

Studies of a Photosynthetic Photoelectrochemical Cell Using Various Electrodes

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Received August 4, 1982; Accepted June 1, 1983

Abstract

We have developed a photochemical cell using a combination of photosynthetic electron transport (photosystem I particles) and the photoreduction of a dye such as flavin mononucleotide (FMN)[†] (6). The overall power conversion efficiency depends on the rate of charge transfer across the electrode surfaces in addition to the efficiency of the photosynthetic and photochemical reactions. For this reason, we studied the effect of varying the nature of the electrodes on the power developed. We found that reticulated vitreous carbon electrodes showed higher power conversion efficiencies than did nickel mesh, platinum, or SnO₂ glass. There are two reasons for this. First, the ratio of actual to apparent surface area is greater for RVC electrodes than for the others. Second, FMN and its photoproducts react better with carbon than platinum electrodes. Substituting RVC electrodes for platinum increased the power conversion efficiency from 1.0 to 3.9%. Platinizing platinum, nickel mesh, or brass electrodes also increased the power developed. However, the photopotential remained stable for several hours only for the platinized platinum electrodes.

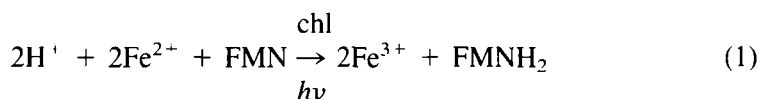
Index Entries: Photosynthetic photoelectrochemical cell; photoelectrochemical cell, photosynthetic; electrodes, for a photosynthetic photoelectrochemical cell.

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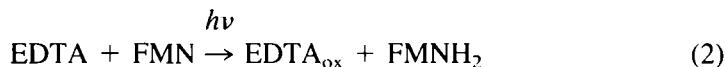
[†]*Abbreviations:* chl, chlorophyll; DCIP, dichlorophenol indophenol; EDTA, ethylenediamine tetraacetic acid; FMN, flavin mononucleotide; PSI, Photosystem I; Pt platinum; PtzPt, platinized platinum; RVC, reticulated vitreous carbon; *p*, electrode current density; TCA, trichloroacetic acid; Tricine; *N*-tris(hydroxymethyl) methyl glycine.

Introduction

We have developed a photoelectrochemical cell that utilizes both photosynthetic electron transport and the direct photoreduction of a dye such as flavin mononucleotide (FMN) (1-6). The photosynthetic contribution [Eq. (1)] involves the chloroplast-mediated reduction of FMN in one compartment of the cell and the oxidation of an electron donor such as $K_4Fe(CN)_6$ or dichlorophenol-indophenol (DCIP) in the other.† We used Photosystem I particles (7) to drive the photosynthetic reaction.



The photochemical contribution involves the direct photoreduction of FMN (6) at the expense of EDTA or a buffer such as Tris or Tricine [Eq. (2)].



Both reactions contribute to the generation of power by the cell as shown by the action spectrum (6).

Initial experimentation resulted in a power output of 20 μW and a power conversion efficiency of $2.5 \times 10^{-3}\%$ (based on a front surface illumination area of 8 cm^2 (1)). Recent improvements have resulted in a maximum power output of 1950 μW and a power conversion efficiency of 1.0% (6).

The power generated by the cell is dependent on several factors (8, 9). These include (1) the separation of charge across a Photosystem I (PSI)-containing membrane resulting in the reduction of the electron acceptor in one compartment of the cell and the oxidation of the electron donor in the other,† (2) the efficiency of the direct photoreduction of the dye, (3) the rates of diffusion of the electroactive species to the electrodes and (4) the rates of reaction of the electroactive species at the electrode surface.

Up until now, most of our increases in the power conversion efficiency have been caused by improvements in either the photosynthetic or photochemical contribution (2-6). In this study, we examined the effect of varying both the area and

†The standard free energy change ($\Delta G^{\circ'}$) for the photosynthetic contribution is given by the following equation.

$$\Delta G^{\circ'} = -n \mathcal{F} (E^{\circ'}_{FMN} - E^{\circ'}_{FeCN})$$

where n is the number of electrons transferred, \mathcal{F} is the Faraday Constant, $E^{\circ'}_{FM}$ is the midpoint potential for the FMN/FMNH₂ couple (-0.19 V), and $E^{\circ'}_{FeCN}$ is that for the $Fe^{3+}2^+Cn_6/Fe^{4+}(CN)_6$ couple (+0.42V). This results in a standard free energy change of +27.2 kcal mol⁻¹. The actual free energy change is slightly different since the FMN is predominantly in the oxidized form and the $Fe^{3+}(CN)_6/Fe^{4+}(CN)_6$ is 3. Nonetheless, light via photosynthesis promotes a charge separation that allows "uphill" electron transport.

Before illumination, there is essentially no dark current. After illumination, the dark current is inversely related to the load resistance since the external circuit is the principal path for the discharge of the potential developed in the light.

types of electrodes used. We have found that substituting vitreous carbon electrodes for the platinum electrodes previously used increased the power conversion efficiency to 4%.

Materials and Methods

The solar cell experimental design and photoresponse measurements for this study remained the same as those previously described (1, 6) except when otherwise stated. Photosystem I (PSI) particles were isolated according to the method Shiozawa et al. (7) as modified by Gross and Grenier (10). Photosystem I particles containing 80 μg chlorophyll were aspirated onto a 1 cm^2 area of a Metrical (cellulose triacetate) filter of 0.45- μ pore size. The filter was placed between the two compartments of the cell. Each compartment contained 32 mL of a solution containing 80 mM Tris-HCl (pH 8.2) or Tricine (pH 8.2) buffer + 100 mM NaCl. The electron acceptor compartment contained 3 mM FMN or 0.5 mM anthroquinone-2-sulfonate (AQS) + 5 mM EDTA as indicated. The electron donor compartment contained either dichlorophenol-indophenol (DCIP) or a mixture of 5.25 mM $\text{K}_3\text{Fe}(\text{CN})_6$ + 1.75 mM $\text{K}_4\text{Fe}(\text{CN})_6$. The mixture of $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{K}_4\text{Fe}(\text{CN})_6$ was necessary to poise the electron donor compartment at the correct redox potential (3, 5). The FMN side was illuminated with white light (tungsten) ($I = 1970 \text{ W/m}^2$) from a slide projector unless otherwise stated). Anaerobicity was maintained by bubbling argon through the cell. Electrodes as indicated were placed in each compartment. The measured areas for the RVC electrodes were corrected for the thickness, i.e., the areas of the sides were included.

The photovoltages were measured across a variable load resistance using a Radiometer Model 26 pH meter as a high impedance voltmeter. Light intensities were measured using a Yellow Springs Instrument's Model 65 Radiometer.

The photochemical contribution was determined after inactivating the PSI particles on the filter using 15% trichloroacetic acid (TCA). Chlorophyll concentrations were measured using the method of Arnon (11).

The SnO_2 electrodes were the generous gift of Dr. T. Kuwana of the Dept. of Chemistry, The Ohio State University. The nickel mesh electrodes were the generous gift of Dr. G. Royer of the Dept. of Biochemistry, The Ohio State University. Reticulated vitreous carbon (RVC) electrodes were obtained from Fluorocarbon Process Systems Division, Anaheim, Ca., and had a porosity of 100 pores per linear inch. FMN was obtained from the Sigma Chemical Co. All other chemicals were of reagent grade.

Results

The Dependence of the Photopower on the Area of Platinum Electrodes Used.

The effect of varying the area of the platinum electrodes was examined using either a mixture of $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{K}_4\text{Fe}(\text{CN})_6$ or $\text{K}_4\text{Fe}(\text{CN})_6$ alone in the donor compartment (Fig. 1). In the presence of $\text{K}_4\text{Fe}(\text{CN})_6$ alone, the power increased sig-

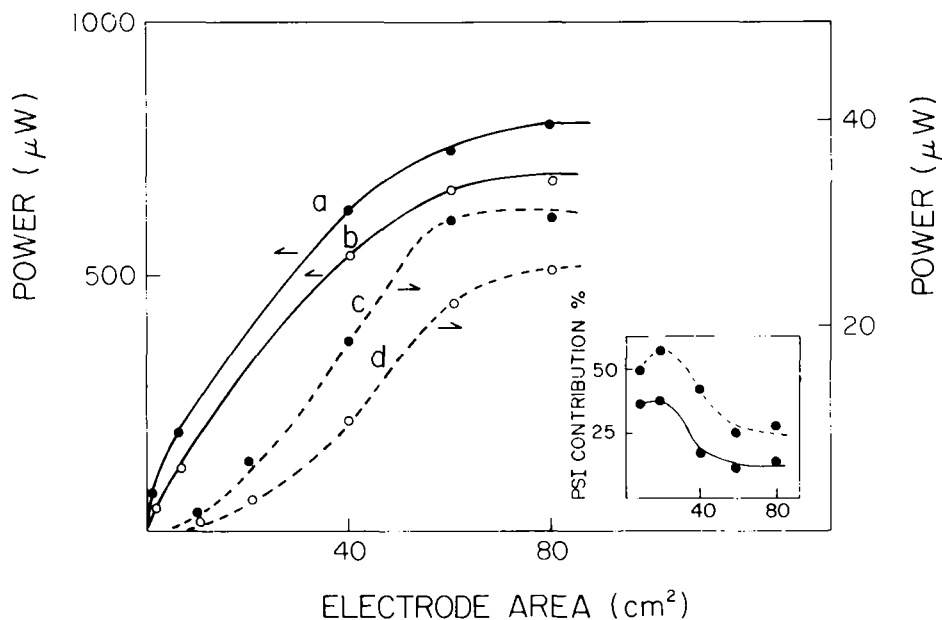


Fig. 1. The effect of electrode area on the maximum power developed using platinum electrodes. The power developed was determined as a function of electrode area for platinum electrodes under the following conditions: (a) Active PSI particles; $K_3Fe(CN)_6 + K_4Fe(CN)_6$ in the donor compartment and FMN in the acceptor compartment; (b) same as (a) except that the PSI particles were inactivated with TCA; (c) active PSI particles; $K_4Fe(CN)_6$ only in the donor compartment; (d) same as (c) except that the PSI particles were inactivated with TCA. In each case, we determined the photovoltage as a function of external load resistance after which the power was calculated using Ohm's law (6). The buffer was 80 mM Tris-Cl (pH 8.2) Other conditions were as described in the Materials and Methods section.

modally as the electrode area was increased reaching a maximum at 80 cm² of platinum per compartment. When $K_3Fe(CN)_6$ was added to the donor compartment, two effects were observed. First, the total power was increased severalfold as observed previously (3, 5, 6). Second, the power increased hyperbolically with increasing electrode areas. As a consequence, the power developed using small electrode areas was a larger fraction of the total possible power than when $K_4Fe(CN)_6$ alone was used in the donor compartment. There are two possible explanations. The first is that the $K_3Fe(CN)_6$ is necessary to poise the donor compartment at the correct redox potential. The second explanation is that there must be a sufficient concentration of $K_3Fe(CN)_6$ to accept electrons from the electrode. The percent of the total power contributed by the photosynthetic reaction was greater at smaller electrode areas. These results suggest that the photochemical contribution may be more sensitive to increases in the electrode area than is the photosynthetic. One possible reason for this is that the electroactive products may be different in the two cases. The product of the photosynthetic reduction of FMN is almost certainly the singly reduced semiquinone whereas the photochemical contribution may also consist of the products of FMN photodestruction (12).

The Effect of Platinizing the Electrodes

Since the apparent surface area is important in determining the effectiveness of the electrodes, we platinized the platinum electrodes to determine whether smaller areas could be used (Table 1). This technique resulted in a greater maximum power output using a 30 cm² platinized platinum electrode than was obtained using an 80 cm² unplatinized platinum electrode. The short circuit current was affected to a greater extent than was the total power. This is particularly evident when comparing the short circuit current drawn per electrode area (electrode current density, ρ). This is reasonable since the electrode characteristics are going to be most important when large amounts of current are being drawn. Similar results were obtained when K₄Fe(CN)₆ plus K₃Fe(CN)₆ (not shown) were used in the donor compartment.

Platinizing the electrodes has several obvious advantages. First, it increases the short circuit current and power. Second, it allows for the use of smaller electrode areas, thus permitting more flexibility in cell design. Finally, it decreases the cost of the cell in the case where the platinum is deposited on either brass or nickel mesh. Unfortunately, the photovoltage decayed after 10–20 min of illumination when either nickel, or platinized nickel or brass was used as electrode materials (Fig. 2). In contrast, the photovoltage was stable for at least several hours when

TABLE 1
The Effect of Platinization of Various Electrodes on the
Photoresponses of the Photosynthetic Photoelectrochemical
Cell Using DCIP as the Electron Donor^a

Electrode	Electrode area, cm	PSI condition ^b	Maximum power output, θ W	Resistance at maximum power output, ohms	Open circuit voltage (Voc), mV	Short circuit current (Isc), mA	Short circuit current density (ρ), μ A-cm
Pt	30	+	153	200	346	2.13	71
		-	98	200	340	1.25	41
PtzPt	30	+	320	80	340	4.65	155
		-	190	100	325	3.75	125
Brass	30	+	30	100	145	1.10	37
		-	25	100	310	1.06	35
PtzBrass	30	+	116	90	265	2.55	85
		-	104	100	260	2.43	81
Ni	150	+	87	300	375	1.7	11
		-	73	300	368	1.3	8.7
PtzNi	150	+	410	50	346	5.8	38
		-	360	60	335	4.7	81

^aConditions were as for Fig. 1 except that 1 mM DCIP was substituted for the K₃Fe(CN)₆/K₄Fe(CN)₆ mixture in the donor compartment. The electron acceptor was FMN.

^b(+) Refers to filters containing active PSI particles. (-) refers to filters containing TCA-inactivated PSI particles.

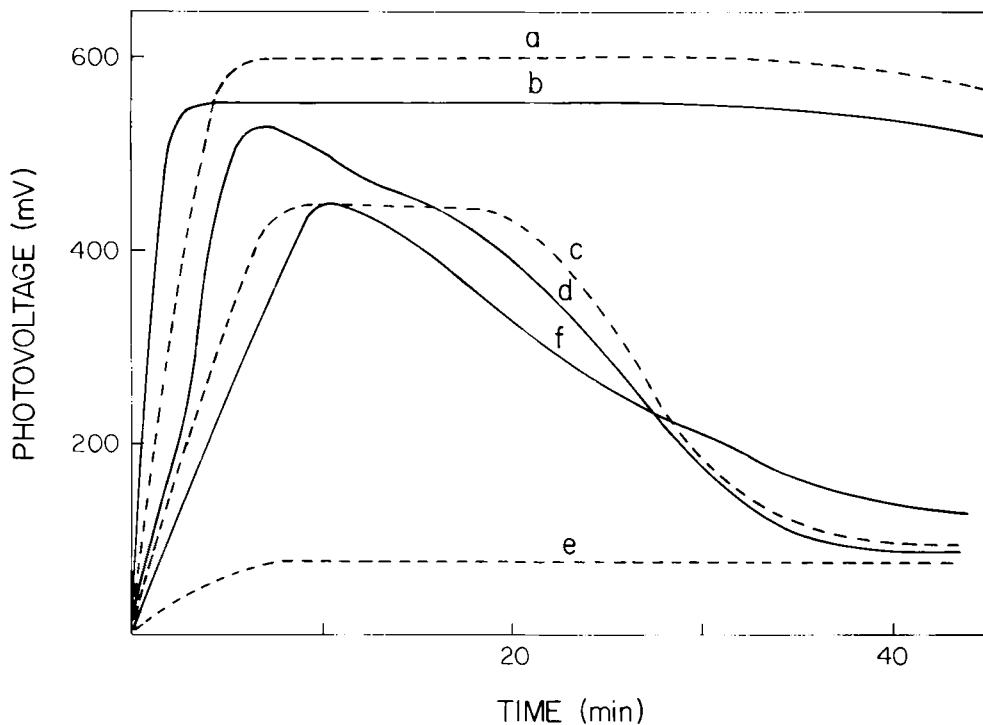


Fig. 2. Stability of the photovoltage for different types of electrodes. The photovoltage was determined as a function of time of illumination for different types of electrodes: (a) platinum; (b) platinized platinum; (c) nickel; (d) platinized nickel; (e) brass; (f) platinized brass. Other conditions were as described for Fig. 1a. The local resistance was 6000Ω .

platinum or platinized platinum electrodes were used (not shown). We observed erosion of the surface of the platinized nickel and brass electrodes during the decay of the photovoltage. We speculate that this is caused by local galvanic effects that short-circuit current flow.

Comparison of the Performance of Platinum Electrodes with Other Types of Electrodes

We compared the effect of apparent electrode surface area on the power developed for four different types of electrodes (Fig. 3). The maximum power obtained increased in the following order: SnO_2 glass, platinum, nickel mesh, and reticulated vitreous carbon (RVC). Thus, we obtained a maximum power of $2200 \mu\text{W}$ with RVC electrodes compared to only $600 \mu\text{W}$ using SnO_2 glass under the same conditions. The reticulated vitreous carbon also showed the greatest short circuit current (13.8 mA) and current density ($0.39 \text{ mA}\cdot\text{cm}^{-2}$ apparent electrode area) (Table 2). The load resistance at maximum power was also the lowest (60Ω). In contrast, the nature of the electrode had little effect on the open circuit voltage. Thus, limitations on the electrodes are most important under conditions in which current is being drawn. Inactivating the PSI particles also had a greater effect on the short circuit current than on the open circuit voltage. Again, the contribution of

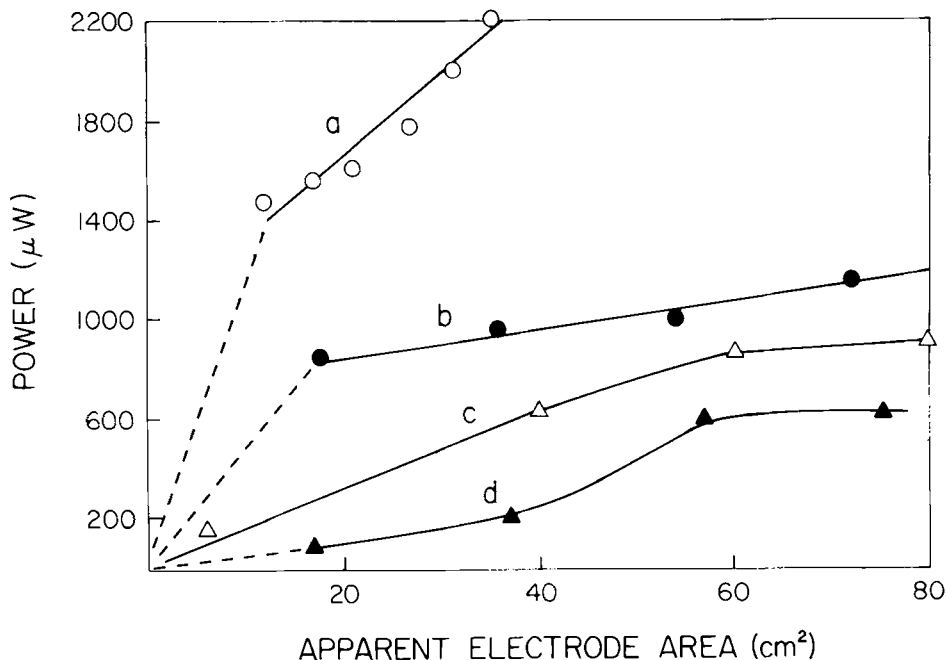


Fig. 3. Comparison of the effectiveness of different types of electrodes on maximum power development. The power developed was determined as a function of apparent electrode area for the following types of electrodes: (a) reticulated vitreous carbon (100S); (b) nickel mesh; (c) platinum; (d) SnO₂ glass. Conditions were as described for Fig. 1a, except that 5 mM EDTA was included in the FMN compartment and 80 mM Na-Tricine buffer was substituted for the Tris buffer in both compartments.

TABLE 2
Comparison of Different Types of Electrodes
with Respect to Power, Voltage, and Current Developed^a

Electrode type	Electrode area, cm ²	PSI condition ^b	Maximum power output, μW	Resistance at maximum power output, ohms	Open circuit voltage (V _{oc}), mV	Short circuit current (I _{sc}), mA	Short circuit current density (ρ), mA-cm ⁻²
RVC	35	+	2180	60	705	13.8	0.39
		-	1916	70	709	10.9	0.31
Pt	80	+	1560	70	708	9.8	0.12
		-	1300	80	707	7.6	0.095
Ni mesh	72	+	1148	80	595	7.2	0.10
SnO	75	+	584	200	645	4.5	0.06

^aConditions were as described for Fig. 3.

(+) refers to filters containing active PSI particles.

(-) refers to filters containing PSI particles inactivated with 15% TCS.

the PSI particles is most important when a maximum current is being drawn. The photovoltage observed with the RVC electrodes was stable for at least several hours (not shown).

Moreover, those electrodes that showed the maximum power (nickel mesh and RVC) also required the least apparent surface area (Fig. 3). One reason why the RVC and nickel mesh electrodes showed the greatest power is that they have a high ratio of actual to apparent surface area. Another reason for the differential power developed with different types of electrodes has to do with electrode selectivity. For example, we have found, using cyclic voltammetry, that reduced FMN reacts much better with carbon paste than with platinum electrodes (13).

The Power Conversion Efficiency as a Function of Electrode Type

We also determined the power conversion efficiency for the different types of electrodes. This involved determining the power output as a function of light intensity after which the efficiencies were calculated (Table 3). The efficiencies were calculated on the basis of the intensity of white light impinging on the front surface of the cell assuming an illuminated area of 8 cm², which represents the area of FMN solution illuminated. This assumption minimizes the contribution of the Photosystem I particles since only 1 cm² of the filter was illuminated. The reticulated vitreous carbon electrodes produced the highest power conversion efficiency (0.14%) even at high light intensities (1970 W·m⁻²). This is in contrast to 0.04% for SnO₂ glass under the same conditions. The effect of electrode material is more striking at low light intensities (39 W·m⁻²) at which we obtain the maximum power conversion efficiencies. In this case, we obtain 3.9% for the reticulated vitreous carbon electrodes compared to 1.8, 0.8, and 0.07% for the platinum, SnO₂ glass, and Ni

TABLE 3
Power Conversion Efficiencies^a of an FMN-PSI Solar Cell
Using Various Electrodes of Maximum Apparent Surface Area

Electrode type	PSI condition ^b	Power conversion	Power conversion
		efficiency at 39.3 W·m ^{-2c}	efficiency at 1970 W·m ^{-2c}
100 S RVC	+	3.9%	0.14%
100 S RVC	-	3.4%	0.12%
Platinum	+	1.8%	0.10%
Platinum	-	1.3%	0.08%
Nickel mesh	+	0.6%	0.07%
SnO glass	+	0.8%	0.04%

^aConditions were as described for Fig. 3 except as otherwise indicated.

^b(+) refers to filters containing active PSI particles. (-) refers to filters containing PSI particles inactivated with 15% TCA.

^cThe power conversion efficiencies were calculated using the intensity of white light incident on the front surface of the cell. Also an area of 8 cm² was used which corresponds to the area of FMN solution illuminated. The area of the PSI-containing filters was 1 cm² so that this method of calculation underestimates the photosynthetic contribution.

mesh electrodes, respectively. The greater power conversion efficiency occurs because the power obtained rises more rapidly with increasing light intensity for vitreous carbon electrodes than for platinum (Fig. 4). For example, half-saturation occurs at $40 \text{ W}\cdot\text{m}^{-2}$ for RVC electrodes compared to $100 \text{ W}\cdot\text{m}^{-2}$ for platinum.

The data shown above was for 100S RVC electrodes. We also examined other types of reticulated vitreous carbon electrodes containing fewer pores per linear inch (80S, 60S, and 45S). They all showed a 30–50% increase in power at high light intensities, but were not as good as the 100S at low light intensities (below $150 \text{ W}\cdot\text{m}^{-2}$).

Discussion and Conclusions

The power conversion efficiency of the FMN-Photosystem I solar cell is dependent on several factors, including the efficiency of the photochemical and photosynthetic process (including different electron donors and acceptors) (1–6), the membrane resistance, and the efficiency of the reaction of the photoproducts at the elec-

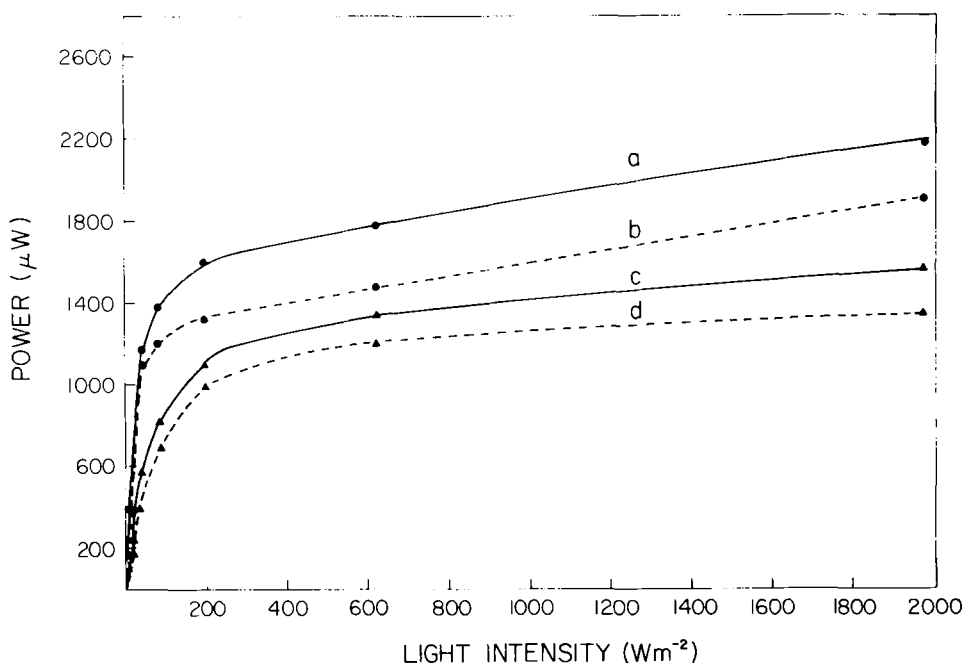


Fig. 4. The effect of light intensity on the power output for platinum and carbon electrodes. The photovoltage was determined as a function of load resistance at several light intensities, after which the power developed was calculated according to Ohm's law. The intensities given refer to the white light incident on the front surface of the cell. (a) RVC electrodes using active PSI particles; (b) RVC electrodes using PSI particles inactivated with TCA; (c) platinum electrodes using active PSI particles; (d) platinum electrodes using PSI particles inactivated with TCA. The electrode area was 40cm^2 . Other conditions were as described for Fig. 3.

trode surface. In this paper, we examined this last factor by varying the area and type of electrodes used. We found that the power obtained could be increased by platinizing some electrodes including platinum, nickel mesh, and brass. However, the only one that showed a stable power development was platinized platinum.

Several other types of electrodes were also examined. It was found that the power developed was greater using reticulated vitreous carbon electrodes than using any of platinum, nickel mesh, or SnO₂ glass. The use of reticulated vitreous carbon electrodes increased the power conversion efficiency from 1.8 to 3.9%. This power conversion efficiency is based on the intensity of white light incident on the front surface of the cell and does not take into account thermodynamic losses caused by sacrificial processes such as the oxidation of the EDTA. Nonetheless, the power conversion efficiency compares favorably with that observed for other photosynthetic solar cells (14, 15).

The higher efficiency observed with the reticulated vitreous carbon electrodes compared to the platinum electrodes is caused by two factors: (1) the large ratio of real to apparent surface area in the case of the RVC electrodes [which amounts to 65 cm²/cm³ (16)] and (2) the electrode selectivity for FMN, which also favors the RVC electrodes. In addition to the higher efficiencies observed, the RVC electrodes have the advantage of being inexpensive and can easily be cut to any size and shape. For example, they have been used by other workers as optically transparent (17) or flow-through (18–20) electrodes.

Acknowledgments

This work was supported in part by US Department of Energy Grant #DE Fg 02-79ER-10538. Any opinions, findings, or conclusions expressed herein do not necessarily reflect the views of DOE.

We wish to thank Mr. Brian Bahnson for construction of the cells.

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