

CoS Supersedes Pt as Efficient Electrocatalyst for Triiodide Reduction in Dye-Sensitized Solar Cells

Mingkui Wang,[†] Alina M. Anghel,[‡] Benoît Marsan,[‡] Ngoc-Le Cevey Ha,[†] Nuttapol Pootrakulchote,[†] Shaik. M. Zakeeruddin,^{*,†} and Michael Grätzel^{*,†}

Laboratory for Photonics and Interfaces, Swiss Federal Institute of Technology, CH 1015, Lausanne, Switzerland, and Département de chimie, Université du Québec à Montréal, C.P. 8888, Succ. Centre-ville, Montréal, QC, Canada H3C 3P8

Received July 17, 2009; E-mail: shaik.zakeer@epfl.ch; michael.gratzel@epfl.ch

In the past decade, nanocrystalline dye-sensitized solar cells (DSCs) have attracted considerable interest in scientific research and industrial applications as a new class of low-cost solar cells.¹ Recent achievements in the long term stability under thermal and light-soaking stress have further enhanced the commercial prospects of DSCs.² The counter electrode (CE) is an important component in DSCs. Fluorine doped tin oxide (FTO) glass loaded with noble metal platinum is commonly used as the CE, Pt exhibiting high electrocatalytic activity for triiodide reduction. In view of the low abundance and high cost of platinum, several previous reports described Pt-free CEs for the DSC,³ including graphite and carbon black, carbon nanotubes, and conducting polymers. However, the device efficiencies have remained below 5% with nonvolatile electrolytes, and no long-term stability data have been reported.³ Conductive plastic substrates, based on polyethylene terephthalate (PET) or polyethylene naphthalate (PEN) films, have been applied to fabricate DSCs,⁴ and an efficiency of 7.2% was reached for a flexible dye sensitized solar cell using a Pt/ITO/PEN counter electrode.⁵ However, these cells contained electrolytes based on volatile solvents, which may permeate through the PEN film under prolonged heat stress. This problem can be avoided by using room temperature ionic liquids (ILs) such as the recently reported eutectic melts⁶ which have emerged as very attractive redox electrolytes for flexible DSC applications.

Apart from the electrolyte it is important to develop alternative noble metal-free materials capable of replacing Pt as electrocatalysts. Cyclic voltammetry experiments have shown that CoS deposited as a quasi-transparent layer on ITO/glass is more electrocatalytic than bulk Pt (disk electrode) for the reduction of triiodide.⁷ Here we report on our striking observation that CoS nanoparticles, deposited electrochemically on flexible ITO/PEN films (see Supporting Information), match the performance of Pt as a triiodide reduction catalyst in DSCs. Remarkably, the novel flexible and transparent CoS loaded counter electrodes showed also excellent stability in IL-based DSCs under prolonged light soaking at 60 °C. Clearly the CoS has an advantage for large scale application as being a much more abundant and cheaper feedstock than Pt, with the cost of cobalt several hundred times lower than that of platinum.

Electrochemical analysis employed cyclic voltammetry and impedance spectroscopy to scrutinize the catalytic activity of the CoS loaded ITO/PEN films. Figure 1a shows the current density (J) as a function of voltage (U) at 20 °C for the iodide/triiodide containing ionic liquid using a CoS derivatized plastic CE in a thin layer symmetrical cell (CE//IL//CE). For comparison, the $J-U$ curve of a Pt loaded ITO/PEN film is also presented. The system behaves

reversibly. At low sweep rates, the limiting current densities (J_{lim}) are determined by the diffusion of the ionic carriers between the two plastic electrodes, which allows us to derive the value of the diffusion coefficient of the triiodide species to be $3.6 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ (see Supporting Information), which is in good agreement with the reported values.^{6b}

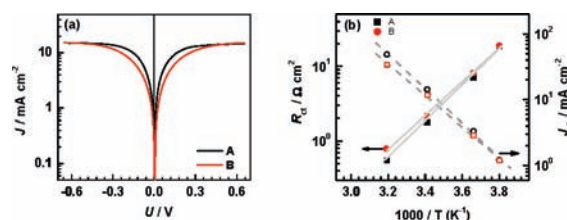


Figure 1. (a) Current–voltage characteristics of thin layer symmetrical cells at 20 °C and (b) Charge transfer resistance–temperature (left ordinate) and exchange current density–temperature data (right ordinate) in the Arrhenius coordinates: (A, black) CoS loaded PEN film and (B, red) Pt deposited PEN film.

The anodic and cathodic branches of the $J-U$ plot (Figure 1a in logarithm scale) show a larger slope for the CoS loaded CE, indicating a higher exchange current density (J_0) on this electrode in terms of the Tafel equation. Using electrochemical impedance spectroscopy, we characterized the catalytic activity of the different counter electrodes for the reduction of triiodide. Figure S1 shows the Nyquist plots obtained from various thin layer symmetrical cells with the same electrolyte composition at 20 °C. Charge transfer resistance (R_{ct}) was obtained by fitting the arc observed at higher frequencies in Nyquist plots (leftmost semicircle) to the Randles circuit shown in the inset of Figure S1. R_{ct} indicates the electron transfer resistance and thus varies inversely with the triiodide reduction activity of the different counter electrodes. Figure 1b presents R_{ct} (left ordinate) for different cells. Compared to the Pt deposited PEN film, the CoS deposited PEN film shows a higher catalytic activity. The CoS deposited PEN film has an R_{ct} of $1.8 \Omega \text{ cm}^2$ at 20 °C, a value less than that of the PEN coated with Pt ($2.2 \Omega \text{ cm}^2$) but greater than that of the widely used thermal platinized FTO/glass CE ($1.3 \Omega \text{ cm}^2$, Figure S2). The exchange current density, J_0 , is calculated from impedance spectroscopy data to be 14.2 and 11.7 mA cm^{-2} at 20 °C for the CoS deposited PEN film and Pt loaded PEN film (see Supporting Information), respectively. This demonstrates that the electrochemical triiodide reduction reaction on the CoS deposited PEN film is comparatively enhanced. The temperature dependence of J_0 (Figure 1b, right ordinate) follows the Arrhenius equation. Compared to the precious metal based catalysts (Pt deposited on ITO/PEN or FTO/glass), the CoS deposited ITO/PEN electrode shows good catalytic activity for triiodide reduction (Figure S2).⁷

[†] Swiss Federal Institute of Technology.

[‡] Université du Québec à Montréal.

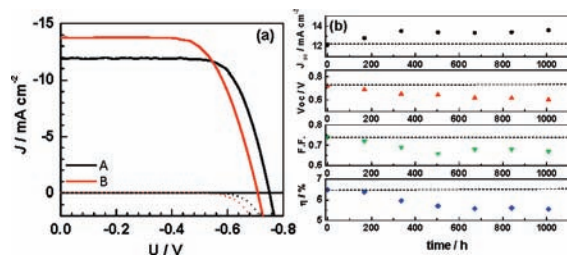


Figure 2. (a) Current–voltage characteristics measured in the dark and under illumination of AM 1.5G full sunlight (100 mW cm^{-2}): devices A and B using CoS and Pt deposited ITO/PEN film as CE, respectively. (b) Detailed photovoltaic parameters of device A measured under an irradiance of AM 1.5G sunlight during successive one sun visible light soaking at 60°C .

Figure 2a compares the performance of two Z907Na sensitized nanocrystalline solar cells employing the same eutectic ionic liquid as the electrolyte but using (A) a CoS/ITO/PEN film and (B) a Pt/ITO/PEN film as the CE under standard simulated AM 1.5 illumination at 100 mW cm^{-2} . The photovoltaic characteristics of device A were V_{oc} , 0.75 V ; J_{sc} , 11.91 mA cm^{-2} ; FF, 0.73 ; and η , 6.5% while those of device B were V_{oc} , 0.71 V ; J_{sc} , 13.7 mA cm^{-2} ; FF, 0.67 ; and η , 6.5% . It is interesting to note that V_{oc} and FF of device A were higher than those of device B which were compensated by a somewhat low J_{sc} value. The observed difference is attributed to the higher proton concentration in the case of Pt/ITO/PEN, shifting the TiO_2 conduction band toward a more positive potential. This lowers the V_{oc} and increases the J_{sc} values. A likely source of protons is the hydrolysis reaction of the titanium/ TiO_x underlayer used to support the platinum catalyst in the case of the commercial Pt/ITO/PEN electrodes. The long-term stability of device A was tested by subjecting it to light soaking at 60°C under full sunlight. As shown in Figure 2b, after 1000 h of light soaking at 60°C , the photovoltaic parameters J_{sc} , V_{oc} , and FF of device A were 13.6 mA cm^{-2} , 0.6 V , and 0.67 , respectively, indicating that the η value retained 85% of its initial value. To the best of our knowledge, this is the first time such a good stability was achieved for a DSC based on the ITO/PEN counter electrode. The novel CoS electrocatalyst is instrumental in bringing about this remarkable performance with a solvent-free electrolyte.

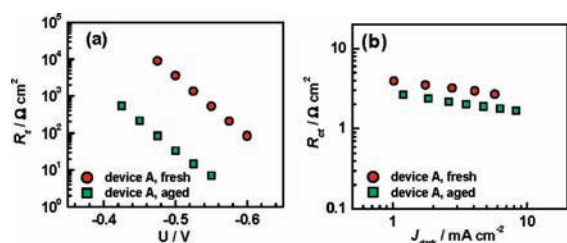


Figure 3. Equivalent circuit components derived from impedance measurements under dark conditions at 20°C for the fresh and aged device A (CoS): (a) Electron transport resistance (R_t) in the TiO_2 film and (b) Charge transfer resistance (R_{ct}) at counter electrode/IL interface.

Electronic impedance measurements were performed to elucidate any changes in the individual circuit elements for the fresh and the aged DSC devices after a long-term light soaking test. Figure 3 compares the electron transport resistance (R_t) in the mesoporous TiO_2 film and the charge transfer resistance (R_{ct}) on the CE/IL electrolyte interface. The TiO_2 conduction band edge (E_{cb}) and/or the Fermi energy level of the redox couple (E_{FP}) movement can be monitored by tracing R_t in the nanocrystalline titania film.⁸ The

logarithm of R_t , which depends on the number of free electrons in the conduction band, shows parallel behavior (Figure 3a). With an identical value of R_t set in Figure 3a, a potential difference of $\sim 120 \text{ mV}$ was found between the fresh and aged device A, which was mainly attributed to the downward shift of the TiO_2 conduction band edge. This corresponds to the drop of V_{oc} ($\sim 120 \text{ mV}$) in device A during the aging process. This effect is quite commonly observed and has been attributed to photoinduced proton intercalation into the titania.^{8c} Finally, a slight decrease in R_{ct} at the CE/IL interface (Figure 3b) was observed upon aging, which can be attributed to the enhanced triiodide reduction or better contact between the electrolyte and the CoS catalyst.⁹ Thus apart from being very active, the new catalyst is also highly durable.

In summary, we have demonstrated, for the first time, that CoS is very effective in catalyzing the reduction of triiodide to iodide in a DSC, superseding the performance of Pt as an electrocatalyst. For the first time, CoS deposited ITO/PEN films were used as the counter electrodes in DSCs yielding 6.5% efficiency under full sunlight in conjunction with a Z907 sensitizer and an eutectic melt electrolyte. Remarkable cell stability under prolonged light soaking and thermal stress was demonstrated rendering CoS an extremely interesting candidate to replace Pt in photoelectrochemical cells employing the iodide/triiodide redox couple. This breakthrough will contribute to lowering the cost of the DSC, fostering large-scale lightweight outdoor applications of mesoscopic sensitized solar cells.

Acknowledgment. Financial support from the Swiss National Science Foundation and the Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged. We thank Dr. Kevin Tabor (G24i Ltd, Cardiff) and Merck AG, Germany, for a free sample of ITO/PEN and Pt/ITO/PEN films and EMIB(CN)₄ ionic liquid, respectively.

Supporting Information Available: Experimental section and Experimental procedures and materials characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737.
- (2) Grätzel, M. *Prog. Photovolt: Res. Appl.* **2006**, *14*, 429.
- (3) (a) Murakami, T.; Grätzel, M. *Inorg. Chim. Acta* **2008**, *361*, 572. (b) Kay, A.; Grätzel, M. *Sol. Energy Mater. Sol. Cells* **1996**, *44*, 99. (c) Trancik, J. E.; Barton, S. C.; Hone, J. *Nano Lett.* **2008**, *8*, 982. (d) Saito, Y.; Kubo, W.; Kitamura, T.; Wada, Y.; Yanagida, S. *J. Photochem. Photobiol., A* **2004**, *164*, 153. (e) Xia, J.; Masaki, N.; Jiang, K.; Yanagida, S. *J. Mater. Chem.* **2007**, *17*, 2845.
- (4) (a) Pichot, F.; Pitts, J. R.; Gregg, B. A. *Langmuir* **2000**, *16*, 5626. (b) Lindstrom, H.; Holmberg, A.; Magnusson, E.; Lindquist, S. E.; Malmqvist, L.; Hagfeld, A. *Nano Lett.* **2001**, *1*, 97. (c) Dürr, M.; Schmid, A.; Obermaier, M.; Rosselli, S.; Yasuda, A.; Nelles, G. *Nat. Mater.* **2005**, *4*, 607.
- (5) Ito, S.; Cevey Ha, N.; Rothenberger, G.; Liska, P.; Comte, P.; Zakeeruddin, S. M.; Péchy, P.; Nazeeruddin, M. K.; Grätzel, M. *Chem. Commun.* **2006**, 4004.
- (6) (a) Bai, Y.; Cao, Y.; Zhang, J.; Wang, M.; Li, R.; Wang, P.; Zakeeruddin, S. M.; Grätzel, M. *Nat. Mater.* **2008**, *7*, 626. (b) Zakeeruddin, S. M.; Grätzel, M. *Adv. Funct. Mater.* **2009**, *19*, 2187.
- (7) Bourguignon, B. Marsan B. Canadian Patent CA 2,544,073, 2007; US Application 20050089681, 2004; EP Application 2004789767, National Entry, 2006.
- (8) (a) Wang, M.; Chen, P.; Humphry-Baker, R.; Zakeeruddin, S. M.; Grätzel, M. *ChemPhysChem* **2009**, *10*, 290. (b) Wang, M.; Grätzel, C.; Moon, S.; Humphry-Baker, R.; Rossier-Iten, N.; Zakeeruddin, S. M.; Grätzel, M. *Adv. Funct. Mater.* **2009**, *19*, 2163. (c) Wang, Q.; Zhang, Z.; Zakeeruddin, S. M.; Grätzel, M. *J. Phys. Chem. C* **2008**, *112*, 7084.
- (9) (a) Toivola, M.; Peltokorpi, L.; Halme, J.; Lund, P. *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 1733. (b) Andrade, L.; Zakeeruddin, S. M.; Nazeeruddin, M. K.; Ribeiro, H. A.; Mendes, A.; Grätzel, M. *ChemPhysChem* **2009**, *10*, 1117. (c) Zaban, A.; Zhang, J.; Diamant, Y.; Meled, O.; Bisquert, J. *J. Phys. Chem. B* **2003**, *107*, 6022.

JA905970Y