

Mercuric Iodide - Photocorrosion Resistant Semiconductor

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Abstract: n - Mercuric Iodide with layer crystal structure is found to resist photocorrosion when used as the anode in photoelectrochemical cells.

1. Introduction

In recent literature, a great deal of attention is given to photoelectrochemical cells as promising devices for conversion and/or storage of solar energy.^{4,9} The advantages of these systems is that the insensitivity of the photoresponse to defects and impurities in the semiconductor - polycrystalline and amorphous materials give results comparable to single crystal slices.^{8,11} However, they are plagued with photocorrosion. Most semiconductors show a noticeable rate of photocorrosion even if best possible redox electrolytes are used.^{6,7} Recently it has been found that semiconducting materials with layered crystal structure (e.g. MoS₂, WSe₂) strongly resist photocorrosion.¹² In this note we report our observations on photocorrosion resistance of red mercuric iodide which is known to have a layered crystal structure.¹⁴

2. Experimental

Red HgI₂ (α) has a layer structure with HgI₂⁻⁴ tetrahedra linked the vertices.¹⁴ The α - phase is stable up to 400° K.¹⁴ Above this temperature, the yellow HgI₂ (β) is more stable. Red HgI₂ behaves as a n - type semiconductor of band gap 2.37 eV.^{2,10} In all experiments analytical grade (BDH brand) HgI₂ is used. HgI₂ made by double decomposition of mercuric chloride with potassium iodide gives identical results.

The photoanode is made by depositing HgI₂ on a platinum foil by vacuum sublimation at ~ 423°K. The yellow form which is deposited reverts to the red α -phase few minutes after cooling to the room temperature. The counterelectrode used is a Pt foil and the electrolyte is 0.1 mol dm⁻³ solution of sodium sulphate. The time development (cathode illuminated at ~ 40 Wm⁻² from a mercury lamp) of the open circuit voltage V_{oc} and the short circuit current density (J_{sc}) is given in Figure 1. V_{oc} and J_{sc} remain practically constant demonstrating the photostability of HgI₂.

3. Results

Oxygen evolution can be seen at the photoanode. In the presence of atmospheric oxygen the cell operates in the photogalvanic mode where O₂ reduction instead of H₂ evolution takes place at the cathode. When the electrolyte is purged with

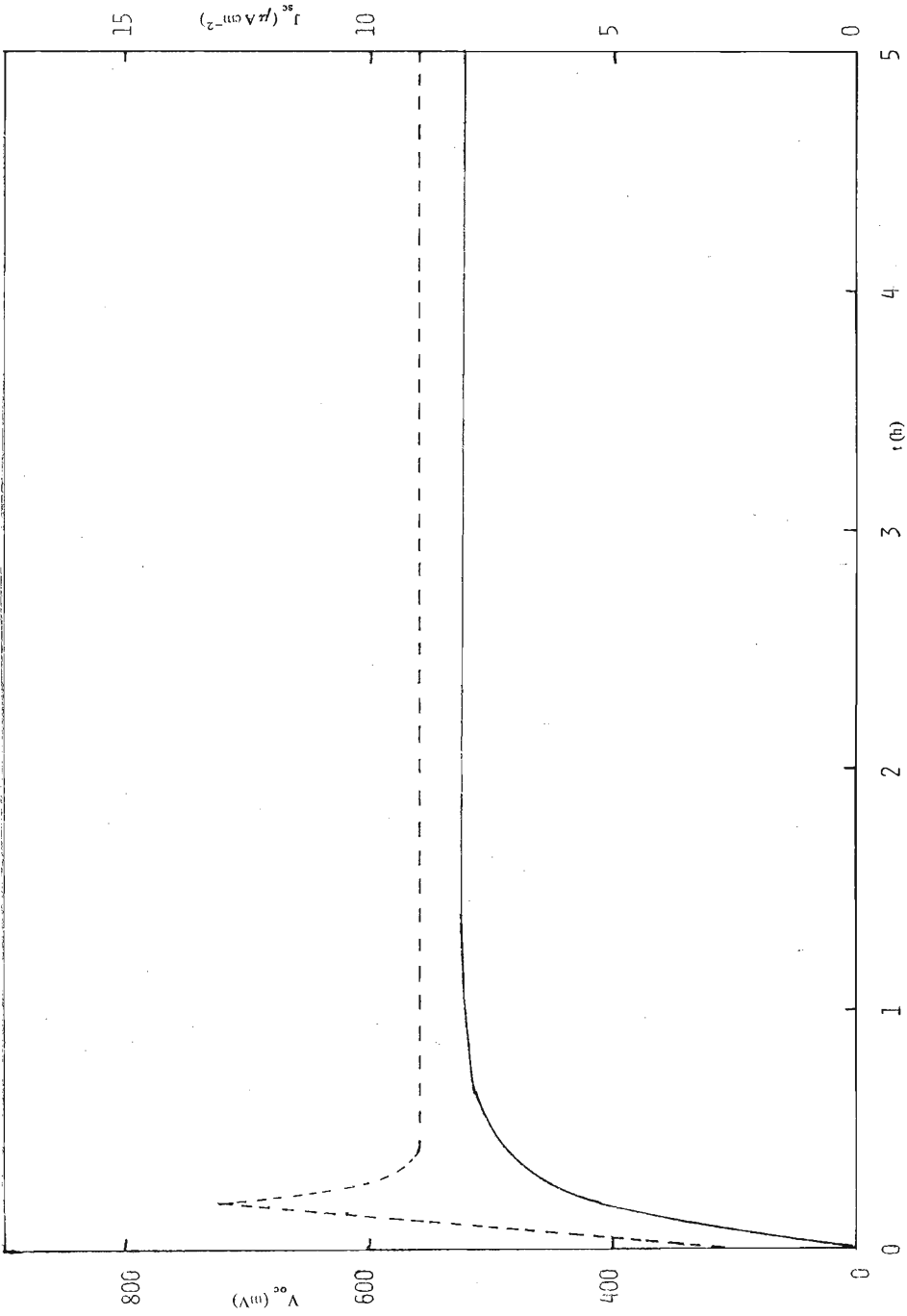


FIGURE 1. --- The plots of V_{oc} vs t (continuous line) and J_{sc} vs t (broken line) when the cathode is illuminated at 40 Wm^{-2} from a mercury lamp.

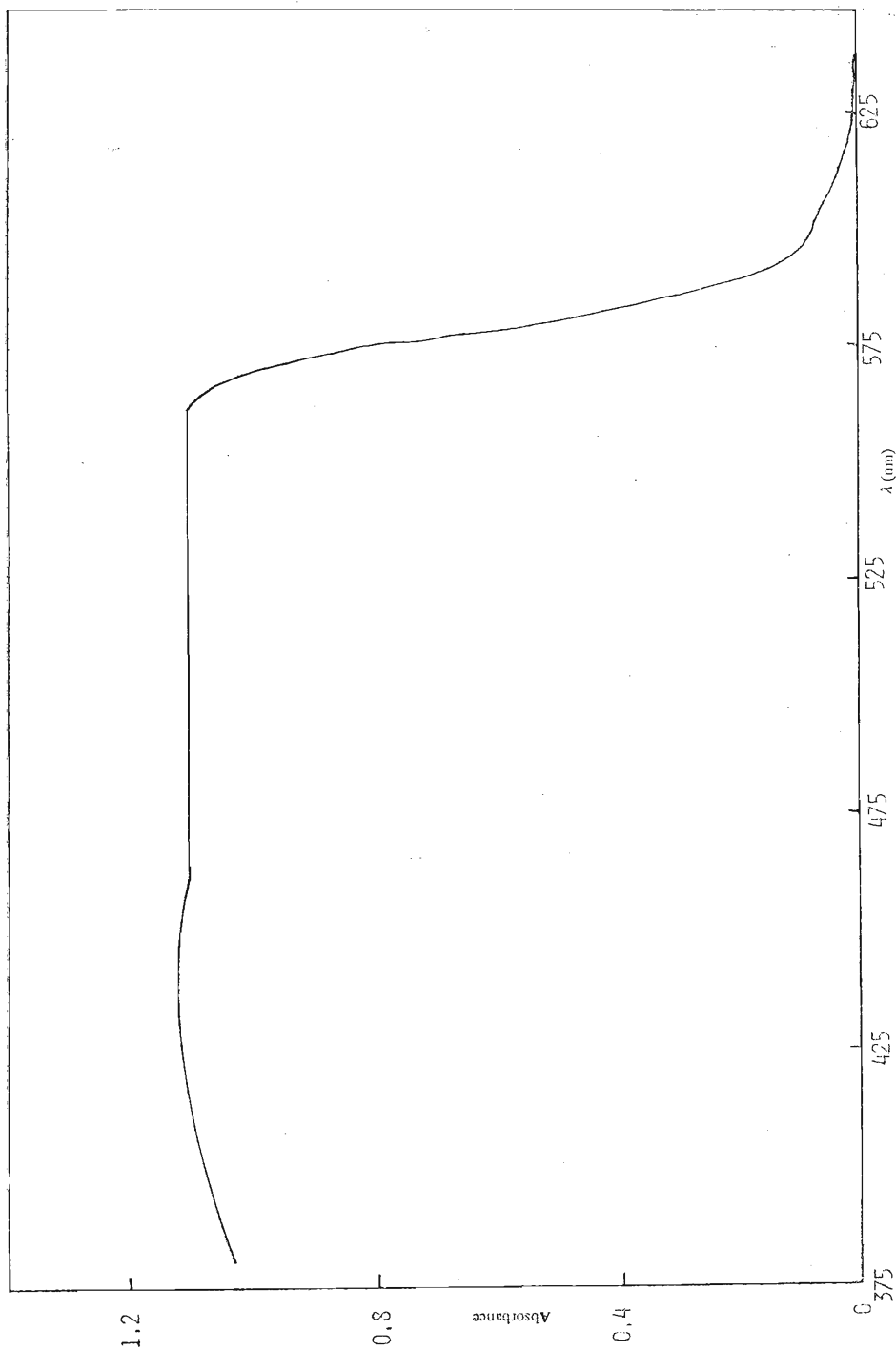


Figure 2 — Diffuse reflectance spectrum of HgI₂.

N_2 , H_2 evolution is seen only when the cell is externally biased. This indicates that H_2O/H_2 redox energy level is lying above the conduction band.⁵

The diffuse reflectance spectrum of polycrystalline HgI_2 powder (measured with a Unicamp Series II (Spectrophotometer) is shown in Figure 2. It is interesting to note the strong and almost constant absorption peak starting at ~ 600 nm.

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