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Comparative study of thylakoids from higher plants for solar energy conversion and herbicide detection

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ABSTRACT

Thylakoid membranes were isolated from seven plant species. The isolated thylakoids were immobilized onto carbon paper electrodes and the photocurrent was measured. Spinach thylakoids showed the largest photocurrent, 80 ± 10 μA per mg protein and 430 ± 60 μA per mg chlorophyll. The electrodes were also tested in a bio-solar cell configuration. Open circuit voltages were the same regardless of the thylakoid source, and spinach thylakoid bio-solar cells had the largest currents. Exposure of the electrodes to diuron, a commonly used herbicide, showed that sensitivity varied by thylakoid source, with spinach having the highest sensitivity and green chard and beet greens having the lowest.

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1. Introduction

Thylakoid membranes, found in the chloroplasts of plants and cyanobacteria, contain all the necessary components for the light-dependent reactions of photosynthesis. Photosynthesis has evolved over time to become extremely efficient, with some components having quantum yields close to 1 [1]. Research groups have sought to take advantage of this efficiency by developing electrodes capable of solar energy conversion using several types of biological or bio-inspired photoelectrocatalysts: chloroplasts [2,3], thylakoids [4–7], photosystems [8–10], photosynthetic reaction centers of bacteria [11,12], or by mimicking electron transfer pathways in photosynthetic complexes [13].

The conversion of solar energy to chemical energy begins with the oxidation of water at the oxygen evolving complex of photosystem II. From here, electrons are transferred to cytochrome b_6f by reduced plastoquinol, which is oxidized back to plastoquinone and the protons are released in the thylakoid lumen. Plastocyanin shuttles electrons from cytochrome b_6f to photosystem I before they are transferred to ferredoxin [14]. The electron transfer can then proceed along two pathways. There is a cyclic pathway where plastoquinone accepts the electrons from the reduced ferredoxin to form plastoquinol which can then continue on in the transfer pathway. A noncyclic pathway also exists where electrons are used by the enzyme ferredoxin-NADP$^+$ reductase to form nicotinamide adenine dinucleotide phosphate (NADPH) [15]. A proton gradient is formed across the membrane by the protons generated in the lumen during photosynthesis which is used by ATP synthase to produce adenosine triphosphate (ATP).

We have previously reported a thylakoid bio-solar cell capable of direct bioelectrocatalysis which had an open circuit voltage of 0.72 V and a short circuit current density of 14 ± 2 μA/cm^2 [5,6]. The photocurrent generated by this system showed a contribution from the first five steps of the photosynthetic electron transfer pathway [16]. The photosynthetic electron transfer pathway is the same for all vascular plants. However, differences in the activities of the components across plant species will affect the photocurrent generation of bio-solar cells incorporating thylakoids from different sources. In this work, thylakoid membranes were isolated from seven plant species and used to make thylakoid bioanodes capable of direct photobioelectrocatalysis. The photocurrent produced at these electrodes was measured and compared. The electrodes were connected with a laccase biocathode to be evaluated in a bio-solar cell configuration as well.

Finally, as a demonstration of a potential application for using thylakoids from different sources, the electrodes were inhibited with diuron, a photosystem II inhibiter used as an herbicide which

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operates by blocking the plastoquinone binding site of photosystem II, preventing the electron transfer to cytochrome b_6f. We have previously reported a biosensor which detects herbicides by measuring the power output decrease due to inhibition of photosynthesis at the thylakoid bioanode [17]. The linear range of detection and different sensitivities of thylakoids from different plant sources was measured.

2. Experimental

2.1. Materials

Organic spinach, arugula, beets, green chard, kale, collard greens, and watercress were purchased from a local supermarket. Tetramethyl orthosilicate (TMOS) and diuron were purchased from Fluka (USA). Toray carbon paper (TGP-H-60, non-wet-proof) was purchased from Fuel Cell Earth (USA). A BCA assay kit from Fisher Scientific was used to determine protein concentrations. All other reagents used were purchased from Sigma (USA). Solutions were prepared with 18 MΩ cm de-ionized water from a Milli-Q system.

2.2. Thylakoid Membrane Isolation

Thylakoid membranes were isolated according to a previous procedure [5]. The same mass of leaves was used for each type of plant (~300 g). After isolation, the thylakoids were suspended in a solution containing 330 mM sorbitol, 2 mM $MgCl_2$, and 50 mM pH 7.8 HEPES (thylakoid isolation buffer). The chlorophyll content and protein concentrations were determined spectroscopically.

2.3. Electrode Fabrication

Catalase from *Aspergillus niger* (Sigma, 9.47 kU/mg, 28.73 mg/mL, 3 μL per 100 μL thylakoids) was added to the thylakoid suspension prior to electrode modification. As per the discussion in Ref. 5, the addition of catalase prevents a decrease in activity due to reactive oxygen species production. A 50 μL aliquot of the thylakoid/catalase mixture was applied to 1 cm^2 Toray® carbon paper electrodes and allowed to dry. A previously reported procedure was use to vapor deposit a thin layer of silica onto the thylakoid layer by hydrolysis of tetramethyl orthosilicate [5,18]. After modification, the electrodes were stored at 4 °C overnight. Laccase biocathodes for bio-solar cell tests were fabricated according to previous procedures [6].

2.4. Photoelectrochemical Analysis

Electrodes were illuminated with a 250 W Halogen lamp at 5200 lumens. Electrochemical experiments were performed using a CHI660E potentiostat. Amperometric measurements were performed by applying a voltage of 0.45 V vs. Ag/AgCl while measuring the current in the absence and presence of light. Control experiments were performed in the exact same experimental setup but with electrodes containing no thylakoids. All experiments were performed in triplicate and reported uncertainties correspond to the standard deviation of those triplicate measurements.

3. Results and Discussion

3.1. Isolated thylakoids from different plant sources

After isolation, the protein and chlorophyll concentrations were determined for the thylakoid suspensions (see Table 1). The protein concentrations are quite similar with only the spinach and beet leaves having significantly lower values (less than half the value of the other five species). The chlorophyll content shows more variance. Again, the spinach and beet leaves have the lowest values, but arugula and watercress also has much lower chlorophyll concentration than some of the other thylakoids. Thylakoid and chlorophyll content is known to have a large seasonal fluctuation along with a dependence on age of the plant [19–22]. Due to these variations, the concentrations for the isolated thylakoids may not be an average representation. Instead, these values are used to normalize the photocurrent generated by each type of thylakoid.

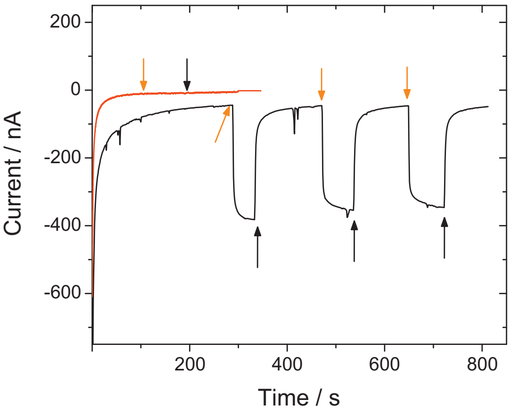

Fig. 1. Amperometric results for a spinach thylakoid electrode (black line) in 0.1 M citrate buffer, pH 5.5, at 0.45 V vs. Ag/AgCl in the absence (black arrows) and presence of light (orange arrows). Results for a control electrode with no thylakoids is also shown (red line).

3.2. Photocurrent generation of thylakoid electrodes

Thylakoids isolated from different plants were immobilized onto carbon electrodes by physical adsorption and covered with a vapor-deposited layer of silica. A potential of 0.45 V vs. Ag/AgCl was applied in 0.1 M pH 5.5 citrate buffer. After the current stabilized, the electrode was illuminated, and the current was allowed to stabilize again. Then the light was turned off. This process was repeated several times for each electrode. Fig. 1 shows representative amperometric data for a spinach thylakoid electrode. Control electrodes containing no thylakoids showed no photocurrent response.

The difference between the current in absence and presence of light was calculated and reported as the photocurrent for each type of thylakoid electrode as shown in Table 1. The photocurrent for thylakoids from different sources varied greatly, from as low as 7 ± 2 nA for kale and watercress up to 350 ± 50 nA for spinach. However, the electrodes were modified with different amounts of protein and chlorophyll depending on the type of thylakoid. Therefore, normalizing the photocurrent by either the protein or chorophyll content would allow for a more accurate comparison of the response, as shown in Table 1. A similar trend is seen for all three cases. Spinach thylakoids have significantly larger photocurrent response (a 4-fold increase) than all of the other thylakoids evaluated. Beet leaves and collard greens show the next largest responses and watercress consistently generated the lowest photocurrent. Thylakoids from arugula, green chard, and kale showed similar responses.

It is not surprising that spinach thylakoids generate the largest photocurrent. Spinach has several advantages as a source for thylakoid isolation. Its leaves are soft which allows for easy cell disruption without too much exposure to the cell vacuolar sap [1]. Minimizing this exposure is important because fatty acids could activate polyphenol oxidases which would result in a decrease in photosynthetic activity [23]. More importantly, spinach has lower

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