

# Dielectric Properties and Structural Investigation of New Binary $\text{Li}_2\text{CO}_3\text{-LiI}$ Solid Electrolyte

Mohd Khari Omar<sup>1</sup>, Azizah Hanom Ahmad<sup>2</sup>

<sup>1</sup>Faculty of Applied Sciences, UniversitiTeknologi MARA, 40450 Shah Alam, Selangor D.E., Malaysia

<sup>2</sup>Institute of Science, UniversitiTeknologi MARA, 40450 Shah Alam, Selangor D.E., Malaysia

**Abstract**—The effect of lithium salt (LiI) addition on dielectric properties and physical structure of  $\text{Li}_2\text{CO}_3$  have been investigated. The samples  $\text{Li}_2\text{CO}_3\text{-yLiI}$  ( $y = 5, 10\text{...}30$  wt. %) were prepared by mechanical milling in solid state reaction. The pelletized samples were used for temperature dependent electrical impedance spectroscopy and FTIR analysis. The analysis of the results indicated that the electrical conductivity,  $\sigma$  of the electrolyte increased from  $10^{-5}$   $\text{Scm}^{-1}$  up to  $10^{-3}$   $\text{Scm}^{-1}$  with the variation of LiI weight percent. The DC conductivity measured in the temperature range 298 – 373K was found to obey Arrhenius law. FTIR studies show some overlapping and shift in peaks between lithium iodide and lithium carbonate.

**Keywords**— EIS, FTIR, LiI,  $\text{Li}_2\text{CO}_3$ .

## I. INTRODUCTION

Lithium based solid electrolyte system or fast ionic conductor have gain popularity because of their potential to be used in various lithium battery applications such hybrid and plug-in vehicle [1]. Besides that, poor mechanical, chemical and thermal behaviors of liquid electrolyte also demand of the use of solid electrolyte for many applications [2]. Lithium ion is known for the behavior of fast conductivity in composite, glass and polymer electrolyte compare to others. Among all the systems, glass electrolyte exhibits several advantage over the others like physical isotropy, absence of grain boundaries, better thermal stabilities and easier to varying the composition. Basic glass structures that have  $\text{PO}_4$  tetrahedral structure can be modified by introducing lithium ion to form 3-D network for ionic conduction pathway [1]. The modified glass structure can be doped with lithium salt, LiI to achieve higher ionic conductivity. This probably caused by the lithium salt that remained independent and did not involve in the structure modification.

In this work, we used LiI and  $\text{Li}_2\text{CO}_3$  to form solid electrolyte compound. We report the results of the variation of LiI weight percent on dielectric and structure of the electrolyte system.

## II. EXPERIMENTAL

The  $\text{Li}_2\text{CO}_3$  - LiI solid electrolyte samples were prepared with different wt. % LiI.

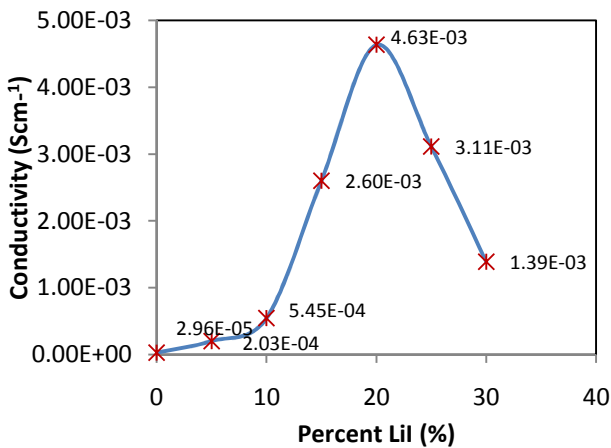
Table 1. Designation of  $\text{Li}_2\text{CO}_3\text{:LiI}$  samples

Composition (wt. %)	Designation
95:5	5%
90:10	10%
85:15	15%
80:20	20%
75:25	25%
70:30	30%

The samples were milled by PM 200 mechanical milling machines at a speed of 250 rpm for 1 hour. The powder was loaded into mold with radius of 1.5 cm and pelletized by ENERPAC hydraulic press at pressure of 200 psi. The electrical impedance of temperature dependant study was conducted in the temperature range of 25 – 100 °C by HIOKI 3531 Z LCR Hi-Tester with frequency range of 50Hz to 1MHz. FTIR spectra were recorded by using Perkin Elmer FT-IR Spectrum 200 in the wave region between 500-4000  $\text{cm}^{-1}$ .

## III. RESULT AND DISCUSSION

The obtained conductivity,  $\sigma$  as a function of LiI is shown in Fig. 1, where conductivity has been plotted against wt. % LiI. It is shown clearly in the graph that the conductivity of the samples increased with the increased of LiI. However this trend stops at 20 wt. % LiI as shown in Fig. 1. The ionic conductivity,  $\sigma$  increased significantly from  $10^{-5}$   $\text{Scm}^{-1}$  up to  $10^{-3}$   $\text{Scm}^{-1}$  as wt. % of LiI increased from 0-20 wt. %. The presence of lithium salt increased the ionic conductivity,  $\sigma$  by increasing the number of mobile ion in the electrolyte [3,4,5]. However,



the ionic conductivity,  $\sigma$  drops as LiI exceed more that 20 wt. %. This is caused mainly by the unnecessary lithium ion which restricted the movement of each charge carrier [4].

The variation of the logarithm of ionic conductivity,  $\sigma$  with the function of inverse absolute temperature for sample 5 wt. % to 20 wt. % LiI is shown in Fig. 2. From the analysis result, the regression values are close to unity, means that the temperature-dependent ionic conductivity for the all samples obeys Arrhenius law and can be described by the equation

$$\sigma_{dc} = \sigma_0 \exp[-(E_{dc}/k_B T)]$$

Where  $\sigma_0$  is the pre-exponential factor,  $E_{dc}$  is the activation energy,  $k_b$  is Boltzman constant and  $T$  is the absolute temperature [6,3,7]. Since the graphs followed Arrhenius relationship, the activation energy for all samples can be calculated from the slopes of the graphs and listed in Table 2. Activation energy,  $A_E$  is the minimum amount of energy needed by molecule to jump into excited state where ions hopping occur. The ionic conduction in solid electrolyte depends on the charge carrier movement into void or interstitial.

The analysis showed that activation energy,  $A_E$  decreased as the wt. % LiI increased. The activation energy for the sample with 5 wt. % LiI showed the highest value of 0.16 eV. Having the highest  $A_E$  value means that the system facing difficulty and require lot of energy to detach the  $Li^+$  which coordinated tetrahedrally to the oxygen of the carbonate group,  $CO_3^{2-}$  to jump into neighboring vacant site [7]. As the result, the ionic conductivity,  $\sigma$  decreased as the activation energy,  $A_E$  increased. From the analysis, increasing the wt. % of LiI provided more free  $Li^+$  in the system, therefore reducing the total energy to break the  $Li^+$  that mainly act as charge carrier.

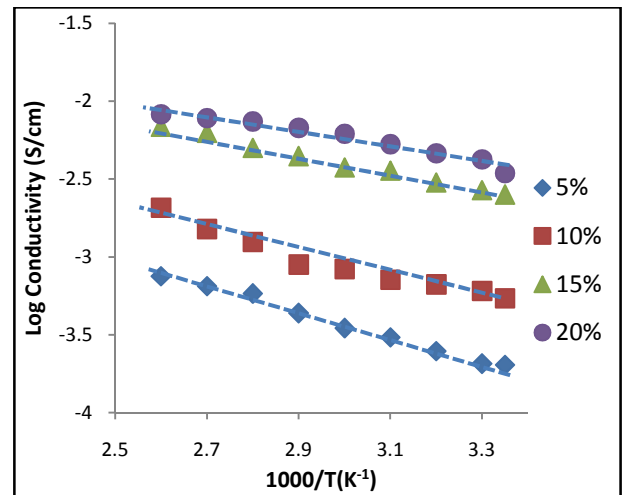


Fig. 2. Arrhenius plots for conductivity of  $Li_2CO_3:LiI$  samples

Table 2. Activation energy with different wt.% LiI

Samples ( $Li_2CO_3-LiI$ )	Activation Energy, (eV)
5 wt. % LiI	0.16
10 wt. % LiI	0.14
15 wt. % LiI	0.12
20 wt. % LiI	0.10

The frequency dependence of the real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) part of the dielectric relaxation at different temperature for sample with 20 wt. % LiI is shown in Fig. 3 and 4. It can be observed that the dispersion of both real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) part were rise sharply toward low frequency region. This phenomenon can be attributes to the occurrence of the electrode polarization and space charge that normally happened in ionic glass and also due to trace quantities of water that may retained by the samples [ 3,7,8,9,10]. Usually, this happened when an electrical stimulus applied caused the charge carrier to agglomerate across the electrode-electrolyte interface creating space charge layer, leading high value of capacitance at the interface [2]. At high frequency region, both dielectric constant,  $\epsilon'$  and dielectric loss,  $\epsilon''$  decreased as the frequency increased. The trend caused by the periodic reversal of the electric field that occurred too fast. Therefore, charge carriers can't get the sufficient time to accumulate at the electrode-electrolyte interface and ions are mainly confined in the bulk of the material [7,2]. Dielectric loss occurs as a result of collision between charge carriers in the system. The variation of real,  $\epsilon'$  and imaginary,  $\epsilon''$  with the function of frequency found to be to a greater extent at higher temperature.

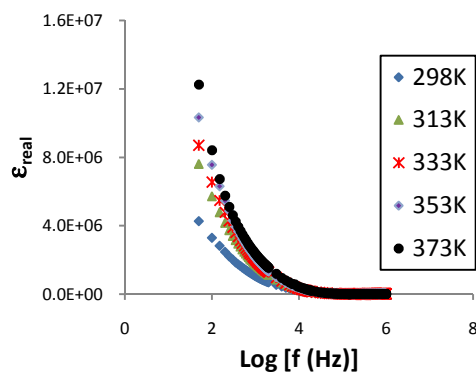


Fig. 3. Variation of real ( $\epsilon'$ ) part of dielectric constant with frequency for  $\text{Li}_2\text{CO}_3\text{-LiI}$  at different temperature

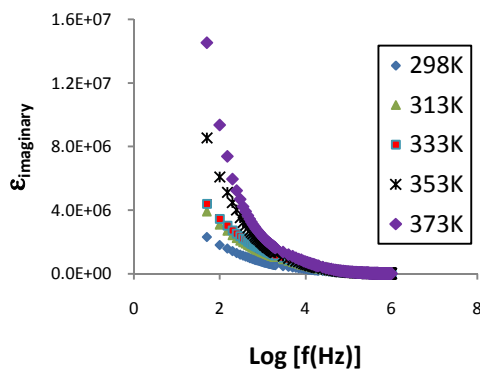


Fig. 4. Variation of imaginary ( $\epsilon''$ ) part of dielectric constant with frequency for  $\text{Li}_2\text{CO}_3\text{-LiI}$  at different temperature

Beside permittivity analysis, the dielectric relaxation can also be studied by electrical modulus of the systems. Fig. 5 and 6 showed the variation of the real part,  $M'$  and imaginary part,  $M''$  of the electrical modulus for sample with 20 wt. % LiI at various temperature.

The analysis showed that both  $M'$  and  $M''$  were observed to increase towards high frequency. The presence of the peaks in the graph at higher frequency proved that all samples are ionic conductor [7]. The peaking curve at the higher frequency region is probably caused by bulk effect. It can be seen clearly (Fig. 6) that the peaks shifted towards higher frequency as the function of temperature. This indicated that the dielectric relaxation process is thermally activated in which the ionic transport is by hopping [7]. In this region, the charge carrier being locked in potential wells so that they can only move in short distance. Vice versa, the long tail in low frequency region represents the frequency range which mobile ion were able to hop from one site to adjacent side and also resulting of the large capacitance associated with the electrode [3,7,11]. The imaginary part,  $M''$  of electrical modulus associated with energy loss during ionic conduction process [3].

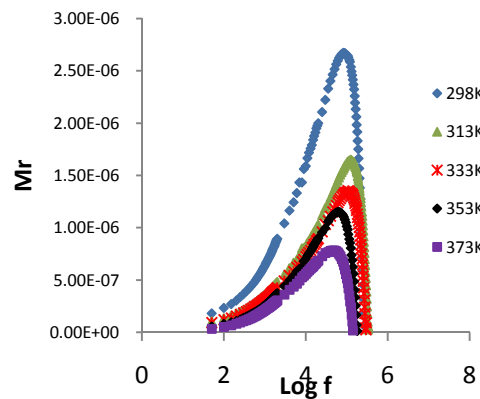


Fig. 5. Variation part of real ( $\epsilon'$ ) modulus with frequency for  $\text{Li}_2\text{CO}_3\text{-LiI}$  at different temperature

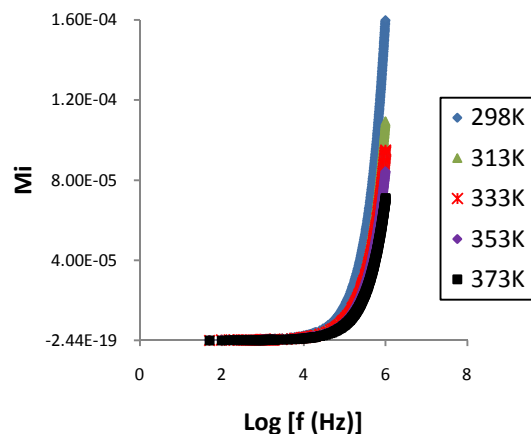


Fig. 6. Part of imaginary ( $\epsilon''$ ) modulus with frequency for  $\text{Li}_2\text{CO}_3\text{-LiI}$  at different temperature

Fig. 7 presented FTIR spectra of pure  $\text{Li}_2\text{CO}_3$  and pure LiI at wavenumber in the range of 400-4000. Theoretically, inorganic carbonate has the same structure as organic carbonate since both have charge of minus two. However, it is better to think that inorganic carbonate have three equivalent C-O stretching and arranged in trigonal planar pattern. They do not have two different C-O and C=O stretching vibration as shown in other organic carbonate.

The result from Fig. 7 depicted that only single C-O stretching appears at band  $1411\text{ cm}^{-1}$  instead of C=O stretch vibration at wavenumber of  $1735\text{-}1750\text{ cm}^{-1}$  [12]. This peak also represents as the fingerprint for  $\text{Li}_2\text{CO}_3$  in IR spectra. Since inorganic carbonate group is planar, there are out-of-plane C-O bending vibration appears at  $857\text{ cm}^{-1}$  and in-plane C-O bending at  $740\text{ cm}^{-1}$ . The peak at  $1589\text{ cm}^{-1}$  in IR spectra of pure LiI can be attributes to the interaction between lithium and iodide [13]. This peak is the important fingerprint for LiI in IR spectra. The other peaks at  $3560$  and  $3404\text{ cm}^{-1}$  are referred to the O-H stretching mode in the LiI. The O-H stretching bonds were appeared due to the hydrate type of LiI which being used in this works.

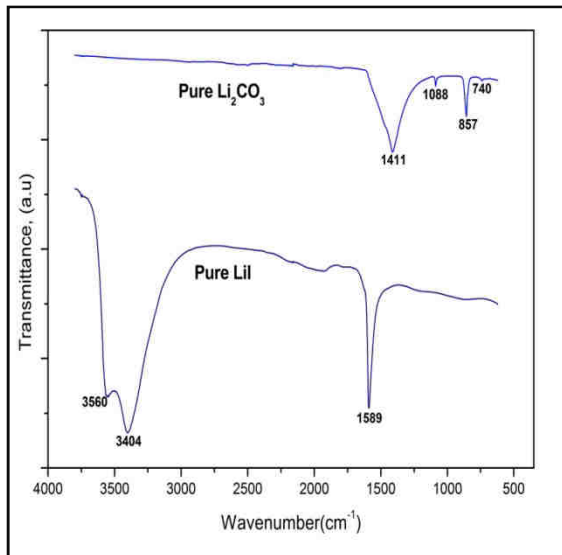


Fig. 7. FTIR spectra of pure  $\text{Li}_2\text{CO}_3$  and LiI in the range of 400-4000  $\text{cm}^{-1}$ .

Fig. 8 showed the IR spectra of the  $\text{Li}_2\text{CO}_3$  – LiI solid electrolyte. In this work, the characteristic peak of  $\text{Li}_2\text{CO}_3$  due to C-O stretching vibration was shifted to lower wavenumber of 1407, 1409 and 1411  $\text{cm}^{-1}$ . This observation indicated that the interaction occurred between C-O stretching vibrations with LiI [14].  $\text{Li}_2\text{CO}_3$  has the monoclinic  $C/2c$  structure and  $\text{Li}^+$  are tetrahedrally coordinated to the oxygen atom of the carbonate.

Since there are interaction occurs, it is possible that lithiated  $\text{Li}^+$  will knock out the weak bonded  $\text{Li}^+$  and replaces their position. Therefore, this Li cation may link the  $\text{CO}_3$  to form 3-D framework structure with staggered  $\text{Li}_2\text{CO}_3$ . This structure is the possible low-energy pathway for  $\text{Li}^+$  migration along the open channel. The fingerprint peak of LiI at 1589  $\text{cm}^{-1}$  also shifted to lower wavenumber of 1473 and 1471  $\text{cm}^{-1}$ . The occurrence of band shift also indicated that complexation had occurred between the two compounds and that both  $\text{Li}_2\text{CO}_3$  and LiI compatible to form solid electrolyte [14].

Two peaks at 3560 and 3404 (Fig. 7) changed from sharp to a broad and shallow peaks at 3434, 3430, 3429 and 3420  $\text{cm}^{-1}$ . This is due to the overlapping of the two O-H peaks at close wavenumber originating from pure LiI [14,4]. Less O-H detected as LiI mix with  $\text{Li}_2\text{CO}_3$  because O-H molecules were dispersed into larger medium. The relative intensity of the O-H stretching vibration of pure LiI at 3560 and 3404  $\text{cm}^{-1}$  also dropped to lower intensity in the electrolyte (Fig. 8). The peaks at 1088, 857 and 740  $\text{cm}^{-1}$  did not show any changes. Therefore, complexation for out-of-plane C-O and in-plane C-O with LiI did not occur as  $\text{Li}_2\text{CO}_3$  mix together with LiI.

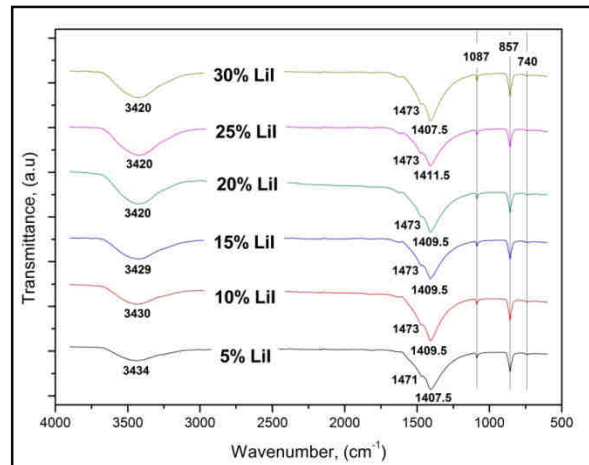


Fig. 8. FTIR spectra of  $\text{Li}_2\text{CO}_3$  with various wt.% of LiI (Li=5-25 wt.%)

#### IV. CONCLUSION

The amount of LiI has been found to affect the ionic conductivity of  $\text{Li}_2\text{CO}_3$  – LiI solid electrolyte. The electrical conductivity of the  $\text{Li}_2\text{CO}_3$  – LiI electrolyte showed the highest conductivity at 20 wt. % LiI. The dielectric analysis has been carried out. The high values of dielectric constant at higher frequency indicated that the samples were ionic conductor. The peaks shifted towards higher frequency as the function of temperature indicated that the dielectric relaxation process is thermally activated. From FTIR analysis, peak shifting revealed that  $\text{Li}_2\text{CO}_3$  and LiI interacted with each other to form  $\text{Li}_2\text{CO}_3$ -LiI solid electrolyte. In this work, we suggest that interaction between compounds created the 3-D framework structure for Li cation migration in the solid electrolyte.

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