

Development of Liquid Electrolyte and Their Applications in Electrochromic Devices

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ABSTRACT

In this study, development and characterization of a novel liquid electrolyte prepared by Ethylene Glycol (EG) and Lithium Chloride (LiCl) and their applications in electrochromism were mainly focused. The electrolyte was optimized and characterized using electrical conductivity, FTIR spectroscopy and cyclic voltammetry. The molar ratio of total oxygen moles of EG to lithium ions of LiCl (O:Li⁺) was varied from 5:1 to 80:1 and the best ionic conductivity of $1.2763 \times 10^{-2} \text{ S cm}^{-1}$ was obtained at room temperature with the molar ratio at 15:1. Electrochemical stability and the application of the electrolyte in electrochromism were studied. In TiO₂/FTO electrochromic film, an impressive reversible colour change between blue and colourless was observed.

1. INTRODUCTION

In recent two couple of decades Electrochromic Devices (ECD) has received much attention ascribed to its potentially low consumption of power in day to day life style. It is a derivative of the rechargeable battery that operates with the same principle as CO₂ emission free energy storage and producing coloring effects [1]. Electrochromic device undergoes changing color or bleaching when voltage is applied due to insertion of ions and electrons [2]. There are few materials showing electrochromic (EC) properties that can be used to make an EC electrode by intercalating ions and electrons [3]. Sandwich electrolyte with those electrodes and a counter electrode can be used to make an electrochromic device. Colour changes are due to the insertion of electrons and ions into the EC material under influence of applied voltage [4]. ECD is normally used to control the light waves and heat waves entering into a building or automobiles made such as displays, architectural glazing, windows, anti glare rear view mirrors, sunroofs for automobiles and agricultural light shields. Normally it is known as "Smart Windows" that serve an important role for energy controlling. In special circumstance, high efficient quick response smart windows in liquid medium are needed such as displays. The main Objective of this study was synthesis a novel liquid electrolyte for ECD having high ionic conductivity and stability.

2. METHODOLOGY

99.9 % LiCl was used as the salt. It was dehydrated before mixing with dehydrated Ethylene Glycol (EG). Dissolving proper amount of LiCl, a set of liquid electrolyte samples were prepared and kept the total ratio of oxygen in EG to Lithium ion in LiCl as n:1 (where, n = 05, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70,

80). Conductivities of liquid electrolyte were obtained at ambient temperature and pressure. Existences of interaction between Li ions and EG have been thoroughly examined using FTIR analysis and the stability has been tested using Cyclic Voltammetry (CV) for different scan rates and up to 500 cycles.

3. RESULTS AND DISCUSSION

3.1 Ionic conductivity of the liquid electrolyte

The ionic conductivities of the liquid electrolyte samples having different molar ratios of oxygen in EG to Lithium ion in LiCl are measured. At room temperature (298 K), conductivities for different compositions of the liquid electrolytes are given in Table 1. In this study, the weight of EG was kept as constant and LiCl amount was varied by keeping the ratio of total oxygen moles of EG to total Lithium ion ratio from 65:1 to 5:1. The maximum conductivity of $1.2763 \times 10^{-2} \text{ S cm}^{-1}$ was obtained for the liquid composition which contains the O: Li ratio of 15:1. However the ionic conductivities obtain at 25 °C for the entire electrolyte samples have shown conductivity above $1 \times 10^{-3} \text{ S cm}^{-1}$ and those values are comparable to standard liquid electrolyte. Ionic conductivity value for the pure EG was $4.45 \times 10^{-6} \text{ S cm}^{-1}$.

Table 1 : Room temperature ionic conductivity values

Electrolyte	Ratio of the total oxygen moles of EG to total Li ⁺ ions of LiCl (O:Li ⁺ ratio)	σ ($\times 10^{-3} \text{ S cm}^{-1}$)
S0	EG only	0.0044
S1	5:1	5.2417
S2	10:1	8.3166
S3	15:1	12.7629
S4	20:1	7.4318
S5	25:1	6.8943
S6	30:1	5.4140
S7	35:1	5.0731
S8	40:1	4.4717
S9	45:1	4.6122
S10	50:1	4.3944
S11	55:1	3.7616
S12	60:1	4.1563
S13	65:1	3.2469

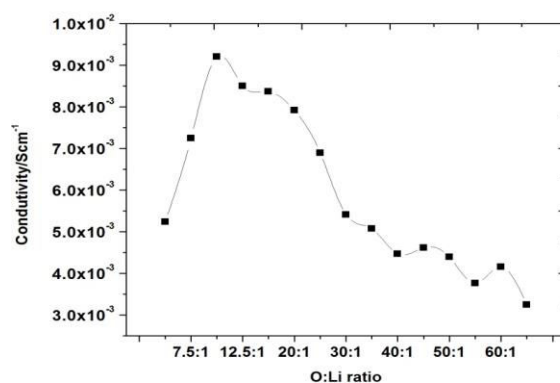


Figure 5: Conductivity Vs. O : Li⁺ ratio of electrolyte measured at room temperature

3.2 Cyclic Voltammetry (CV)

The Influence of TiO₂/FTO electrode in electrochemical liquid electrolyte and performance of electrochromic device were analyzed by using three electrode systems. 1.8182 g of LiCl was dissolved in 20g of EGto obtain the weight ratio of 15:1of O to Li⁺ as the electrolyte for CV analysis. TiO₂/FTO, silver/silver chloride (Ag/AgCl) and Glassy carbon electrode (GCE) were used as working electrode, reference electrode and counter electrode, respectively.

In order to study the recyclability of the TiO₂ electrode, the cyclic voltammetry testswere performed for a number of continuous cycles (Fig. 2) in the potential window between -2.0 V to 0.25 V (Vs SCE). As seen in Fig.2, up to the 500th cycle, the device does not change its electro activity sharply. It is clearly see that the 475th and 500th cycles are overlapped due to the high stability of the electrolyte. These results indicate that the TiO₂ electrode has satisfactory redox stability. The current drop up to 500 cycles was less than 1×10⁻³ A.

It shows two oxidation and reduction peaks due to presence of lithium in liquid electrolyte which causes two chemical processes in the electrolyte system. Oxidation and reduction peaks are representing the chemical process one which happens at the carbon counter electrode surface. Since TiO₂ is a cathodically ion insertion material, in accordance with the following equation, the electrochromic process is the reversible insertionand extraction of the Li⁺ ions into/from the TiO₂ lattice. The blue coloration of the film can be removed by the electrochemicaloxidation

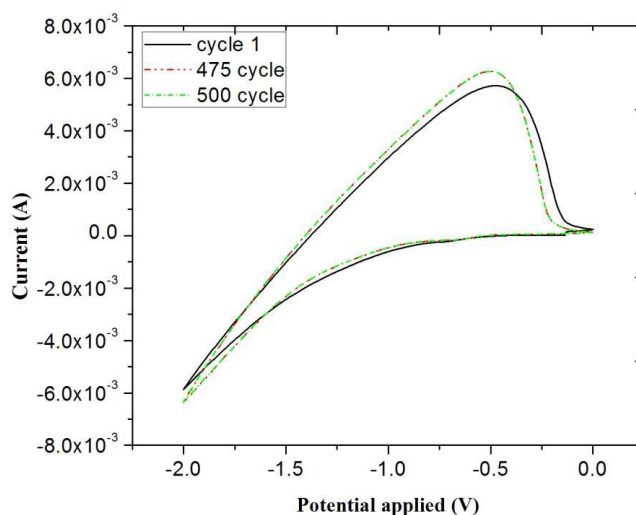
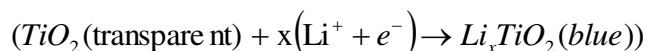


Figure 6 : The graph of WE current Vs Potential applied. Tested for 500 cycles using cyclic Voltammetry, where WE-TiO₂ /FTO (15Ω cm⁻¹), RE- Ag/AgCl, CE-C and Scan rate of 100mV/s

Figure 3 and 4 shows cyclic voltammograms of the TiO₂ electrode at different scan rates. As can be seen from the figure 4, with the increasing scan rate, the shift of the anodic peak potential or position does not change significantly. This indicates the improved kinetic performances of the TiO₂ as electrochromic material.

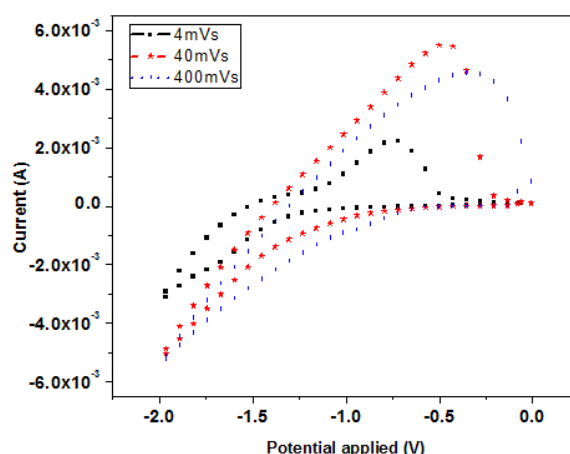


Figure 7: The graph of WE Current Vs Potential applied. Tested for different scan rates under cyclic Voltammetry, where WE- TiO_2/FTO ($15 \Omega\text{cm}^{-1}$), RE- Ag/AgCl , CE- C and Scan rate of 4 - 400 mV/s.

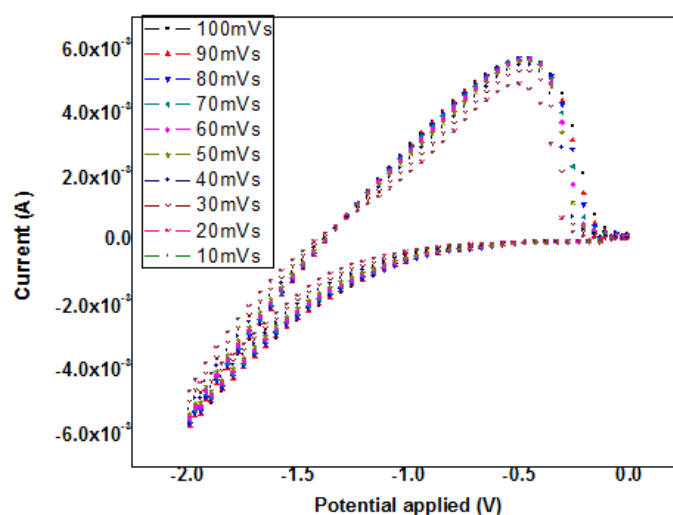


Figure 8 : The graph of WE Current Vs Potential applied. Tested for different scan rates under cyclic Voltammetry where WE- TiO_2/FTO ($15 \Omega\text{cm}^{-1}$), RE- Ag/AgCl , CE- C and Scan rate: 10 - 100 mV/s.

3.3 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transformed infrared spectroscopy was conducted in order to get a better understanding of the solubility and structural behavior of these blends. FTIR spectra taken between the wavenumber 4500 and 500 cm^{-1} of several systems shown in figure 5 were compared. To better understand, the outlook of the LiCl/EG interactions, peaks in the middle of the FTIR spectra were investigated in depth. We focused particular attention on the $4000\text{-}700 \text{ cm}^{-1}$ region, where the peaks associated with the functional groups directly involved and finger print region was not evaluated. The peaks composing the bands in the $3100\text{-}3600$ and $900\text{-}1200 \text{ cm}^{-1}$ regions are correspond to the (O-H) and (C-O) stretching vibrations[5]. This analysis allowed us to identify one type of (O-H) vibrations in the $3200\text{-}3600 \text{ cm}^{-1}$ region and two bands in the $900\text{-}1200 \text{ cm}^{-1}$ region. The band detected in the EG/LiCl complexes at 3277 cm^{-1} increases in

wavenumber as the concentration of LiCl in the electrolyte rises. According to the previous vibrational studies carried out, this peak was ascribed to the O-H stretching vibration of EG molecules hydrogen-bonded to chloride ions and weakly bonded to EG molecules[6]. Peaks occurring at 1366 and 1325 cm^{-1} are scribed to the C-O and deformation vibrational modes of CH_2 . However, as expected, the bands peaking at 1330 and 1406 cm^{-1} has shifted with salt concentration compare with EG.

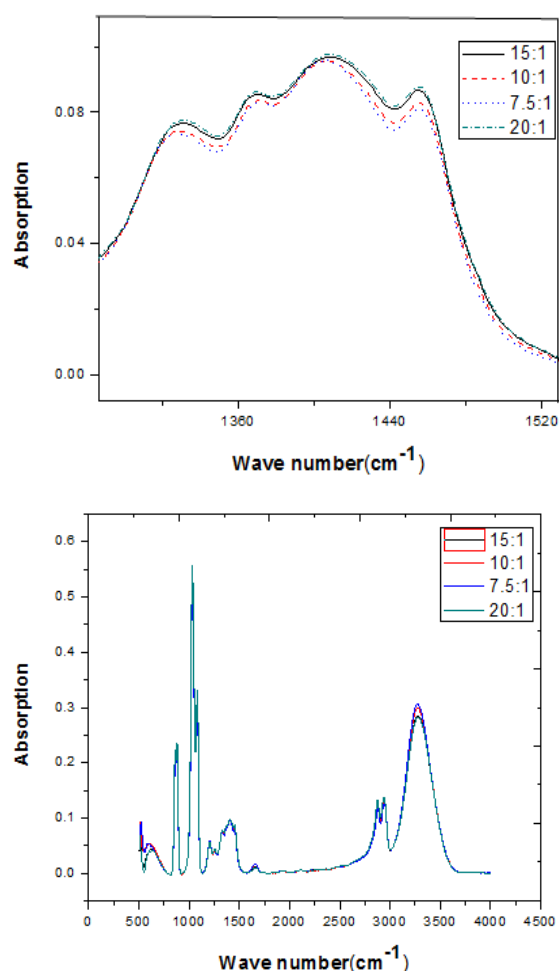


Figure 9 : FTIR curves for liquid electrolytes of 1: 7.5 to 1 : 20, Li to O ratio taken using Bruker Tensor 27.

CONCLUSION

A novel Li^+ based liquid electrolyte has been synthesized and characterized. On the basis of electrical and electrochemical studies, the following conclusions have been drawn. The liquid electrolyte offers relatively high ionic conductivity at room temperature. The best ionic conductivity is $1.2763 \times 10^{-2} \text{ S cm}^{-1}$ for the electrolyte comprising O: Li molar ratio at 15:1. Studies based on AC impedance spectroscopy and cyclic voltammetry indicate the essential requirement of the electrochemical reversibility and electrochemical stability. Possibility of using this novel liquid electrolyte for electrochromic devices was tested. On TiO_2/FTO film an impressive reversible colour change between blue and colourless states could be observed.

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