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A BIOLOGICAL SOLAR CELL

M. SEIBERT
A. F. JANZEN

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A BIOLOGICAL SOLAR CELL

Michael Seibert
Solar Energy Research Institute
1617 Cole Boulevard
Golden, Colorado 80401
U.S.A.

A. Frederick Janzen
Photochemical Research Associates, Inc.
London, Ontario
Canada

ABSTRACT

Recent reports have demonstrated the possibility of employing photoactive, biological-membrane components in photoelectrochemical cells. Present studies in our laboratories have led to the attachment of a much simpler biological complex, the bacterial photosynthetic reaction center isolated from *Rhodospseudomonas sphaeroides*, directly onto a SnO_2 semiconductor electrode. Light-induced photovoltages (70mV) and photocurrents ($0.5 \mu\text{A}/\text{cm}^2$) not attributable to Dember effects have been observed in photoelectrochemical cells employing reaction-center-coated, SnO_2 working electrodes. Such "reaction-center electrodes" may serve as model systems for future organic photovoltaic devices.

1. INTRODUCTION

Recent studies have demonstrated the possibility of employing photoactive, biological-membrane components, including chloroplasts, chloroplast fragments, photosystem I particles, purple membrane fragments, and bacterial reaction centers, in photoelectrochemical cells (1) for the conversion of solar energy into electricity. In most cases the biological component was incorporated into liposomes, bilayer lipid membranes, or lipid impregnated filters. Unfortunately, the geometry necessitated by the lipid systems (2 half-cells separated by the lipid) would be quite cumbersome in any practical solar energy conversion device. Consequently, our approach has been to deposit the simplest photosynthetic complex that carries out a light-induced charge separation (the bacterial reaction center) directly onto one of the electrodes of an electrochemical cell. Reaction centers, which are bacteriochlorophyll-containing protein complexes and can be isolated in pure form, are quite stable (except at high light intensities). In theory, they can convert up to 15% of the incident solar energy into chemical potential of charge separation at the point where the bacteriochlorophyll dimer (electron donor) is oxidized and the iron/quinone (acceptor) is reduced (2). Therefore, photoelec-

trochemical cells incorporating reaction centers might someday approach the efficiencies of semiconductor photovoltaic devices if light-induced stability problems can be overcome.

2. METHODS

The experimental cell (Fig. 1) consisted of a reaction-center-coated, SnO_2 working electrode and a platinum counter electrode. The SnO_2 was antimony-doped (an n-type semiconductor) and situated on a glass substrate. The reaction centers were isolated from *Rhodospseudomonas sphaeroides* R-26, a purple, non-sulfur, photosynthetic bacterium. They were transferred to the working electrode by dipping the electrode directly into a concentrated reaction-center suspension. Red light ($>600 \text{ nm}$) was used to elicit the photoresponses, and the cell electrolyte contained 0.1 M Na_2SO_4 and 0.05 M hydroquinone in tricine ($\text{pH}=7.0$) buffer.

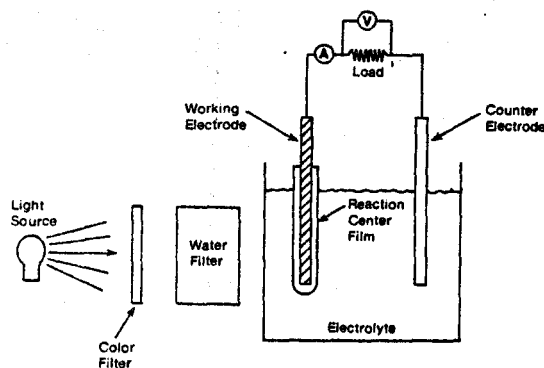


Fig. 1. The experimental photoelectrochemical cell.

3. RESULTS

Figure 2A shows that a reaction-center-coated, SnO_2 electrode can typically generate an open-circuit photovoltage of 37 mV. The maximum value observed thus far is 70 mV. A maximum photovoltage of about 495 mV is possible (the difference between the midpoint redox potential of the bacteriochlorophyll primary donor, +450 mV, and that of the iron/quinone acceptor, -45mV). Mismatching of the energy levels of the reaction-center molecules with the energy levels of the SnO_2 as well as charge recombination within the reaction-center film, could account for the small photovoltages. Typical short-circuit photocurrents observed are about $0.3 \mu\text{A}/\text{cm}^2$ with a maximum of about $0.5 \text{ A}/\text{cm}^2$. The residual photovoltage after autoclaving indicated in Fig. 2B is probably due to a Demer effect (1).

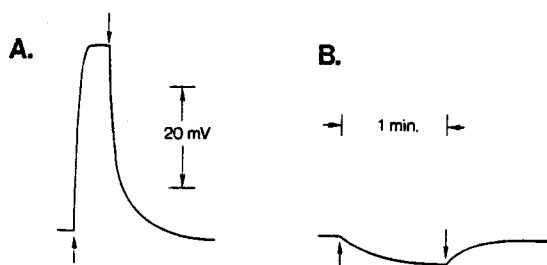


Fig. 2. Open-circuit photovoltage produced by a reaction-center-coated, SnO_2 electrode exposed to red light in an electrochemical cell. A. Freshly-coated electrode. This electrode acts as a photocathode since the midpoint potential of the iron/quinone acceptor in the reaction center is more positive than the flat-band potential of SnO_2 (NHE scale). The kinetics of the photovoltage vary with the age of the sample.* B. Autoclaved electrode. Upward and downward arrows indicate light on and off, respectively.

If electrons pumped across the reaction center during the primary photoact of photosynthesis do equilibrate with the electrode, the action spectrum of the photocurrent measured in the external circuit should correspond to the absorbance spectrum of the reaction centers. This, in fact, has been observed (2).

Figure 3 shows our present model explaining

*The aging process ultimately reverses the polarity of the photo-induced responses, and this will be the subject of future research.

reaction-center-driven electron transport at a SnO_2 semiconductor/reaction-center film/electrolyte interface. The reaction centers, of course, are the source of the light-induced photovoltage and photocurrent one can measure at the load resistor depicted in Fig. 1. The abbreviations used in the figure are defined in the legend. The thick arrow represents light-induced excitation of the bacteriochlorophyll dimer. The thinner arrows

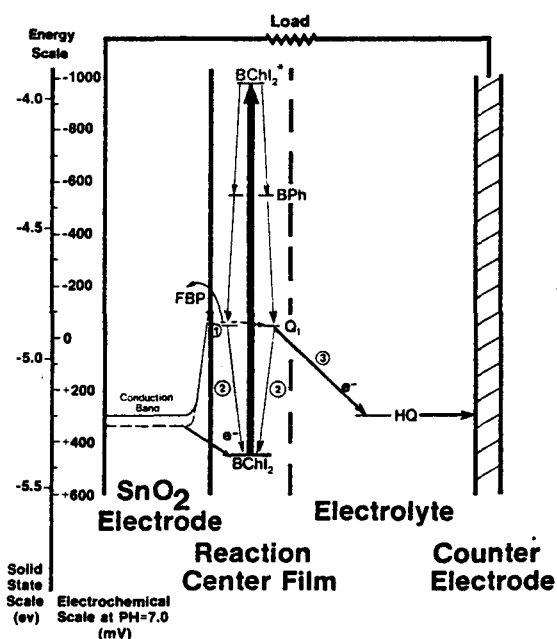


Fig. 3. Model to explain reaction-center-driven electron transport at a SnO_2 semiconductor/reaction center/electrolyte interface. Abbreviations: FBP, flat-band potential; BChl_2 , bacteriochlorophyll dimer electron donor; BChl_2^* , first excited singlet state of the BChl_2 ; BPh, bacteriopheophytin; Q_1 , iron/quinone electron acceptor; HQ, hydroquinone. See the text for an explanation of the model.

denote electron transport reactions resulting from reaction-center photochemistry. The thin dashed lines denote the energy level shifts occurring when the light is turned on. When the reaction-center-coated, SnO_2 electrode is immersed in the photoelectrochemical cell, the Fermi level of the semiconductor equilibrates with the redox potential of the electrolyte (hydroquinone) causing the SnO_2 conduction band to "bend down".

When the light is turned on, electrons in the reaction center film accumulate at Q_1 . From here they could: 1) go into the SnO_2 ; 2) re-reduce the BChl_2^+ formed during the primary charge-separation act, or; 3) equilibrate with the hydroquinone in the electrolyte. Step 1 does not occur due to the barrier of the flat-band potential. Steps 2 and 3 probably both occur, but step 3 is slightly favored. At the same time, electrons from the SnO_2 conduction band tunnel across the barrier created by the band-bending phenomenon to re-reduce any oxidized BChl_2 available. This causes a further bending of the conduction band (e.g., the thin dashed line). The potential generated across the external load resistor is the difference between the light-induced level of the conduction band and the potential of the hydroquinone in the electrolyte.

4. CONCLUSIONS

We conclude that charge separation generated across the reaction-center molecule as a result of the primary photochemistry of photosynthesis can be electrically coupled directly to semiconductor electrode materials. Such reaction-center electrodes can be used in a photoelectrochemical cell to generate photovoltages and photocurrents in an external circuit. These electrodes may lead to new methods of probing the primary photochemistry of photosynthesis and, in addition serve as model systems for future inorganic or organic photoelectrochemical devices.

5. ACKNOWLEDGEMENTS

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