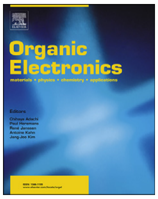
Organic Electronics 44 (2017) 159–167

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel



Inkjet-printed platinum counter electrodes for dye-sensitized solar cells

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ARTICLE INFO

Article history:
Received 17 December 2016
Received in revised form
4 February 2017
Accepted 11 February 2017
Available online 16 February 2017

Keywords:
Dye-sensitized solar cells
Inkjet printing
Platinum
Catalyst
Stability

ABSTRACT

In this study, inkjet printing method was successfully demonstrated to produce catalytic platinum layers for dye-sensitized solar cells. Our work includes meticulous optical, morphological, and electrocatalytical analyses of precisely inkjet-patterned counter electrodes as well as traditionally drop-cast samples. Similar catalytic performance was obtained with both methods ($R'_{CT} = 1.2\ \Omega\ cm^2$ for drop-cast and $R'_{CT} = 1.6\ \Omega\ cm^2$ for inkjet-printed) at same Pt loading (ca. 2.5 $\mu g/cm^2$), and correspondingly almost same cell efficiencies ($\eta_{drop\text{-}cast} = 6.5\%$ and $\eta_{printed} = 6.7\%$). All the cells exhibited high stability by keeping their efficiencies after being subjected to a 1000 h aging test under 1 Sun and 35 °C at the open circuit condition. These results highlight the potential of inkjet printing to realize precisely patterned and no-material-wasting counter electrodes by controlled dispensing of the functional solution.

1. Introduction

Dye-sensitized solar cells (DSSCs) have been widely investigated due to the potential of their possible utilization in low-power electronics [1]. The traditional device structure of a DSSC employs a dye-impregnated photo electrode (PE) and a counter electrode (CE) that consists of a platinum (Pt) catalyst layer loaded over a fluorine tin oxide (FTO) coated glass substrate [2]. PE and CE remain separated through a thermoplastic layer (typically a Surlyn or Bynel foil) and exchange the holes and electrons through a redox mediator (traditionally I_3^-/I^- based redox couple). Though many alternatives for catalysts have been tested [3], the conventional Pt catalyst layer in DSSC is still the most widely used material due to its high catalytic activity, good adhesion, superior transparency, and high stability [4]. On the other hand, its high cost motivates to develop cost efficient deposition methods without compromising the optimum performance of the cell operation [5,6]. For small area DSSC, the Pt layer is typically produced over clean FTO-glass by drop casting, namely, placing a drop (4–5 μl) of a 5–10 mM chloroplatinic acid hydrate ($H_2PtCl_4 \cdot 6H_2O$) solution (in 2-propanol) to the center of the planned active area at room temperature, and the platinization is completed upon the thermal decomposition of the drop-cast layer at 385–410 °C [7]. With this technique, the best catalytic activity obtained in terms of charge transfer resistance (R'_{CT}) is 0.4 $\Omega\ cm^2$ with 10 $\mu g/cm^2$ platinum loading [8].

The characteristics of the catalyst layer in a DSSC affect the maximum potential power conversation efficiency related to the losses in R'_{CT}, which also depends on the electrolyte composition [9,10]. Depending on the platinization technique, the CEs fabricated with high Pt loading amounts generally provide favorable low R'_{CT} values, however, with a compromise in the short-circuit current density as a result of less sunlight harvested in case of bifacial illumination [11]. Table 1 summarizes some examples of CEs employing differently prepared Pt layers on FTO-glass along with the Pt layer transmittance and thickness outcomes as well as R'_{CT} of the electrolyte/catalyst surface. In addition to these techniques, other methods for Pt catalyst deposition include electrochemical deposition [12,13], vacuum thermal decomposition [14], electrospinning [15], spin coating [16], dip coating [17], doctor-blading

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http://dx.doi.org/10.1016/j.orgel.2017.02.015
1566-1199/

Table 1
Physical and electrical properties of CEs with various platinization methods in the presence of different electrolytes. T_{550} (%) = Pt layer transmittance at 550 nm wavelength, d (nm) = Pt layer average thickness, L (μg/cm^2) = Pt loading, MPN = 3-methoxypropionitrile, ACN = Acetonitrile, VLN = Valeronitrile.

Method	T_{550}	d	L	R'_{CT}	Electrolyte
Drop casting [8,20],[a]	96	4.6[b]	10	0.4	I^-/I_3^- in MPN
Drop casting[a,c]	93	1.2[b]	2.5	1.2	I^-/I_3^- in MPN
Drop casting[a,c]	90	2.4[b]	5.1	–	I^-/I_3^- in MPN
Sputtering [21]	92[d]	2	4.3[b]	1.2	I^-/I_3^- in MPN
Spray coating [22],[a]	88	9[b]	19	1.6	I^-/I_3^- in ACN-VLN
Electrodeposition [23]	99	0.64	1.4[b]	8	I^-/I_3^- in ACN-VLN
Electrodeposition [23]	66	6.4	14	2	I^-/I_3^- in ACN-VLN
Inkjet printing[a,c]	90	4.6[b]	9.8	0.7	I^-/I_3^- in MPN
Inkjet printing[a,c]	95	1.1[b]	2.4	1.6	I^-/I_3^- in MPN

[a] Followed by thermal decomposition.
[b] Calculated from thickness of the Pt layer = Pt loading/Pt density (21.45 g/cm^3).
[c] Current study.
[d] Data extracted from related figure or measurement results.

[18], and atomic layer deposition [19].

Here we report a versatile method of Pt precursor solution deposition, i.e., the inkjet printing of the traditional Pt precursor that is used to fabricate small area DSSC devices through the drop casting technique. Integrating the inkjet printing technique in the DSSC manufacturing proposes numerous advantages such as controlled dispensing of the solution with no waste of expensive Pt, drop-on-demand patterning as well as non-contact and direct-write materials deposition with no additional printing mask along with high purity. Moreover, realizing the inkjet printing of Pt was the last step to achieve 100% inkjet printed DSSC after inkjet printed mesoporous photoanode [24] and our inkjet printed sensitizer and electrolyte reports [25,26].

The inkjet printing for this study was performed with 5 mM chloroplatinic acid hydrate ($H_2PtCl_4 \cdot 6H_2O$) solution (in 2-Propanol) using a disposable silicon based piezoelectric inkjet cartridge storage and jetting unit. The jetting module has 16 identical nozzles embedded on a single line and each nozzle consists of a piezoelectric driven pumping chamber and an orifice to the ambient with 21.5 μm diameter. The distance between the substrate and the nozzle orifice is mostly adjusted to be minimum by the user in order to reduce the ambient interaction, which may increase the inaccuracy of the desired drop position on the substrate [27]. A user defined driving signal is applied to the chamber to form droplets and after the drops are ejected from the nozzles, they travel until the substrate and the amount of dispensed ink is altered by a user-defined parameter "drop spacing" (DS), which is the distance between the centers of two neighboring drops on the substrate. Aforementioned Pt precursor solution exhibits complete wetting over the FTO due to the low surface tension of the precursor along with the Lewis type acid-base interaction [28].

The drop formation and reliable jetting of inkjet printing inks are related to their physicochemical characteristics of the ink such as viscosity, surface tension, density, boiling point, and particle size [29]. For example, a rapid evaporation rate and big particles in the liquid can lead to a deviation in the travel path of the drop between the nozzle orifice and the substrate, eventually clogging the jetting nozzles [30,31] or an ink with sub-optimal properties may result in drops with axis-asymmetric tails or secondary unwanted droplet formation called "satellite drop" which jeopardizes printing quality as well [32]. For an ideal print output satellite-free drops following a vertical and linear trajectory with a proper speed are aimed [29,33,34].

In this study, platinization ink was characterized prior to the inkjet printing process and the jetting trajectory of the ejected drops was evaluated by implementing a special algorithm on the extracted images from stroboscopic camera built-in the inkjet printer [30]. Altered drop spacing controllably changed the amount of platinum deposited on the FTO-glass substrates, and the charge transfer resistance and transparency of the films were systematically varied. Additionally, due to the good jetting obtained we were able to pattern FTO-glass precisely without a mask (Fig. 1 a) which is vital for printed electronics [35].

2. Experimental Section

2.1. Materials

Chloroplatinic acid hydrate ($H_2PtCl_4 \cdot 6H_2O$) and all the solvents were purchased from Sigma Aldrich. All chemicals were used without further purification. 3-methoxypropionitrile based high stability electrolyte (EL-HSE), TiO_2 nanocrystalline (18-NRT) and scattering (WER2-0) pastes were obtained from Dyesol. Dye N719 was purchased from Solaronix.

2.2. Measurements

The transmittance spectra of bare and platinum coated FTO-glass substrates were captured with a UV–Vis spectrophotometer (Perkin Elmer lambda 950) using air as the background. The goniometric behaviors of the sessile drop on the FTO-glass substrate and pendant drop on air were investigated with a CAM 200 optical tensiometer (KSV instruments). The recorded images from both experiments were analyzed by using a built-in image analysis software in order to calculate the contact angle of the drop on the substrate and the surface tension of the solution in accordance with Young and Laplace equation. A scanning electron microscope (SEM) (Zeiss Ultra 55 FEG-SEM) and a MultiMode 8 atomic force microscope (AFM) equipped with a NanoScope V controller (Bruker Corporation, Billerica, MA) were used to examine the platinized surfaces. Obtained images from AFM were handled by using NanoScope 8.15 software (Bruker) without any image correction (except flattening). Keithley 2400 source meter was used to measure the current-voltage (I-V) characteristics of the solar cells (0.17 cm^2 masking area) which were illuminated in a solar simulator (Peccell Technologies, Japan, Model PEC-L01) with a Xe lamp and light intensity of 1 Sun (1000 W/m^2). The calibration of the simulator was carried out with a silicon reference solar cell (PV Measurements Inc.). Electrochemical impedance spectroscopy (EIS) data was recorded at open circuit voltage conditions using Zahner-Elektrik IM6 potentiostat under the same illumination as the photovoltaic performance measurements and the data was fitted by Zview2 software (Scribner Associates Inc.). In this study all data fitting was carried out in accordance with the typical equivalent circuit model [36].

2.3. Fabrication of counter electrodes (CE) and CE-CE symmetrical cells

Identical system components and assembly technique were employed to produce inkjet-printed and drop-cast platinum based CE-CE symmetrical cells. The reference CEs were platinized by drop casting of 5 mM $H_2PtCl_4 \cdot 6H_2O$ solution (in 2-propanol) on cleaned and UV treated FTO-coated glasses with 15 Ω/sq sheet resistance. The digitally printed samples were prepared by heating the substrate during the printing process (50 °C) and altering the amount of ejected solution systematically. After the deposition of the platinum precursor with different methods (inkjet printing and drop casting) the layers were sintered at 385 °C for 15 min. Two identical CEs were sandwiched by a Surlyn frame foil spacer