PHOTOELECTROCHEMICAL BEHAVIOR OF A DYE-SENSITIZED NANOPARTICULATE SEMICONDUCTOR ELECTRODE IN A BIOFUEL CELL

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Dye-sensitized photoelectrochemical solar cells based on nanoparticulate semiconductors are of considerable technological interest\(^1\). Concurrently, there have also been numerous studies of the generation of electrical energy using enzymatic processes\(^2\). However, the combination of these two approaches in a single light-assisted fuel cell has been little investigated. In the present study, the electrochemical characterization of such a photoelectrochemical biofuel cell will be presented.

Nanoparticulate SnO\(_2\) on indium-tin oxide conducting glass was used as the photoanode. The semiconductor particles were coated with porphyrin-based sensitizer dyes (D). After electron injection into the semiconductor particles by the excited dye molecules (D\(^+\)), the resulting oxidized dye molecules (D\(^2+\)) were reduced by NADH (nicotinamide adenine dinucleotide, reduced form) to regenerate the sensitizer. The two-electron oxidation product, NAD\(^+\), was reconverted to NADH by enzymatic reactions during which methanol fuel is oxidized by an enzymatic system employing alcohol dehydrogenase, aldehyde dehydrogenase and formate dehydrogenase.

Figure 1 shows the open circuit voltage (OCV) of the photoanode, determined as the equilibrium potential of the photoanode in the open-circuit state. The OCV thus measured may be different from that determined by the commonly-employed voltage sweep method, which is affected by variables such as the scan rate, as shown in Figure 2.

The oxidized form of the electron donor (NAD\(^+\)) was not reduced at the photoanode, and such reduction is not an important recombination reaction for this cell. Other possible recombination reactions such as the reduction of SnO\(_2\) (intercalation or reconstitution) and \(\text{H}_2\) evolution were not observed within the voltage window that is usually used (Figure 3). Therefore, the main recombination reaction in this system is postulated to be reduction of oxidized dye by the injected electrons in conduction band. Thus, the electrochemical behavior of the photoanode and the electrochemical equilibrium reactions under OCV conditions will be directly determined by the electrochemical properties of the D\(^+/D^-\) and D\(^2+/D^-\) couples. There are many variables that can affect the electrochemical behavior of D\(^+/D^-\) and D\(^2+/D^-\) in the biofuel cell. Examples are the concentration and diffusion of NADH, the light intensity, the physiochemical properties of the dye-coated electrode, and the amount of fuel and enzyme. The effect of some of the factors that can affect the electrochemical behavior of the photoanode will be discussed, as well as details of the electrochemical reactions at the photoanode.

References

Figure 1. The variation of the OCV with cell resting time

Figure 2. The current-voltage curve at various scan rates

Figure 3. Cyclic voltammetry of SnO\(_2\) and ITO electrodes (scan rate: 1 mV/sec)