

COMMENTS

On Septum-Based Photoelectrochemical Cells

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We write to comment on the recent report by Kondapaneni et al.¹ and earlier papers by Tien and co-workers,² which imply that so-called semiconductor septum (SC-SEP) photoelectrochemical cells (PEC) provide special advantages and higher power conversion efficiencies compared to conventional, two-electrode PEC cells. A simple electric circuit analysis of these cells shows that they are equivalent to a conventional dark galvanic or electrolytic cell wired in series with a conventional PEC cell. Failure to consider the *overall* electrochemical process (which involves four electrodes in two separate, series cells) has clouded the issue of power conversion efficiency in papers describing SC-SEP devices. In particular, claims of efficient visible-light water photolysis with CdSe-based cells^{2b} need to be reconsidered in view of the fact that in these cases a galvanic cell (which one should think of as a battery or sacrificial anode) is used to drive the photoproduction of hydrogen. In the most "efficient" of these cells, the anode material (carbon or brass) is oxidized at potentials *negative* of the hydrogen/water formal potential, so the SC-SEP cell is driving an overall electrochemical reaction (active metal + H⁺ → metal salt + 1/2H₂) that is in fact thermodynamically downhill. Such cells can run only as long as the battery is charged and therefore should be considered as photocatalytic rather than photosynthetic devices.

Circuit Analysis of SC-SEP Cells. An SC-SEP cell can be represented, in a general way, as shown in Figure 1A. A "semiconductor septum", which consists of a polycrystalline semiconductor such as n-TiO₂¹ or n-CdSe² either alone or grown on a nonporous metal foil, separates two solution compartments. The semiconductor facing solution 1 is irradiated and photooxidizes reduced species R₁ (water¹ or polysulfide²) to oxidized species O₁. At the remaining three dark electrodes, oxidation and reduction reactions also occur to complete the circuit. When the cell operates in a regenerative (photosynthetic) mode, O₁' = O₁, O₂' = O₂, etc., but in a sacrificial (photocatalytic) cell these species may differ.

The same cell may be redrawn in a way to make it easier to understand, as shown in Figure 1B, by decomposing it into two cells—a conventional PEC and a dark cell—that are wired in series. The PEC cell works, as is well understood,³ to generate a photopotential and photocurrent via electron-hole separation in the space-charge region near the semiconductor/solution interface. At open circuit, under intense illumination, there is little band-bending, and the electron quasi-Fermi level is near the conduction band edge potential. The photovoltage is then ideally the difference between this potential and the O₁/R₁ formal potential. As current flows, this potential difference decreases by the amount of band-bending, and the maximum power point is achieved where the photovoltage × current product is a maximum. The operation of the dark cell (either an electrolytic or galvanic cell) is also well understood.

Photochemical Energy Conversion in SC-SEP Cells. One may analyze the performance of SC-SEP devices in terms of the three possible modes of operation of the dark cell.

(a) *Regenerative.* In this case, the processes occurring at M and M₂ in the dark cell are the reverse of each other, i.e., O₂' = O₂ and R₂' = R₂. The open circuit potential under these conditions

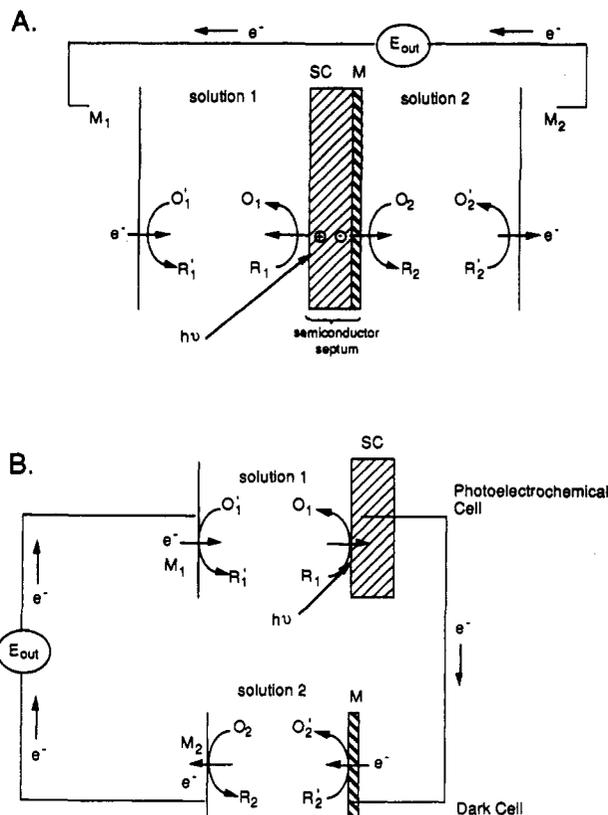


Figure 1. (A) Diagram of a semiconductor septum (SC-SEP) photoelectrochemical cell. Illumination of the n-type semiconductor facing solution 1 results in electron-hole pair separation and photocurrent in the direction shown. The output voltage (E_{out}) is measured between electrodes M₁ and M₂. (B) Equivalent representation of the SC-SEP cell in which the semiconductor-metal ohmic contact is expanded into a wire connecting two separate cells; one is a conventional PEC cell and the other is a dark galvanic or electrolytic cell. The two cells are connected in series, and $E_{out} = E_{PEC} + E_{dark}$.

is zero in the dark cell, and under conditions where current flows, the dark cell acts simply as a resistive load on the PEC cell.

(b) *Sacrificial.* The dark cell behaves as a battery and can bias the PEC cell. However, in this case, one is consuming reactants in the dark cell irreversibly. The output voltage measured between M₁ and M₂ is then the sum of the voltages of the battery and photocell, which are wired in series: $E_{out} = E_{dark} + E_{photo}$.

(c) *Storage.* In this case, the PEC drives the dark cell, as in (a), but in an electrolytic process that stores the solar energy converted in the PEC cell. Again, the dark cell acts as a load on the photocell, reducing the voltage output measured between M₁ and M₂.

One may conclude from this equivalent circuit analysis that the output voltage of the SC-SEP cell exceeds that of the simple PEC cell of the same M/solution/SC composition only in case (b). In terms of practical energy conversion devices, cases (a) and (c) are less efficient than the simple PEC cell. Case (b) results in a higher output voltage but only at the cost of irreversible decomposition of materials. The latter is strictly equivalent to biasing the PEC with an external power supply. There is, therefore, no real advantage to constructing cells of this type.

Comparison with Multijunction PEC Cells Involving Bipolar Electrodes. The SC-SEP cells described in refs 1 and 2 bear a superficial resemblance to semiconductor bipolar electrode array

cells previously described by us⁴ and others.⁵ In both cases, cells are wired in series, although in the case of PEC bipolar arrays, the purpose of this arrangement is to drive energetically demanding overall electrochemical processes, such as the decomposition of water to hydrogen and oxygen, that cannot be driven by the photovoltage of a single two-electrode PEC cell. One may think of these arrays as nearly equivalent to case (c) above, i.e., a PEC cell driving a dark electrolytic cell, except that several PEC cells in series replace the single cell shown in Figure 1B.

While series bipolar arrays offer the advantage of photolyzing water without added electrical power input, their power conversion efficiencies are generally low. Effectively, each CdSe/polysulfide/CoS cell in the series array generates a few tenths of a volt of photovoltage at its maximum power point, and at least four cells in series are needed to drive the water electrolysis reaction (which requires at least 1.23 V) at an appreciable rate.^{4b,c} The price one pays for adding up the photovoltages of n such cells is that n photons are required per electron. Put another way, the illuminated area of a series bipolar PEC array containing n compartments is n times that of a single PEC cell producing the same photocurrent, albeit with $1/n$ times the photovoltage.

For the water photolysis reaction, the theoretical limit of solar conversion efficiency at a CdSe/polysulfide/CoS array is ca. 2.8%.^{4c} In cases where the semiconductor bandgap is poorly matched to the solar spectrum (e.g., TiO₂), power conversion efficiencies are much lower.^{4a} Significantly higher efficiencies have been realized in the Texas Instruments Si microsphere system,⁵ which uses two illuminated p-n junctions in series to drive the photolysis of HBr. In this case, only two photons are

required per electron, the semiconductor bandgap is well matched to the solar spectrum, and less overpotential is required to drive the oxidation of Br⁻ than the oxidation of H₂O.

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