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PHOTOINDUCED ELECTRODIALYSIS

Basic principles of photoinduced electro dialysis, photoelectrodialysis, have been discussed. The process consists in a coupling of electrochemical reactions occurring at an illuminated semiconductor-redox electrolyte interface with an ionic transport through ion-exchange membranes. The semiconductor photoelectrodes used in experiments were *n*-type CdS plates of about 3 cm² active surface area fabricated by pressing CdS powder under 60–70 MPa and sintering it at 1000–1100 K in argon atmosphere. A vacuum-evaporated titanium film on the sintered CdS plate was made to provide an electric contact with copper wire. Some photoelectrodes were also made by anodizing a metal cadmium substrate in a Na₂S/NaOH solution at current density of 10.5 A m⁻². A sulfide/polysulfide redox solution served as a liquid junction and platinum as a counterelectrode. Domestic cation- and anion-exchange membranes and 0.01 M NaCl solution were used in the photoelectrodialytic experiments.

Results of desalination point to the coupling between the redox reactions and the transport of ions through ion-exchange membranes but a considerable mismatch between these two elements of the system accounts for the low efficiency.

1. INTRODUCTION

Interest in solar energy conversion and storage has a long history and a comprehensive background. Most of the attempts reported in the literature have aimed at transforming the energy of sun light into heat and electricity. The efforts proved fruitful, yielding two practicable solutions — solar collectors and silicon solar cells [1]. Both types of converters have been either applied or recommended as applicable to the water desalination, e.g., in distillation [2]–[4] or in electro dialysis [5]. In the past several years, the different approaches to the problem of energy conversion and storage have come together in a concept of a system initiating the way in which green plants capture and transform light quanta. This artificial system (which Calvin [6] has called a “synthetic chloroplast”) need not necessarily be a point-by-point imitation of nature itself but it should be capable of a similar

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function. The processes occurring at a semiconductor–electrolyte interface in a liquid junction photocell seem to offer a promising way that may lead to development of such a system. This is because of a certain similarity between these processes and those involved in photosynthesis.

Liquid junction photocells are constructed by placing a semiconductor and a counterelectrode in a common electrolyte. The semiconductor–electrolyte interface is an element in which solar energy conversion occurs. A major factor which had limited the applications of the cells for a long time was the photocorrosion of the semiconductor electrode. But this problem has partly been solved for semiconductors of larger band gaps (greater than 1eV) by an appropriate selection of redox electrolytes [7]–[9]. In the case of semiconductor photoanode, the reductant of such a redox couple oxidizes on the anode surface to be subsequently reduced on the counterelectrode. The reverse holds for the photocathode: the oxidizer of the redox couple is reduced on the photocathode surface and regenerated on the counterelectrode. To prevent photocorrosion it is necessary that these redox reactions compete efficiently with electrode dissolution reaction.

In 1978 MURPHY [10] proposed several model photoelectrochemical energy conversion systems which couple electrochemical reactions occurring in the semiconductor–electrolyte junction with mass and charge transport through ion-exchange membranes. Photoelectrodialysis was one of these model systems. The process was tested experimentally [11], [12] and the results obtained have inclined us to repeat the experiment with another semiconductor (*n*-CdS). The results and a detailed analysis of the process are presented in this paper.

2. EXPERIMENTAL

2.1. MATERIALS

All of the chemicals used in this study were analytically pure. CdS was that of a special grade designed for luminophores. The membranes used were domestic KESD cation-exchange and AESD anion-exchange membranes. Both types of the membranes have already been tested in the electro dialysis experiments [13].

2.2. PREPARATION OF POLYCRYSTALLINE CdS PHOTOELECTRODES

Two preparation methods were employed. One of them consisted in anodizing metallic cadmium in 1 M Na₂S + 1 M NaOH solution for 5 h at a current density of 10.5 A m⁻². The electrodes obtained were thoroughly rinsed with distilled water,

etched superficially by repeated immersion in concentrated CH_3COOH , and finally washed. The other method involved pressing of CdS powder in a steel form at a pressure of 60 to 70 MPa and sintering it in this form at 1000 to 1100 K under argon. The sintering process took 1 to 2 h, and cooling of the sintered pellets to room temperature proceeded at a rate of 20 deg h^{-1} . The pellets were then etched in concentrated HCl for several seconds, rinsed with distilled water and placed in 1 M $\text{Na}_2\text{S} + 1 \text{ M KOH}$ solution for 1 to 2 h in order to remove elemental sulfur from their surfaces. Following the washing with distilled water, the pellets were dried at 383 K for 24 h. They had a diameter of $30 \pm 0.2 \text{ mm}$ and a thickness of $2 \pm 0.5 \text{ mm}$. A vacuum-evaporated titanium film and a protecting nickel layer were made to provide an electric contact with copper wire and counterelectrode. Except for the illuminated part, the surfaces of the electrode were additionally covered with an epoxy resin layer. The photoactive surface area of the electrode (3.14 cm^2) was subject to photoetching by the TENNE [14] method.

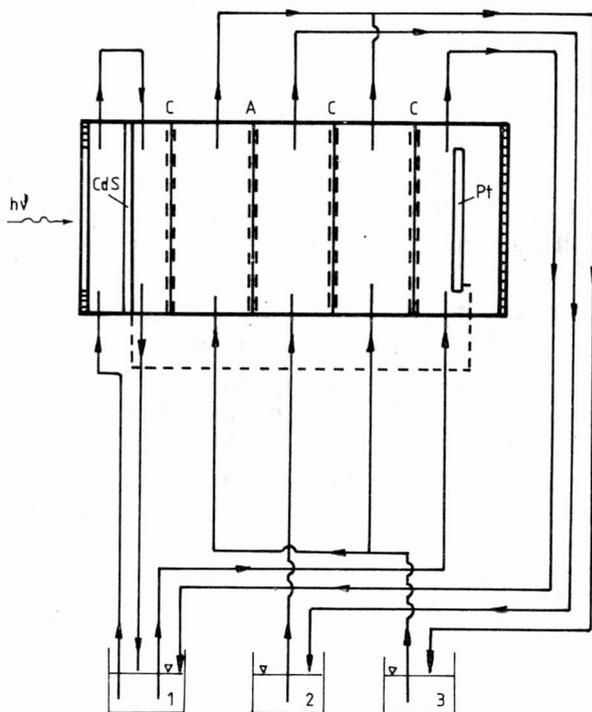


Fig. 1. Schematic representation of the photoelectrodialytic system

C - cation-exchange membrane, A - anion-exchange membrane, 1 - redox electrolyte, 2 - dialysate, 3 - concentrate

3. PHOTOELECTRODIALYSIS

The experimental photoelectrodialyzer is shown schematically in fig. 1. It consisted of two parts: a CdS|0.1 M Na₂S+0.1 M KOH+0.01 M S half-cell and a membrane stack together with a platinum counterelectrode. The apparatus was made of organic glass. Rubber gaskets (1 mm thick), along with the membrane stack, formed the compartments of the electro-dialyzer. The additional "buffer compartment" was incorporated to the membrane stack. The compartment was to limit the contamination of the dialysate by co-ions leakage through cation-exchange membrane. Each of the membranes had a working surface area of 3.14 cm². Volumes of the circulated redox, concentrate, and dialysate solutions were 100 cm³ for each of them. Desalination was carried out for 0.01 M NaCl solution. To follow the course of the process, the Cl⁻ concentration in the dialysate was determined. The source of light was an incandescent-mercury MIX F 450 W Polam lamp which had been placed at a distance of about 30 cm from the window of the apparatus.

3. RESULTS AND DISCUSSION

The system shown in fig. 2 is, in principle, a liquid junction photocell in which the electro-dialytic membrane stack has been placed between the photoelectrode and the counterelectrode. While the illuminated surface of the *n*-CdS photoelectrode functions as an anode, the opposite dark surface is a cathode, from which the charge is transported to the counterelectrode through a metal contact. However, this membrane-photocell combination has to meet two major requirements which are, in fact, contradictory.

i) To prevent photoanodic dissolution, it is necessary to use highly concentrated electrolytes containing a stabilizing redox couple. Fulfilment of this requirement creates an unfavourable environment for the working membranes. As a consequence, a significant drop in the membrane selectivity and co-ions leakage may be expected. This negative effect may be limited only if efficient and stable low-concentration liquid junction photocells are invented. However, the results of recent studies [15] indicate that a stable performance of photocell is associated with very high concentrations of the liquid junction. The application of the buffer compartment, as suggested MURPHY [12], may protect to some extent the dialysate against contamination, but it does not decrease the redox electrolyte loss or increase the process efficiency.

ii) The membranes should not obstruct the light incident on the photoanode and the electrolyte layer on its surface should be as thin as possible. The result is that the electrolyte should be passed from the photoanode surface (compartment I) to the membrane stack contact (compartment II) through an appropriate tubing. To estimate how critical this element might be to the functioning of the system, we did

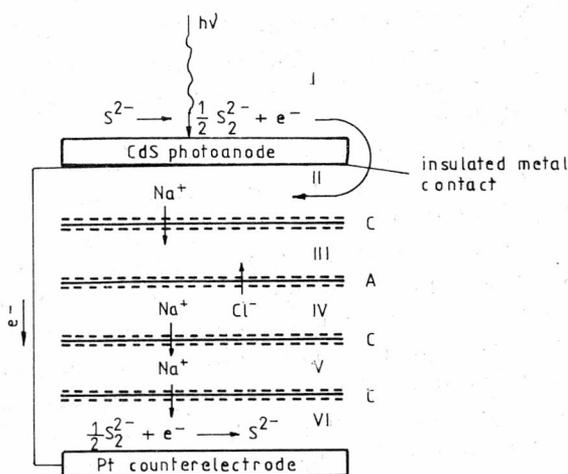


Fig. 2. Schematic representation of photoelectrodialysis

C and D are cation- and anion-exchange membranes, respectively

the following analysis. Using the redox electrolyte described earlier, we measured the open-circuit photovoltage of the cell having a platinum counterelectrode placed at a distance of 5 mm from the photoanode surface. The voltage varied from 420 to 450 mV for CdS electrodes produced by electrodeposition onto a cadmium substrate, and from 500 to 550 mV for electrodes prepared from sintered CdS. Current-voltage characteristic of the electro dialytic membrane stack shows that the voltage of the photocell falls beyond the range which is advantageous for the membranes (above 650 mV). Moreover, the loading of the photocell with additional resistance of the I to II electrolyte junction would shift its effective voltage further beyond this range. The voltage that can be obtained from the photocell is limited from above and approaches 1 V for most of the semiconductors.

Photoelectrodialysis experiments were performed in two variants. In the first, the redox solution flowed from compartment I to compartment II through the 10 cm long external channel. The photoelectrodes used were the electrodeposited CdS electrode and the sintered CdS pellet. Another experiment was carried out with the external channel blocked and the redox solution flowing through four 1 mm diameter holes made in the electrodeposited photoanode. The volume and the concentration of the solutions were chosen carefully to ensure a good accuracy of the measured concentration changes in the course of desalination and to keep the concentration level close to the initial value. We measured the desalination effects in mols per hour of ionic current flow. The results obtained in the tests with the redox solution passing externally were 1.4×10^{-6} and 1.6×10^{-6} mol \cdot h $^{-1}$ for the electrodeposited and the sintered CdS electrodes, respectively. Shortening of the redox solution path by passing it through the holes in photoanode instead of the external

channel brought about an increase in the ionic current flow which amounted to $2.4 \times 10^{-6} \text{ mol} \cdot \text{h}^{-1}$. No significant decrease in this parameter could be observed with prolonged time of the experiments. This proved the stability of the photoanodes used in this study. The presence of co-ion leakage was indicated by noticeable increase in dialysate alkalinity.

The results presented above show that the elements of the system which had earlier been thought of as being critical to the process efficiency were found to be critical indeed. While it is relatively easy to decrease the resistance of the junction, it was practically impossible to eliminate leakage of co-ions through the cation-exchange membrane. The redox electrolyte concentration which we used in our study was approximately one tenth of that usually employed for the stabilization of CdS. The removal of KOH from the redox solution may substantially abate co-ion leakage owing to the elimination of the mobile hydroxyl ion. On the other hand, however, this can make elemental sulfur settle on the photoanode surface.

Both the analysis of the system and the interpretation of the experimental results indicate that not only the nature of the physicochemical processes occurring in the semiconductor-electrolyte junction, but also the character of the membrane transport account for the considerable mismatch of these elements. A simple connection by electrolyte does not yield an effective system of solar energy conversion and storage in the form of chemical energy. It may be expected that an efficient and feasible solution will be achieved when energy conversion is really coupled with membrane transport. Such a coupling is likely to be obtained, if e.g., a semiconductor is placed in the membrane phase or the photoactive membrane is designed in a different manner.

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FOTOINDUKOWANA ELEKTRODIALIZA

Przedstawiono podstawowe zasady fotoindukowanej elektrodializy — fotoelektrodializy. Proces ten polega na połączeniu reakcji elektrochemicznych, przebiegających na oświetlonej powierzchni półprzewodnika kontaktującego się z roztworem redoks, z transportem przez membrany jonowymiennie. Jako półprzewodnikowych fotoelektrod w eksperymentach użyto tabletek z siarczku kadmowego typu *n* o powierzchni aktywnej ponad 3 cm², wytworzonych przez prasowanie proszku CdS pod ciśnieniem 60–70 MPa i następnie spiekanie go w temperaturze 1000–1100 K w atmosferze argonu. Próżniowo naniesiona warstwa tytanu tworzyła na spiekanej tabletkie kontakt z przewodem miedzianym. Użyto także fotoelektrod wytworzonych przez anodyzowanie podłoża kadmowego w roztworze Na₂S–NaOH przy gęstości prądu 10,5 Am⁻². Siarczkowo-wielosiarczkowy roztwór redoks tworzył ciekłe złącze z półprzewodnikiem, przeciwelektrodą była elektroda platynowa. W eksperymencie fotoelektrodializy użyto krajowych membran kationo- i anionowymiennych oraz 0,01 mol roztworu NaCl.

Uzyskane odsolenie wskazuje na sprzężenie między reakcjami redoks i zachodzącym przez membrany jonowymiennie transportem jonów, ale istniejące niedopasowanie tych dwóch elementów systemu obniża efektywność procesu.

ФОТОЭЛЕКТРОДИАЛИЗ

Представлены основные принципы фотоиндуктированного электро dialиза — фотоэлектро dialиза. Этот процесс состоит в соединении электрохимических реакций, происходящих на освещенной поверхности полупроводника, имеющего контакт с раствором redox, с транспортом через ионозаменные мембраны. В экспериментах, в качестве полупроводниковых электродов, применили таблетки из сернистого кадмия типа *n* активной поверхности свыше 3 см², изготовленные посредством прессования порошка CdS под давлением 60–70 МПа, а затем спекания в температуре 1000–1100 К в атмосфере аргона. Вакуумно нанесенный слой титана образовал на спекаемой таблетке контакт с медным проводом. Употребили также фотоэлектроды, изготовленные посредством анодизации металлического кадмиевого основания в растворе Na₂S/NaOH при плотности тока 10,5 Ам⁻². Сульфидно-полисульфидный раствор redox образовал жидкое соединение с полупроводником, контркатодом был платиновый электрод. В эксперименте фотоэлектро dialиза употребили отечественные катионо- и анионозаменные мембраны, а также 0,01 mol раствор NaCl.

Полученное обессоление указывает на связь между реакциями redox и происходящим транспортом ионов ионозаменными мембранами, но существующее несогласование этих двух элементов системы понижает эффективность процесса.