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The effect of various concentrations of PVDF-HFP polymer gel electrolyte for dye-sensitized solar cell

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ABSTRACT

A PVDF-HFP gel electrolytes based DSSCs were fabricated successfully, where gel electrolytes with 2.5 wt.%, 5 wt.%, 10 wt.% and 15 wt.% PVDF-HFP are included, respectively. Linear sweep voltammetry (LSV), photocurrent–voltage measurements and electrochemical impedance spectra (EIS) were measured. As the results shown, the apparent diffusion coefficient (D_{app}) of I^- and I_3^- decreased as PVDF-HFP increased. D_{app} of I^- and I_3^- are decreased from 1.87×10^{-6} to 0.67×10^{-6} cm^2/s and 3.28×10^{-6} to 0.88×10^{-6} cm^2/s, respectively. For the solar cell measurements, the short circuit current density (J_{sc}) were affected by the ion motilities, which was decreased from 11.58 mA/cm^2 to 8.17 mA/cm^2, and the energy converting efficiency (η %) was decreased from 5.17% to 2.79%. For electrochemical impedance spectra (EIS) measurements, the ionic diffusion impedance for the redox-couple (I^-/I_3^-) in the gel electrolyte was also increased with the concentration of PVDF-HFP from 0.61 Ω to 8.17 Ω. In the Bode Plots, the electron lifetime (τ_e) of the 2.5 wt.% and 5 wt.% PVDF-HFP electrolytes was increased from 40.52 ms to 48.48 ms and 41.29 ms, respectively. However, τ_e was decreased in the concentrations of 10 wt.% and 15 wt.% PVDF-HFP, due to the ion motilities that were decreased by excessing PVDF-HFP polymer. For gel electrolyte, the cell of 2.5 wt.% PVDF-HFP exhibited a better J_{SC} of 10.89 mA/cm^2, a higher energy conversion efficiency (η) of 4.75%, a higher fill factor (FF) of 61.26%, and a smaller R of 1.06 Ω than the 15 wt.% PVDF-HFP based cell.

1. Introduction

Dye sensitized solar cell (DSSC) is consisted of TiO_2 on the transparent conducting oxide (TCO) glass (photo-electrode), a ruthenium based dye, a redox electrolyte and platinum (Pt) counter electrode [1]. When sunlight illuminates the solar cell, electrons are injected from the photo-excited dye molecule into the conduction band of TiO_2. The electrolyte provides electrons back to the dye molecule and then the dye returns from the excited state to the ground state ($3I^- \rightarrow I_3^- + 2e^-$). The electrons of TiO_2 arrive from the external circuit to counter electrode. The redox couple (I^-/I_3^-) is regenerated at the interface between the electrolyte and the counter electrode ($I_3^- + 2e^- \rightarrow 3I^-$) [2].

Liquid electrolytes have technical limitations of sealing up and long-term stability [3]. To overcome these limitations, many researchers use solid or quasi-solid-state electrolytes such as ionic liquids [4], organic and inorganic hole-transport materials [5], and polymer electrolytes [6–8]. In many polymer electrolytes, PVDF-HFP in DSSC has been known [6] to be useful because of its photoelectron stability and chemical stability. PVDF-HFP also shows superior mechanical strength and high ionic conductivity [9], and it is stable in the TiO_2 and Pt nanoparticles for redox electrolytes of DSSC [10].

In this paper, gel electrolytes were fabricated by adding 2.5 wt.%, 5 wt.%, 10 wt.% and 15 wt.% PVDF-HFP into liquid electrolytes, respectively. The purpose is to fabricate various weight percentages of PVDF-HFP, which will affect the ionic impedance. The photovoltaic performances and electrochemical properties of solar cells were measured.

2. Materials and methods

2.1. Preparation of the electrolytes

The liquid electrolytes contained 0.1 M LiI (Merck), 0.05 M I_2 (Aldrich), 0.6 M IonLic DMPII (Solaronix) and 0.5 M 4-tert-butylpyridine (Aldrich) in 3-methoxypropionitrile (MPN) (Aldrich). PVDF-HFP polymers (MW 400,000, Aldrich) of 2.5 wt.%, 5 wt.%, 10 wt.% and 15 wt.% were respectively added into liquid electrolytes to fabricate gel electrolytes. The gel electrolytes were heated and stirred at 75 °C for 6 h.

2.2. Preparation of dye sensitized solar cells

The TiO_2 nanoparticles (P25), polyethylene glycol (Aldrich), 2,4-pentanedione (Alfa Aesar) and TritonX-100 were dispersed in D.I.

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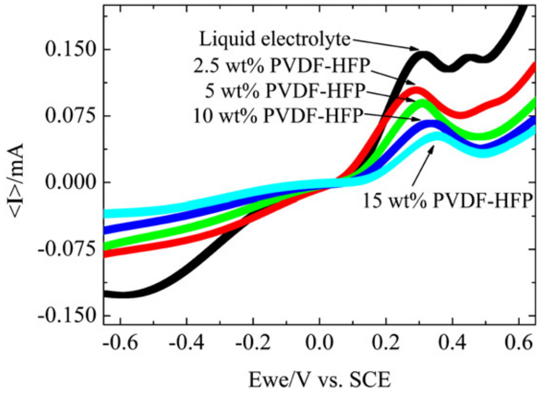

Fig. 1. Steady-state voltammograms of various electrolytes.

Water. The colloid of TiO_2 was deposited on FTO conductive glass substrate by spray coating method (with a working area of 1 cm^2). The working electrode was sintered at 450 °C for 30 min and then it was immersed in the solution of 0.3 mM N719 dye (UniRegion Bio-Tech) for 24 h. The DSSCs were fabricated by sandwiching the electrolyte between the working electrode and the counter electrode. The Pt counter electrode was coated on Indium Tin Oxide (ITO) glass by sputtering.

2.3. The features of various concentrations of PVDF-HFP polymer gel electrolyte measurements

Linear sweep voltammetry (LSV) is a method in which the current at the working electrode is measured while the potential between the working electrode and the reference electrode is swept linearly in time. The LSV measurements were conducted with an electrochemical work station (Bio Logic, SP-150). In this study, the steady-state current–voltage (I–V) curves for electrolyte contain various types. For the LSV, the Pt ultramicroelectrode is used as working electrode, the Pt wire as counter electrode and the Ag/AgCl as reference electrode. The potential was cycled from −0.65 to 0.65 V at a scan rate of 10 mV/s. The apparent diffusion coefficient (D_{app}) values of I^- ions and I_3^- ions were calculated from the anodic and cathodic steady-state current (I_{SS}) using the following Eq. (1) [11]:

$$I_{SS} = 4nFrCD_{app} \tag{1}$$

where n = 2 is the electron number in the electrode reaction, F is the Faraday constant, r is radius of the microdisk electrode, and C is the bulk concentration of electroactive species.

2.4. The features of dye-sensitized solar cell measurements

The photocurrent–voltage measurements were recorded by a Keithley 2400 source meter under stimulated 1 sun illumination (AM1.5G, 100 mW/cm^2). Measurement parameters are open-circuit voltage (V_{OC}), short circuit current density (J_{SC}), fill factor (FF), and energy conversion efficiency (η %). The FF and η are calculated using the V_{OC} and J_{SC}. The FF is calculated using the Eq. (2) [12]:

Table 2
Characteristics of DSSCs with various electrolytes based cells.

Sample	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	η (%)	R (Ω)	τ_e (ms)
LE	11.58	0.72	61.85	5.17 ± 0.15	0.61	40.52
2.5wt-PH	10.89	0.71	61.26	4.75 ± 0.09	1.06	48.48
5wt-PH	9.87	0.71	62.42	4.37 ± 0.17	1.15	41.29
10wt-PH	8.88	0.70	59.49	3.68 ± 0.19	6.83	35.39
15wt-PH	8.17	0.69	49.58	2.79 ± 0.14	8.17	30.06

$$FF = \frac{JmaxVmax}{J_{sc}V_{oc}} \tag{2}$$

where I_{max} and V_{max} are the maximum output values of current and voltage, respectively. The efficiency is calculated using the Eq. (3) [12]:

$$\eta = \frac{J_{sc}V_{oc}FF}{P_{in}} \tag{3}$$

where P_{in} is the power of incident light. The electrochemical impedance spectra (EIS) measurements were conducted with an electrochemical work station at an amplitude of 0.7 V over a frequency range of 50 mHz to 1 MHz. The Nyquist plot was applied to measure the impedance of the DSSC with gel electrolyte containing various weight percentages (wt.%) of PVDF-HFP, in which a clear feature with three semicircles was displayed. The Bode Plots of impedance data plotted as phase angle vs frequency, for the three DSSCs with various weight percentages (wt.%) of PVDF-HFP.

3. Results

3.1. Diffusion behavior of I^- and I_3^- ions in the liquid electrolyte and gel electrolytes

The components of the liquid electrolyte were LiI, and I_2, dissolved in MPN. PVDF-HFP of 2.5 wt.%, 5 wt.%, 10 wt.% and 15 wt.% were respectively added into liquid electrolytes to fabricate gel electrolytes. It is well-known that the diffusion of I^- and I_3^- ions in the electrolyte has an important effect on the performance of the DSSC. To determine the D_{app} of I^- and I_3^- ions, LSV was employed at 25 °C. Fig. 1 shows the steady-state current–voltage (I–V) curves of the reduction of I_3^- ions and the oxidation of I^- ions. The anodic I_{SS} (upper plateau) refers to the electrochemical oxidation of I^-, while the cathodic I_{SS} (lower plateau) refers to the electrochemical reduction of I_3^-. As the results shown, the apparent diffusion coefficients (D_{app}) of I^- and I_3^- decreased with the increasing of PVDF-HFP concentrations. It would be caused by that the PVDF-HFP can decrease the ion motilities (I^-/I_3^-) in the electrolyte [13]. Therefore, D_{app} was decreased. D_{app} of I^- and I_3^- were decreased from 1.87×10^{-6} to 0.67×10^{-6} cm^2/s, and 3.29×10^{-6} to 0.88×10^{-6} cm^2/s, respectively, as shown in Table 1.

Table 1
The steady-state current and the apparent diffusion coefficient values of I^- and I_3^- in various electrolyte.

Sample	I_{SS} (I^-) (mA)	I_{SS} (I_3^-) (mA)	D_{app} (I^-) (10^{-6} cm^2/s)	D_{app} (I_3^-) (10^{-6} cm^2/s)
Liquid electrolyte (LE)	0.145	0.127	1.87	3.29
2.5 wt.% PVDF-HFP (2.5 wt-PH)	0.104	0.078	1.35	2.02
5 wt.% PVDF-HFP (5 wt-PH)	0.089	0.068	1.14	1.76
10 wt.% PVDF-HFP (10 wt-PH)	0.068	0.049	0.88	1.32
15 wt.% PVDF-HFP (15 wt-PH)	0.052	0.034	0.67	0.88