QUASI SOLID-SATE DYE SENSITIZED SOLAR CELLS BASED ON PLASTICIZED POLYMER ELECTROLYTE COMPLEXES WITH MIXED IONIC SALTS

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Energy is an essential need in modern society. From the beginning of mankind they have searched for different sources of energy. Out of all the energy sources electrical energy has become the most attractive candidate due to its user friendliness. Although, there are many renewable energy sources used to generate electricity, solar energy has become the most prominent one, because it is freely available abundantly. There are lots of methods to convert solar energy to electricity, but Dye Sensitized Solar Cells (DSSCs) have grabbed the higher attraction of scientists due to its easy fabrication, comparable high energy conversion efficiency and low cost. One of the major disadvantage of DSSCs is usage of liquid electrolytes. Therefore, in this study we are reporting use of gel polymer electrolyte in DSSCs to improve the power conversion efficiency.

This report contains performance of DSSCs with gel polymer electrolytes composed of Polyacrylonytrile (PAN) and different salts.

The effect of CsI and LiI binary mixture of gel polymer electrolytes on the efficiency enhancement in DSSCs was investigated. Electrolyte with the binary mixture of CsI:LiI =1:1 (by weight) shows the highest ionic conductivity 2.9×10^{-3} S cm^{-1} at 25 °C. Highest solar cell performance with an energy conversion efficiency of ~ 4.8% under the irradiation of one Sun is due to the mixed cation of the cell. The solar cell with only CsI as the iodide salt gave an energy conversion efficiency of ~ 3.9% while it was ~ 3.6% for the cell with only LiI. This is an

efficiency enhancement of 23%. The DC polarization measurements showed predominantly ionic behavior of the electrolyte.

PAN incorporated TPAI gel electrolyte used in this work exhibited an ionic conductivity of 2.6 mS cm^{-1} at 25 °C, and the DSSCs fabricated with this gel electrolyte showed V_{oc}, J_{sc} , ff and efficiency values of 0.71 V, 11.8 mA, 51 % and 4.2 % respectively, under 1 sun irradiation. The efficiency of the cell increases with decreasing solar irradiance achieving up to 10% efficiency and 80% fill factor at a low irradiance value of 3mW cm^{-2}. The main reason for the lower efficiencies at higher intensities is attributed to transport limitation of the redox mediators at high irradiation intensities. The results open up new vistas on efficiency improvement by optical manipulation and control of DSSCs.

PAN based gel polymer electrolytes with LiI, tetrapropyl ammonium iodide and 1-butyl-3-methylimidazolium iodide were studied. The LiI composition was optimized for both the conductivity enhancement and the DSSC performance employing fixed amounts of tetrapropyl ammonium iodide and 1-butyl-3-methylimidazolium iodide according to the chemical formula $(PAN)_{10}(EC)_{25}(PC)_{20}(BMII)$ $(TPAI)_{0.75}(LiI)_n(I_2)_{n/10}$. Where, EC and PC represent ethylene carbonate and propylene carbonate, respectively, and the molar proportion of polyacrylonitrile (PAN) is relative to the polymeric repeating unit. The highest room temperature ionic conductivity of 3.9×10^{-3} S cm^{-1} was shown by the sample with LiI molar fraction n =1.75, out of the prepared set of electrolytes. The best cell with a single meso-porous layer of TiO_2 showed an efficiency of 5.41 % and J_{sc} of 20.61 mA cm^{-2} with the electrolyte having the triple iodide system. The incorporation of LiI into the binary iodide system has enhanced the efficiency by 30 % and the J_{sc} by 62 % for DSSCs with single layer TiO_2.

PAN based gel polymer electrolytes with different size of alkaline cations such as LiI, NaI, KI, RbI and CsI were also studied. The electrolytes were fabricated according to the stoichiometric proportion $(PAN)_{10}(EC)_{25}(PC)_{20}(MI)_{1.2}(I_2)_{0.12}$. The ionic conductivity of the electrolyte with relatively larger cations, K^+, Rb^+ and Cs^+ is more or less equal while for electrolytes containing smaller cations such as Na^+ and Li^+ exhibits lower values in the temperature range from 0 °C to 60 °C. FTIR spectroscopy was used to explain the charge transport mechanism in these electrolytes. The electrolytes were employed in DSSCs based on a TiO_2 double layer (compact and meso-porous) with a N719 dye sensitizer. The open circuit photovoltage (V_{oc}) of the cells

increases with the cation radius. The efficiency and fill factor of the DSSCs also increase with the cation size and exhibits the maximum efficiency of 3.48 % for the CsI containing sample. However, the highest short circuit current density (J_{sc}) of 9.43 mA cm^{-2} has shown by the RbI containing sample. This enhancement in V_{oc} with increasing cation size is attributed to the decrease in recombination rate of electrons in the conduction band of TiO_2 and I_3^- in the vicinity of the TiO_2 electrode and to the conduction band shift resulting from cation adsorption to TiO_2. The influence of the cation on the DSSC performance is discussed in terms of the co-ordination, intercalation and the adsorption of the cations at the nano-crystalline TiO_2 surface and conductivity of the electrolyte. In liquid electrolyte based DSSCs the J_{sc} has been reported to decrease with increasing size of the cation but in this work the J_{sc} follows an opposite trend highlighting a major difference between liquid and quasi-solid electrolytes in relation to the DSSC performance.

A series of gel electrolytes containing the alkaline iodides LiI, NaI, KI, RbI and CsI and polyacrylonitrile (PAN) was fabricated together with the non-volatile plasticizers ethylene carbonate (EC) and propylene carbonate (PC). A similar series was fabricated with the inclusions of performance enhancers (additives) tetrapropylammonium iodide (Pr_4NI), the ionic liquid 1-methyl-3-propyl imidazolium iodide (MPII) and 4-tert-butylpyridine (4TBP). The ionic conductivity of the electrolytes was studied in order to investigate its dependence on the nature of the alkaline cation in presence or absence of additives. The conductivities were higher for the electrolytes with the larger cations, namely K^+, Rb^+ and Cs^+. A significant conductivity enhancement was observed in presence of the additives, and this effect was especially noticeable for samples with the smaller cations. The highest conductivity for electrolytes with additives, 3.96 mS cm^{-1} at 25 °C, is exhibited by KI containing samples.

Quasi-solid state DSSCs were assembled using the above mentioned series of gel electrolytes and TiO_2 photo-anodes prepared with a meso-porous TiO_2 layer overlaid on a compact spin coated layer of the same oxide. A clear trend of open circuit voltage (V_{oc}) and efficiency enhancement with increasing cation size is observed for additive free cells. However, additives enhanced V_{oc}, short circuit current density (J_{sc}), fill factor (*ff*) and energy conversion efficiency

in all the series of DSSCs were investigated. All the cells with additives have shown V_{oc} and ff higher than 0.7 V and 60%, respectively. The maximum J_{sc} and efficiency given by KI based DSSC reached 11.35 mA cm^{-2} and 5.26%, respectively. The performance enhancers or additives used in this work are responsible for 348.0, 216.9, 76.5, 35.8 and 22.4% efficiency enhancement for LiI, NaI, KI, RbI and CsI containing solar cells, respectively.

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