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ELECTRICAL CHARACTERIZATION OF TETRABUTYLAMMONIUM IODIDE BASED POLYMER FREE GEL ELECTROLYTE

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Gel Electrolytes (GE) have been extensively studied due to their long term stability and durability and they have attracted worldwide attention due to the ability of use them in the practical applications like solar cells and rechargeable batteries. The most of the GE systems studied are polymer gel electrolytes. In this work, a polymer free GE system was fabricated by adding a innert filler, fumed silica, to tetrabutylammonium iodide ($Bu_4N^+I^-$) salt dissolved in a solvent mixture of ethylene carbonate (EC) and propylene carbonate (PC). A series of GEs, x% EC: x% PC ; y% Bu_4N+I^- , were prepared by varing the weight of salt as y=20,15,12,and 10. In every sample, EC to PC weight ratio was 1:1 and the amount of fumed silica added was 10% of the total weight of EC,PC and $Bu_4N^+I^-$. The ionic conductivities of fumed silica added GEs with different salt concentrations are in the order of $\sim 10^{-3}$ S cm^{-1} at room temperature. The highest conductivity of 6.51×10^{-3} S cm^{-1} at 24 ^{o}C was obtained for the sample with composition 40% EC: 40% PC: 20% $Bu_4N^+I^-$. The DC polarization testa were carried out and the results verified that the prepared electrolytes were predominantly ionic conductors with negligible electronic conductivity. FT-IR studies were carried out to investigate the interactions of Bu_4N^+ ions with the ether oxygen of EC and PC. The vibrational modes of EC and PC do not show major changes with the addition of the salt to the EC + PC solvent. Dye sensitized splar cells of configuration Glass/FTO/TiO_2 working electrode/dye(N719)/gel electrolyte/ platinized FTO/ glass were fabricated using the optimized GE and it showed a maximum short circuit current density(J_{sc}) of 9.30 mA cm^{-2}, open circuit voltage (V_{oc}) of 651.4 mV and efficiency of 3.73% exhibiting the ability to use the proposed GE system in solar cells.

KeyWords : gel electrolyte, propylene carbonate, ethylene carbonate, tetrabutylammonium iodide, fumed silica,FT-IR

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1. Introduction

Dye sensitized solar cells (DSSC) are emerging as low cost alternative source to photovoltaic semiconductor junction devices. These solar cells conventionally used liquid electrolytes, which have several drawbacks like solvent eveporation and leakage, corrotion of the platinum electrode, desorption and photo degradation of the dye, and ineffective sealing of cells for long term applications. Therefore, to overcome the above problems, these liquid electrolytes have been replaced by solid and gel type electrolytes. Althouhg the solid electrolytes are used to replace the liquid electrolytes, they show lower energy conversion efficiency compared to liquids due to poor contact with the dye coated TiO_2 surface. However, the gel electrolytes show good device properties, while drastically reducing the above mentioned problems caused by liquid electrolytes. Therefore, in the past few decades, the most of the researches have been focused on synthesizing gel electrolytes incorporating a polymer. Due to numerous advantages of polymer gel electrolytes, lithium ion conducting polymer electrolytes are being developed for lithium rechargeable- batteries and iodide ion conducting polymer electrolytes for dye sensitized photo-electrochemical(PEC) solar cells. Conventionally, PGEs were formed by incorporating a host polymer, the ionic salt and the plastilizers such as ethylene carbonate(EC) and propylene carbonate(PC). For DSSCs, the gel electrolyte should be developed with iodide salts and many studies have been done incorporating alkaline metal iodides in PAN based and PEO based PGEs. There, the effect of changing the size of the cation on the performance of the electrolyte and the solar cell have also[1,2] been studied.

The photocurrent density (J_{sc}) is an important parameter of a solar cell and it depends on the mobility of the iodide ions. When the cation is large, the iodide ion mobility increases[2] and it enhances the J_{sc}. Therefore by incorporating a salt which contain a bulky cation compared to the iodide ion, such as quaternary ammonium iodide salts, the performance of DSSCs can be enhanced. These quaternary ammonium iodide salts are tetrapropylammonium iodide($Pr_4N^+I^-$), tetrabutylammonium iodide($Bu_4N^+I^-$), and tetrahexylammonium iodide ($Hex_4N^+I^-$) and the radius of the cation increases respectively. These three salts have been used with host polymers and reasonably good cell performance have been reported[3-7]. In this study, we have focused on a gel electrolyte incorporating quaternary ammonium iodide salt, $Bu_4N^+I^-$. This new gel system was prepared by using EC, PC and by adding an inner filler fumed silica, which create a network structure to form the gel electrolyte. The samples were characterized using complex impedence analyser and DC polarization test. Finally, DSSCs were fabricated using the gel electrolyte with optimized conductivity and the fabricated cells were characterized.

2. Experiment

2.1. Materials

Ethylene carbonate (EC) (Aldrich,99%), propylene carbonate(PC) (Aldrich), fumed silica(Aldrich,7nm grain size, surface area 350-430 m^2 per g) and $Bu_4N^+I^-$ (tetrabutylammonium iodide) were used as starting materials. $Bu_4N^+I^-$ was vaccume dried for 24 hours at 80 °C and SiO_2 was heated at 500 °C for 24 hours. EC and PC were used as recieved. Titanum dioxide powder (TiO_2), iodine, glacial acetic acid, tetraisopropoxide (TIP) triton-X-100, ethanol were purchased from Aldrich. Fluorine doped tin oxide glass plates (FTO)(sheet resistance 16 ohms/cm^2) were used as a substrate for coating TiO_2 paste. Ruthenium dye (N719) [ditetrabutylammoniumcis-bis(isothiocyanato)bis(2,2E -bipyridyl-4.4E - dicarboxylato)ruthenium(II)] was purchased from Solatronics to use as the sensitizer.

2.2. Sample preparation

Different compositions of EC,PC,$Bu_4N^+I^-$ and fumed silica were used in order to obtain a polymer free gel electrolyte. For that the weight ratio between EC and PC was kept unchanged. That is, it was kept 1:1 ratio for all the samples. The total weight ratio of EC,PC and $Bu_4N^+I^-$ was always kept as 1g. Fumed silica was added as a percentage of the total weight. At first, appropiately weighted amounts of EC,PC and $Bu_4N^+I^-$ were magnetically stirred at room temperature for 24 hrs with constant amount of silica. A gel electrolyte sample with LiI was also prepared in the same manner for comparison. The compositions of the gel electrolytes are given in the table 1.

Table 2.1: Compositions of gel electrolytes prepared by varying EC,PC and $Bu_4N^+I^-$ or LiI. The total weight of EC,PC and the salt was 1g and amount of added fumed silica is 10% of total weight.

Electrolyte	EC(x %)	PC(x %)	$Bu_4N^+I^-$ (y %)	LiI(y%)
A	40	40	20	-
B	42.5	42.5	15	-
C	44	44	12	-
D	45	45	10	-
E	40	40	-	20

Solar cell characterization was done only for the electrolyte sample A, which gives the highest conductivity. For that the electrolyte samples were prepared by adding I_2 while keeping the I^-:I_2 molar ratio at afixed value of 10:1. The I_2 was added for the EC,PC and salt solvent, which has been stirred until I_2 dispersed well in the solvent and then fumed silica was added and stirred for 3 to 4 hours.

2.3. Fabrication of the DSSCs

Initially the TiO_2 colloidal particles were prepared in order to prepare the photo-electrode. For that, first 2.2 ml of acetic acid was added to 20 ml of tetraisopropoxide. Then 25 ml of ethanol was added to the mixture and a steam was passed through the solution until the mixture turn in to light blue colour. Then 50 ml of water was added (drop by drop) and it was stirred for 12 hrs. Finally the solution was autoclaved at 150 ^{o}C for 3 hrs. Afterthat 20 ml of the autoclaved TiO_2 colloidal was taken. Then 55 ml of acetic acid was added and it was ground well using a motor. Next 5 drops of triton-X-100 were added and was mixed well. Finally 20 ml of ethanol was added. This colloidal was sprayed on the FTO glass plate using hand spray method. Then the glass plates were sintered at 500 ^{o}C for 30 mins. Afterthat the glass plates were allowed to cool at about 80 ^{o}C. Then the plates were diped in the Ruthenium dye(N719) for 12 hrs. DSSCs were fabricated by sandwiching the gel electrolyte in between platinized electrode and dye absorbed TiO_2 electrode with configuration glass/FTO/TiO_2/dye/gel electrolyte/ counter electrode.

2.4. Solar cell and material characterization

2.4.1. Conductivity studies

The electrical conductivities of the prepared samples were measured using a schlumberger SI 1260 Impedence analyser (Solatron), in the frequency range from 20 Hz to 10 MHz. The gel electrolyte was sandwiched between two stainless steel electrodes in a homemade cell holder and the temperature was varied from 25 ^{o}C to 60 ^{o}C at approximately 5^{o}C intervals. The temperature of the sample was allowed to stabilize at each measuring temperature for about 30 minutes.

2.4.2. DC polarization measurements

In order to estimate the ionic nature of the GEs, the DC polarization test was carried out at room temperature. The samples were sandwiched between two stainless steel blocking electrodes and a small voltage of about 1V was applied. The current was measured with time and this was repeated for all gel samples.

2.4.3. Solar cell characterization

Current voltage characteristics of the solar cells were measured under the irradiance of 100 mW cm^{-2} simulated sunlight using a homemade setup coupled with Keithley 2000 multimeter via computer controlled software. In order to get the simulated sunlight with above intensity, Xenon 500 lamp was used.

2.4.3 FT-IR Measurements

FT-IR spectra were obtained for the GE samples A,D and E, tetrabutylammonium iodide salt and a mixture of ethylene carbonate and propylene carbonate (EC+PC) using Thermo Nicolet 6700 FT-IR spectrometer in the range 600 to 4000 cm^{-1}.

3. Results and Discussion

The conductivity plots for gel electrolyte samples with different salt concentrations and constant amount of fumed silica are shown in figure1.

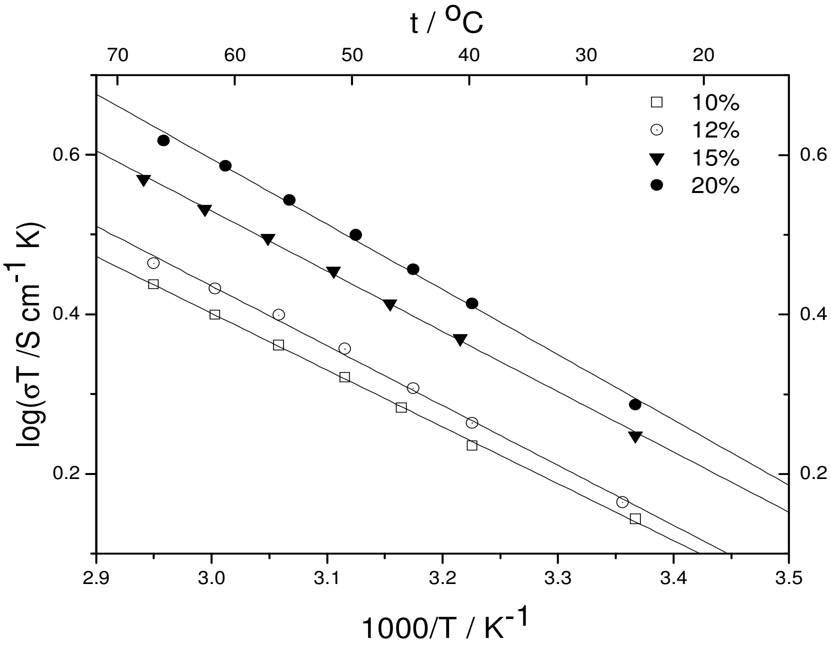

Figure 1. The ionic conductivities of GE samples with different salt concentrations

The conductivity variation of all GEs well obeys Arrhenius relationship:

$$\sigma T = \sigma_o \exp[-E_a / KT] \qquad (2)$$

within the tested temperature range, where E_a is the activation energy, σ_o is the pre-exponential factor, k is the Boltzmann constant and T is the absolute temperature[8]. All curves have a linear behavior for log(σT) vs. 1000/T agreeing with the theory. The highest ionic conductivity of 6.51×10^{-3} S cm^{-1} was obtained at room temperature for the sample containing 20% of salt and 40% of each EC and PC. With the increase of the salt concentration the conductivity increases and can be attributed essentially to an increase of number of free ions.

However, further addition of salt (more than 20% salt) was not possible due to the difficulty of dissolving the salt in the EC and PC solvent mixture. We can speculate a decrease in the conductivity with the further increase of salt due to the formation of large number of ion pairs and higher ionic aggregates. Here silica acts as a gelling agent which immobilizes the liquid medium to produce a gel electrolyte. Fumed silica is an electrochemically inert material and because of the enormous surface area (50-400 m^2/g) of these particles, the surface functional groups (silanol, siloxane) play a major role in creating bonds with EC,PC and salt ions and forming a network.

Dc polarization tests were performed for all the gel electrolytes using stainless steel blocking electrodes. An abrupt current change was observed with the current dropping to 1/10 of the initial current within the first few minues. After about 60 minutes, current reached to a very low stable value. Hence, all these electrolytes show mainly the ionic nature and the electronic conductivity is negligible.

The electrolyte consists of EC and PC, where each molecule has three oxygen atoms for possible coordination of cation (figure 2). Also an anion may interact with the $-CH_3$ moity of PC. These ion- solvent interactions may lead to changes in several vibrational modes of EC and PC.

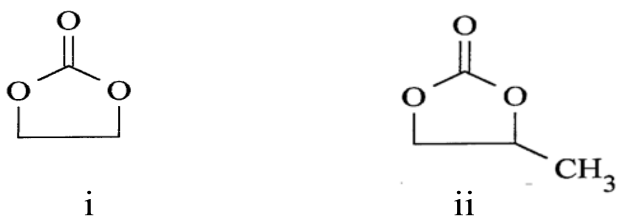

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Figure 2. The chemical structures of (i) Ethylene Carbonate and (ii) Propylene Carbonate

The FT-IR spectra in the region 860 to 910 cm^{-1} of , pure $Bu_4N^+I^-$, EC+PC, gel electrolyte samples A,D, and E are shown in figure 3. The FT-IR spectrum of $Bu_4N^+I^-$ has two peaks at 870 and 880 cm^{-1} which belongs to the cation. The peak at 894cm^{-1} of spectrum (b) is attributed to the ring breathing mode of EC, which shows in the (c),(d), and (e) spectra of gel electrolytes as well[9]. However, in spectrum (e), which is belonging to the sample E, has an extra peak at 903 cm^{-1} . When oxygen atoms of EC molecules coordinate with cations present in the solution, there will be changes in the above mode. This has been observed by many researches. For example, a polymer gel electrolyte based on PAN, EC and $LiClO_4$ studied by Wang *et al.*[9] observe a peak growing at around 900cm^{-1}, other than the peak at 890cm^{-1} belonging to EC. However, in spectra (c) and (d) there is no corresponding peak or shoulder at around 900cm^{-1} showing that the cation of the $Bu_4N^+I^-$ has no strong interactions with the oxygen atoms of EC. Sample D, which has the highest $Bu_4N^+I^-$ concentration has a broad peak appearing at around 880cm^{-1} corresponding to the salt $Bu_4N^+I^-$.

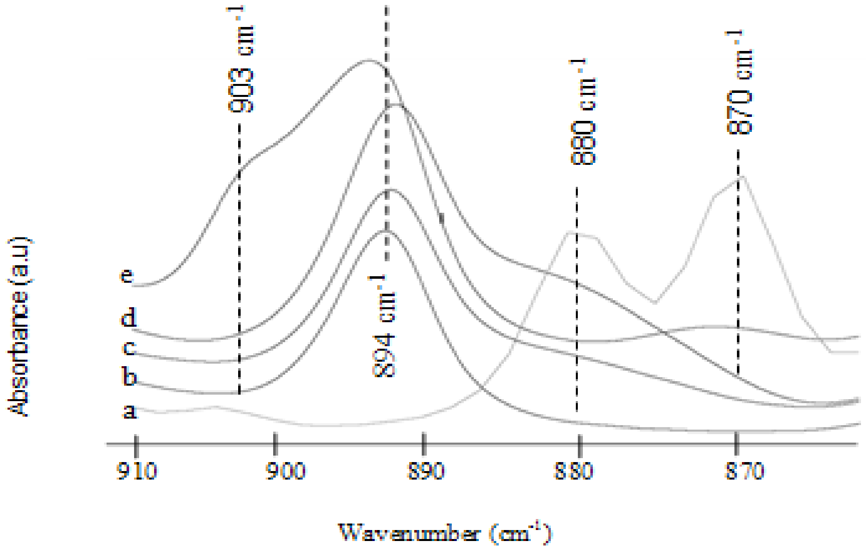

Figure 3. FT-IR spectra attributed to the ring breathing mode of EC in the region 860-910 cm^{-1}, (a) Pure $Bu_4N^+I^-$; (b)EC+PC; (c) EC+PC+10% $Bu_4N^+I^-$ salt+10% silica; (d) EC+PC+20% $Bu_4N^+I^-$ salt+10% silica; (e) EC+PC+20% LiI salt +10% silica.

This fact is evident from a few other modes, namely, ring bending of EC and symmetric ring deformation of PC situated at 714cm^{-1} and the C=O symmetric stretching mode of EC (~1800 cm^{-1} and 1770cm^{-1}) and PC(~1800cm^{-1})[9-11]. The symmetric stretching mode of EC (figure 4) is a very strong broad band which has split into two with the peak positions at 1787 cm^{-1} and 1770 cm^{-1}. The same mode of PC has a very strong broad IR band peaked at 1787cm^{-1} (figure 4). In spectrum e, this band has broadened while it is not in spectra (c) and (d), again showing the absence of interactions between $Bu_4N^+I^-$ and solvent molecules.

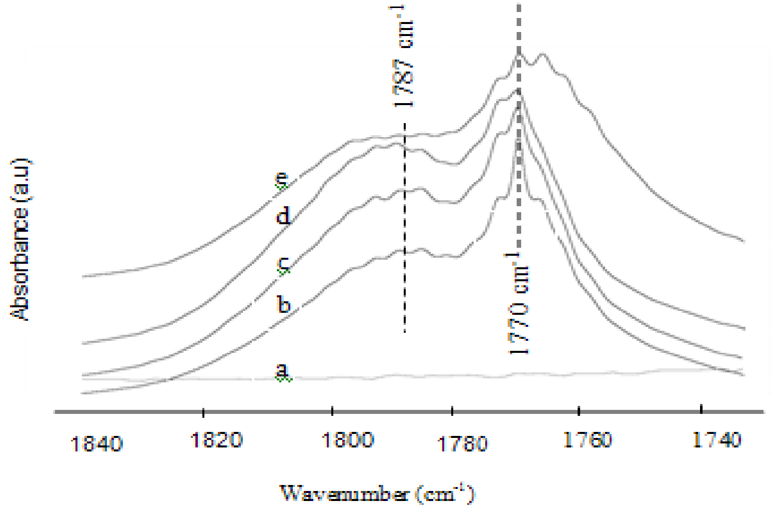

Figure 4. FT-IR spectrum of C=O streching band in EC and PC in the region 1700-1850cm$^{-1,}$ (a) Pure $Bu_4N^+I^-$; (b)EC+PC; (c) EC+PC+10% $Bu_4N^+I^-$ salt+10% silica; (d) EC+PC+20% $Bu_4N^+I^-$ salt+10% silica; (e) EC+PC+20% LiI salt +10% silica.

Ring bending mode of EC and symmetric ring deformation mode[10,11] of PC is centered at 714cm^{-1} and a growing shoulder can be observed at 729 cm^{-1} in FT-IR spectra of sample E, without such a shoulder for samples C and D, showing the presence of strong Li^+ interactions with EC and PC but no strong interactions with the cation of $Bu_4N^+I^-$.

The reason for Li^+ ion coordination with EC and PC is that Li^+ ions have a very high surface charge density and low-lying orbitals available for electron pair acceptance, is prone to get linear, tetrahedral or even octahedral coordination by these ligands, while such coordination is impossible for the $Bu_4N^+I^-$, which have no low –lying empty orbitals to get coordinated by the ligands. $Bu_4N^+I^-$ has a bulky cation and low surface charge density preventing interactions with solvent molecules.

The photocurrent- photovoltage(I-V) characteristics of three solar cells of configuration glass / FTO / TiO_2 /dye / gel electrolyte / counter electrode were measured using the gel electrolyte sample with the highest conductivity. Solar cell parameters such as open circuit voltage(V_{oc}) and the short circuit current density (J_{sc}) were measured and the fill factor (FF%) and effciency (η%) are calculated. It showed a J_{sc} of 9.39 mA cm^{-2} , V_{oc} of 651.4 mV and efficiency of 3.73% exhibiting the ability to use the proposed GE system in solar cells. The short circuit current density, 9.39 mA cm^{-2} is rather a good value compared to quasi solid state solar cells reported using quaternary ammonium iodide salts and ruthenium dye complexes[3-6].

4. Conclusion

A polymer free gel electrolyte was prepared by incoporating the a bulk cation salt $Bu_4N^+I^-$, plastilizers EC and PC and a innert filler, fumed silica and the conductivity for these samples were studied. The gel electrolyte samples shows a highest conductivity for the sample with 20% (0.2g) salt (0.4g of EC and PC). Dc polarization tests were performed for all the gel electrolytes using blocking electrodes and all the electrolytes showed mainly the ionic nature and the electric conductivity is negligible. DSSCs were fabricated for the gel electrolyte with highest conductivity in order to see how much of efficiency could be obtained from this new system. This system, without using a polymer, incorporating $Bu_4N^+I^-$ shows efficiency of 3.73%. FT-IR spectrums give information about how efficiency the cation of the salt ($Bu_4N^+I^-$) coordinates with EC and PC in the gel electrolyte. The $Bu_4N^+I^-$ didnot show any coordination with EC and PC, because Bu_4N^+ ions have no low-lying empty orbitals. It was shown that a gel electrolyte can fabricate without using a polymer and can obtain reasonable efficiencies for DSSCs compared to polymer gel electrolytes.

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