XRD, Conductivity and FTIR Studies on LiI-Li$_2$WO$_4$-Li$_3$PO$_4$
Prepared by Low Temperature Sintering

A.H. Ahmad$^1$ and A.K. Arof$^2$

$^1$Faculty of Applied Science, MARA University of Technology,
40500 Shah Alam, Selangor D.E, Malaysia
$^2$Physics Department, Faculty of Science, University of Malaya,
50603 Kuala Lumpur, Malaysia

Abstract. Different amounts of Li$_3$PO$_4$ were mixed to a fixed ratio of LiI:Li$_2$WO$_4$, ground and pelletised before subjected to sintering at 70°C for 7 days. XRD shows that the product formed after sintering process is most likely Li$_6$P$_4$W$_6$O$_{32}$ due to peaks present at 10.6°, 22.4°, 24.0°, 24.4°, 26.2°, 32.4° and 34.0°. Conductivity studies show that the sample with 25 wt.% Li$_3$PO$_4$ exhibits the highest room temperature conductivity of $3.42 \times 10^{-3}$ Scm$^{-1}$. Conductivity is expected to occur through channel-like structures which could have formed due to corner or edge sharing of polyhedra. FTIR studies have shown the existence of WO$_4$ tetrahedra and WO$_6$ octahedral at 850 cm$^{-1}$ and 952 cm$^{-1}$, and phosphate tetrahedral at 564 cm$^{-1}$, 700 cm$^{-1}$, 890 cm$^{-1}$ and 1030 cm$^{-1}$.

1. Introduction
Lithium ion conductors are prepared by melt quenching technique [1,2,3]. In cases where lithium iodide is one of the chemical components, melting is done under vacuum and quenched in liquid nitrogen [4,5]. These materials can exhibit at room temperature electrical conductivity as high as $10^{-3}$ Scm$^{-1}$. For example LiI-Li$_2$O-B$_2$O$_3$ has been shown to exhibit conductivity of $10^{-2}$ Scm$^{-1}$ at 300°C [6]. Most of the materials produced by the rapid quenching method are glasses. However, these are also crystalline compounds that exhibit high electrical conductivity at room temperature and various methods of preparation are ballmilling, solid state reaction and sol-gel technique [7,8,9].

In this work, Li$_3$PO$_4$ has been added to LiI-Li$_2$WO$_4$. The three components were ground and thoroughly mixed. The mixture was then pelletised and calcined at 70°C to initiate the reaction and maintained at that temperature for 7 days. The product was analyzed by X-ray diffraction (XRD) and by Fourier Transform Infrared Spectroscopy (FTIR). The electrical conductivity was determined by impedance spectroscopy.

2. Experimental Description
2.1. Preparation of Solid LiI-Li$_2$WO$_4$-Li$_3$PO$_4$ Electrolyte. The sample 0.2 wt.% LiI-0.8 wt.% Li$_2$WO$_4$ system was found to exhibit the highest electrical conductivity in the LiI-Li$_2$WO$_4$ family. Different amounts of Li$_3$PO$_4$ was added to the binary system. The three components were mixed and ground thoroughly and the finely mixed powder was pelletized, put on a glass slide and finally placed in a test-tube plugged with glass wool. The pelletized samples were calcined at 70°C for 7 days. For each composition of LiI-Li$_2$WO$_4$-Li$_3$PO$_4$, three test samples were prepared.

2.2. X-Ray Diffraction. X-ray diffraction measurements were performed using the X-ray Phillip Expert Diffraction system. The diffractograms were taken at 2θ angles between 10° to 70°.

2.3. Measurement of Electrical Conductivity. The electrical conductivity of the sample was measured by the ac impedance technique. Complex impedance was measured using the HIOKI 3520-01 LCR HI Tester that was interfaced to a computer. The measurements were carried out at room temperature in the frequency range 42 to 10$^6$ Hz.
2.4. Fourier Transform Infrared Spectroscopy. FTIR measurement was done using the Perkin Elmer FT-IR Spectrometer SPECTRUM 2000, and was performed using the KBr method. The spectrum was obtained in the 400 to 4000 cm\(^{-1}\) region at 1 cm\(^{-1}\) wave number resolution.

3. Results and Discussion
The XRD diffractogram of the various LiI-Li\(_2\)WO\(_4\)-Li\(_3\)PO\(_4\) (Fig. 1) samples showed peaks at 10.6°, 18.5°, 21.5°, 22.4°, 23.5°, 24.0°, 25.0°, 26.2°, 30.3°, 32.4°, 34.0°, 35.5° and 37.0°. The peaks at 10.6°, 22.4°, 24.0°, 24.4°, 26.2°, 32.4° and 34.0° are also found in the diffractogram of Li\(_6\)P\(_4\)W\(_8\)O\(_{32}\) (JCPDS pattern: 40-1061). The peaks at 10.6°, 24.0°, 26.2°, 32.4° and 34.0° are also peaks observed in pure Li\(_2\)WO\(_4\). The peak at 22.4° is also found in the Li\(_3\)PO\(_4\) diffractogram. Hence after 7 days of sintering at 70°, it can be deduced that the compound Li\(_6\)P\(_4\)W\(_8\)O\(_{32}\) has formed but with some Li\(_3\)PO\(_4\) and Li\(_2\)WO\(_4\) leftovers. Within this 20° range peaks attributed to LiI are not observed. It may be possible that the iodine component in LiI has vaporized during sintering.

In order to justify that the peaks at 10.6°, 24.0°, 26.2°, 32.4° and 34.0° are representative of Li\(_6\)P\(_4\)W\(_8\)O\(_{32}\), the intensity of the peaks was plotted with respect to Li\(_3\)PO\(_4\) content (Fig. 2). If these peaks are representative of Li\(_2\)WO\(_4\), then the intensity of the peaks should continue to decrease and the appearance of new peaks and the shifting of the peak to higher angle as the amount of lithium phosphate (LP) is increased.

Fig. 1. XRD pattern of LiI-Li\(_2\)WO\(_4\)-Li\(_3\)PO\(_4\) solid electrolyte for 20 = 10-40°.

Fig. 2. Intensity of the peaks versus wt.% Li\(_3\)PO\(_4\).

Fig. 3. XRD pattern to show the splitting of the peaks or the appearance of new peaks and the shifting of the peak to higher angle as the amount of lithium phosphate (LP) is increased.

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