

Semiconductor Electrodes

XXXIX. Techniques for Stabilization of n-Silicon Electrodes in Aqueous Solution Photoelectrochemical Cells

Fu-Ren F. Fan,* Bob L. Wheeler,* and Allen J. Bard*

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

and Rommel N. Noufi*

Solar Energy Research Institute, Photo Voltaic Division, Golden, Colorado 80401

A number of different approaches have been used in the stabilization of small band gap n-type semiconductors against photocorrosion in photoelectrochemical (PEC) cells. Such stabilization is necessary in the design of practical cells for conversion of solar energy to electricity, and is of critical importance in photoelectrosynthetic systems where the photogenerated holes produce species (e.g. O_2 , Cl_2) at quite positive potentials at the semiconductor surface. 1) One approach involves the utilization of thin films of metals (1) or semiconductors (2) to protect the surface. For example, n-GaAs electrodes can be stabilized in a solution of Fe(II) EDTA by a thin ($\leq 60 \text{ \AA}$) film of gold (3). 2) Use of nonaqueous solvents (4) in PEC cells has been shown to aid in the stabilization of the semiconductor electrode by decreasing the extent of solvation of the oxidation products. A similar approach involves the use of concentrated electrolytes in aqueous solutions. Wrighton and co-workers (5) have recently demonstrated that n-MoSe₂ and n-MoS₂ electrodes are stable in concentrated LiCl solutions even in the presence of chlorine evolution. 3) The deposition of polymer layers on the semiconductor surface can also decrease photocorrosion. Noufi and co-workers (6) have described the stabilization of n-GaAs and n-Si by the electrodeposition of polypyrrole films on the surface.

We demonstrate here that by combining these approaches even better stabilization can be accomplished and describe the photo-oxidation of Fe^{2+} at n-Si electrodes covered by thin gold and thicker polypyrrole film and immersed in a concentrated electrolyte aqueous solution.

Electrodes were fabricated from n-Si single crystals (0.4 to 0.6 Ω cm) donated by Texas Instruments. Ohmic contacts were made with In-Ga alloy. They were connected to a copper wire with silver epoxy cement. The crystals were mounted in a glass tube with all sides insulated with 5 min epoxy and covered by silicone rubber sealant leaving an area of 0.2-0.5 cm^2 exposed. The surfaces of some crystals were polished with sand paper (600 grit), followed by etching in conc. HF for 15-20 sec. This pretreatment gave no improvement, compared with these unpolished electrodes, in the adhesion of the polypyrrole films and in the stability of the polypyrrole-covered n-Si electrodes. Immediately prior to electrodeposition of polypyrrole or Au, the electrodes were etched, if not otherwise mentioned, with an etchant containing $HNO_3:HF:acetic$ acid (3:3:1) and bromine (one drop of Br_2 per 100 ml of solution) for 10-15 sec and then with conc. HF for 15-20 sec. This etching procedure produced more efficient etching than that simply with conc. HF. The electrodes were then rinsed thoroughly with water, methanol and acetonitrile.

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The electroplating of Au on n-Si was carried out at -1.6 V vs. SCE from a gold plating solution that was prepared by mixing 30 ml of VIGOR fine gold plating solution (Vigor Co. New York, NY) with 20 ml of 2.5 M NaCN solution. The polypyrrole films were synthesized potentiostatically (0.75 V vs. SCE) with the electrode surface simultaneously illuminated with the red light ($> 590 \text{ nm}$, 100-150 mW/cm^2) from a 450 W Xe lamp. The solutions used in this electrodeposition, $CH_3CN/0.1 \text{ M}$ tetra-n-butylammonium BF_4^- , were prepared as reported by Noufi et. al. The thicknesses of the polypyrrole and the Au films were estimated from the charge measured during electrodeposition, as discussed by Noufi et. al. (6).

The PEC behavior of naked or modified n-Si electrodes were compared in three different redox solutions: (A) 0.5 M $FeSO_4$ and 0.15 M $Fe_2(SO_4)_3$ in 0.5 M H_2SO_4 ; (B) 0.15 M $FeSO_4$ and 0.15 M $Fe_2(SO_4)_3$ in 0.1 M Na_2SO_4 at pH 1; (C) 0.5 M $FeCl_2$, 0.15 M $FeCl_3$ and 1 M HCl in 11 M LiCl.

For comparison, the light source used in all experiments, if not otherwise mentioned, was a sunlamp, which was separated from the PEC cell by a water IR filter of path length $\sim 14 \text{ cm}$. The light intensity impinging on the window of the PEC cell was 41 mW/cm^2 . The stability of the photoelectrodes was tested here based on two criteria: (A) constant

steady-state photocurrent vs. time of illumination at a load resistance of $10\ \Omega$ and (B) constant fill factor (f.f.) and onset photopotential (V_{on}) (or invariant shape of the photovoltaammtric curve) with time of illumination.

The photocurrents of naked n-Si photoelectrodes under the illumination with a light intensity of $41\ \text{mW}/\text{cm}^2$ decayed to small values ($< 20\ \mu\text{A}/\text{cm}^2$) within three potential scan cycles between -0.2 and $0.7\ \text{V}$ vs. SCE at $100\ \text{mV}/\text{sec}$ in solution (A), (B), or (C). The attachment of polypyrrole film ($\sim 3500\ \text{\AA}$) on n-Si electrodes did, as reported by Noufi et al. (6b), decrease the rate of photodegradation of n-Si electrodes in both electrolyte solutions (A) and (B). As shown in Fig. 1(A), the photoelectrodes still showed fairly ideal photovoltaammtric curves even after ten potential scan cycles between -0.2 and $0.7\ \text{V}$ vs. SCE. However, the V_{on} shifted in a positive direction with scanning. The photocurrent (through a load resistance of $10\ \Omega$) produced by a PEC cell, composed of a polypyrrole coated single crystal n-Si photoelectrode and a Pt counter electrode in solution (A) or (B), decayed continuously with time, indicating the occurrence of slow passivation of the electrode even under these conditions. (See also curve a in Fig. 2.)

By the addition of $11\ \text{M}$ LiCl to the redox solution (solution C) the suppression of the anodic photodegradation of the photoelectrodes was further improved. As shown in curve b of Fig. 2, the photocurrent decayed initially and then reached a steady state value ($2.1\ \text{mA}/\text{cm}^2$) after 2-3 hrs upon continuous illumination with a light intensity of $41\ \text{mW}/\text{cm}^2$. Parallel to this behavior, the photovoltaammtric curves changed continuously during the first 2-3 hrs of illumination and then reached a steady state. (See Fig. 1(B).) The drawn-out character of the steady state photovoltaammtric curves shown in curve d of Fig. 1(B) suggests that an insulating layer was formed on the n-Si surface or that the polypyrrole film was photodegraded during the first 2-3 hrs of illumination. The results shown in the following experiments involving a gold underlayer favor the first possibility.

The third type of photoelectrode was prepared by electroplating $10\text{-}20\ \text{\AA}$ of Au on n-Si and then overlaying $\sim 3300\ \text{\AA}$ of polypyrrole on the Au photoelectrochemically. This type of electrode has been tested in solution (C). Very stable photocurrent and photovoltaammtric curves were obtained with extended time of illumination. As shown in Fig. 1(D), the fill factor and the onset photopotential were only slightly changed after illumination with $41\ \text{mW}/\text{cm}^2$, giving a steady state photocurrent

density of $3.1\ \text{mA}/\text{cm}^2$ at a load resistance of $10\ \Omega$ for more than 48 hrs. Only a slight decay of the photocurrent was observed, even in the first 2-3 hrs of illumination (see wave c in Fig. 2), indicating that the $10\text{-}20\ \text{\AA}$ of Au underlayer together with the polypyrrole coating suppresses the photodegradation of the n-Si electrodes quite effectively. However, the $10\text{-}20\ \text{\AA}$ of Au layer alone could not stabilize the n-Si electrode even in solution (C).

Under a light intensity of $41\ \text{mW}/\text{cm}^2$, a PEC cell composed of one of the third type of photoelectrodes and one Pt counter electrode in solution (C) gave a short-circuit photocurrent density of $3.5\ \text{mA}/\text{cm}^2$, a fill factor of 0.65 and an open-circuit photovoltage of $0.40\ \text{V}$, corresponding to a power conversion efficiency of 2.3%. Under illumination with a stronger light intensity ($150\ \text{mW}/\text{cm}^2$ from a tungsten-halogen lamp), the photocurrent at a load resistance of $10\ \Omega$ decayed very slowly with time ($\sim 10\%$ decrease of the initial photocurrent, $12\ \text{mA}/\text{cm}^2$, after the first 8-hr illumination and 5% more decrease after the second 8-hr illumination). The decay rate of the photocurrent increased with an increasing temperature of the PEC cell.

In conclusion, polypyrrole films on a metal underlayer on n-Si photoelectrodes substantially improves their stability against photodegradation in an aqueous electrolyte containing $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple. The addition of $11\ \text{M}$ LiCl to the solution further improves the suppression of the anodic photodegradation. The increased stability can be attributed to the following: 1) The highly concentrated LiCl solution substantially decreases the activity of H_2O thus decreasing its reactivity with the electrode surface (5). 2) Li^+ and/or Cl^- may also diffuse into the interstitial regions of the polypyrrole film and decrease penetration of water. 3) Both the gold and polypyrrole serve to remove photo-generated holes rapidly from the silicon surface before degradation occurs. In this way, they are analogous to stabilizing solution redox species (e.g. Se^{2-}) which are rapidly oxidized preferentially. 4) The gold layer improves the adhesion of the polypyrrole to the Si surface and blocks pinholes in the film.

Since the polypyrrole film is highly colored, it blocks some of the light impinging on the electrode surface and thus decreases the efficiency. Improvements should be possible by optimizing the metal and polymer layer thicknesses and by investigating electrolytes other than the $\text{Fe}^{3+}/\text{Fe}^{2+} - \text{LiCl}$ systems to improve both the solar energy conversion efficiency and the stability.

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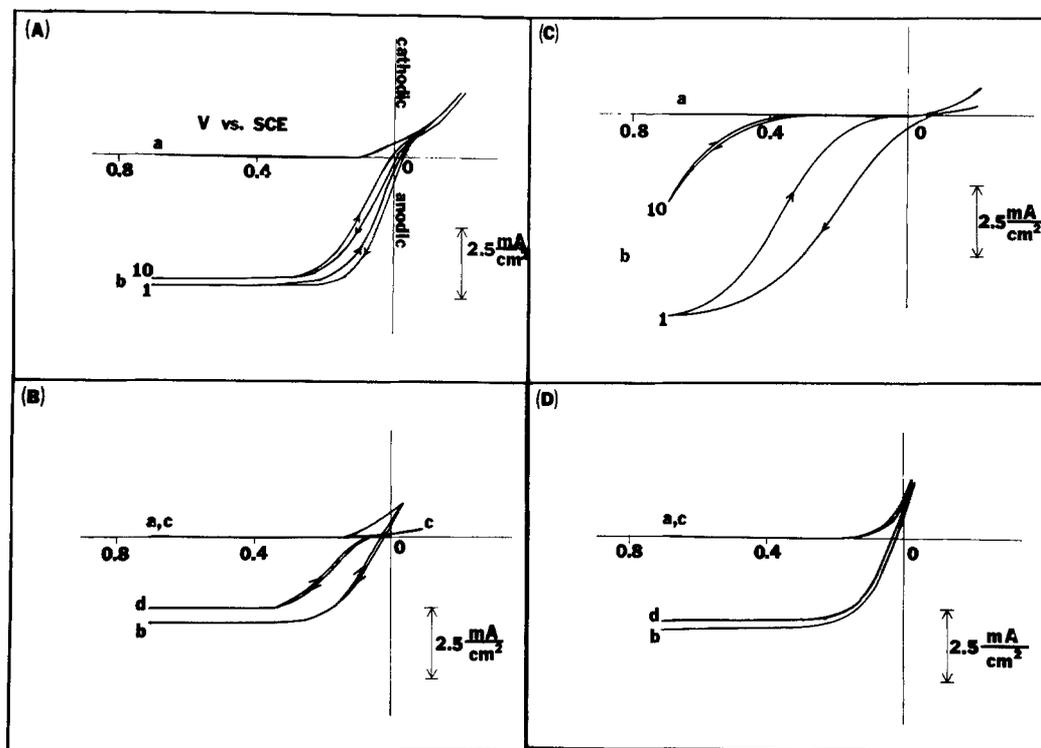


Fig. 1 Voltammetric curves of modified n-Si electrodes in the dark and under illumination (41 mW/cm^2 from a sunlamp). Scan rate 100 mV/sec . (A) n-Si electrode coated with $\sim 3500 \text{ \AA}$ of polypyrrole in 0.5 M FeSO_4 , 0.15 M $\text{Fe}_2(\text{SO}_4)_3$ and 0.5 M H_2SO_4 . (a) dark, (b) under illumination; 1: the first cycle; 10: the tenth cycle. (B) n-Si electrode coated with $\sim 3300 \text{ \AA}$ of polypyrrole in 0.5 M FeCl_2 , 0.15 M FeCl_3 , 1 M HCl and 11 M LiCl . (a) Fresh electrode in the dark, (b) Steady state photovoltammeteric curve of fresh electrode, (c) Voltammeteric curve of the same electrode after illumination for more than 3 hrs., (d) Steady state photovoltammeteric curve of the electrode after illumination for more than 3 hrs. (C) n-Si electrode coated with 20 \AA of Au in 0.5 M FeCl_2 , 0.15 M FeCl_3 , 1 M HCl and 11 M LiCl . (a) dark, (b) under illumination; 1: the first cycle; 10: the tenth cycle. (D) n-Si electrode coated with $\sim 15 \text{ \AA}$ of Au and then with $\sim 3300 \text{ \AA}$ of polypyrrole in 0.5 M FeCl_2 , 0.15 M FeCl_3 , 1 M HCl and 11 M LiCl . (a) Fresh electrode in the dark, (b) Steady state photovoltammeteric curve of fresh electrode, (c) Dark voltammeteric curve of the same electrode after illumination for 48 hrs., (d) Steady state photovoltammeteric curve of the electrode after illumination for 48 hrs.

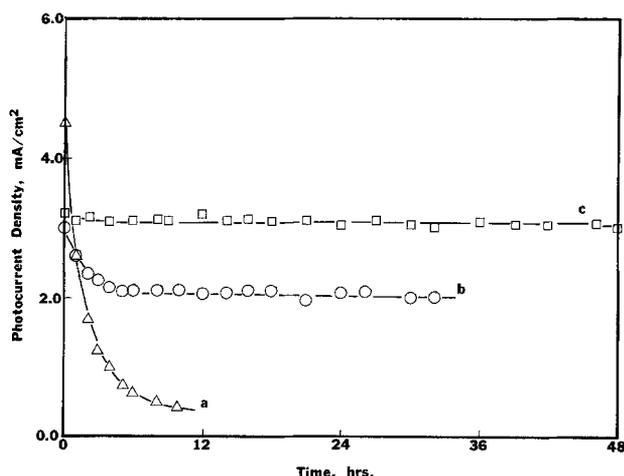


Fig. 2 Photocurrent (at load resistance of 10 Ω) vs. time. Light intensity 41 mW/cm^2 from a sunlamp. (a) n-Si electrode coated with $\sim 3500 \text{ \AA}$ of polypyrrole in 0.5 M FeSO_4 , 0.15 M $\text{Fe}_2(\text{SO}_4)_3$ and 0.5 M H_2SO_4 . (b) n-Si electrode coated with $\sim 3300 \text{ \AA}$ of polypyrrole in 0.5 M FeCl_2 , 0.15 M FeCl_3 , 1 M HCl and 11 M LiCl . (c) n-Si electrode coated with $\sim 15 \text{ \AA}$ of Au and then with $\sim 3300 \text{ \AA}$ of polypyrrole film in 0.5 M FeCl_2 , 0.15 M FeCl_3 , 1 M HCl and 11 M LiCl .

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