{LiTi}_2(\text{PO}_4)_3$ di dalam semua sampel. Nilai konduktiviti ionik bagi elektrolit pepejal ini dianalisa menggunakan IS di suhu bilik. Nilai konduktiviti tertinggi adalah 1.06×10^{-4} and 9.854×10^{-6} S/cm untuk $\text{Li}_{1.2}\text{Ti}_{1.8}\text{Al}_{0.2}(\text{PO}_4)_3$ dan $\text{Li}_{1.2}\text{Ta}_{0.9}\text{Al}_{1.1}(\text{PO}_4)_3$ pada suhu bilik. Tingkah konduktiviti dipertingkatkan apabila sampel didopkan dengan aluminium, $x = 0.2$ untuk LTAP dan $x = 0.1$ untuk komposisi LTaAP. Nilai konduktiviti ionik yang tinggi bagi LTAP-0.2 adalah kerana data ketumpatan dan puncak bendasing yang lebih rendah seperti yang dilaporkan melalui XRD. LTAP mempunyai tingkah konduktiviti yang lebih baik berbanding komposisi LTaAP yang mungkin disebabkan sifat keras semulajadi tantalum di dalam nisbah stoikiometri LTaAP yang akhirnya memperluas sempadan bijian dan mengurangkan konduktivitinya. Walau bagaimanapun, daripada analisis konduktiviti AC, nilai konduktiviti untuk LTAP-0.2 dan LTaAP-0.1 adalah di dalam julat $0 < s < 1$.

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LIST OF SYMBOLS AND ABBREVIATIONS

3D	3 dimensional
%	Percentage
ϵ	Dielectric permittivity
Ω	Ohms
π	Pi
τ	Relaxation time
ϵ'	Dielectric constant
ϵ''	Dielectric loss
ρ_b	Bulk density
ϵ_0	Dielectric permittivity of free space
=	Equal to
\leq	Less than
$^\circ$	Degree
$^\circ\text{C}$	Degree celsius
A	Area
\AA	Armstrong's
Al	Aluminium
Al_2O_3	Aluminium oxide
AR	Analytical reagent
Au	Gold
cm	Centimeter
C_0	Capacitance of dielectric constant
CPE	Constant phase element
Cu	Copper
d	Diameter

EDX	Elemental dispersive x-ray
EEC	Electrical equivalent circuit
FESEM	Field emission scanning electron microscope
FTIR	Fourier transform infra-red
FWHM	Full width at half maximum
g	Gram
h	hour
Hz	Hertz
ICSD	Inorganic crystal structure database
IS	Impedance spectroscopy
JCPDS	Joint committee on powder diffraction standard
kg	kilogram
Li	Lithium
Li ₂ CO ₃	Lithium carbonate
LISICON	Lithium ion super ionic conductor
Log	Logarithm
LLTO	Lithium lanthanum titanate oxide
LTaAP	Lithium tantalum aluminium phosphate
LTAP	Lithium titanium aluminium phosphate
m	Meter
MA	Mechanical activation
M''	Imaginary electric modulus
M'	Real electric modulus
MHz	Mega hertz
NASICON	Sodium super ionic conductor
NH ₄ H ₂ PO ₄	Ammonium dihydrogen phosphate
PO ₄	Phosphate
R	Resistance
R _b	Bulk resistance
R _{gb}	Grain boundary resistance
RT	Room temperature
S	Siemens
SC	Scandium
s.g	Space group

SCO	Solid conducting oxide
SEs	Solid electrolytes
SEM	Scanning electron microscopy
SW	Scandium Wolframate
t	Thickness
Ta	Tantalum
Ta ₂ O ₅	Tantalum oxide
tan δ	Loss tangent
Ti	Titanium
XRD	X- Ray diffraction
Z''	Imaginary impedance
Z'	Real impedance
A	Alpha
β	Beta
θ	Theta
μ	Micro
σ	Conductivity
σ_{ac}	AC conductivity
σ_b	Bulk conductivity
σ_{gb}	Grain boundary conductivity
ν	Frequency
ω	Angular frequency



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JOURNALS

- i. **Mohammed Isah Kimpa**, Mohd Zul Hilmi Mayzan, Fahmiruddin Esa, Jibrin Alhaji Yabagi, Muhammad Muhammad Nmaya and Mohd Arif Agam (2017). Synthesis of NASICON Structured Solid Electrolyte $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ for Lithium Ion Batteries. *Advanced Science Letter (Accepted/Scopus Index)*
- ii. **Mohammed K. Isah**, Chong. M. Kit, Fahmiruddin Esa, Mohd Z.H. Mayzan, Jibrin A. Yabagi and Mohd A. Arif (2017). Characterization of $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ Solid Electrolytes Prepared Using Sol-Gel Method. *Journal of Engineering and Applied Sciences (Accepted/Scopus index)*.
- iii. **Mohammed Isah Kimpa**, Mohd Zul Hilmi Mayzan, Fahmiruddin Esa, Jibrin Alhaji Yabagi, Muhammad Muhammad Nmaya and Mohd Arif Agam (2017). Physical Characterization and Electrical Conductivity of $\text{Li}_{1.2}\text{Ti}_{1.8}\text{Al}_{0.2}(\text{PO}_4)_3$ and $\text{Li}_{1.2}\text{Ta}_{0.9}\text{Al}_{1.1}(\text{PO}_4)_3$ NASICON Material. *International Journal of Integrated Engineering (Accepted/Scopus index)*.
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CHAPTER 1

INTRODUCTION

1.1 Background

The inexpensive oil is going to last after few more years and the search for the alternative energy sources is very important. Since the tapping of energy from non-conventional sources such as wind, solar, or nuclear sources has certain limitation, research focus has been shifted to batteries and fuel cells as a source of energy storage (Guin *et al.*, 2017; Zhang *et al.*, 2017). Much attention has been paid to rechargeable lithium batteries as a future energy storage due to its higher energy density and longer charge retention (Anantharamulu *et al.*, 2011; Xu *et al.*, 2004a).

The advent of solid state batteries must be understood in the context of the challenges faced by modern storage systems, especially Li-ion batteries. Existing Li-ion batteries, apart from the storage and active components, contain considerable quantities of auxiliary materials and cooling equipment (Guin & Tietz, 2015). Loss of battery quality due to continuous charging and discharging cycles, flammability, dissolution of the electrolyte, and from vehicle to grid utilization has been another important concern. Solid state batteries are being extensively studied and researched with a view to solving these problems such as excellent physical and chemical stability, Li⁺ ion conduction, free from leakages and is durable (Baek *et al.*, 2017; Giarola *et al.*, 2017)

Lithium-based solid electrolyte is one of the best candidates for the application in batteries due to its high potential and low weight for high-energy density storage in batteries (Pérez-Estébanez *et al.*, 2014). The lithium transition metal phosphates have found application in the field of electrochemical energy storage, especially those with

NASICON structure, because of their good electrochemical performances and capability to answer safety concerns surrounding oxide chemistry (Arbi *et al.*, 2015).

NASICON is an acronym of Sodium (**Na**) Super Ionic **C**onductor which is derived from family of $\text{NaZr}_2\text{P}_3\text{O}_{12}$ (NZP) by partial replacement of P by Si with Na excess to balance the negatively charged framework (Eckert & Martins Rodrigues, 2017; Khireddine *et al.*, 1997; Santagneli *et al.*, 2016) to yield the general formula $\text{Na}_{1+x}\text{Zr}_2\text{P}_{3-x}\text{Si}_x\text{O}_{12}$ with a wide range of stoichiometry where x can assumed any value between 0 and 3 (Moreno-Real *et al.*, 2002). The structural and electrical properties of Nasicon-type compounds vary with the composition of its framework (Yi *et al.*, 2014).

The compound has unusual property of accommodating 40 to 45 elements in its structure and also have some special structural features such that all the atoms, except oxygen, can be substituted by various atoms of different oxidation states and radii, giving the resulting compositions different chemical and physical properties, while at the same time retaining the main crystal structure (Ahmadu, 2014). This make it amiable for diverse applications for block engines, electrical vehicles and mobile electronic devices (Yang *et al.*, 2015).

NASICON was first sensitised by Hong and Goodenough in 1976 (Siebert & Fabry, 1999). NASICON compounds crystallize with a rhombohedral structure in the $R\bar{3}c$ space group, but cell distortion leading to a monoclinic symmetry has also been found and discussed (Hiromichi Aono, 1994). The compounds are built on framework of $\text{M}[\text{A}_2\text{B}_3\text{O}_{12}]$, where M, A, and B are monovalent, tetravalent and pentavalent cations, respectively. These compounds present a good ionic conductivity by the monovalent M^+ cations. The structure of the compound can be described as a covalent anionic skeleton $[\text{A}_2\text{B}_3\text{O}_{12}]^-$ constituted of AO_6 octahedra and BO_4 tetrahedra which form 3D interconnected channels in which two types of interstitial sites are available for the M^+ conductive cations (Leo *et al.*, 2002). Conduction happens when M^+ moves from one interstitial site to another through “bottlenecks” formed by triangle of oxygen ions (Fuentes *et al.*, 2001).

Among many solid electrolytes available (Balagopal *et al.*, 1999), NASICON has been extensively tested for the use in power sources and is better than other electrolyte materials such as Perovskite-type, Garnet-type and sulfide-based glasses (Ma *et al.*, 2016) due to their high excellent conductivity at room temperature as well as good stability under atmosphere (Mustaffa and Mohamed, 2015).

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