**Effect of MnO₂ Filler on the Electrical and Dielectric Properties of Binary Li₂CO₃/LiI Electrolyte**

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**Graphical abstract**

Inorganic electrolyte consisting of Li₂CO₃ and LiI with the incorporation of MnO₂ as fillers was prepared by a mechanical milling technique. The effects of ceramic filler concentration on the electrolyte host system were investigated by deploying electrical impedance spectroscopy, EIS measurement at a temperature range of 298-373K. It was revealed that incorporating 9 wt. % MnO₂ filler in Li₂CO₃/LiI electrolyte significantly enhanced the electrical conductivity from 4x10⁻³ S/cm up to 8x10⁻³ S/cm. Nano-particle inorganic oxides have been found to act as ions dissociation enhancer in solid electrolytes. Dielectric analysis was performed to investigate the ions migration process in solid electrolyte. The dielectric study showed that the ionic conductivity of the electrolyte was observed to increase as a function of temperature, suggesting that the system is thermally assisted. The plots of electrical conductivity, as a function of temperature have been varied from 298 – 373K and were found to obey the Arrhenius law.

**Keywords**: Li₂CO₃/LiI, MnO₂, Electrical Impedance Spectroscopy (EIS)

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1.0 INTRODUCTION

Nowadays, lithium ion batteries have become the official power sources for portable electronic devices and undoubtedly represent the most promising portable energy sources ever invented [1]. The demands for smaller, lighter and higher energy density solid electrolyte are tremendous and lead to the many attempts to discover a new possible method to achieve favorable properties of the electrolyte. Current studies have discussed different explanation that responsible for the conductivity progress with the incorporation of filler such as higher dissociation of salt, space charge induced enhancement effect and improvement in the level of amorphous phase [2,3].

Basically, nanoparticle ceramic filler possess two common features: 1) large specific surface area and 2) grains covered by various Lewis basic or acidic groups [4]. The interaction between Lewis groups with the salt species responsible for the conductivity enhancement observed in the system [5]. Introduction of nanoscale ceramic filler such as Al₂O₃, TiO₂ and MnO₂ have been found to be effective in improving the transport properties, resistance to crystallization and the stability of the electrode/electrolyte interface. [6,7,8]. It is observed that the incorporation of ceramic fillers helps to improve the conductivity by dissociating ions pair into cations and anions so that the number of available charge carriers increases [9,10].

Our purpose in this work is to increase the ionic migration rate of Li₂CO₃-LiI by adding different amount of MnO₂ filler. The electrical impedance spectroscopy measurement at different temperature was carried out to study the effect of the filler on the electrical and dielectric behavior of electrolyte.
2.0 EXPERIMENTAL

2.1 Materials

Lithium carbonate (Li2CO3, MW = 73.89 g/mol, CAS = 554-13-2, purity = 99.0%, Aldrich) in powder form, lithium iodide (LiI, MW = 133.85 g/mol, CAS = 85017-80-7, Purity = 99.999%, Aldrich) in crystalline powder form, and manganese (IV) oxide (MnO2, MW = 86.94 g/mol, CAS = 1313-13-9, Purity = 99%, Aldrich).

2.2 Preparation of Li2CO3/LiI-MnO2 Solid Electrolyte

The composition of the host electrolyte Li2CO3/LiI is 80:20. The MnO2 filler were added to the host system at different percentage (3, 6, 9, 12%). The Li2CO3/LiI-MnO2 electrolytes were prepared by deploying planetary ball mill technique model PM 200 at the speed of 250 rpm for 90 minutes to improve particle distribution homogeneity. The milled powders were palletized by utilizing mould with diameter of 1.5 cm. The powders were pressurized at 200 psi for approximately 3-5 minutes.

2.3 Characterization Technique

Electrical impedance spectroscopy measurement was carried out by HIOKI 3531 Z LCR Hi-Tester with frequency range of 50Hz to 1MHz. The variations of the temperature (298K-373K) were performed to identify the effect of the temperature on the samples conductivities properties.

3.0 RESULTS AND DISCUSSION

The conductivity of the solid electrolytes was found to be directly proportional with the increase of MnO2 in the Li2CO3/LiI host electrolyte. The highest conductivity was observed for the sample containing 9 wt. % of MnO2 with conductivity of 8.28 x10^{-3} S/cm, as shown in Fig. 1. 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 [11,12]. 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 either travel along or between these interconnected pathways, give a rise to the ionic conductivity of the system [11].

The presence of MnO2 filler had also increased the ionic conductivity by multiplied the number of charge carriers in the electrolyte. The MnO2 filler 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 [13,14]. Thus, the strength of lithium ion-anion interaction was reduced and “freeing” the lithium ion. However, the conductivity declined as the MnO2 were further increased beyond 9 wt. % in the system. 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 [15]. Therefore, the mobility of the ions also decreased.

The dependence of the conductivity of Li2CO3/LiI-MnO2 electrolyte on temperature is given in Fig. 2. The regression values were found close to unity and the electrolyte obeyed the Arrhenius law and can be described by the Eq. 1

$$\sigma_{dc} = \sigma_0 \exp(-E_{dc}/k_BT)$$

where \(\sigma_0\) is the ionic conductivity, \(E_{dc}\) is the activation energy, \(k_b\) is Boltzman constant and \(T\) is the absolute temperature [16,17]. Fig. 2 depicts the conductivity of the electrolytes at various temperature increases with MnO2 filler. The Arrhenius plots for the higher filler concentration remained linear against the highest temperature. This may occurred due to the fact that MnO2 filler helped in preventing ionic transport deterioration at high temperature [18].

![Figure 1](image1.png)

**Figure 1** Variation of conductivity as a function of wt. % MnO2 in Li2CO3/LiI

![Figure 2](image2.png)

**Figure 2** Arrhenius plots for the conductivity of Li2CO3/LiI-MnO2 at different temperature
The variation of real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts of dielectric relaxation curve at different temperature are shown in Fig. 3 and 4 respectively. The dispersion of conductivity at low frequency region was high and decreased towards the high frequency region as illustrated in the figures. The charge carriers were accumulated across the electrode-electrolyte interface at low frequency region creating space charge layer, leading to high value of capacitance at the interfaces [19,20,21]. As the frequencies increased, the high periodic reversal reduced the contribution of charge carriers towards dielectric constant [20,21]. This may arose due to insufficient time for the charge carriers to accumulate at the electrode-electrolyte interface and ions were mainly confined in the bulks of material [22].

Fig. 5 and 6 show the frequency dependent of the real, ($M'$) and imaginary, ($M''$) parts of modulus study and it can be observed that both parts of modulus decreased towards low frequency region due to the fact that electrode polarization has made insignificant contribution to the system [21]. This region also represented the frequency range in which the mobile ions were able to hop from one site to adjacent site [23]. On the other hand, the high frequency region represented the state where charge carriers were locked in potential well and could only move in short distance [23]. The heights of the peaks were found to decrease with the increase in temperature, suggesting a plurality of relaxation mechanisms [24]. The presences of the peaks at the higher frequency region in the modulus study indicated that the electrolyte system is ionic conductor [21]. The peaks were shifted towards higher frequency as the function of temperature, showing that the relaxation process was thermally assisted [19].
4.0 CONCLUSION

The incorporation of MnO$_2$ filler has led to significantly enhance the ionic conductivity from 4.63 x 10$^{-3}$ up to 8.28 x 10$^{-3}$ S/cm. The role of filler is not limited to the sole action of ions dissociator, but also promoting specific interaction between ionic species and filler surface group as the additional site for ionic migration pathways. The dielectric analysis also showed that the transport mechanism in electrolyte system is an ionic conductor and the relaxation process was thermally assisted. The additions of MnO$_2$ filler also helped to prevent ions deterioration and retain ionic migration pathways at high temperature since ceramic fillers are stable and possess high melting temperature as the boundary line was successfully shown on the LCD monitor. The result of the distance test showed that the hue (H) element is almost consistent whereas the saturation (S) varies by roughly 49.3% and value (V) by 30.5%. As for the range of detection, the minimum range was 12 cm where the maximum range was up to 15 meter. The accuracy of the 4 base colors detection was about 80%.

References


