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# A low-cost quasi-solid DSSC assembled with PVDF-based gel electrolyte plasticized by PC–EC & electrodeposited Pt counter electrode

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ABSTRACT

A low-cost quasi-solid dye-sensitized solar cell (DSSC) with a photoelectric conversion efficiency of 1.79% was assembled using PVDF-based gel electrolyte plasticized by PC–EC and electrodeposited Pt counter electrodes. Its morphology, chemical structure, electrochemical and photoelectric properties were examined by SEM, FTIR, EIS and *I–V* tests, respectively. The results showed that PC–EC plasticized gel electrolyte can greatly prevent the α-phase formation of PVDF, and had the loose structure & many interpenetrating holes due to the effective intercalation of PC & EC into PVDF chains through their dipole interaction. It made the migration or diffusion of iodide ions to electrodes easier. Furthermore, its conductivity was increased to 2.34 mS/cm from 1.00 mS/cm of unplasticized gel electrolyte. $V_{oc}J_{sc}$, FF & $\eta$ values of DSSC plasticized by PC–EC were all enhanced. Compared with Pt electrode obtained by thermal decomposition, electrodeposited Pt electrode had the lower charge-transfer resistance and the better contact with gel electrolyte in quasi-solid DSSC due to its orderly grain arrangement, more even, denser and larger active surface. Meanwhile, its process also had little influence on ITO sheet resistance. Thus, its quasi-solid DSSC has the higher photoelectric conversion efficiency.



## 1. Introduction

Since DSSC based on the mechanism of a fast regenerative photoelectrochemical energy conversion was first reported by O'Regan and Gratzel in 1991 [1], DSSC has become one of the most promising new generation solar cells due to relatively high photoelectric conversion efficiency, simple fabrication process and low cost. At present, its efficiency has amounted to higher than 12% [2,3] from 7.12% since 1991 [1]. In DSSC, the electrolyte is responsible for charge transport between photoanode and counter electrode. Most high-efficiency DSSCs have been constructed with liquid electrolytes with $I^-/I_3^-(I_5^-)$ redox couple dissolved in volatile organic solvents. However, the evaporation of toxic solvents and the leakage of liquid electrolytes as well as the sealing problem will significantly limit their practical application. Thus, many attempts have been made to solve these problems by replacing liquid electrolytes with quasi-solid or solid-state electrolytes, such as polymer-based electrolyte, hole transport materials and ionic liquids [4–6]. Poly(vinylidene fluoride) (PVDF) is usually used as porous separators or the matrix of gel polymer electrolytes due to its good insulation, affinity to liquid electrolytes, electrochemical stability, thermotolerance and easy filming in lithium batteries. And it is also applied in quasi-solid DSSC as the matrix of gel electrolytes due to its high adhesion strength with Pt counter electrode and $TiO_2$ photoanode. But alone PVDF is difficult to provide the suitable pore structure and only gains the low efficiency for DSSC [7]. Thus, interpenetrating-polymer-network (IPN) PVDF composites copolymerized with other monomers are interested to act as gel polymer electrolyte of DSSC [7–9]. However, IPN structure is difficult to control and its synthesis process is also complex, which is not adapted to the mass production of DSSC. If PVDF can gain the suitable pore structure through the more simple modification, it will bring the great convenience for the preparation and assembly of DSSC. It is reported that higher ionic mobility occurs in the amorphous phases rather than in the crystalline phases of polymers in polymer-based electrolytes [10,11]. But many polymers tend to crystallize at room temperature. It is known that plasticizers can reduce crystalline phases to gain more amorphous phases in polymers. Considered the easy addition reaction of traditional phthalates such as dioctyl phthalate &

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dibutyl phthalate with iodine, propylene carbonate (PC) and ethylene carbonate (EC) can be chosen to plasticize PVDF due to their same polar ester group and good dissolution to $I^-/I_3^-(I_5^-)$ redox couple. PC and EC are usually used as the solvent of electrolyte in batteries, while their application as the plasticizer of PVDF-based gel electrolyte in DSSC is not intensively researched. The chemical structure & morphology of PC or EC plasticized PVDF and their influence on the photoelectric property of DSSC need to be cleared. In our work, *N*-methyl-2-pyrrolidone (NMP) is selected as the solvent of PVDF-based gel electrolyte due to its good affinity to $I^-/I_3^-(I_5^-)$ redox couple, better dissolution to PVDF and lower cost than PC & EC. And PC–EC mixed regent with mass ratio of 1/2 was determined to plasticize PVDF because of the higher conductivity of its gel electrolyte.

For high performance DSSC, counter electrode with high electrocatalytic activity towards the reaction of $I_3^-(I_5^-) + 2e^- = 3I^-(5I^-)$ and high electrical conductivity is required. Pt is regarded as an outstanding counter electrode material due to its great conductivity and electrocatalytic activity [12]. Pt is usually prepared by thermal decomposition [13], electrodeposition [12,14], magnetron sputtering deposition [15] and so on. Yoon et al. [16] prepared the counter electrodes on FTO glass for DSSC through these three techniques and examined the performances of Pt. The results showed that the electrodeposited Pt counter electrode had higher solar energy conversion efficiency of 7.6% than other Pt counter electrodes. Some researchers [17–19] studied the thickness effect on the performance of Pt counter electrode for the DSSC. It was found that Pt electrodes only with 2 nm thickness can exhibit good electrochemical activity towards the reaction of $I_3^-(I_5^-) + 2e^- = 3I^-(5I^-)$. When its thickness amounted to 10 nm, Pt mirror is formed and can utilize the light once again. Therefore, photoelectric conversion efficiency may be more enhanced if the thickness of Pt electrodes can reach more than 10 nm. But the thickness of Pt electrodes needs to be low enough in order to reduce the cost. Fortunately, electrodeposition is easy to control the thickness of Pt film deposited on ITO or FTO glass and its process was simple and fast.

In this work, gel electrolyte with PC–EC plasticized PVDF as matrix was prepared and Pt counter electrodes were also prepared through cyclic-voltammetry electrodeposition & thermal decomposition, respectively. Obtained gel electrolyte and Pt counter electrodes were simultaneously applied to assemble DSSC. Their morphology, chemical structure, electrochemical and photoelectric properties were analyzed by SEM, FTIR, EIS and *I–V* tests, respectively.

## 2. Experimental

### 2.1. Materials

$I_2$, NaI, PC, EC, NMP, $H_2PtCl_6$, $H_2SO_4$, ethanol, isopropanol were purchased from Aladdin Industrial Inc., China. N719 dye and ITO glass were purchased from Jinge Solar Energy Co., China. Solef 5130-PVDF was purchased from Solvay Co., France. About 20 nm-sized $TiO_2$ powders were self-made through sol-gel method.

### 2.2. Preparation of gel electrolyte

Sol electrolyte was obtained after 15 g PC–EC with mass ratio of 1/2 and 15 g PVDF were successively added into NaI(0.6 M) $-I_2$(0.05 M)/NMP(100 g) solution, dispersed via ultrasonic for 20 min, and evenly stirred at 70 °C for 3 h. It was casted on a clean glass slide and became the film after dried in a vacuum oven at 70 °C for 12 h. Gel electrolyte film with the thickness of ~100 μm was obtained after peeled off from the glass slide. It was cut into sheets with area of $0.5 \times 0.5\ cm^2$. Gel electrolyte film without PC–EC plasticizer was also prepared with the same process.

### 2.3. Preparation of dye-sensitized $TiO_2$ photoanode

$TiO_2$ pastes were prepared according to [5] and printed with the thickness of 10–20 μm and the area of $1 \times 1\ cm^2$ on the centre of ITO conductive face through the screen-print technology. It was heated in thermostatic muffle furnace at 200 °C for 30 min and subsequent 450 °C for 30 min. $TiO_2$ porous film with the thickness of 10–20 μm was formed after natural cooling. Subsequently, it was soaked into 0.5 mmol/L ethanol solution of N719 for 24 h. Dye-sensitized $TiO_2$ photoanode was obtained after dried in air.

### 2.4. Preparation of Pt counter electrode

Pt counter electrodes were prepared through thermal decomposition or electrodeposition. Their thickness was dominated to about 2 μm. Film thickness was measured on Alpha-Step D-100 KLA-Tencor Profiler. (1) Thermal decomposition: 0.05 mL isopropanol solution of chloroplatinic acid with concentration of 40 mmol/L was pipetted onto ITO conductive surface, dried in air and subsequently pyrolysed at 400 °C for 15 min. Thus, Pt counter electrode was obtained. (2) Electrodeposition: ITO conductive surface with area of $0.5 \times 0.5\ cm^2$ exposed was used as working electrode. Pt electrode was used as counter electrode. Ag/AgCl electrode dipped into the saturated KCl aqueous solution was used as reference electrode and 4 mmol/L $H_2PtCl_6$ and 0.5 mol/L $H_2SO_4$ mixed aqueous solution was used as the electrolyte. Pt counter electrode was gained through cyclic voltammetry method with variable potential scan from −0.2 V to 0.5 V for 8 laps at the scan rate of 10 mV/s.

### 2.5. Assembly of quasi-solid DSSC

Quasi-solid DSSCs were simply assembled according to Fig. 1 with above dye-sensitized $TiO_2$ photoanode, gel electrolyte film and Pt counter electrode. The conductive edges about 5–10 mm width of two electrodes were remained for tests.

### 2.6. Measurements

Morphologies of samples were observed on Hitachi S-4800 field emission scanning electron microscopy. The FTIR spectra of samples were obtained by the KBr-pellet method on PE Spectrum GX FTIR analyzer at a resolution of $4\ cm^{-1}$ with 32 scans over the

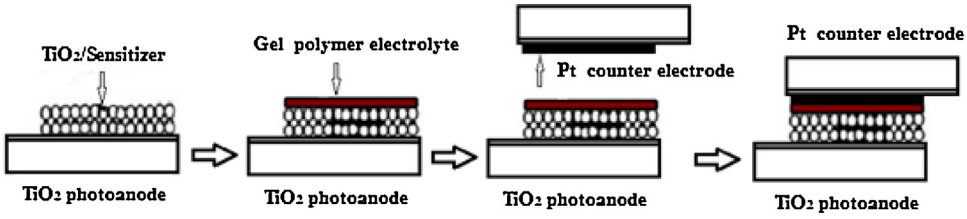


**Fig. 1.** Diagram of Quasi-solid DSSC assembly process.