A novel electrochemical proton pump

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Protons are transported electrochemically from one aqueous phase to the other phase *via* an oil phase containing a hydrophobic quinone compound (vitamin K_3) using a pair of solid polymer electrodes set at the oil/water boundaries.

In recent years the mechanism of photosynthesis has evoked great interest with a view to constructing efficient solar energy conversion and storage systems. In this respect, production of hydrogen and reduction of carbon dioxide on semiconductor photocatalysts and assembled molecules is called artificial photosynthesis and has been studied very intensively.[1] However, the function of the proton pump of photosynthesis[2,3] has not attracted much attention in the field of artificial light energy conversion systems, although it is one of the key functions of photosynthesis.

Pioneering work on the proton pump mimicking the biological system has been reported by Anderson *et al.*[4] using a liquid membrane containing vitamin K_1 and coenzyme Q_{10}. More recently, similar systems have been reported by Kobuke and Hamache[5] using a liposomal membrane and by Imanishi and co-workers[6] using a liquid membrane. The membranes contained electron carriers and separate aqueous solutions having electron donors in one phase and electron acceptors in the other phase. As the electrons were passed from electron donors to electron acceptors through the electron carriers in the membranes, protons were co-transported. Therefore, in these systems the difference in the electrochemical potentials of two aqueous phases gave the driving force for the proton transport. Eschegoyen and co-workers[7] have demonstrated through electrochemistry the cation transport through the oil phase *via* the redox reactions of quinone compounds dissolved in the oil phase. The reactions were driven by two sets of electrochemical systems.

Our proton pumping system is unique in that the redox reaction of quinone compounds takes place at the oil/water interfaces using a pair of electrodes placed at the interfaces. In this system no net chemical change occurs, except the transport of protons and the counter ions. As a whole, therefore, the electric energy is converted to the chemical potential as acid concentration.

The electrochemical experiments were carried out using Nafion® membrane electrodes loaded with a porous platinum layer on one side of the membrane. They were prepared according to the literature.[8] These electrodes have been applied to fuel cells[9] and organic electrochemistry.[10,11] The membrane electrodes with an apparent surface area of 0.79 cm^2 were fixed to two-compartment and three-compartment cells, as shown in Figs. 1 and 2. The platinum deposited side of the Nafion® membrane electrodes faced the oil phase. As the oil, we used dichloroethane containing no supporting electrolytes. Potassium chloride was added to the aqueous phases as the supporting electrolyte at a concentration of 0.05 mol dm^{-3}. A platinum counter electrode with an apparent surface area of 1.0 cm^2 was used in the two-compartment cell.

Before constructing the proton pump system, we searched for the quinone compounds to be used in the system. For this purpose, electrochemical properties of quinones at the oil/water boundary were studied using the two-compartment cell.

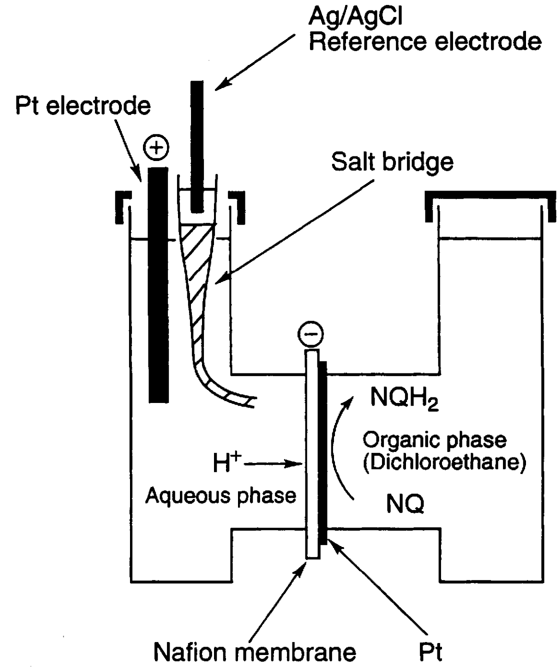


Fig. 1 Two-compartment cell for cyclic voltammetry

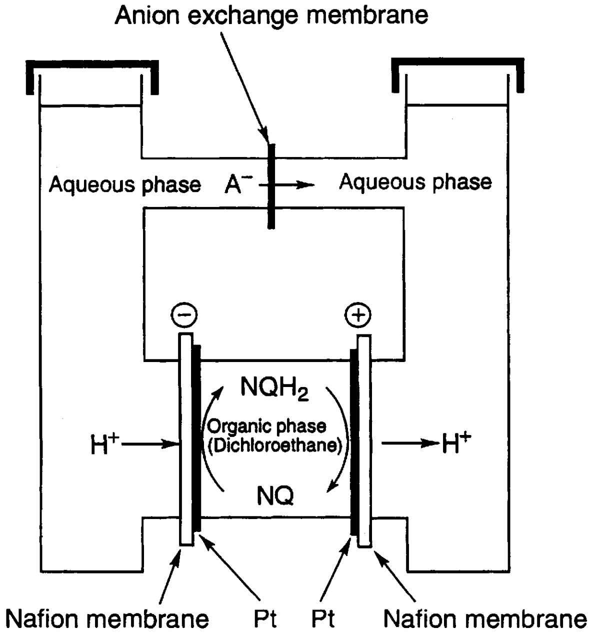


Fig. 2 Three-compartment cell for proton transfer experiments

Hydrophobic quinone compounds were dissolved in the oil phase and their electrochemical reactions on the Pt-loaded

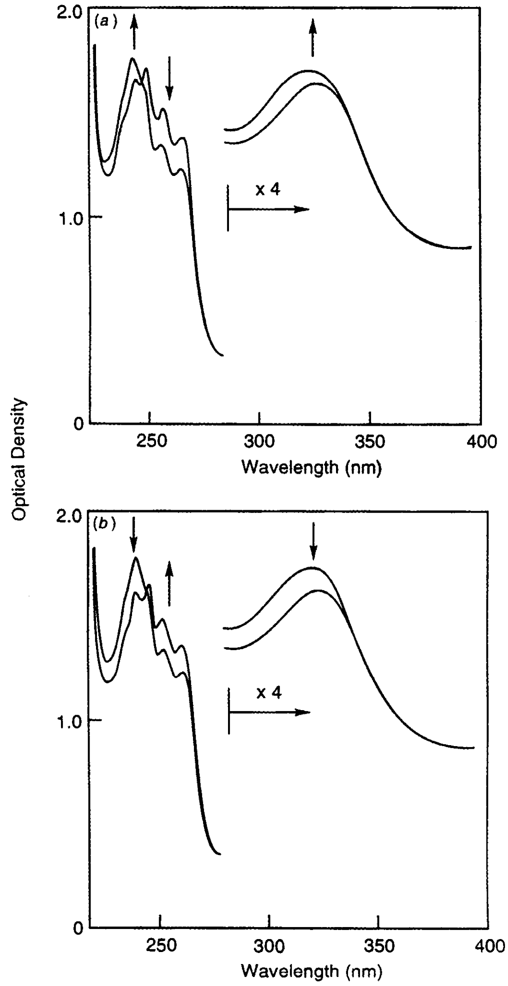
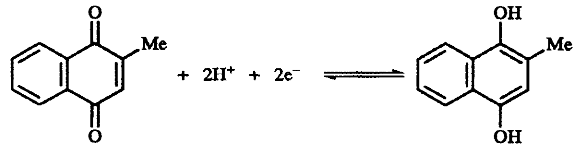


Fig. 3 (*a*) Spectral change of NQ (1.0×10^{-4} mol dm^{-3}) in dichloroethane by electrochemical reduction at −1.0 V *vs.* Ag/AgCl for 3 h under anaerobic conditions in the two-compartment cell. (*b*) Spectral change of the above solution by oxidation at 0.0 V *vs.* Ag/AgCl for 3 h. Trends of spectral changes with time are shown by arrows.

Nafion® electrode were followed by cyclic voltammetry. From the experimental results, we found that vitamin K_3, or 2-methyl-1,4-naphthoquinone (NQ), shows redox reactions on the electrode surface, the redox potential being at *ca.* −0.68 V *vs.* Ag/AgCl.

In order to determine the reduced form of NQ and the reversibility of the redox reaction in our system, NQ was electrochemically reduced at −1.0 V *vs.* Ag/AgCl in the two-compartment cell under argon atmosphere. As the reduction proceeded, new absorption bands peaking at 245 and 322 nm grew as shown in Fig. 3(*a*). The absorption bands agreed with those of 2-methyl-1,4-naphthohydroquinone (NQH_2). By applying 0.0 V *vs.* Ag/AgCl (oxidative potential) to the Nafion® membrane electrode after the electrochemical reduction of NQ, the absorption peaks due to NQH_2 decreased and the bands due to NQ reappeared as shown in Fig. 3(*b*). These results confirm the two-electron and two-proton redox reactions between NQ and NQH_2 (Scheme 1) on the Nafion® membrane electrode at the water/oil interface. Protons involved in the reactions are expected to be supplied from and released to the aqueous phase through the Nafion® membrane, which separates the water/oil boundary and has good affinity to water.

When other quinone compounds were studied, we sometimes observed degradation products of quinone compounds on the platinum layer of the Nafion® membrane electrodes during electrolysis and poor reversibility of the reactions.



Scheme 1

On the basis of the above results, we carried out the proton transfer experiments using the redox couple of vitamin K_3 in the three-compartment cell. *Ca.* 2.5×10^{-4} dm^3 of dichloroethane solution containing NQ and NQH_2 (5.0×10^{-3} mol dm^{-3}, respectively) was added to the middle compartment. Each of the two compartments at both ends contained 8.0×10^{-3} dm^3 aqueous sodium chloride (5.0×10^{-3} mol dm^{-3}). The pH of the solution was adjusted to pH 3.0 by adding hydrochloric acid. A bias voltage of 0.4 V was applied between the two electrodes and maintained using a potentiostat during electrolysis. In the absence of NQ and NQH_2 in the organic phase, the current was less than 0.2 μA and no pH change was observed in the aqueous phases even after application of the voltage over several hours. No current flowed when the aqueous liquid junction was disconnected. On the other hand, when NQ and NQH_2 were dissolved in the organic phase and the aqueous liquid junction was connected, *ca.* 13 μA current kept flowing. After an electric charge of 100 mC had passed, the pH changes of both aqueous phases were measured. They were in good agreement with those expected from the electric charge passed in the system; the amount of protons transported between the aqueous phases corresponded to 98% of the electrons passed as current. These results prove that protons are carried through the NQ–NQH_2 redox system added to the organic phase. The neutrality of the solutions is maintained by the transfer of chloride ions through the anion exchange membrane in the cell.

By means of the novel proton pump system, we have demonstrated the electrochemical concentration of acid using a suitable quinone compound and platinum loaded Nafion® membrane electrodes. It is important that no chemical changes occur in the system. A new solar energy conversion system mimicking the photosynthesis could be constructed by utilizing the proton pump if it is operated photoelectrochemically or photocatalytically using semiconductor electrodes or semiconductor particles in place of the two porous platinum layers.

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