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Exploration on the P(VP-co-VAc) copolymer based gel polymer electrolytes doped with quaternary ammonium iodide salt for DSSC applications: Electrochemical behaviors and photovoltaic performances

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ABSTRACT

Gel polymer electrolytes (GPEs) consisting of poly(1-vinylpyrrolidone-co-vinyl acetate) P(VP-co-VAc) with the different tetrapropylammonium iodide (TPAI) salt concentration are prepared. The dielectric and electric dispersion behaviors of the GPEs are studied by dielectric relaxation spectroscopy at room temperature. The dielectric studies imply that dielectric constant (ε') and dielectric loss (ε'') values decrease with increase in frequency at lower frequency region whereas frequency independent behavior is observed in the high frequency region. The trend of the dispersion part of the electric modulus shows a shift towards higher region of frequency indicating shorter relaxation time with an increase in TPAI concentration. The GPE samples were observed to obey Arrhenius behavior and the highest ionic conductivity obtained is 1.60×10^{-3} S cm^{-1} at room temperature. The GPE samples are then fabricated into dye sensitized solar cells for photovoltaic studies. Highest efficiency of 3.07% is obtained with short circuit current density of 6.86 mA cm^{-2}, open circuit voltage of 727 mV and fill factor of 62%.

1. Introductions

As a result of the declining resources on earth, solar energy is expected to be an important source of energy in the coming future and dye sensitized solar cells (DSSC) is a strong candidate to be the upcoming generation of solar cells. DSSCs are known to be an incredible alternative to the conventional solar cells [1,2]. The first prototype of DSSC was reported in 1991 by O'Regan and Gratzel and since that time, DSSC are getting serious attention and interest over the past decades. This is due to some of the advantages that DSSC have over the conventional solar cells. For instance, DSSCs are simple and easy to be prepared and cheap in the cost of productions [3,4]. DSSCs are known to have high photovoltaic efficiencies of 12%. However, these DSSCs are based on liquid electrolytes. Thus, common problems like potential of evaporation, leakages, desorption, photo degradation of the dye, and corrosion of the platinum secondary electrode are to be expected. These problems are holding back the development of the DSSCs [5–7]. Fortunately, researchers haven't given up on these highly potential DSSCs yet. A lot of effort has been put in search for the alternative for the liquid electrolytes and it has given rise to the all-solid, quasi-solid and ionic liquid type of electrolytes to replace the liquid electrolytes. The quasi-solid or also known as gel type of electrolytes attracted a large number of attentions due to its high performances and excellent long term performances [8,9].

Gel electrolytes (GPEs) consist of a polymer host, solvents, mobile ion providers and some other additives. In general, polymer content is usually low, rendering very low viscosity gel electrolytes but a significantly high amount of organic solvent can be retained inside the polymer matrixes. This would straighten the limitation issues of leakage and volatilization. GPEs are excellent in contacting and filling properties with electrodes, reasonable high photovoltaic performances and high thermal stability. Unfortunately, even with so many advantages, GPEs still have drawbacks that need to be addressed in order to replace the liquid electrolytes. One of the main concerns would be the low electrical and photovoltaic performance over the liquid electrolytes. Studies reported that the gel network inside the polymer matrixes had hindered the charge transport and the gelators may have reacted with other components of the electrolytes which may cause the reduction of the performances of the gel electrolytes [10–12].

A lot of research has been done to overcome this problem and usage of co-polymer instead of the normal conventional polymer was proved to be efficient in improving the performances of the polymer electrolytes. Co-polymers have two types of properties that usually contradict with each other. These properties are

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electrical performances and mechanical stability. Most polymers would excel in one property and perform badly in the other. As for co-polymer, when these two properties actually co-exist, it could open up a big opportunity for the researchers to fine tune and adjust their gel electrolytes so that it could become more efficient. A widely known co-polymer in the polymer electrolyte field is the PVdF–HFP where it has the co-existence of crystalline PVdF and amorphous PHFP phases [13,14].

For any reaction to happen inside the DSSC, the gel polymer electrolytes have to be the anion conductor or in most case it has to be the iodide ions (I^-) conductors. The iodide ion conduction contributes to the overall ionic conductivity of the electrolytes in the DSSC. It is the major factor that determines the circuit current density (J_{sc}) and hence the photovoltaic efficiency of a DSSC. The reason to this is that the iodide ion while participating in the redox reaction, also shuffles between the photo-electrode and the counter electrode. Quaternary ammonium salts such as TPAI, TBAI and THAI are some of the widely used ionic salts in the gel electrolytes. The quaternary ammonium salts also produces cations instead of the iodide ions. Reports show that cations affects many parameters that could influence the solar cell performances. This includes the strength of the sensitizer surface attachment, the energetics of the semiconductor and sensitizer, the charge transport rate, the dynamics of interfacial electron transfer, and the rate of iodide oxidation [15–17].

The present work, is aiming to clarify the electrical conduction and the dielectric behavior of the P(VP-co-VAc) based GPEs and to optimize the GPE samples to be used in the applications of the DSSCs. In this article, the electrical and dielectric properties of the GPEs together with the photovoltaic performances of the cells will be reported.

2. Experimental

2.1. Materials and GPE sample preparations

Poly(1-vinylpyrrolidone-co-vinyl acetate) P(VP-co-VAc) (Mw, ~50,000), ethylene carbonate (EC), propylene carbonate (PC), tetrapropylammonium iodide (TPAI) and Ruthenium dye (N719) were purchased from Sigma Aldrich. Iodine (I_2) was purchased from Friedemann Schmidt Chemical. P(VP-co-VAc) and TPAI were dried in vacuum oven at 50 °C for 24 h prior to use. The materials were weighed appropriately following the composition as shown in Table 1. EC and PC were mixed with the weight ratio of 1:1 and remained unchanged for all the samples. The variation of the GPE composition was done by changing the ratio of the P(VP-co-VAc) and TPAI. The weight of iodine was calculated at one tenth of the total amount molar weight of iodine to the weight of the iodide salts added. TPAI and iodine pellet were added into the mixture of EC and PC and were stirred on a magnetic stirrer at 60 °C until complete dissolution of the TPAI and iodine. P(VP-co-VAc) were then added into the mixture batch by batch (1 g maximum each) with continuous stirring at 80 °C. The mixture was then stirred at 100 °C for 30 min for complete dissolution and homogeneity of the electrolytes. The whole stirring process was done in a tightly closed container to avoid any losses due to evaporation and sublimation of iodine. The low viscous mixture was then slowly cooled to room temperature which resulted in gel polymer electrolyte. This procedure was then repeated for different compositions of the GPEs (See Table 2).

Table 1
The compositions of P(VP-co-VAc) gel polymer electrolyte samples with different concentration of TPAI salts.

Electrolytes	TPAI (%)	P(VP-co-VAc) (g)	TPAI (g)	I_2 (g)	EC (g)	PC (g)
P0	0	5.000	0.0	0.000	1.5	1.5
P10	10	4.459	0.5	0.041	1.5	1.5
P20	20	3.919	1.0	0.081	1.5	1.5
P30	30	3.378	1.5	0.122	1.5	1.5
P40	40	2.838	2.0	0.162	1.5	1.5

Table 2
The dc ionic conductivity and activation energy of the GPEs sample with different concentration of TPAI.

Electrolytes	Ionic conductivity, σ_{dc} (S cm^{-1})	Activation energy, E_a (kJ mol^{-1})
P0	3.83×10^{-7}	1.2869
P10	4.28×10^{-4}	0.9579
P20	8.89×10^{-4}	0.9960
P30	1.60×10^{-3}	0.6495
P40	8.61×10^{-4}	1.0675

2.2. Characterization of the electrolytes

The dielectric properties of the GPE samples were carried out using a computer controlled HIOKI 3532-50 LCR Hi-Tester over the linear frequency f ($f = \omega/2\pi$, where ω is angular frequency) range from 50 Hz to 1 MHz at room temperature (27 ± 1 °C). Frequency dependent values of capacitance C_p and parallel resistance R_p of the sample holder loaded with the electrolyte sample were measured in parallel mode for the determination of the dielectric/electrical functions of the GPE samples. The frequency dependent real part Z' and imaginary part Z'' of complex impedance $Z^*(\omega)$ of the electrolyte films were evaluated by the following equation:

$$Z^*(\omega) = 1/Y^*(\omega) = Z' - jZ'' = R_p/\left(1 + (\omega C_p R_p)^2\right) - j\left[\left(\omega C_p R_p^2\right)/\left(1 + (\omega C_p R_p)^2\right)\right] \quad (1)$$

The ionic conductivity of the GPE samples were calculated by following equation:

$$\sigma_{dc} = l/R_b A \quad (2)$$

where σ_{dc} is ionic conductivity in S cm^{-1}, l is thickness of the thin film sample in cm, R_b is bulk resistance in Ω obtained from Cole–Cole impedance plot, and A is surface area of the sample touching on the electrodes in cm^2. The electrochemical impedance spectroscopy (EIS) measurements were performed using an electrochemical cell composing two identical stainless steel electrodes separated by the gel polymer electrolyte. The thickness of the GPE is controlled with a 0.75-mm-thick Teflon® spacer in between the electrodes. Temperature variation of the conductivity of each sample was obtained by taking measurements at approximately 10 °C intervals in the temperature range 30–100 °C. At each temperature, the sample was allowed to stabilize for about 30 min before the measurement was taken.

2.3. DSSCs fabrication and characterizations

The DSSCs were fabricated with the configuration as shown in Fig. 1. The GPEs were sandwiched in between the dye-sensitized TiO_2 electrode and a platinum (Pt) coated FTO glass. Fluorine doped tin oxide (FTO) (8 Ω cm^{-2}) conducting glasses were cleaned with distilled water and ethanol. The TiO_2 paste was prepared by mixing 0.5 g of D25 TiO_2 and 0.075 g of Triton X-100 as the dispersing agent in 2 ml of nitric acid (pH = 1). The paste was then ground in a mortar for 30 min. Then, the TiO_2 paste was doctor bladed on the cleaned FTO substrate and air-dried. The TiO_2 film was sintered at 450 °C for 30 min. The TiO_2 film obtained was 12 μm