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. 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. However, they are plagued with photocorrosion. Most semiconductors show a noticeable rate of photocorrosion even if best possible redox electrolytes are used. Recently it has been found that semiconducting materials with layered crystal structure (e.g. MoS$_2$, WSe$_2$) strongly resist photocorrosion. In this note we report our observations on photocorrosion resistance of red mercuric iodide which is known to have a layered crystal structure.

2. Experimental
Red HgI$_2$ (α) has a layer structure with HgI$_{2-4}$ tetrahedra linked the vertices. The α-phase is stable up to 400°K. Above this temperature, the yellow HgI$_2$ (β) is more stable. Red HgI$_2$ behaves as a n-type semiconductor of band gap 2.37 eV. In all experiments analytical grade (BDH brand) HgI$_2$ is used. HgI$_2$ made by double decomposition of mercuric chloride with potassium iodide gives identical results.

The photoanode is made by depositing HgI$_2$ 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 photo-stability of HgI$_2$.

3. Results
Oxygen evolution can be seen at the photoanode. In the presence of atmospheric oxygen the cell operates in the photogalvanic mode where O$_2$ reduction instead of H$_2$ evolution takes place at the cathode. When the electrolyte is purged with...
Figure 1. The plots of $V_{oc}$ vs $t$ (continuous line) and $I$ vs $t$ (broken line) when the cathode is illuminated at 40 W/m² from a mercury lamp.
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Figure 2 — Diffuse reflectance spectrum of HgI₂.
N₂, H₂ evolution is seen only when the cell is externally biased. This indicates that H₂O/H₂ redox energy level is lying above the conduction band.

The diffuse reflectance spectrum of polycrystalline HgI₂ 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.

References