

# An Anion-Permeable Polymeric Coating for the Protection of a Semiconductor Photoelectrode against Decomposition

J. M. BOLTS and R. P. MARIELLA, JR.,\* *Allied-Signal Corporation, P.O. Box 1021R, Morristown, New Jersey 07960*

## Synopsis

An anion-permeable polymeric film has been applied to the surfaces of cadmium sulfide photoanodes to decrease the rate of electrode corrosion which is observed during the photoelectrochemical oxidation of aqueous species. Although the rate of surface corrosion was reduced, film adhesion problems were observed.

## INTRODUCTION

We wish to report the results of using an anion-permeable organic polymer film for the protection of cadmium sulfide electrodes against photoelectrochemical corrosion. This anion-permeable film contains immobilized quaternary ammonium cations, and includes the three structures shown in Figure 1. The film was made by the reaction of *N,N*-dimethylpropane-1,3-diamine with a 15% dimethylformamide solution of a 1:1 styrene/vinylbenzyl chloride copolymer. The use of similar materials for producing ion exchange membranes has been described previously.<sup>1</sup>

The film was applied to the surfaces of cadmium sulfide electrodes, in order to protect the electrodes against photocorrosion in aqueous electrolyte solutions. The surfaces of compound semiconductor photoelectrodes have been stabilized by a variety of surface coatings;<sup>2-10</sup> in addition, films containing immobilized ammonium ions have previously been applied to the surfaces of graphite and platinum electrodes.<sup>11</sup> However, the degree of protection against decomposition which may be realized when such ammonium-containing films are applied to semiconductor electrode surfaces has not been previously investigated.

The photodecomposition of cadmium sulfide electrodes in aqueous electrolyte solutions leads to the deposition of elemental sulfur on the electrode surface and the dissolution of the  $\text{Cd}^{+2}$  into the aqueous phase.<sup>12</sup> Coating the CdS surface with a polymer that was permeable to anions but not cations would therefore be expected to retard photocorrosion while still allowing the transport and sustained oxidation of anionic species in the electrolyte solution. In the present study, the photocorrosion of CdS was monitored in competition with the photoelectrochemical oxidation of cyanide anions to cyanate in solution.

\*Present address, Lawrence Livermore National Lab, Mail Stop L228, CA 94550.

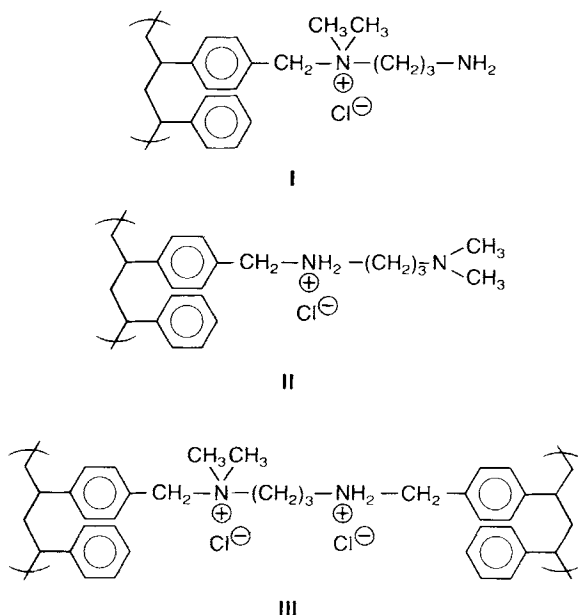


Fig. 1. Structures of the chemical components of the anion-permeable film are shown schematically.

### EXPERIMENTAL

The diamine and copolymer solution were mixed and immediately brushed onto the surface of a CdS photoelectrode, which had been etched and mounted as reported previously.<sup>12</sup> A hard, clear film formed within minutes. Residual dimethylformamide was driven off by baking the coated electrode in air for 1 h at 95°C. By viewing a cleaved portion of a coated electrode with a microscope with a calibrated ocular, we estimated that the films were typically 10  $\mu\text{m}$  thick. These films had immobile quaternary ammonium ions, each with an associated, mobile  $\text{Cl}^-$ . Coated electrodes were equilibrated overnight in 0.1M NaOH/20mM NaCNO/5mM NaCN to allow the removal of the  $\text{Cl}^-$ .<sup>13</sup>

Photoelectrochemical experiments were performed with the CdS photoanode short-circuited to a platinum counter electrode through a precision resistor. The voltage drop across the resistor was monitored with a strip chart recorder as a measure of the current. No reference electrode or externally applied bias voltage was employed. The electrolyte solution (2 mL) contained 20mM NaCNO and 5mM NaCN with 0.1M NaOH as the supporting electrolyte salt. The source of light was the 477 nm line from an argon ion laser. The light intensity, as measured by an Eppley Thermopile, was approximately 25  $\text{mW}/\text{cm}^2$ . Although an initial spike in photocurrent up to 0.3  $\text{mA}/\text{cm}^2$  was observed when the laser first illuminated the CdS electrode, the typical steady state currents were 0.1  $\text{mA}/\text{cm}^2$  or less. Measured open-circuit photovoltages ranged from 0.6 to 0.68 V. Atomic absorption analysis was used to measure the  $\text{Cd}^{+2}$  concentration in the electrolyte solution after each run, which typically lasted 1 h.

TABLE I  
Integrated Charge Flow  $Q$ , Measured Concentration of  $\text{Cd}^{+2}$  and Percentage  
of CdS Photocurrent Due to Photodecomposition,  $\zeta^a$

Electrode ID	$Q$ (mC)	$\text{Cd}^{+2}(m)$	$\zeta$
1. Coated	20	0.50	9%
2. Coated	6	0.13	7%
3. Coated	63	0.15	1%
4. Uncoated	71	22	105%

<sup>a</sup>For electrode 4, the light intensity was reduced so that the photocurrent was comparable to that observed for coated electrodes 1–3, approximately  $0.1 \text{ mA/cm}^2$ .

## RESULTS AND DISCUSSION

The total current flow observed in the external circuit is the sum of the current associated with the oxidation of solution species plus the current arising from self oxidation of the CdS. The integrated charge represented by the measured concentration of  $\text{Cd}^{+2}$  in the electrolyte solution was compared to the total charge flow in order to determine the fraction of current arising from the photocorrosion process. Since the  $\text{CNO}^-$  concentration was much higher than that of the  $\text{Cd}^{+2}$ , and since the potential for the reduction of  $\text{Cd}^{+2}$  to  $\text{Cd}^0$  is  $-0.403 \text{ V vs. NHE}^{14}$  it was assumed that no  $\text{Cd}^{+2}$  was reduced at the platinum electrode.

As shown by the data in Table I, the photocurrents observed with uncoated CdS electrodes were found to arise almost exclusively from photodecomposition. In contrast, CdS electrodes bearing the polymeric films consistently showed markedly lower rates of photocorrosion.

The current densities which we observed with our coated electrodes were approximately 100 times lower than those which have been reported for electropolymerized films on platinized GaAs.<sup>10</sup> These relatively low current densities are attributed to the thickness of the films made by the brush-on technique; the  $10 \mu\text{m}$  polymer coatings reported herein are approximately 100 times thicker than those prepared by electropolymerization. When a coated CdS electrode is initially exposed to light, a current spike is seen, comparable to that from an uncoated CdS electrode; the current then decays rapidly to the much lower level. We interpret the initial spike as the photoelectrochemical oxidation of the  $\text{CN}^-$  which was already in the anion-permeable film; the much lower steady state level reflects the kinetically slow process of ion exchange between the  $\text{CNO}^-$  which is formed within the film and the  $\text{CN}^-$  solution. We do not know if the film itself participates in the photoelectrochemical process; however, if the illumination is turned off for 5 min or more, reilluminating the coated electrode does reproduce the behavior of initial current spike/rapid decay, suggesting that long term chemical changes to the anion-permeable film are not important in this case. Visual inspection of the coated electrode surfaces at the conclusion of most photoelectrochemical experiments revealed no apparent changes in the appearance of the polymer films. However, in some cases, microscopic blisters were observed, showing partial detachment or peeling of the film from the electrode surface. Such

phenomena have previously been observed for polymer coatings on compound semiconductor substrates.<sup>5-8</sup>

### CONCLUSIONS

An anion-permeable organic polymer film was applied to the surfaces of cadmium sulfide photoanodes. When used for the photoelectrochemical oxidation of dilute aqueous  $\text{CN}^-$  to  $\text{CNO}^-$ , the polymer-coated cadmium sulfide electrodes underwent significantly less corrosion than did the uncoated electrodes. However, in some cases, microscopic blisters could be seen within the films after the coated electrodes were used in photoelectrochemical cells. In addition, the observed current densities were relatively low. Therefore, although this anion-permeable film afforded a measure of protection for the CdS photoanodes, it will be necessary both to prepare thinner films and to address the adhesion problem in order to increase the utility of this technique.

The authors gratefully acknowledge the assistance of Dr. Fred Chlanda.

### References

1. F. Chlanda, L. Lee, and K. Liu, U.S. Pat. 4,116,889 (1978).
2. B. Parkinson, A. Heller, and B. Miller, *Appl. Phys. Lett.*, **33**, 521 (1978).
3. P. K. Ghosh and T. G. Spiro, *J. Am. Chem. Soc.*, **102**, 5543 (1980).
4. A. B. Bocarsly and S. Sinha, *J. Electroanal. Chem.*, **140**, 167 (1982).
5. R. Noufi, D. Tench, and L. F. Warren, *J. Electrochem. Soc.*, **127**, 2310 (1980).
6. R. Noufi, D. Tench, and L. F. Warren, *J. Electrochem. Soc.*, **128**, 2596 (1981).
7. R. Noufi, A. J. Nozik, J. White, and L. F. Warren, *J. Electrochem. Soc.*, **129**, 2261 (1982).
8. R. Noufi, *J. Electrochem. Soc.*, **130**, 2126 (1983).
9. J. M. Bolts and M. S. Wrighton, *J. Am. Chem. Soc.*, **101**, 6179 (1979).
10. G. Horowitz, G. Tourillon, and F. Garnier, *J. Electrochem. Soc.*, **131**, 151 (1984).
11. N. Qyama, T. Ohsaka, and T. Okajima, *Anal. Chem.*, **58**, 979 (1986).
12. A. B. Ellis, S. W. Kaiser, J. M. Bolts, and M. S. Wrighton, *J. Am. Chem. Soc.*, **99**, 2839 (1977).
13. R. M. Wheaton and W. C. Bauman, *Ind. Eng. Chem.*, **43**, 1088 (1953).
14. A. Bard and L. Faulkner, *Electrochemical Methods*, Wiley, New York, 1980.

Received January 24, 1989

Accepted January 31, 1989