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BIOLOGICAL SOLAR CELLS

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ABSTRACT

Recent reports have demonstrated the possibility of employing photoactive, biological membrane components in photoelectrochemical cells. Such systems have produced small photovoltages and photocurrents. 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 an SnO₂ electrode. The light-induced primary charge separation processes which occur across the reaction center macromolecule have been coupled to the electrode, and in a two-electrode configuration photovoltages as high as 70 mV and photocurrents as high as 0.5 $\mu\text{A}/\text{cm}^2$ have been observed in an external circuit. The phenomena are not due to "biological" Dember effects. Such "reaction center electrodes" may be the forerunner of future biological solar cells or may serve as model systems for future organic photovoltaic devices.

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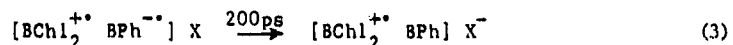
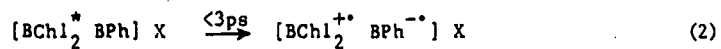
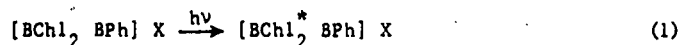
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INTRODUCTION

Recent studies have demonstrated the possibility of employing photoactive, biological components in photoelectrochemical cells [1]. Such cells have used chloroplast membranes [2], chloroplasts [3,4], photosystem I particles [5], purple membrane fragments containing bacteriorhodopsin [6,7], bacterial reaction centers [8], and chlorophyll [refs. 9-11 are recent examples but there is a substantial amount of literature in this area]. In most cases, the biological component was incorporated into liposomes or bilayer lipid membranes, and the stability enhanced by using polymers or lipid-impregnated filters. Unfortunately, since the interiors of liposomes are inaccessible to contemporary electrodes, definitive electrochemical studies are very difficult. Lipid bilayers often trap solvents and have small working surfaces. Furthermore, the geometry necessitated by lipid bilayer systems (two-half cells separated by the bilayer) would be quite cumbersome and impractical in any foreseeable biological solar energy conversion device. On the other hand, chloroplast membranes [2,3] and chlorophyll [9,11] have been deposited directly onto the surface of various types of electrodes thus simplifying the cell. Unfortunately, the photoeffects have been either small or rather unstable.

Bacterial reaction center complexes are the simplest biological units that carry out the primary photochemistry of photosynthesis. They have been isolated from photosynthetic bacteria and are relatively stable (at high concentration under room temperature and light conditions). Physically, a reaction center is an 80,000 molecular weight protein complex containing a number of chlorophyllous chromophores, and it carries out the following charge separation process with a quantum efficiency of one:



where BChl_2 is a bacteriochlorophyll dimer (the primary electron donor); BPh is a bacteriopheophytin; and X is the classical primary acceptor, an iron-quinone complex (for a detailed discussion see ref. 12). One can calculate the amount of incident solar energy available as the chemical potential of charge separation at the level of $[\text{BChl}_2^{+\bullet} \text{ BPh}] \text{ X}^-$ (which has a half-life of about 50 ns) as follows:

$$\eta = 100 \frac{E_D - E_A}{E_P} \int_{380\text{nm}}^P I_\lambda P_\lambda d\lambda \quad (4)$$

where E_D is the redox midpoint potential of the primary donor couple, $\text{BChl}_2/\text{BChl}_2^{+\bullet}$; E_A is the redox potential of the acceptor, X^-/X ; E_P is the photon energy at the longest effective wavelength for photosynthesis, P ; I_λ is the fraction of the total solar irradiance available at wavelength λ , and P_λ is the ratio of the photon energy at P relative to that at wavelength λ . I_λ for air mass 1.2 can be found in ref. 13. In the case of

Rhodospseudomonas sphaeroides, E_D is 0.45 V, E_A is -0.18 V, E_p is 1.43 eV, and P is 865 nm. From this information one can calculate a value of 19.3% for η , assuming that the sample is sufficiently dense to absorb all incident light between 380 and 865 nm. Thus reaction centers approach the efficiency of the best photovoltaic devices in their ability to convert sunlight into chemical potential.

We [14] and others [15] have suggested that reaction centers might be coupled directly onto electrodes to serve as model systems for potential future solar energy conversion devices. This paper reports the first successful direct electrical coupling of a photosynthetic reaction center to an electrode.

METHODS

Reaction center complexes were isolated from the purple non-sulfur photosynthetic bacterium, Rhodospseudomonas sphaeroides R-26 (a mutant strain of ATH 2.4.1 lacking highly unsaturated carotenoids), using the method of Dutton *et al.* [16]. They were suspended in 10 mM Tris-HCl buffer (pH = 8.0) at a concentration of 266 μ M. Reaction centers were transferred to working electrode surfaces by dipping the electrodes directly into the concentrated reaction center suspension. Excess liquid was removed from the lower part of the electrodes, and the electrodes were allowed to dry in the dark under ambient conditions.

Platinum electrodes were platinized using standard methods, carbon and aluminum electrodes were made by sputtering the materials onto glass, and SnO₂ coated glass was purchased from Corning Glass Works (Corning, N.Y.).

The experimental cell consisted of the working electrode and either a platinized platinum or SnO₂ counter electrode. The electrolyte contained 0.1 M Na₂SO₄ and 0.05 M hydroquinone in either water or Tricine buffer (pH = 7.1). The light source was a Unitron tungsten lamp (Unitron Instruments, Inc., Woodbury, N.Y.) focused through both a Corning CS2-62 red filter which cuts off light below 600 nm and a 7 cm water filter. Photovoltages and photocurrents were measured in the external circuit with a Keithley Instruments Model 177 multimeter (Cleveland, Ohio) using various load resistors connected in parallel or series, respectively, with the meter. Absorbance spectra were obtained with a Cary 219 spectrophotometer (Varian, Palo Alto, Calif.). Action spectra were measured at very low light intensity using a tungsten light source focused through a 1/4 m Bausch and Lomb monochromator (6 nm bandwidth). The reciprocal of the quantum flux necessary to elicit a 14 μ V response across a 10 k Ω resistor was plotted as a function of the wavelength.

RESULTS

Table I, row A, presents the results obtained when reaction center complexes were dried as a thin film on the surface of a platinized platinum working electrode. Small open circuit photovoltages and short circuit photocurrents were observed routinely, and the photoeffects lasted for at least several days. If these phenomena were due to the direct electrical coupling to the electrode (and hence the external circuit) of the light-induced charge separation associated with the primary processes of photosynthesis, one would not expect to observe photo-induced voltages and currents if the biological molecules were inactivated. Autoclaved reaction centers are not photoactive. The fact that autoclaved reaction-center-coated platinum electrodes (Table I, row B) exhibit photoeffects of the same order as unautoclaved electrodes demonstrates that biologically active electron transfer is not involved. Clay-

Table I. PHOTOEFFECTS IN REACTION-CENTER-COATED, PLATINIZED PLATINUM ELECTRODES

Working Electrode Condition	Photovoltage (mV) ^a	Photocurrent (μA) ^b
A. Freshly Coated Electrode	2.1	1.07
B. Autoclaved Electrode	3.65	0.32

^aOpen circuit.

^bShort circuit.

ton (personal communication) has suggested that a "biological" Dember effect [1] could account for the phenomena illustrated in Table I. The absence of any coupling of the primary charge separation to the electrode is probably due to rapid back reactions across the reaction centers catalyzed by the platinum electrode itself.

If this be the case, the use of other electrode materials might overcome the problem. Consequently, we made reaction center electrodes using carbon, aluminum, and SnO₂-coated glass. The former two electrode materials were not suitable because the dark voltages observed after coating were unstable. On the other hand, Figure 1A shows the results obtained with a reaction-center-coated, SnO₂ electrode. The maximum open circuit photovoltage observed in this case was 37 mV; however, photovoltages of 70 mV have been observed in other samples. A maximum photovoltage of about 630 mV (the difference between the midpoint redox potential of the BChl₂ primary donor, +450 mV, and that of the X acceptor, -180 mV) is expected, but mismatching of the energy levels of the reaction center molecules with the energy levels of the SnO₂, as well as electrical leaks back across the reaction center film, could account for the

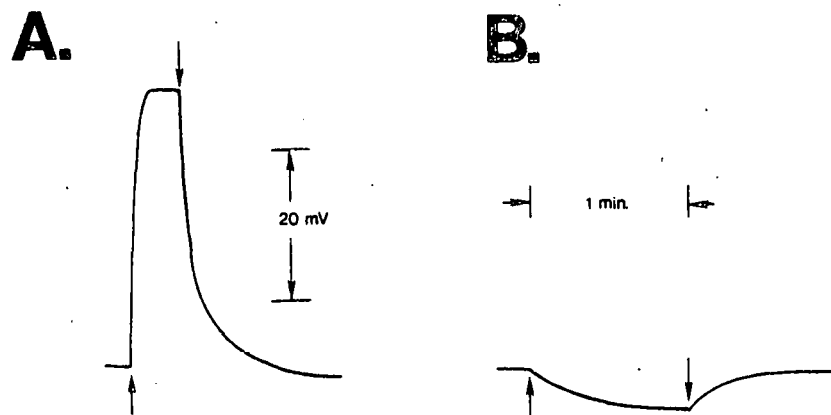


Figure 1. Open circuit photovoltage produced by a reaction-center-coated, SnO₂ electrode exposed to red light in an electrochemical cell. Upward and downward facing arrows indicate light on and off, respectively. A. Freshly coated electrode. B. Autoclaved electrode.

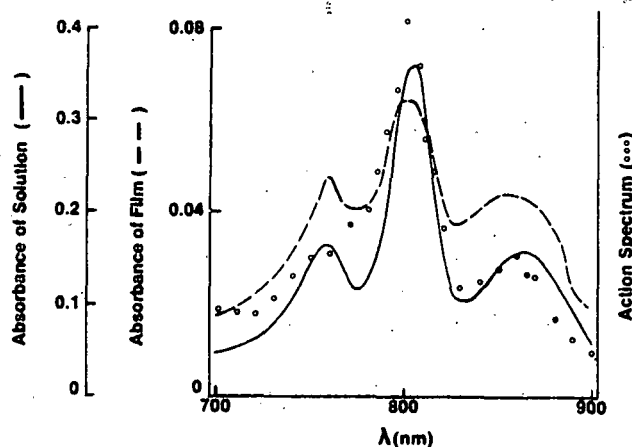


Figure 2. A comparison of reaction center solution, film, and action spectra. See the methods section for experimental detail.

small photovoltages observed. The maximum short circuit photocurrent thus far observed has been on the order of $0.5 \mu\text{A}/\text{cm}^2$. Figure 1B shows the residual photovoltage after autoclaving. It is probably due to a Dember effect as discussed above.

If electrons pumped across the reaction center during the primary photoact of photosynthesis do couple to the electrode, one would expect that the action spectrum of the photocurrent measured in the external circuit would correspond to the absorbance spectrum of the reaction centers. Figure 2 compares the solution absorbance spectrum, the absorbance spectrum of a thin reaction center film, and the action spectrum of the photocurrent. The absorbance spectrum of the film is distorted with respect to the solution spectrum due to the effects of light scattering. However, the action spectrum follows the solution spectrum closely above 800 nm. The peaks in the spectra at around 800 nm and 860 nm are due to bacteriochlorophyll absorption. The absence of a bacteriopheophytin peak at about 760 nm in the action spectrum presently remains unexplained.

DISCUSSION

The charge separation generated across the reaction center molecule as a result of the primary photochemistry of photosynthesis can be electrically coupled to some types of electrode materials. We have demonstrated that such reaction center electrodes can be used in a photoelectrochemical cell to generate photovoltages and photocurrents in an external circuit. Consequently, such reaction center electrodes might be the harbinger of a future biological photocell or might serve as a model system for future inorganic or organic photovoltaic devices.

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