Integrated Multijunction Photovoltaic/Electrolyte System for Water Photoelectrolysis

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The direct photoelectrolysis of water has been termed the "Holy Grail of Photoelectrochemistry" (1). Aside from the pure scientific interest in the direct splitting of water, the promise of direct water splitting at the semiconductor electrolyte interface implies benefits such as cost and energy savings over coupled photovoltaic (PV)-electrolysis systems for hydrogen production. However, the lack of a combination of a stable, efficient light absorption system coupled with suitable semiconductor-redox energetics has kept photoelectrochemistry from reaching this goal.

The ability of an illuminated semiconductor electrode to spontaneously drive an electrochemical reaction of interest is determined by its band gap (the energy separation between the valence and conduction band edges) and the position of the valence and conduction band edges relative to the vacuum level (or other reference electrode). This fixed energy is given by the energetic position where these bands terminate at the semiconductor/electrolyte interphase. The energetic position of these band edges is determined by the chemistry of the semiconductor/electrolyte interface, which is controlled by the composition of the semiconductor, the nature of the surface, and the electrolyte composition. So even though an illuminated semiconductor electrode may generate sufficient energy to effect an electrochemical reaction, the energetic position of the band edges may prevent it from doing so. For spontaneous light-driven water splitting, the oxygen and hydrogen redox reactions must lie between the valence and conduction band edges, and this is almost never the case.

In earlier work, we identified p-type gallium indium phosphide (p-$GaInP_2$) as perhaps an ideal semiconductor for water splitting. However, while its bandgap is in the ideal range (1.83 eV), the energetics of its band edges are not correct for water splitting, needing an additional 500mV bias. While it is possible to move the band edges to some extent, it is still insufficient to effect water splitting (2).

Our approach then moved to engineering solid state designs to integrate a bias voltage to effect the water decomposition reaction. The device concept was patterned after the well known $GaInP_2$/GaAs p/n,p/n tandem cell device grown at NREL. The solid state tandem cell consists of a gallium arsenide (GaAs) bottom cell connected to a gallium indium phosphide ($GaInP_2$) top cell via a tunnel diode interconnect. The top junction bandgap of the $GaInP_2$ at 1.83 volts is designed to absorb the visible portion of the solar spectrum and the bottom GaAs junction (bandgap of 1.42 eV) absorbs the near infrared portion of the spectrum transmitted through the top junction. Our device differs from the standard solid-state tandem cell in that a PEC Schottky-type junction has replaced the top p/n junction. This device then is a PEC Schottky barrier device, voltage biased with an integrated PV device. Operationally, under illumination, electrons flow towards the surface and holes towards the back ohmic contact.

For this device configuration to work properly, the GaAs cell must provide sufficient voltage to overcome the bandedge mismatch between the $GaInP_2$ and the water redox reactions and also provide additional voltage to overcome any overvoltage losses from the hydrogen and oxygen evolution reactions.

Because these tandem systems operate by requiring two photons (one per junction) to produce one electron in the external circuit, great care is taken in the solid-state systems to match the photon absorption characteristics such that equal number of photocarriers are generated in the top and bottom cells. However, when the photocurrent-matched configuration is placed in an aqueous environment, the system either produces no current in the external circuit, or decomposes (3). A thicker, top p-type layer, and the resultant mismatch of electron-hole formation in the two-junction region appears to be the key for proper operation. The key to making this particular system work is the requirement for the bottom cell to be the limiting electron provider. Under illumination then, this configuration will spontaneously split water with an efficiency of about 12% (4). However, the photocurrent shows a steady decay indicating corrosion. Work has continued to find other materials with greater resistance to corrosion.

This report will discuss our monolythic water splitting system, as well as our work on some new materials and our attempts to control bandedge energetics.

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References

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