et al[9] investigated the 0 ls peak intensities as a function of the radiation angle of x-ray beam, and found no intensity change at all. Thereupon, they concluded that the 0 ls species which gives a peak at 531.3eV can exist only on the surface.

Winograd *et al*[7,11] have assumed that Ni^{3+} ion can be formed on the cation defect sites of surface NiO, and assigned the peak at 531.3eV to surface Ni_2O_3. This assignment, however, fails to account for the binding energy shift of 0^{2-} ion. As regards to Ni_2O_3, the binding energy shift of Ni $2p_{3/2}$ should be expected, but not that of the 0 ls. In addition, there are little possibilities that the peak might be due to NiO(H) as stated in section (I) of the results.[3,4,14]

Acknowledgements. This work was supported by a grant from the Korea Science and Engineering Foundation.

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Comparisons of Stability and Spectral Response of n-Si Electrodes Modified with Polyaniline and Polypyrrole in Aqueous Solutions[1]

Jin-Doo Kim and Kang-Jin Kim*

Department of Chemistry, Korea University, Seoul 136

Jung-Kyoon Chon

Department of Chemistry, Han Kuk University of Foreign Studies, Seoul 131. Received April 17, 1987

Modification of n-Si electrodes coated by photogalvanostatically with polyaniline and polypyrrole in aqueous solutions considerably enhanced the stability and the spectral response of the photoelectrodes. A polypyrrole coated electrode incorporated with redox couple $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ yielded a photocurrent density of 400 $\mu A/cm^2$ for about 120 hours. Broad spectral responses over 300-850 nm were observed for both polymer coated electrodes of which polypyrrole coated one showed better current conversion efficiency.

Introduction

Recently the use of n-type semiconductors as the photoanodes to the electrolysis of water has aroused a great deal of interest which stems from the expectation that the light-stimulated electrode process may offer fairly good means of converting solar energy to electrical or chemical energy.[2-5] To achieve an efficient utilization of the immense solar energy, it is desirable for an semiconductor electrode to possess the small band gap among other things.[6] Theoretical calculations show that the optimum band gap of a phototelec-

trode for the electrolysis of water is 1.3 ± 0.3 eV which corresponds to the absorption of light of 1000 ± 250 nm.[3,7] An n-Si semiconductor has a favorable band gap of 1.14 eV and it is one of the cheapest semiconductors, well-understood in the solid state physics, and most nearly perfect crystalline material available. Unfortunately, an electrode of small band gap, including n-Si, has a drawback of corrosion in aqueous electrolyte solutions under illumination. The photogenerated holes not only corrode the semiconductor itself, but may introduce surface states where the recombination reactions with electrons convert the absorbed energy into

Polymer Coated n-Si Electrode

Bull. Korean Chem. Soc., Vol. 8, No. 5, 1987 363

heat or radiation.[8] Although n-type semiconductors such as TiO_2 and SnO_2 are subject to less photocorrosive reactions, they capture only small fraction of the solar spectra in the short wavelength region.

One promising approach of several proposed techniques to defeat the photocorrosion is to modify the surface of photoelectrode with conducting polymer films, such as polypyrrole, polyaniline, polythiophene, and poly-N-vinylimidazol.[9,10] The polymer-coated n-Si electrode exhibited the decrease of corrosion and the enhancement of stability, which are attributed to the effective injection of the photogenerated holes to the electrode surface across the polymer film[11] in addition to the isolation of the semiconductor surface from the electrolyte solution.

There are, however, few reports of extensive studies on modified electrode coated in particular from aqueous solutions and little thought seems to have been given to the spectral response of the photoelectrodes. To obtain further insight on better stability for the purpose of studying water electrolysis, in the present paper, some characteristics were investigated by cyclic voltammetry on the n-Si electrodes modified by deposition with polyaniline and polypyrrole from aqueous solutions and the results were compared with those of modified Pt electrodes.

Experimental

Chemicals. Aniline(99%) and pyrrole(96%) obtained from Fluka were purified by vacuum distillation.[12] Tetraethylammonium tetrafluoroborate, tetrabutylammonium chloride, and tetrabutylammonium bromide from Fluka were used as supporting electrolytes without further purification.

Electrodes. The n-Si electrodes used were constructed from a prepolished, (100) orientation, single crystal wafer doped with phosphine at $2 \times 10^{18}/cm^3$. A square piece of about 0.25 cm^2 was cut from the wafer, back ohmic contact was made with chemically vacuum diposited Al, and a Teflon-coated Cu wire was connected to the contact with silver epoxy, Dotite type D-500(Fujikura Kasei Co.). All surfaces except the front were insulated with RTV silicone rubber adhesive (Steven Industries, Bayone, N.J.). Before using, the electrodes were etched for 20-30 seconds in a 4:1:1 HNO_3:HF:CH_3COOH solution and throughly rinsed with doubly distilled water.

Electroconducting polypyrrole films were deposited electrochemically onto n-Si electrodes and Pt electrodes. Film deposition was monitored by measuring the charge passed and the film thicknesses were estimated assuming 24 mC/cm^2 charge density yielded a 0.1 μm film.[13-15] Polyaniline films were deposited similarly.[16,17] All polymer coated electrodes were kept in appropriate electrolyte solutions to avoid film degradation.

Electrolytic Cell. The electrochemical experiments were carried out in a three compartment cell which consisted of a photoelectrode as a working electrode, a Pt coil counter electrode, and a Ag/AgCl reference electrode. The working and the counter compartments were separated by a fine fritted glass disc, and the reference compartment was connected through a Luggin capillary to the working compartment. Two sets of glass capillaries were used to remove dissolved oxygen and to prevent oxygen to dissolve into the solution, respectively, with purified N_2 gas.

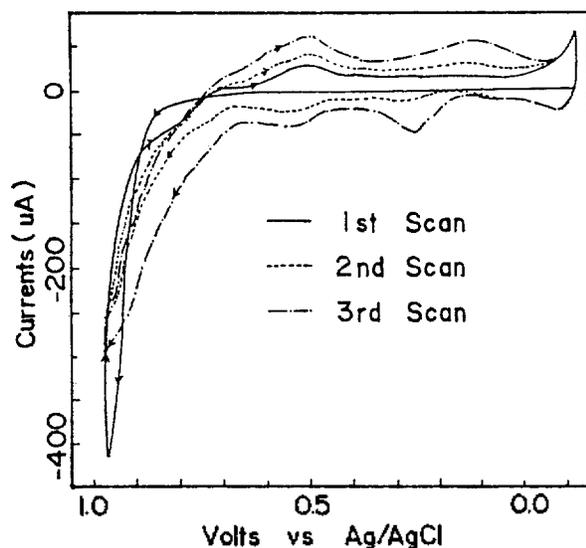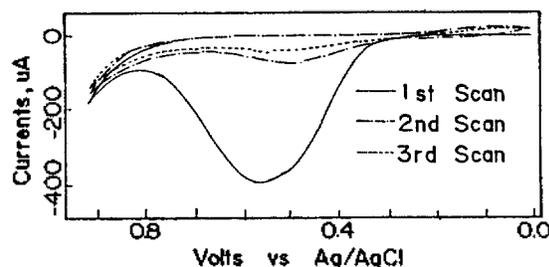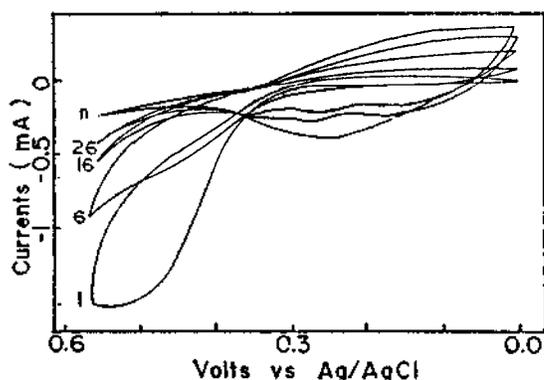**Figure 1.** Cyclic voltammograms of 0.1 M aniline in 1.0 M H_2SO_4 at a Pt electrode. Scan rate was 50 mV/sec.

Figure 2. Typical cyclic voltammograms of 0.010 M pyrrole in 0.5 M KNO_3 at a Pt electrode. Scan rate was 100 mV/sec.

Instruments. A potentiostat/galvanostat system of conventional adder design was constructed in this laboratory and calibrated with a keithley 610 C solid state electrometer. In addition, a good potential reading was confirmed by a polarogram of a solution of $CdSO_4$ in HCl and an excellent reproducibility was obtained by a cyclic voltammetry of a $K_3Fe(CN)_6$ solution at a Pt wire. An XYR-2A X-Y recorder (TOA Electronics Ltd, Japan) was employed to record the current/potential curves. The 150W xenon lamp installed in a Hitachi 650-60 spectrofluorimeter was utilized as a light source and the electrolytic cell was inserted into the cell compartment of the spectrofluorimeter for measurements.

Results and Discussion

Cyclic Voltammogram. Figure 1 illustrates typical cyclic voltammograms between -0.13 V and 0.94 V of 0.1 M aniline in 1.0 M H_2SO_4 at a Pt electrode. On the first sweep, from approximately 0.86 V it shows the anodic current associated with the oxidations of aniline and base electrolyte solution. On the reverse sweep the current is higher than on the forward one over 0.80 + 0.08 V. This occurs because the coated polyaniline faciliates the oxidation of aniline, which is a common observation when a surface phase is formed by a nucleation and growth mechanism.[18] The cathodic peaks at 0.48 and 0.095 V and the anodic peaks at 0.24 and 0.56 V on the second sweep are presumably due to the reduction and

364 *Bull. Korean Chem. Soc., Vol. 8, No. 5, 1987*

Jin Doo Kim et al.

Figure 3. Repeated cyclic voltammograms of 0.010 M pyrrole in 0.5 M KNO_3 at a Pt electrode. Scan rate was 50 mV/sec. The n is larger than 50.

the oxidation of the polyaniline film coated on the Pt, respectively. The current near the switching potential on the second sweep is lower than that on the previous sweep, which implys that the polyaniline coated Pt electrode appears to require larger overvoltage for oxygen evolution than a bare Pt electrode. On further sweep, all peaks were increased due to the growth of the polymer film.

Figure 2 shows the cyclic voltammograms of 1.0×10^{-2} M pyrrole in 0.1 M KNO_3 at a Pt electrode. The initial sweep yielded a broad anodic current probably due to the multiple oxidation reactions involved. Apparently their oxidation potentials are so close each other that the peaks are heavily overlapped. However, the anodic current at around 0.55 V continued to be very low and very little oxidation is seen from the second sweep while the anodic reactions near 0.50 V are still discernible. It is speculated that the irreversible damage on the polypyrrole film caused by taking the potential as positive as 0.92 V yielded a non-efficient conducting surface layer of decomposition product.[18]

It is noted between 0.00 V to 0.35 V of Figure 2 that the current is slightly increased in the second sweep. To observe this more clearly the sweep was reversed at 0.56 V and the result is depicted in Figure 3. The current around 0.50 V was progressively decreased as the sweep proceeded, because that the oxidation rate of pyrrole at a polypyrrole coated Pt electrode was slower than that at a bare Pt electrode. However, both anodic and cathodic currents were continuously increased on repeating the sweep in the potential region up to about 0.35 V where the currents were presumably associated with the oxidation and the reduction of the polypyrrole film, respectively. The gradual increase in current certainly reflects the increase of surface area due to the film growth.

The photocurrents of n-Si electrode coated with polypyrrole were evaluated for three different methods of deposition from a KNO_3 aqueous solution: photogalvanostatic deposition with a current density of 400 A/cm² for 1 minute and with 40 A/cm² for 10 minutes, and photopotentiostatic deposition at 0.8 V. Because of the difficulties of reproducing the substrate surface and the film thickness, the effect of deposition method on the photocurrent were considered rather qualiative. Nevertheless, Figure 4 demonstrates that the net photocurrent is the highest for the photogalvanostatic deposition with a larger current density. Presumably semiconductor photodegradation[19] occurred to a less extent in the process during deposition.
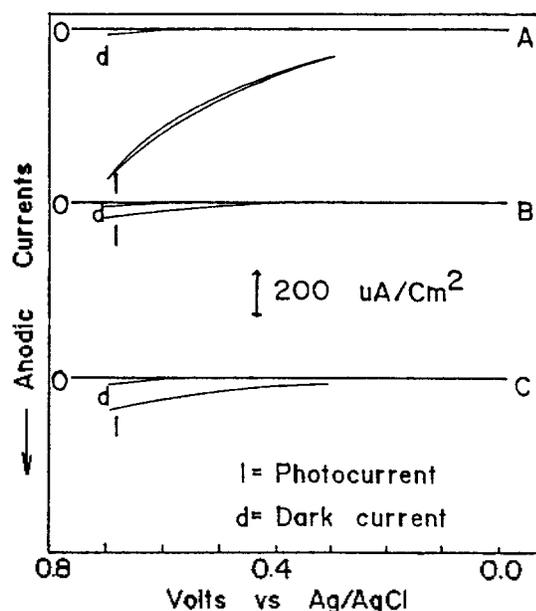
Figure 4. Cyclic voltammograms of polypyrrole-coated n-Si electrodes prepared by (a) photogalvanostatically with 400 A/cm² for 1 minute; (b) photopotentiostatically at 0.80 V, and (c) photogalvanostatically with 40 A/cm² for 10 minutes, under a 150 W Xe lamp. Slitwidth was 20 nm.
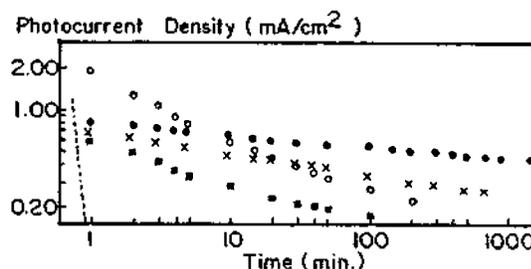

Figure 5. Comparisons of anodic photocurrent densities under a 150 W Xe lamp with 20 nm slitwidth for (○) polypyrrole-coated n-Si electrode in 1.0 M KCl; (●) Fe-PP-n-Si in 1.0 M KCl; (×) polypyrrole-coated n-Si electrode in 1.0 M $K_4Fe(CN)_6$; (■) polyaniline coated n-Si electrode in 1.0 M KNO_3; and (---) bare n-Si electrode in 1.0 M KNO_3. A potential of 0.8V was applied to ensure conduction condition.

Polyaniline film on n-Si electrode exhibited a similar photocurrent-potential behavior as polyaniline, namely, the photogalvanostatic deposition with a current density of 400 A/cm² for 1 minute showed the highest net photocurrent.

Stability. The band gap of n-Si semiconductor, 1.14 eV, is highly favorable for optimum utilization of solar evergy. However, in contact with aqueous media the semiconductor becomes very rapidly passivated under illumination. To evaluate a long-term sustained photocurrent flow a few representative modified n-Si electrodes were compared for stability against degradation.

Figure 5 shows the variation of anodic photocurrent density versus time for the electrodes studied in aqueous solutions. Dark currents were corrected for each measurement. The comparsions were made with a polyaniline coated n-Si electrode in 1.& M KCl, a polypyrrole coated n-Si in 1.& M K_4Fe $(CN)_6$, and a Fe-PP-n-Si in 1.0 M KCl, where the last electrode was a polypyrrole coated n-Si electrode incorporated
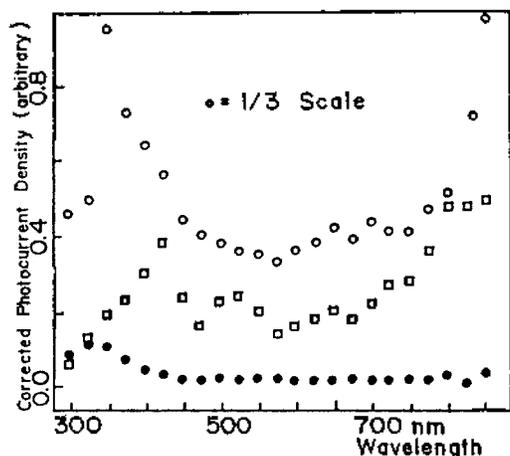
Figure 6. Spectral dependence of corrected photocurrent densities for (●) bare, (□) polyaniline-coated, and (○) polypyrrole-coated n-Si electrodes.

with Fe $(CN)_6^{4-}$ within the polymer film by a potential cycle between -0.30 and 0.70V for 10 hours in 1.0 M $K_4Fe(CN)_6$.

The longest stability, as far as has been checked, was obtained from the Fe-PP-n-Si electrode. The redox couple, $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$, incorporated within the polypyrrole film appeared to cause a fast charge transfer between the couple and the photogenerated holes. The passivation by the holes seemed to be greatly reduced as a result. Furthermore, the Fe-PP-n-Si electrode had a nearly constant photocurrent density of about 400 $\mu A/cm^2$ for at least 120 hours which is comparable to the best reported stability with a similar electrode.[20] However, the incorporated redox couples were slowly exchanged with anions of supporting electrolyte if immersed for a long period of time[19] as evidenced by the experimental observation that the photocurrent density was diminished much faster than that of which the electrode was kept in $K_4Fe(CN)_6$. In general, conducting polymer coating greatly enhanced the stability of a bare n-Si with which photocurrent decayed to the level of background within a minute. Polypyrrole yielded more stable photoelectrodes than polyaniline.

The initial loss of photocurrent for both Fe-PP-n-Si and polypyrrole-coated n-Si in $Fe(CN)_6^{4-}$ was likely caused by the absorption of the anion. The absolute values between electrodes may not belegitimate to compare due to difficulties of reproducing film thickness and substrate surface as pointed above.

Photocurrent Action Spectra. In order to compare the relative current conversion efficiencies for modified n-Si electrodes the corrected photocurrent spectra were obtained as a function of wavelength of incident radiation over the region of 300-850 nm with a wavelength scan rate of 480 nm/min. For the correction the measured photocurrent density was divided by the lamp intensity which was monitored by a Spectraphysics model 404 power meter.

Figure 6 shows typical results for a polyaniline coated and a polypyrrole coated n-Si electrodes in 1 M KNO_3 at 1.0 and 0.8 V, respectively. Also included are the data of a bare n-Si electrode which was pretreated before measuring the action spectrum by illuminating it with the lamp at 1.0 V until the photocurrent became a nearly steady value. It can be stated from the gragh that the polypyrrole coated electrode has higher quantum efficiency by a factor of roughly six over the

spectral region studied than the polyaniline coated one. The bare n-Si electrode was considered to be almost passivated before measurement. The spectra show broad maxima near 350 and 400 nm which approximately coincide with the absorption minima of polyaniline and polypyrrole films,[10,17] respectively, when extrapolated to the respective potentials applied in this study. It is also noted that the photocurrent densities of the polymer coated electrodes tend to show a slight increase towards the long end of the spectra where two opposing effects are possibly involved. Since the photocurrent arises mostly from the interband excitation,[21] it starts to flow at around 1100 nm which very closely corresponds to the band gap of an n-Si semiconductor. Consequently the efficiency of the interband energy transfer should be high with a photon energy close to the band gap and the photocurrent of n-Si electrode will be continuously increasing towards the long wavelength region. On the other hand, polyaniline and polypyrrole themselves absorb strongly beyond about 600 nm.[10,17] Therefore, the photocurrent gained by the efficient energy transfer may be largely offset by the absorption of light by the polymer film, leaving only a slight tendency of increment. These spectral responces are encouraging because the spectral energy of sunlight at the earth's surface has considerably large intensities up to 1100 nm with a maximum near 450 nm.[22]

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Chromatographic Behavior of Cryptand[2,2] Modified Resin on Metal Cations

Moo-Yul Suh*, Tae-Yoon Eom, and In-Suk Suh

Korea Advanced Energy Research Institute, P.O.Box 7 Daejeon 300-31

Si-Joong Kim

Department of Chemistry, Korea University, Seoul 132. Received May 18, 1987

Cryptand[2,2] was grafted to low crosslinked styrene-divinylbenzene copolymer by substitution reaction with chloromethylated styrene-divinylbenzene copolymer. This resin was stable in concentrated acid and base, and showed a good resistance to heat. The pH, time, and concentration dependence of the adsorption of metal ions by this resin were studied. Studies on the chromatographic separation of lanthanides, Cu^{2+}, and UO_2^{2+} were also carried out with various eluents. These studies demonstrate that this resin has the applicability to the preconcentration and separation of metal ions.

Introduction

Many investigations have been devoted to the synthesis of macrocyclic compounds, their complexing properties, characterization of the solid complexes, and selective complex formation of the compounds with metals[1-4]. Recently, these compounds were used in the field of analytical chemistry such as solvent extraction, chromogenic reagent, ion-selective electrode, and liquid chromatography[3,5-8].

In liquid chromatography, macrocyclic compounds were used as a coating material on silica gel or as a modifier of an eluent to separate various cations, anions, organic compounds, and optically active compounds[3,7-10]. Polymers modified with macrocyclic compounds were also used rather frequently as a stationary phase due to their excellent properties in chromatography[3,11-13]. Many kinds of these polymeric compounds which can selectively adsorb inorganics and organic compounds have been prepared by condensation, by substitution, and by copolymerization with various crown ethers or cryptands. Although several attempts have been made to separate alkali and alkaline earth cations by the pioneering works of Blasius *et al.*[11-13], the study of the applications to the heavy metals containing the lanthanides and actinides was not found, so far.

In a previous paper[14], we reported that cryptand[2,2] forms a stable complex with UO_2^{2+} but not with lanthanide cations of +3 valence state in aqueous solution. It is of interest to extend these particular properties of cryptand[2,2] to analytical work. In this study, we describe the synthesis of styrene-divinyl benzene(DVB) resins modified with cryptand[2,2] as a functional group, their adsorption characteri-

stics for various metal cations, and their application to the chromatographic separation of rare earth cations, UO_2^{2+}, and Cu^{2+}.

Experimental

Reagents. Cryptand[2,2] was the reagent grade chemical obtained from Merck and other chemicals used for the preparation of resin carried a certified purity. All other reagents were in analytical grade and used without further purifications. N(Me)$_4$OH was prepared from N(Me)$_4$Cl using the method of G. Anderegg *et al*[15]. N(Me)$_4$NO$_3$ stock solution was prepared by neutralizing the N(Me)$_4$OH solution with conc-HNO$_3$.

Synthesis of Resin. The styrene-DVB copolymer(II) modified with cryptand[2,2] (I) was synthesized as illustrated in Figure 1. The fine bead of styrene-DVB was prepared by suspension copolymerization of styrene and DVB at 90°C as described elsewhere[16-18]. The crosslinkages of copolymers were adjusted to 1% and 4% by varying the amount of DVB added in the reaction mixture.

Chloromethylation of dried styrene-DVB copolymer was carried out by refluxing with chloromethylmethylether for 5 hours. A catalytic amount of ZnCl$_2$ was added to the mixture. After the reaction was completed, the solution was removed by decantation and the product was washed successively with dioxane-water, water and methanol, and was dried at 50°C for 3 days in an oven.

The substitution reaction of chloromethylated copolymer (III) with cryptand[2,2] proceeded as follows. Five grams of chloromethylated copolymer was added to 200m*l* of benzene