

A. C. EFFECT ON THE PHOTOPOTENTIAL AT THE CADMIUM SULPHIDE-ELECTROLYTE INTERFACE

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Faradaic rectification brought about by light was observed during an examination of the effect of sinusoidal current on the electrode system CdS-aqueous ammoniacal ammonium perchlorate. When the CdS electrode was irradiated by intense white light, a frequency dependent Faradaic rectification was observed, the effect increasing negatively by about 60mV in the frequency range upto 1000 c/s, reaching a saturation value around 300 c/s.

Keywords: A. C. Effect; Photopotential; Cadmium Sulphide-Electrolyte Interface

INTRODUCTION

EARLIER we reported marked photopotentials at the cadmium sulphide-aqueous ammonium perchlorate system (Kuppusami *et al.*, 1979).

Faradaic rectification has been reported both experimentally and theoretically for the system electrolyte-metal electrode (Doss & Agarwal, 1951; Oldham, 1957; Vdovin, 1958; Barker, 1959; and Levich & Grafov, 1962). The same effect was examined in a semiconductor-electrolyte system by earlier workers (Gurevich & Myamlin, 1964; and Myamlin & Pleskov, 1967). Assuming that the passage of current is associated with an oxidation-reduction reaction at the interface, the passage of a sinusoidal current, which has no preferred direction, has been shown to lead to the appearance of a constant potential difference in the system (Gurevich & Myamlin, 1964; and Myamlin & Pleskov, 1967). The sign of this Faraday shift was shown to be determined by the difference in the exchange currents due to holes and electrons, indicating the degree of participation in the reaction of the two energy bands of the semiconductor at potentials close to the equilibrium value. On semiconductors one can expect a greater Faradaic effect with the same current amplitude as the exchange current density. i_0^s is generally much less than the exchange current density on metals i_m^0 .

In this background, we examined the effect of sinusoidal current on the system cadmium sulphide-aqueous ammonium perchlorate rendered alkaline by addition of

ammonia. However, in the normal dark system we observed no Faradaic rectification. On the other hand when the electrode was irradiated by intense white light, a frequency-dependent Faradaic rectification was observed, the effect increasing negatively by about 60mV in the frequency range upto 1000 c/s reaching a saturation value around 300 c/s.

This photo-Faradaic rectification effect seems to be connected with the fast surface states, which may control the kinetics of charge transfer across the semiconductor-electrolyte interface.

EXPERIMENTAL

A glass vessel having two compartments with an optical glass window was employed. The semiconductor electrode taken was a sintered polycrystalline CdS layer on a ceramic substrate. Annular ohmic indium contact was provided for the CdS layer on top. The ceramic pellet bearing the CdS layer was attached to a glass tube support. The counter electrode was platinised platinum. A saturated calomel electrode was the reference to measure the Faradaic rectified potential of the CdS electrode. An a.c. source of 3V was connected to the main cell. Care was taken to see that the a.c. was filtered off in the d.c. measuring circuit and vice versa by connecting a condenser and a choke appropriately.

The light source was a 24V, 200W projector lamp kept at a constant distance of 4cm from the cell.

The electrolyte used was aqueous ammonium perchlorate of concentrations 1.0, 0.5 and 0.1N rendered alkaline to a pH of 9.5 by addition of aqueous ammonia solution to ensure satisfactory stability of the CdS electrode.

OBSERVATIONS

In the dark, with the application of different frequencies, from the lowest to 1000 c/s, the Faradaic rectified e.m.f. recorded between the CdS electrode and the calomel electrode was almost invariant. When irradiated with light, the potential across CdS calomel electrodes in 0.1N ammonium perchlorate with ammonium hydroxide was around -210mV at zero frequency and with increasing frequency it fell off sharply to about -255mV at 50 c/s, -270mV at 300 c/s and remained almost constant with very little variation upto the measured frequency of 1000 c/s. These experiments were repeated in electrolyte solutions of 0.5, and 1.0N of ammonium perchlorate. In all these cases, the same trend was observed and the fall was steep upto 50 c/s, the magnitude being -290mV , for 0.5N and -270mV for 1.0N solutions. These studies are preliminary and detailed investigations are under way.

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