

# CONDUCTIVITY AND IONIC MOBILITY STUDIES ON $\text{Li}_2\text{WO}_4\text{-LiI-Al}_2\text{O}_3$ BY EIS AND NMR TECHNIQUES

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## Article history

Received

2 July 2015

Received in revised form

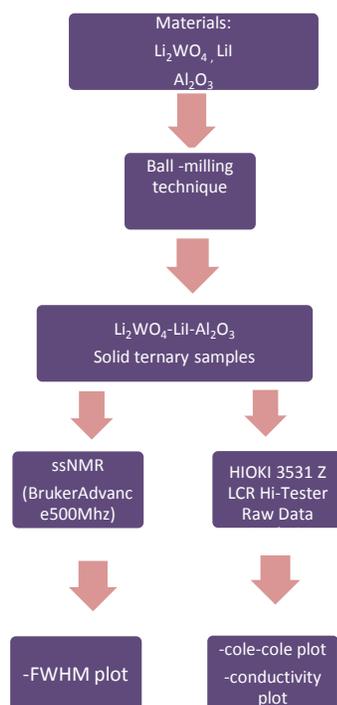
3 April 2015

Accepted

25 June 2015

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## Graphical abstract



## Abstract

$\text{Li}_2\text{WO}_4\text{-LiI-Al}_2\text{O}_3$  solid electrolytes have been found to be a potential electrolyte for battery applications due to its high electrical conductivity at ambient temperature. The binary solid electrolyte with incorporation  $\text{Al}_2\text{O}_3$  was prepared in solid state reaction and characterized by Electrical Impedance Spectroscopy (EIS) and  $^7\text{Li}$  Magic Angle Spinning (MAS) solid state Nuclear Magnetic Resonance (ssNMR) technique. Maximum electrical conductivity of  $3.35 \times 10^{-3} \text{ Scm}^{-1}$  was recorded for the sample containing 20 wt.% of LiI. The conductivity improved up to  $3.92 \times 10^{-3} \text{ Scm}^{-1}$  as 5wt.% of  $\text{Al}_2\text{O}_3$  was added into the optimum composition of the binary system. Mobility of the charge carrier in the sample was investigated and NMR result showed that the electrolyte with high ionic mobility contribute into high electrical conductivity.

Keywords: Solid state electrolyte, impedance spectroscopy, ionic conductivity, solid state nuclear magnetic resonance

## Abstrak

Elektrolit pepejal  $\text{Li}_2\text{WO}_4\text{-LiI-Al}_2\text{O}_3$  telah dijumpai sebagai bahan berpotensi tinggi dalam pembuatan bateri kerana mempunyai kebolehan mengalirkan arus elektrik yang tinggi pada suhu bilik. Pepejal elektrolit peringkat kedua dengan kerjasama  $\text{Al}_2\text{O}_3$  telah disediakan dalam keadaan reaksi pepejal dan telah dicirikan oleh teknik Spektroskopi Impedans Elektrik (EIS) dan pusingan sudut ajaib  $^7\text{Li}$  Resonans Magnetik Nuklear keadaan pepejal (ssNMR). Pengaliran arus tertinggi sebanyak  $3.35 \times 10^{-3} \text{ Scm}^{-1}$  telah direkodkan untuk sampel yang mengandungi 20 berat peratus LiI. Peningkatan pengaliran arus elektrik kepada  $3.92 \times 10^{-3} \text{ Scm}^{-1}$  telah dicapai apabila 0.5 peratus berat  $\text{Al}_2\text{O}_3$  telah ditambah kepada komposisi optimum sistem  $\text{Li}_2\text{WO}_4\text{-LiI}$  kedua. Kebolehan bergerak caj pembawa dalam sampel telah dikaji dan keputusan menunjukkan bahawa elektrolit dengan kebolehan bergerak caj yang tinggi menyumbang kepada pengaliran arus elektrik yang tinggi.

Kata kunci: Elektrolit keadaan pepejal, spektroskopi impedans, pengaliran ion, resonans magnetik nuklear keadaan pepejal

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## 1.0 INTRODUCTION

Solid state lithium batteries have attracted great attention because of their reliability properties and high safety compared to liquid type electrolytes. Lithium solid electrolyte which is one of the components for the lithium batteries requires favorable properties such as high lithium ion,  $\text{Li}^+$  conductivity, stable against chemical reaction and wide electrochemical window to allow utilization of high voltage cathode and anode material [1]. Inorganic solid electrolytes are widely recognized to be important material to fabricate solid state lithium batteries because they provide an effective conduction path for the charge carriers to pass through [2, 3, 4].

The variation in electrical conductivity is closely dependant on the amount and the mobility of charge carrier. To improve the electrical conductivity, it is necessary to optimize the amount of charge carrier and mobility of the ions since the low number of charge carriers will result in low ionic migration rate and excessive amount of charge carrier will caused the charge carrier to collide with each other, hence the conductivity decreased [5, 6, 7, 8]. In general, electrical conductivity of the glassy electrolyte can be increased by increasing the number of charge carrier or reducing the internal resistance in the system [9, 10]. It was reported that lithium iodide, LiI is the best candidate for elevated temperature operation for lithium battery due to thermodynamically stability of anion toward lithium anode while tungstate,  $\text{WO}_4$  in another work, shows good performance as an electrolyte in  $\text{Sc}_2(\text{WO}_4)_3$  and their structure found to be quite similar to the conducting compound such as NaSICON [11]. Our earlier work agrees with literature [3, 11] where tungstate glass build up three dimensional networks with large size of tunnel where ionic migration expected to occur.

Composite electrolyte is a promising future candidate for all-solid-state lithium battery because of their transport characteristic, mechanical properties and hygroscopic resistance that can be freely adjusted by varying the chemical composition or microstructure. The introduction of inert filler such as  $\text{TiO}_2$ ,  $\text{SiO}_2$  and  $\text{CeO}_2$  resulted in enhanced ionic conductivity [12]. The addition of inorganic filler caused great improvements of interfacial ionic transport via grain boundaries parallel to the direction of current flow in polymer electrolyte [13]. Nanoscale  $\text{Al}_2\text{O}_3$  exhibits two important features that aiding ionic conductivity in electrolyte such as large specific surface areas and grains covered with various Lewis acidic group [14].

Nuclear magnetic resonance (NMR) methods are well-suited for studying ionic environments and mobility in disordered electrolytes. In a recent initial investigation of PEO/LiI/Al<sub>2</sub>O<sub>3</sub> composite electrolytes, wide-line  $^7\text{Li}$  NMR spectra were utilized to study the coexistence of mobile and immobile Li phases as functions of temperature and composition [13].

In this work, we used  $\text{Li}_2\text{WO}_4$  and LiI to form the binary solid electrolyte and  $\text{Al}_2\text{O}_3$  as the filler. We report the result of the optimum binary system and the effect of the  $\text{Al}_2\text{O}_3$  filler on the electrical conductivity and ionic mobility of the electrolyte system.

## 2.0 EXPERIMENTAL

The binary solid electrolyte samples were prepared by mixing the appropriate weight ratio of lithium iodide, LiI (Aldrich) and lithium tungstate,  $\text{Li}_2\text{WO}_4$  (Aldrich). The powders were ground by planetary milling machine (model PM 200) at speed of 250 rpm for approximately 1 hour. The powders were pelletized by using ENERPAC hydraulic press with a mould of 1 cm radius at a pressure of 200 psi. The electrical conductivity of the samples (pellet) with different compositions was characterized by using HIOKI 3531 Z LCR Hi-Tester at ambient temperature (frequency range 50 Hz to 1 MHz). The different weight percent (5, 10, 15 and 20 wt.%) of alumina,  $\text{Al}_2\text{O}_3$  was added to the optimum composition of the binary LiI- $\text{Li}_2\text{WO}_4$  systems. The samples were characterized using impedance spectroscopy technique. The ionic mobility of the samples was characterized by deployed NMR spectrometer (model Bruker Advance 500 Mhz).

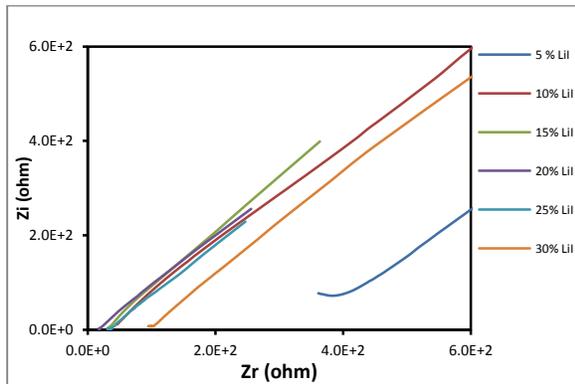
## 3.0 RESULTS AND DISCUSSIONS

The variations of the Impedance spectra of the binary samples with different LiI content are shown in Figure 1. The result depicted that the spectra consisted of spikes with different inclination for different amount of LiI (wt.%). The spikes at higher frequencies can be attributed to grain boundary effect while the semicircle at lower frequencies probably caused by the resistance of the grain (bulk) [15]. Basically, the electrical conductivity of pure  $\text{Li}_2\text{WO}_4$  is very low that is equal to  $10^{-6} \text{ Scm}^{-1}$ . The electrical conductivity was calculated by using the following equation

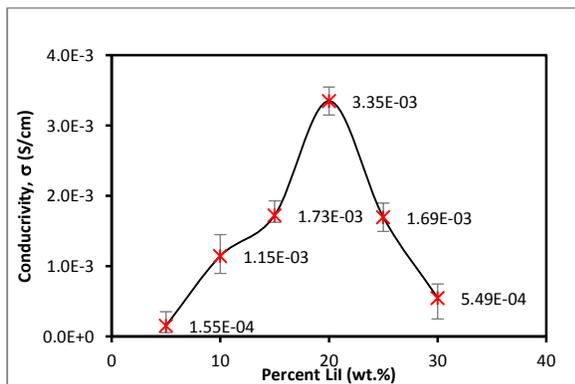
Conductivity,  $\sigma = t/A \cdot R_b$

Where,  $t$  = thickness of sample (cm)  
 $A$  = contact area of the sample (cm<sup>2</sup>)  
 $R_b$  = bulk resistance of the sample (S)

Figure 2 shows the variation of electrical conductivity of LiI-Li<sub>2</sub>WO<sub>4</sub> with different amount of LiI (wt.%). The conductivity values of the samples were increased as the different amount of LiI (wt.%) were introduced into the system. This could be due to the increases of the charge carriers numbers lithiated from LiI [16]. The maximum electrical conductivity of  $3.35 \times 10^{-3}$  Scm<sup>-1</sup> was obtained from the sample containing 20 wt.% of LiI. The conductivity was dropped after further addition of LiI beyond 20 wt.% in the system. This may arise due to the fact of having too much mobile ions in the electrolyte system which restricted the movement and caused the charge carrier to collide with each other.

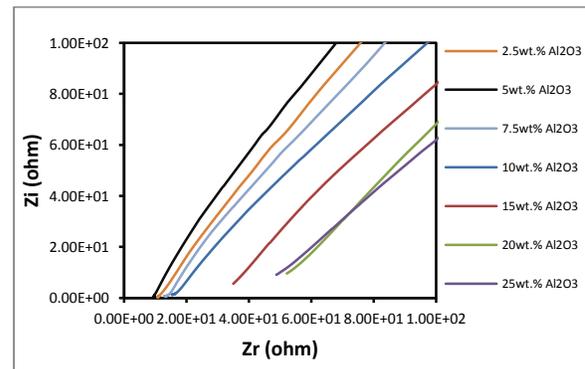


**Figure 1** Impedance spectra of Li<sub>2</sub>WO<sub>4</sub> with different amount of LiI (wt.%)

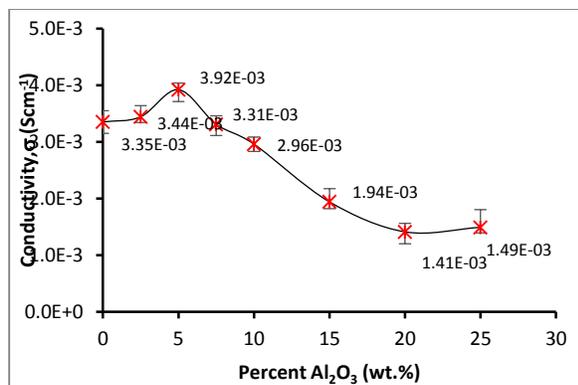


**Figure 2** Variation of conductivity for Li<sub>2</sub>WO<sub>4</sub> with different amount of LiI (wt.%)

The optimum composition of Li<sub>2</sub>WO<sub>4</sub>-LiI was selected in order to prepare electrolyte system with incorporation of Al<sub>2</sub>O<sub>3</sub> ceramic filler. Figure 3 demonstrates the impedance spectra of samples with different amount of Al<sub>2</sub>O<sub>3</sub> (2.5, 5, 7.5, 10, 15, 20, 25 wt.%). The variations of the electrical conductivity of the electrolyte system are shown in Figure 4. The electrical conductivity for the sample containing 5 wt.% of Al<sub>2</sub>O<sub>3</sub> was increased up to  $3.92 \times 10^{-3}$  Scm<sup>-1</sup>. The conductivity enhancement could be assigned to the Lewis acid-base type interaction between ionic species with oxygen and OH surface groups on the grains. This interaction could be able to provide transient hopping site, which created favorable high-conducting pathways for migration of ions [17, 18]. At the highest conductivity composition, the filler grains could move close enough to each other such that the high conducting regions within the vicinity of the grains became interconnected. Therefore, the ionic species could be able to travel either along or between these interconnected pathways, hence give a rise to the ionic conductivity of the system [18]. Besides, the Al<sub>2</sub>O<sub>3</sub> filler also was an effective lithium ion dissociating media in this system due to the ability of filler to interact with the anion in the system via a sort of 'ion-ceramic complex' formation [19,20]. Thus, the strength of lithium ion-anion interaction was reduced and "freeing" the lithium ion. However, the electrical conductivity of electrolyte was dropped with further increment of Al<sub>2</sub>O<sub>3</sub>. This could be attributed to the fact that the higher concentration of filler caused the grains positioned too close to each other and lead to the geometrical constriction or blocking effect [21]. Therefore, the mobility of the ions also decreased.



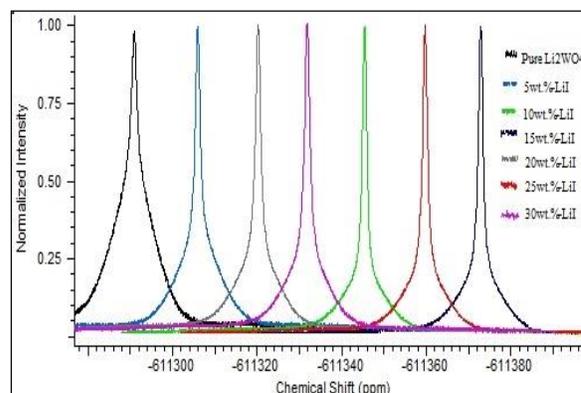
**Figure 3** Impedance spectra of Li<sub>2</sub>WO<sub>4</sub>-LiI with different amount of Al<sub>2</sub>O<sub>3</sub>



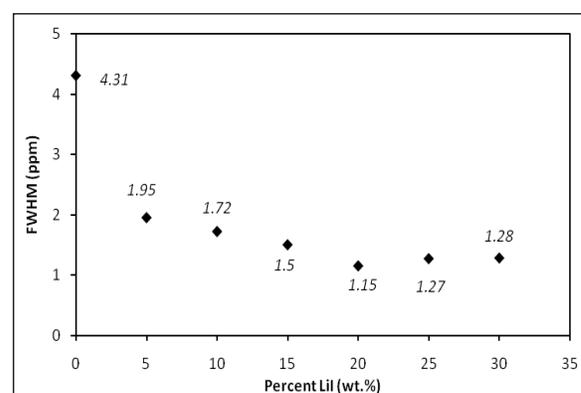
**Figure 4** Variation of conductivity for Li<sub>2</sub>WO<sub>4</sub>-LiI with different amount of Al<sub>2</sub>O<sub>3</sub>

The static solid state <sup>7</sup>Li NMR measurement was carried out in order to study the dynamic behavior of lithium ion in electrolyte system. Figure 5 shows the spectra of the binary electrolyte system. Each spectrum was differing from each other based on their peak width. The mobile lithium ions yield partially narrowed spectra and the nuclei contributing to this part of the signal was assumed to be associated with the ionically conductive lithium ions in the system [13]. Basically, the different between EIS and NMR measurement is that the impedance data reflects the total conductivity including both the bulk and grain boundary contribution while NMR result could be attributed to the bulk resistance alone [22].

The variation of line width as a function of amount of LiI (wt.%) are shown in Figure 6. The sample of the pure Li<sub>2</sub>WO<sub>4</sub> has showed high value of 4.31 ppm which indicates that the system posses low ionic mobility. The FWHM values were found to be decreased as the amount of LiI (wt.%) were increased in the system. The presence of LiI in the system provides another source of charge carriers for ionic conduction. Thus, give the rise for the concentration of mobile charge carriers. The FWHM values were continue to decrease until the system reach certain amount of LiI (20 wt.%). As the LiI was increased beyond 20 wt.%, the line width also increased. This could be due to the high concentration of charge carriers that lead to the collisions between charge carriers that may occur during ionic migration process toward limited conduction pathways.



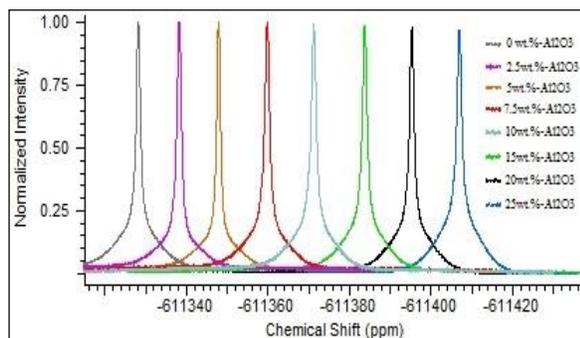
**Figure 5** The <sup>7</sup>Li NMR spectra of Li<sub>2</sub>WO<sub>4</sub> with different amount Al<sub>2</sub>O<sub>3</sub> (wt.%)



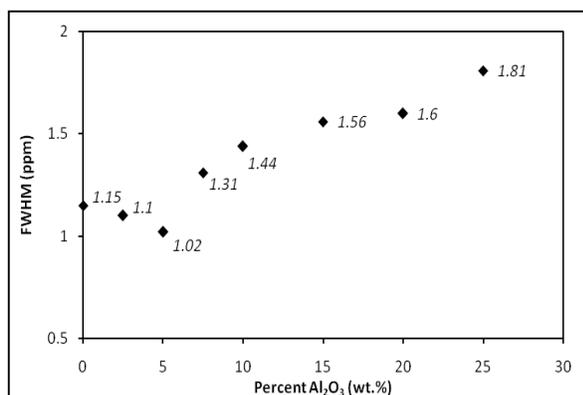
**Figure 6** Line width (FWHM) of Li<sub>2</sub>WO<sub>4</sub> with different amount Al<sub>2</sub>O<sub>3</sub> (wt.%)

Figure 7 shows the static NMR spectra of the Li<sub>2</sub>WO<sub>4</sub>-LiI with different amount of Al<sub>2</sub>O<sub>3</sub> (wt.%). The line width (FWHM) against amount of Al<sub>2</sub>O<sub>3</sub> were plotted to distinguish the peak width as a function of Al<sub>2</sub>O<sub>3</sub> in the electrolyte system as shown in Figure 8. The line width of the sample with 2.5wt.% of Al<sub>2</sub>O<sub>3</sub> has made no significant different with the sample without Al<sub>2</sub>O<sub>3</sub> filler. The lowest line width was found as the amount of Al<sub>2</sub>O<sub>3</sub> was increased up to 5wt.% in the system. Figure 8 depicts the narrowest line width that is equal to 1.02 ppm indicates that the sample exhibit the highest ionic mobility among the samples. The ionic mobility was increased with the presence of the Al<sub>2</sub>O<sub>3</sub> in the system could be due to the availability of free ions that were increased respectively based on the interaction between Al<sub>2</sub>O<sub>3</sub> and lithium ions that were tetrahedrally coordinated to the oxygen atoms of the tungstate group, WO<sub>4</sub><sup>2-</sup>. The interaction between Lewis acid group with oxygen and OH also contributes to the

ionic mobility by providing transient hopping site for the ionic migration.



**Figure 7** The  ${}^7\text{Li}$  NMR spectra of  $\text{Li}_2\text{WO}_2\text{-LiI}$  with different amount  $\text{Al}_2\text{O}_3$  (wt.%)



**Figure 8** Line width (FWHM) of  $\text{Li}_2\text{WO}_2\text{-LiI}$  with different amount  $\text{Al}_2\text{O}_3$  (wt.%)

## 4.0 CONCLUSION

The maximum electrical conductivity of  $3.35 \times 10^{-3} \text{ Scm}^{-1}$  of the electrolyte is obtained from the sample containing 20 wt.% of LiI. The incorporation of  $\text{Al}_2\text{O}_3$  filler has led to significantly enhanced ionic conductivity up to  $3.92 \times 10^{-3} \text{ S/cm}$ . The role of filler is not limited to the sole action as ions dissociator, but also promoting specific interaction between ionic species and filler surface group as the additional site for ionic migration pathways. From the analysis, we conclude that the lowest line width (high ionic mobility) and highest electrical conductivity occur concurrently.

## Acknowledgement

The author would like to thank Universiti Teknologi Mara (UiTM) for supporting this study by Research Incentive Fund grant No. 600-RMI/FRGS 5/3 (9/2014). Author also would like to thank Dr. Fauzi Mohd Som (RRIM Research Centre, Malaysian Rubber Board, 47000 Sungai Buloh, Selangor D.E) and all members of Ionic and Coating lab (ICC), UiTM for their assistance and support through the work.

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