



Effect of Pan Based Gel Polymer Electrolytes of Alkaline Iodide Series on Photo Electrochemical Solar Cells

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ABSTRACT

The nature of the cation and its concentration in the electrolyte noticeably influence on the efficiency of nanocrystalline dye-sensitized solar cells (DSSCs). In this work gel electrolytes suitable for DSSCs were studied using iodide salts with different cation sizes such as LiI, NaI, KI, RbI and CsI. The stoichiometric proportion (PAN)10(EC)25(PC)20(MI)1.2(I2)0.12 was followed in the preparation of electrolytes. The abbreviations of EC and PC represent ethylene carbonate and propylene carbonate respectively and the molar proportion of polyacrylonitrile (PAN) is relative to the polymeric repeating unit.

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 ionic conductivity values. This behavior was consistent for all measured temperatures in the range from 0 °C to 60 °C. The interactions between ion and donor sites in the host polymer and solvent molecules, as revealed by FTIR spectroscopy, were used to explain the charge transport mechanism in these electrolytes. The electrolytes were employed in DSSCs based on a TiO₂ double layer (compact and meso-porous) with a N719 dye sensitizer. Open circuit photovoltage (V_{oc}) of the cells increases with the increasing cation radius. This enhancement in V_{oc} with increasing size of cation is attributed to the decrease in recombination rate of electrons in the conduction band of TiO₂ and I³⁻ in the vicinity of the TiO₂ electrode and to the conduction band shift resulting from cation adsorption to TiO₂. The efficiency and fill factor of the DSSCs also increase with the increasing cation size and exhibits the maximum efficiency of 3.48 % for the DSSC with electrolyte containing CsI. However, the highest short circuit current density (J_{sc}) of 9.43 mA cm⁻² is shown by the RbI containing sample. The influence of the size of cation on the DSSC performance is discussed in terms of the co-ordination, intercalation and the adsorption of the cations at the nanocrystalline TiO₂ 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.

KEYWORDS: quasi-solid-electrolyte, dye-sensitized, solar cell, polyacrylonitrile

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Introduction

DSSCs provide a technically and economically viable alternative to present day P-N junction photovoltaic devices which have grabbed high attention after the groundbreaking report by O'Regan and Grätzel in 1991[1] and soon after that, the energy conversion efficiency of DSSCs were improved to ~ 12%. Also, DSSCs have attracted worldwide attention mainly due to the low production cost and the simple and environmental friendly cell preparation methods compared to those of conventional silicon-based solar cells [1-3]. Generally, the DSSC is composed of a nano-crystalline TiO₂ working electrode which sensitized with a dye, a platinum counter electrode and an electrolyte comprising a redox couple with compatible redox potentials to the Fermi level of the photo-electrode. So far, the redox couples I⁻/I³⁻ and Co²⁺/Co³⁺ have mostly been used in order to obtain good solar cell performances [2-4].

Statement of the Problem

DSSCs, despite their myriad advantages, do have a disadvantage like temperature sensitive and volatile liquid electrolyte, therefore potential instability and danger of evaporation. Polymer electrolytes as an alternative approach to address these issues, on the other hand, need to be further examined for the conductivity of charge carriers in order to improve efficiency and stability of DSSCs.

Objective of the Study

Investigation of the effect of the size of the alkaline cation in the electrolyte on the efficiency of DSSCs in order to fabricate commercially viable solar cell

Materials and methods

Alkaline metal iodides MI (M = Li, Na, K, Rb, Cs) as salts, polyacrylonitrile (M_w = 150,000), iodine (I₂), ethylene carbonate (EC), propylene carbonate (PC), and sensitizing dye, ruthenium 535-bis TBA were used as starting materials. For the gel electrolyte preparation the method described in our previous work is used []. Five different gel electrolyte samples were prepared according to the stoichiometric formula (PAN)₁₀(EC)₂₅(PC)₂₀(MI)_{1.2}(I₂)_{0.12} in order to get a good gel and to keep the molar concentration of the electrolyte constant, where PAN represent one monomer of the polymer. The composition of the electrolytes is given in Table 1. Three DSSCs were fabricated in each composition of electrolyte and performance of DSSCs was studied with the aim of understanding the effect of mixed salts. V-I characteristics of fabricated DSSCs were obtained while exposing them to one sun and using eDAQ Potentiostat and e-coder. The area of cell exposure to light was 11mm².

Table 1. The composition of electrolyte series (PAN)₁₀(EC)₂₅(PC)₂₀(MI)_{1.2}(I₂)_{0.12}.

| Sample | Salt (MI) | PAN/g | EC/g | PC/g | Salt/g × 10 ⁻² | I ₂ /g × 10 ⁻³ |
|--------|-----------|-------|--------|--------|---------------------------|--------------------------------------|
| A | LiI | 0.1 | 0.4151 | 0.3851 | 3.0384 | 5.76 |
| B | NaI | 0.1 | 0.4151 | 0.3851 | 3.4025 | 5.76 |
| C | KI | 0.1 | 0.4151 | 0.3851 | 3.7682 | 5.76 |
| D | RbI | 0.1 | 0.4151 | 0.3851 | 4.8208 | 5.76 |
| E | CsI | 0.1 | 0.4151 | 0.3851 | 5.8977 | 5.76 |

Results and Discussion

The ionic conductivity in these electrolytes is due to both, the cations as well as iodide anions. The implications probably may be of the variation of the cation size or, in a Coulombic model, the charge density on the ionic conductivity. Salt dissociation, polymer cross linking, mobility of ions, ion coordination and shielding by polymer chains all are linked to cation size and charge density

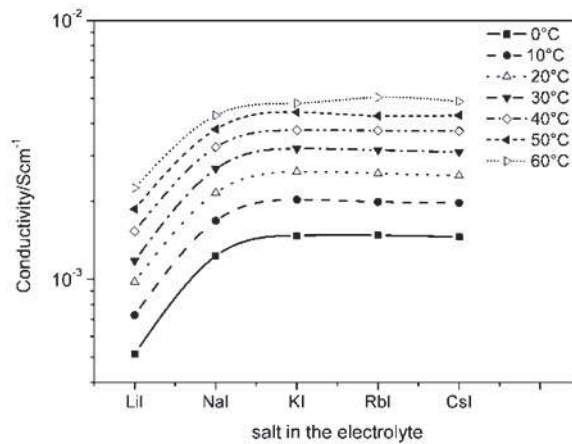


Figure 1. Ionic conductivity variation with the alkaline iodide salt (MI) in $(\text{PAN})_{10}(\text{EC})_{25}(\text{PC})_{20}(\text{MI})_{1.2}(\text{I}_2)_{0.12}$ electrolyte samples at different temperatures.

The short circuit current density (J_{sc}) and open circuit photovoltage (V_{oc}) of the DSSCs are shown in the Figure 2 as a function of the alkaline salt in the electrolyte. The observed 39% enhancement in V_{oc} (from 0.49 to 0.68 V) with increasing size of the cation can be attributed to the decrease of the recombination of electrons in the conduction band of TiO_2 with I_3^- in the electrolyte at the vicinity of the TiO_2 electrode and to the specific shift of the conduction band resulted by cation adsorption or intercalation to TiO_2 .

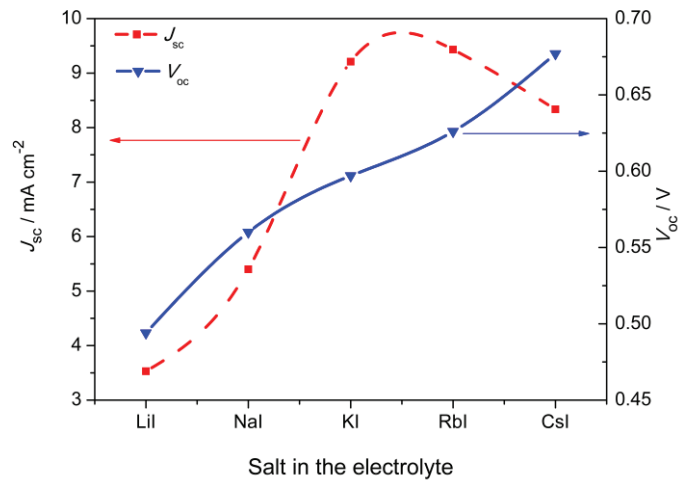


Figure 2: The short circuit current density (J_{sc}) and open circuit photovoltage (V_{oc}) of the DSSCs

Conclusion

The efficiency and the fill factor of DSSCs fabricated in this study increase with the cation size and exhibit a maximum of 3.48 % of efficiency and 61.6 % FF for the CsI containing sample with this single salt electrolyte. The efficiency improvement of the DSSCs is predominantly governed by the V_{oc} change of about 39%. However, the highest J_{sc} , of 9.43 mA cm⁻¹ and the corresponding efficiency of 3.46 % are shown by the RbI containing sample under 1000 W m⁻² irradiance. *The ionic conductivity for the electrolyte and all the DSSC parameters, J_{sc} , V_{oc} , FF and power efficiency of this series of quasi-solid state DSSCs generally increase with decreasing charge density of alkaline cations in the electrolytes. The only exception is a slightly lower J_{sc} given for the CsI containing DSSC. The Cs^+ was found to be the*

most suitable cation, in the alkaline series to be used in a single salt containing quasi-solid-electrolytes DSSCs.

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