Supplementary Information.

Electrodeposited PEDOT-on-Plastic Cathodes for Dye-Sensitized Solar Cells

Jennifer M. Pringle,* Vanessa Armel and Douglas R. MacFarlane

Experimental.

3,4-ethylenedioxythiophene (EDOT, 97%) was obtained from Sigma-Aldrich and used as received. Lithium bis(trifluoromethansulfonyl)amide (LiTFSA) was purchased from 3M and used as received. The ITO-PEN (sheet resistance < 15 ohm/cm², thickness 200 μ m) and platinised plastic electrodes¹ (platinum/titanium alloy on PEN, sheet resistance < 5 ohm/cm²) were purchased from Peccell.² The poly(3,4-ethylenedioxythiophene) was prepared by electrodeposition from a 0.1M solution of EDOT in 0.1 M LiTFSA in acetonitrile. The ITO-PEN was used as the working electrode, with a large surface area platinum counter electrode and a silver pseudo reference electrode. The films (ca. 1 x 1.2 cm²) were grown at constant current (1.5mA) for between 5 and 45 seconds. The electrocatalytic activity of the PEDOT-on-ITO-PEN electrodes (1 cm²) was assessed by cyclic voltammetry using a Pt counter and Pt pseudo reference electrode, calibrated using ferrocene, in an electrochemical cell containing 10 mM LiI, 1 mM I₂ and 0.1 M LiClO₄ in acetonitrile. Scan rates of 20 mV/sec were used, and data was acquired using an EG&G PAR VMP2/Z multi-channel potentiostat. Profilometry of the PEDOT films was recorded using a Dektak 150 Profilometer.

For comparative purposes, DSSCs were assembled that utilize FTO glass anodes, in combination with the new plastic cathodes. While there is significant interest in the development of plastic anodes for DSSCs and many researcher groups, including ours, are working in this area, the performance and consistency of these anodes is currently rather limited. Thus, to enable a valid

comparison of the PEDOT-on-plastic counter electrodes with those of the standard platinised glass cathodes, all of the other parameters in the standard DSSC assembly procedure (working electrode, dye, electrolyte, filling and sealing procedure) was left unchanged.

For the solar cell assembly and testing, working electrodes were prepared by screen printing two transparent layers (~6 μ m each) from a paste of 18 nm TiO₂ particles (JGC Catalysts and Chemicals Ltd., Kitakyushu-Shi, Japan) onto FTO glass and one scattering layer of 400 nm TiO₂ (~6 μ m thick), followed by sintering (working electrode area 0.16cm²). The working electrodes were also treated with TiCl₄. Before dyeing they were heated to 500 °C then 110 °C for 30 minutes each. The electrodes were dyed by immersion into a solution of 0.5mM N719³ (Dyesol, purified⁴) in a 1:1 volume mixture of acetonitrile and tert-butyl alcohol and stored for 24 hours in the dark before rinsing with acetonitrile and drying under nitrogen.

The platinised FTO glass counter electrodes were prepared by thermal decomposition of H_2PtCl_6 in isopropanol (0.05 M) at ca. 450 °C for 15 minutes, cooled to room temperature and used immediately. The working and counter electrodes were sandwiched together and sealed with a 25 µm Surlyn (DuPont) gasket and filled with the electrolyte solution (either acetonitrile or ionic liquid-based) by back filling under vacuum. Wires were soldered onto the glass or plastic electrodes using an ultrasonic solder. For consistency, comparison of the cell performance using the different types of counter electrolyte, dye, TiO₂ layer etc.

Photovoltaic testing was performed using simulated sunlight (AM 1.5, 1000 W m⁻²) using an Oriel solar simulator with an AM 1.5 filter. A Keithley 2400 source meter was used to record the current-voltage plots, from 1000 to -300 mV, with 10 mV steps and a settling time of 30 ms for acetonitrile-based cells, 300 ms for the [emim][SCN] ionic liquid-based cell and 100 ms for the

more fluid [emim][B(CN)₄] ionic liquid cell. Two different ionic liquid mixtures were tested; either I₂ (0.2M) in 1-ethyl-3-methyl imidazolium thiocyanate ([emim][SCN], 35%) and 1-propyl-3-methylimidazolium iodide (65%) and 4-tertbutylpyridine (0.5 M), or a mixture composed of 1ethyl-3-methylimidazolium tetracyanoborate ([emim][B(CN)₄]); 1-ethyl-3-methylimidazolium iodide; dimethylimidazolium iodide; guanidinium thiocyanate; iodine; *N*-methylbenzimidazole at a molar ratio of 16:12:12:1:1.67:4.⁵

The acetonitrile-based electrolyte was composed of acetonitrile/valeronitrile (85:15 vol%), iodine (0.03 M), 4-tertbutylpyridine (0.5 M), 1-butyl-3-methylimidazolium iodide (0.6M) and guanidinium thiocycanate (0.1 M).

For the long-term stability test, the cell was stored in the dark at room temperature in air, without any extra sealing, and retested immediately prior to submission of this article (4.5 months after initial assembly).

SEM images were recorded using a JEOL840A SEM, operated at 20kV, at the Monash Centre for Electron Microscopy. A 1nm thick AuPd conducting layer was applied to the samples using a Cressington 208HR sputter coater.

Results.



Figure 1. The influence of electrodeposition time on the roughness of the PEDOT-on-ITO-PEN film. At least 2 data points were collected for each deposition time.



Figure 2. The dependence of the electrochemical activity (as indicated by the peak current density) of the PEDOT-on-ITO-PEN films on deposition time (in 0.1M tetrabutylammonium tetrafluoroborate in acetonitrile, Pt r.e., Ag wire pseudo r.e., 50 mV/sec).



Figure 3. Cyclic voltammograms of PEDOT-on-ITO-PEN, grown using a range of deposition times, compared to the platinised FTO glass and Pt/Ti alloy on ITO-PEN showing the Γ/I_3 redox couple in acetonitrile. Although the increased deposition time results in a significant increase in the roughness of the PEDOT film, there is little change in the peak currents of the CV, indicating that in the electrochemical cell the process is not limited by the electrocatalytic activity of the PEDOT but, rather, is diffusion limited. However, the thickest film, deposited for 45 seconds, shows a wider peak separation than the thinner films, which is not desirable, and thus these films were not used in the DSSC assembly and testing.





References.

- 1. M. Ikegami, K. Miyoshi, T. Miyasaka, K. Teshima, T. C. Wei, C. C. Wan and Y. Y. Wang, *Appl. Phys. Lett.*, 2007, **90**, 153122/1.
- 2. <u>http://www.peccell.com/</u>.
- 3. M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Mueller, P. Liska, N. Vlachopoulos and M. Graetzel, *J. Am. Chem. Soc.*, 1993, **115**, 6382.
- 4. M. K. Nazeeruddin, S. M. Zakeeruddin, R. Humphry-Baker, M. Jirousek, P. Liska, N. Vlachopoulos, V. Shklover, C.-H. Fischer and M. Graetzel, *Inorg. Chem.*, 1999, **38**, 6298.
- 5. Y. Bai, Y. Cao, J. Zhang, M. Wang, R. Li, P. Wang, S. M. Zakeeruddin and M. Gratzel, *Nat. Mater.*, 2008, 7, 626.