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Rapid, 5 min, low temperature aqueous platinization for plastic substrates for dye-sensitized solar cells

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ABSTRACT

This paper reports a rapid (5 min), low temperature (120 °C) method to platinize the counter electrodes of dye-sensitized solar cell (DSC) devices. This new method uses aqueous solutions and is based on chemical bath deposition of an activating Pd layer followed by Pt only using H₂ gas as the reductant. This method has been tested on flexible, plastic substrates (indium tin oxide-coated polyethylene terephthalate or polyethylene naphthalate, ITO-PET or ITO-PEN, respectively). We report device efficiencies up to 7.2% on ITO-PET which is comparable to devices made using high temperature (400 °C) processing on rigid, fluoride-doped tin oxide (FTO) glass counter electrodes. The method is scalable and suitable for continuous roll-to-roll production.

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1. Introduction

Typically dye-sensitized solar cells (DSCs) are fabricated by high temperature sintering of the TiO₂ photoanode (450–500 °C) and platinum-coated counter electrode (400 °C) [1]. However, low temperature manufacturing of DSC devices is beneficial to reduce energy processing costs and to broaden the range of substrates available to flexible materials such as plastics which require processing temperatures ≤150 °C. Previous methods to prepare Pt counter electrodes on flexible substrates have included sputtering, electrochemical deposition and chemical reduction. For example, Ikegami et al. deposited a Pt/Ti bilayer on ITO-PEN using vacuum sputtering to make a fully plastic DSC which had a conversion efficiency of 4.3% [2]. By comparison, Grätzel electrodeposited Pt onto ITO-PEN to make a flexible DSC with a conversion efficiency of 7.2% and a 15 μm thick TiO₂ photoanode [3]. Kang et al. [4], Park et al. [5], and Chen et al. [6] used chemical reduction to prepare Pt counter electrodes by spreading an isopropanol solution of H₂PtCl₆ onto ITO-coated plastic followed by reduction in a H₂O/ethanol solution of NaBH₄. By contrast, Sun et al. [7] fabricated Pt counter electrodes using ethylene glycol to reduce H₂PtCl₆·6H₂O at 180 °C.

Here, we report an aqueous, low temperature (120 °C) and scalable method using chemical bath deposition (CBD) combined with H_{2(g)} as a reducing agent to produce flexible platinized ITO-coated plastic electrodes at scales ranging from 1 cm² to A4 size. Optical

transmission, device performance and counter electrode-counter electrode data are reported.

2. Experimental

The substrates used were indium tin oxide-coated polyethylene terephthalate (ITO-PET) (15 Ω per square, from Optical Filters), ITO-coated polyethylene naphthalate (ITO-PEN) (15 Ω per square from G24i), Ti foil (>99.6%, 1 mm, Advent Research Materials) and TEC7 or TEC8 (7 Ω per square or 8 Ω per square, respectively) supplied by NSG Pilkington. The substrates were activated using PdCl₂ (procedure in electronic [Supplementary information – ESI S1](#)). These activated substrates were then immersed in Pt solution made by dissolving potassium hexachloroplatinate in DI water (0.0029 g in 60 ml of H₂O) to make a 100 μM solution where the pH was adjusted to between 4.0 and 4.5 using HCl_(aq) or KOH_(aq). Hydrogenation of this layer was then carried out by bubbling H_{2(g)} over the immersed substrate for 2 min, then leaving for 4 min before washing with DI water and isopropanol, followed by drying with N_{2(g)}.

TiO₂ photoelectrodes (2 layers of Scotch tape were used to give a 12 μm thick layer of TiO₂) were prepared as described previously [8] and were dyed by immersion in a 400 μM t-butanol/CH₃CN (Aldrich, 1:1 v/v) solution of ruthenium-bipyridyl N719 (Solaronix) for 12 h at room temperature. To make full DSC devices, counter and photoelectrodes were sealed together at 120 °C using 50 μm Surlyn gasket (DuPont) and the gap was filled with electrolyte

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(0.05 M of I₂, 0.1 M of LiI, 0.6 M of C(CH₃)₄Ni and 0.5 M of 4-butylpyridine in CH₃CN).

UV-visible spectroscopy was carried out on a PerkinElmer Lambda 35 spectrometer. Current-voltage (I-V) data of DSC devices were measured with a Xe arc lamp solar simulator (ABET) and a Keithley 2400 at 1 Sun calibrated using a certified crystalline Si reference cell (Oriel 91150 V). Counter electrode-counter electrode (CE-CE) devices were also studied using the same electrolyte sweeping from -1.5 to 1.5 V at 2 mV/s.

3. Results and discussion

The aim of this method has been to enable fabrication of platinized counter electrodes for DSC devices at low enough temperatures to allow transparent plastic substrates to be used (i.e. <120 °C), and which uses only aqueous-based solutions to avoid the use of organic solvents which can make scale-up very difficult due to dangers associated with threshold exposure limits, and flammability and explosion risks [9]. Pd was used as a seed layer because it deposits more easily using a H₂ reductant, it lowers the Pt loading, it is half the cost of Pt and it can improve device lifetime by reducing any potential Pt corrosion in the corrosive I₂-based electrolyte [10]. A further aim was to make the counter electrode as transparent as possible to facilitate illumination through the counter electrode (i.e. reverse illumination). UV-Vis spectra (Fig. 1) show that depositing Pt from higher H₂PtCl₆ concentration solutions (1 mM versus 0.1 mM) corresponds with lower transmittance at 320 nm (ESI Fig. 3). We ascribe this to increased Pt deposition from the higher concentration solution. Transmittance data were also compared between an ITO-PEN substrate platinized using our low temperature CBD method and one with sputtered Pt (ESI Fig. 4). The data show that the low temperature CBD method gives higher transmittance from 350–850 nm. This may indicate either lower Pt loading or smaller Pt particle size for the CBD method samples.

Counter electrode-counter electrode devices have been studied using rigid, fluoride-doped tin oxide (FTO)-coated TEC glass substrates to ensure a fixed distance between electrodes (Fig. 2). The low temperature CBD platinization method has been compared with a high temperature (400 °C) sintering of a commercial Pt paste (PT1, Dyesol). The data show significant current for both CBD produced and sputtered Pt electrodes showing that both are active for I₃⁻ reduction and I⁻ oxidation. Both types of electrode also reach their mass transport limitations in the bias voltage range (0.75–1.0 V) which is also similar to that reported for other Pt

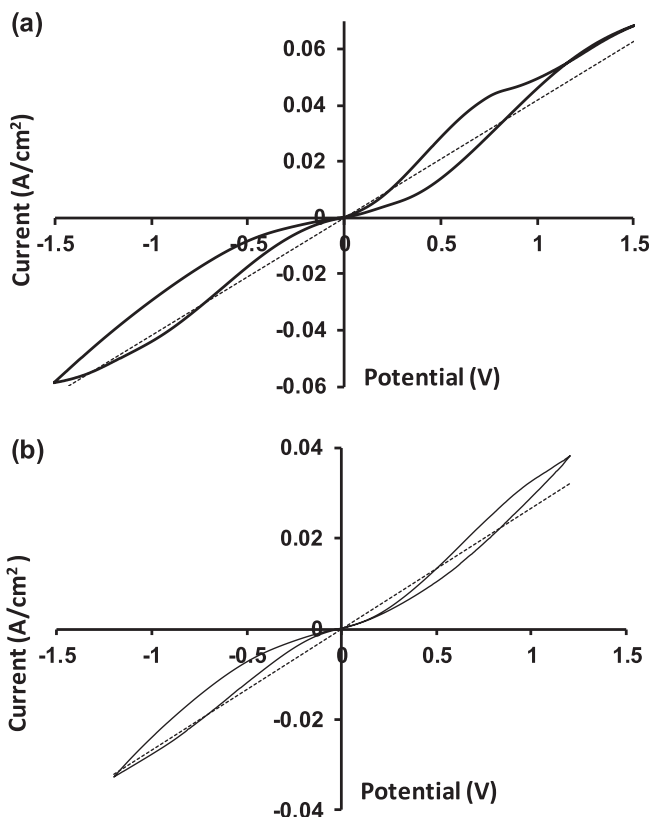


Fig. 2. Current-voltage data for counter electrode-counter electrode devices for (a) low temp. Pt and (b) commercial Pt paste (Dyseoil PT1) sintered at 400 °C. Scan rate 2 mV/s, electrolyte I⁻/I₃⁻ in CH₃CN.

counter electrodes [11]. The limiting current densities (which are a measure of the diffusion of electrolyte charge carriers) are 45 mA/cm² for the CBD electrode and 33 mA/cm² for the sputtered electrode. In line with this, the gradient of the line for the CBD electrode is higher at lower voltage bias indicating a higher charge exchange current density. In addition, the redox peak (-1.5 to 0 V) is related to the reaction (I₃⁻ + 2e⁻ → 3I⁻) which occurs at the CE of the DSC; accelerating this reaction is the key role of the Pt catalyst [12]. By comparison, the redox peaks (0–1.5 V) correspond to the reaction (3I⁻ → I₃⁻ + 2e⁻) which occurs at the dye-oxide interface and so is less important to the CE discussion. Thus, the cathodic peak's current density (I_{pc}) and potential (V_{pc}) are directly proportional to the ability of the CE to reduce I₃⁻. The data show the peak anodic to cathodic currents of the CBD approach is 58.6 versus 32.3 mA/cm² in line with higher catalytic activity of the CBD approach. Peak anodic to cathodic current densities barely change with successive scans, indicating that the Pt film is electrochemically stable.

Current-voltage data for DSC devices (Table 1) show that the best performing devices match the efficiency for devices reported by electrodeposited Pt (η = 7.2%, [3]). Photocurrents from devices made using this new low temperature CBD method are higher than ones made using sputtered Pt on ITO-PEN substrates (ESI Table 1) leading to higher overall efficiencies for the CBD method (mean efficiency 6.1% versus 4.7%). Other low temperature approaches have reported similar efficiencies, but they have often used external stimulation (e.g. UV light) to catalyse the reaction. However, this could either directly degrade some plastics, and/or generate free radicals by interaction with the TiO₂ photoanode if used in an all-in-one approach such as that reported by Fu et al. [13]. Large area monolithic devices (10 cm² active area) have also been fabricated using sub-samples taken from a A4-sized ITO-PET sheet that

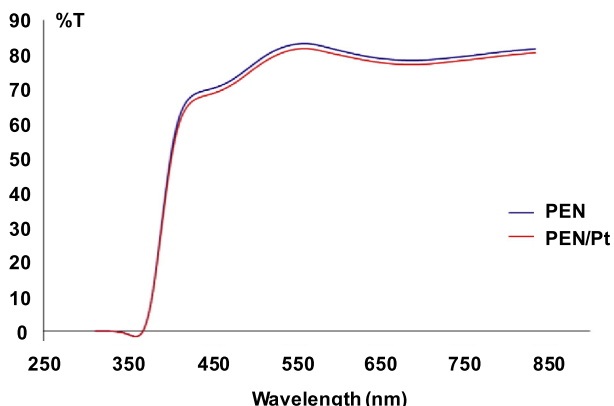


Fig. 1. UV-visible spectroscopy of indium tin oxide-coated polyethylene naphthalate (ITO-PEN) substrate before/after Pt deposition by CBD.

Table 1

Current-voltage (I-V) data for glass TEC 7 TiO₂ photoelectrode with low temperature Pt on polyethylene-indium tin oxide (PET/ITO) counter electrode dye-sensitized solar cell devices. η = power conversion efficiency; FF = fill factor; J_{sc} = short circuit current; V_{oc} = open circuit voltage.

η (%)	FF (%)	J_{sc} (mA/cm ²)	V_{oc} (V)
<i>TEC 7 TiO₂ photoelectrode (1 cm² devices)</i>			
6.32	0.53	16.01	0.75
6.91	0.60	15.10	0.76
6.56	0.60	14.58	0.67
7.22	0.58	16.64	0.75
3.34	0.36	13.63	0.77
<i>TEC 15 TiO₂ photoelectrode (10 cm² devices)</i>			
0.87	0.30	41.59	0.71
1.04	0.31	47.21	0.71

had been processed using the low temperature CBD method described in this paper. The device testing data (Table 1) show lower fill factors (FF \approx 0.30) and short circuit currents ($J_{sc} \approx 4.44$ mA/cm²) were obtained which is ascribed to the un-optimized monolithic device architecture which leads to overall efficiencies of ca. 1.0%.

4. Conclusions

To our knowledge, this is the highest efficiency platinumized PET at 25 °C with no external energy source to catalyse the reaction ($\eta = 7.2\%$). The data show that by hydrogenation of PdCl₂ to make an initial Pd activation layer followed by hydrogenation of H₂PtCl₆, a highly transparent, conductive Pt coating can be rapidly achieved (5 min). Our data also show that this method is suitable for forward and reverse illumination DSC devices and also for scaled DSC devices, and we have demonstrated this for A4 sized substrates. Transmission data show that the amount of Pt deposited can be controlled by modifying the concentration of the Pt solution. Electrochemical measurements of counter electrode-counter electrode devices show good catalytic activity and high chemical stability to redox cycling for the CBD-produced electrodes.

Conflict of interest

None.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mblux.2018.100001>.

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