[October, 1983] © *1983 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.,* ***56***, *2873—2876 (1983)*

A Photochemical Storage Battery with an *n*-GaP Photoelectrode

Yoshiro Yonezawa,* Makoto Okai, Masato Ishino, and Hiroshi Hada
Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606

(Received December 27, 1982)

We have constructed a photochemical storage battery with an *n*-GaP Photoelectrode. A two-compartment cell, *n*-GaP|aqueous $K_3[Fe(CN_6]-K_4[Fe(CN)_6]$||aqueous $NiSO_4$|Pt, is capable of being charged by the irradiation of the photoelectrode. The current efficiency of nickel deposition on the storage electrode was 80%. When we drew electrical energy out of the dattery, the deposited nickel could act as a Ni electrode in the Ni^{2+} solution. The power efficiency of the storage battery amounted to about 2%. We could recharge the battery more than five times after discharge.

In an earlier paper, we proposed a concept of a solid-state photogalvanic cell.[1] We would now like to introduce a new term; a "photochemical storage battery," as a substitute, because it is less abstract and so less likely to cause unnecessary confusion regarding the concept. Active materials stored photoelectrochemically on the electrode surface can yield electrical energy whenever necessary. We have actually made up four kinds of batteries and found that the TiO_2 |aqueous $Ce(SO_4)_2-Ce_2(SO_4)_3$||aqueous $AgNO_3$|Pt cell has especially excellent characteristics. Such a regenerative storage of light energy is one of the most remarkable advantages of photochemical storage batteries in contrast to usual photovoltatic cells. This aspect has been pointed out by several investigators recently.[2,3]

Two methods for storing light energy as solid materials on the electrode surface have been reported thus far. One of them, proposed by us,[1] is to use a half-cell of metal ion/metal, such as Ag^+/Ag and Cu^{2+}/Cu, while the other is to use a half-cell of either metal sulfide or metal hydroxide, such as $Ag_2S/Ag,S^{2-}$, $Ni(OH)_2/Ni, OH^-$, and $Cd(OH)_2/Cd,OH^-$, as introduced by Hodes *et al.*[2] and Ang and Sammells.[3] Though the *n*-TiO_2 photoanode is photochemically stable, the band-gap energy (3.05 eV, 405 nm) is rather large; therefore, the incident light available for energy storage is limited to the near-ultraviolet† region. In contrast, *n*-GaP has a smaller band-gap energy (2.25 eV, 550 nm), but a photoanode made of it might suffer irreversible decomposition in an electrolyte solution. Recently, Memming has stressed that the anodic dissolution of the illuminated *n*-GaP electrode can be suppressed by adding the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ couple to the electrolyte at pH=6.5—9.5.[4] As the flat-band potential of *n*-GaP is *ca.* −1.0 V at pH=1 and the standard redox potential of this couple is +0.36 V *versus* a normal hydrogen electrode (NHE), various kinds of metal ion/metal combinations can be used as active materials for the storage electrode in the battery. In this report, we have chosen the Ni^{2+}/Ni couple (−0.25 V *versus* NHE) and tried to improve the power efficiency of the battery by using the *n*-GaP photoanode.

Experimental

The experimental setup of a photochemical storage battery and the procedure were almost the same as those reported previously.[1] A schematic representation of the battery was given in a figure of that paper. Single crystals of *n*-GaP, in the form of wafers 0.2—0.3 mm thick, were provided by the Sanyo Electric Co., Ltd. They were of a 99.999% purity, doped with S at the concentration of $(2—3)\times 10^{17}$ cm^{-3}. The *n*-GaP photoelectrode(P) was prepared according to the method of Nakato *et al.*[5] The surface area to be exposed to the electrolyte solution was 1 cm^2. A storage electrode(A) was made of a platinum-black disk 3 cm^2 in area, while the counter electrode(C) was made of platinum and had a 5-cm^2 area. The two compartments were separated by three sheets of ion-exchange membrane(M). Each membrane was 1.7 cm^2 in area and *ca.* 0.2 mm thick. They were CSV (proton-permeable membrane), ACH-45 T (anion-specific membrane), and CSV, provided by the Tokuyama Soda Co., Ltd. Tne electrolyte solution in the compartment of the P- and C-electrodes consisted of aqueous solutions of 0.2 M-K_2SO_4, 0.05 M $K_3[Fe(CN)_6]$, and 0.05 M $K_4[Fe(CN)_6]$, while tnat in the A-electrode compartment consisted of aqueous solutions of 0.05 M K_2SO_4, 0.2 M $NiSO_4$, and 0.06 M $NiCl_2$. In order to keep the pH of the solutions between 6.5—7.0, it was sometimes necessary to add either H_3BO_3 or NH_4Cl to the electrolyte soulution in the A-electrode compartment. All the potentials given in this peper were measured *versus* NHE.

As the light source, a high-pressure 500 W mercury lamp (Ushio Denki Co., Ltd.) was used in combination with a cut-off filter VY-45 (Toshiba Co., Ltd.) and a water filter to select a longer-wavelength light of more than 450 nm. The incidentlight intensity between 450—540 nm was 3.1 mW cm^{-2} according to both ferric oxalate actinometry[6] and photoelectronic measurement by means of a photometer IL-600 (International Light Co., Ltd.). The amount of the Ni atom deposited on the storage electrode was determined by the aid of a Jarrel-Ash AA-780 atomic-absorption spectrophotometer.

Results and Discussion

The polarization curves of the *n*-GaP electrode were measured by using a potentiostat/galvanostat HA-104 (Hokuto Denko Co., Ltd.). The electrolyte solution was composed of K_2SO_4, $K_3[Fe(CN)_6]$, and $K_4[Fe(CN)_6]$, whose concentrations were the same as those used for the photochemical charging of the battery. The typical behavior of the *n*-type semiconductor electrode was observed: the dark current was not evident at an electrode potential more positive than −0.4 V, but it then increased steeply with the cathodic polarization. The anodic photocurrent flowed at an electrode potential more positive than —0.8 V, and

---

† 1 M=1 mol dm^{-3}.

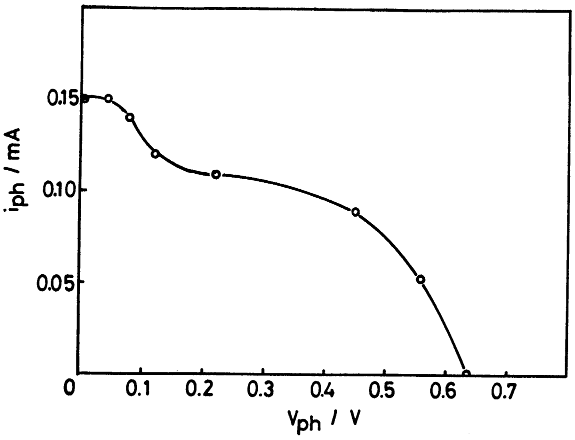

Fig. 1. Curve of photocurrent, i_{ph}, against photovoltage, V_{ph}, for the n-GaP battery: n-GaP|$K_3[Fe(CN)_6]$–$K_4[Fe(CN)_6]$||Ni^{2+}|Pt.

its saturated value was 155 μA cm^{-2}.

Figure 1 shows a curve of the photocurrent against the photovoltage during irradiation. The photocurrent flowed from a storage electrode to the GaP electrode. The net electrochemical reactions are as follows:

$$n\text{-GaP} + h\nu \longrightarrow e^- + p^+, \quad (1)$$

$$Ni^{2+} + 2e^- \longrightarrow Ni, \quad (2)$$

$$K_4[Fe(CN)_6] + p^+ \longrightarrow K_3[Fe(CN)_6], \quad (3)$$

where e^- and p^+ denote an electron and a positive hole respectively. The photocurrent under the short-circuit condition was 0.15 mA; the apparent quantum efficiency (the number of electrons passed per s divided by the number of incident photons for the 450—540 nm region per s) was *ca.* 13%. The photovoltage under the open-circuit condition was 0.63 V. On illuminating the battery for photochemical charging, the potential of the A-electrode shifted from +0.4 V to −0.2 V within 900 s, but after that it remained constant. After the cell had been illuminated for 7200 s (the quantity of electricity flowing was 1.08 C), the A-electrode was switched off from the P-electrode. Stored energy was stable in the dark for more than 24 h under the open-circuit condition. Electrical energy was drawn out by connecting the A- and C-electrodes through the external load resistance(L). We also tried to deposit the Ni atom on the A-electrode by using a galvanostat (electrochemical charging). Under a constant charging current of 2 mA, the potential of the A-electrode shifted from +0.4 to −0.3 V within 60 s, and after that remained constant. The current-voltage curve of the battery charged by 1.0 C in this manner was measured by changing the load resistance and was then compared with that charged photochemically (Fig. 2). The two cells show almost the same features: a short-circuit current of 4.3 mA and an open-circuit voltage of 0.75 V. The observed open-circuit voltage is somewhat larger than the difference in the standard electrode potential between Ni^{2+}/Ni and $[Fe(CN)_6]^{3-}$/$[Fe(CN)_6]^{4-}$. The discharge current with the load resistance was initially constant, but it gradually decreased with the discharge time. We could hardly draw any electrical energy out of the battery either before charging or after a nearly complete discharge. The change in the performance of the battery during the cycle of photochemical charging and discharge has been examined (Fig. 3). The battery was capable of being recharged more than five times after discharge.

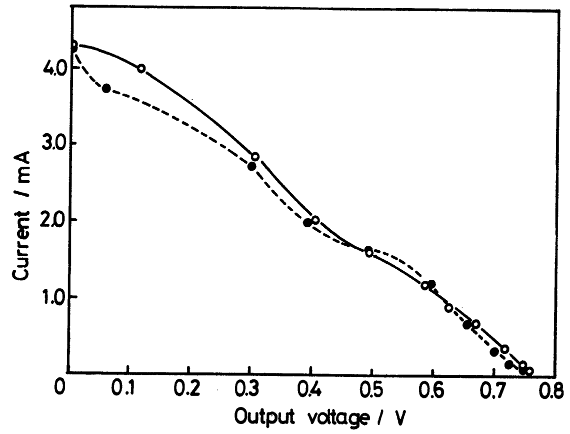

Fig. 2. The current-voltage characteristics of the battery: Pt|$K_3[Fe(CN)_6]$–$K_4[Fe(CN)_6]$||Ni^{2+}|Pt.
○; Photochemical charging, ●; electrochemical charging.

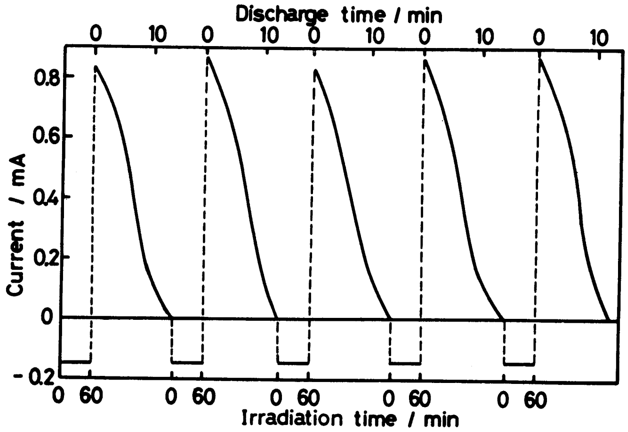

Fig. 3. Current of the battery during photochemical charging upon illumination of the n-GaP electrode and during discharge through A- and C-electrodes. The current of negative value corresponds to charging current when 2 Ω external resistance is inserted between P- and A-electrodes and that of positive value corresponds to discharge current with 700 Ω load.

We have also examined the dependence of the amount of deposited Ni, Q_{Ni}, on the quantity of electricity passed through while charging the battery, Q_{ch}. The quantity of electricity flowing during irradiation was determined by integrating the total photocurrent. Figure 4 shows the linear relation observed for both photochemical and electrochemical charging. It is shown that the Ni deposition proceeds in this battery with a current efficiency of 80%. It should be noted, however, that the efficiency was considerably lowered when we used a platinum disk instead of the platinum-black disk as the A-electrode.

We have also investigated the behavior of the battery

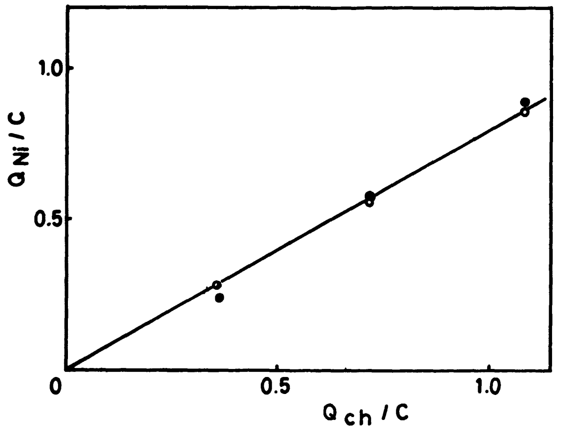

Fig. 4. Relation between the quantity of electricity flowed during charging, Q_{ch}, and the amount of Ni deposited on a platinum-black electrode, Q_{Ni}.
○; Photochemical charging, ●; electrochemical charging.

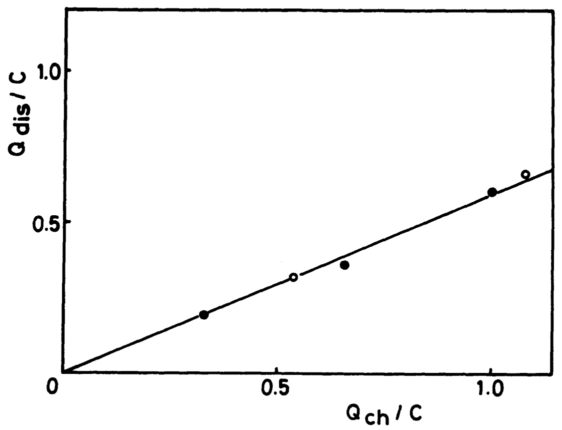

Fig. 5. Dependence of the quantity of electricity flowed during discharge, Q_{dis}, on Q_{ch}.
○; Photochemical charging, ●; electrochemical charging.

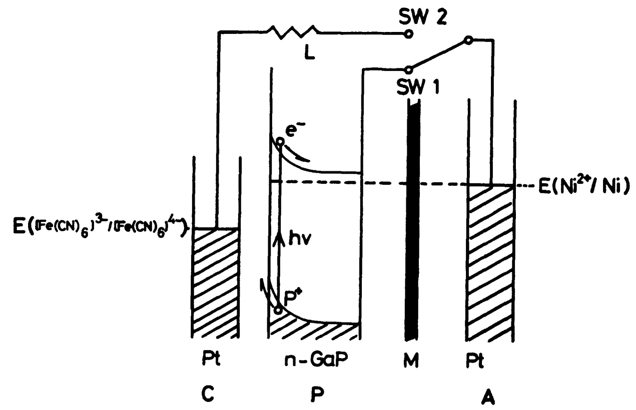

Fig. 6. Energy-level diagram of an illuminated battery.

during discharge. After photochemical charging, the battery was discharged for an appropriate period, and the quantity of electricity flowing during that period, as determined from the discharge current, was compared with the amount of dissolved Ni. The latter value was evaluated approximately by subtracting the amount of Ni left on the A-electrode after discharge from the hypothetical amount of Ni deposited while charging the battery, *i.e.*, 80% of the quantity of electricity flowing during charging. Under such an approximation, it was deduced that the amount of Ni dissolved was almost the same as the quantity of electricity flowing during discharge; *i.e.*, Ni in quantities of about 0.0, 0.20, and 0.45 C was dissolved during the discharge of the battery by amounts of 0.0, 0.22, and 0.42 C respectively. We could thus determine that the deposited Ni at the A-electrode acts as a Ni electrode in the Ni^{2+} solution. Figure 5 shows the linear relation between the quantity of electricity flowing during discharge, Q_{dis}, and that during charging, Q_{ch}. In this case, Q_{dis} was determined by integrating the total current over the discharge time until the current fell off to *ca.* 1% of its initial value. Though the conversion efficiency of Q_{ch} to Q_{dis} seems to be sensitive to the discharge condition,[1] about 55% of the Q_{dis} could be drawn out of the battery as an effective discharge current. We suppose that the discrepancy between the efficiencies of conversion from Q_{ch} to Q_{Ni} and from Q_{ch} to Q_{dis} is due to the somewhat poor discharge condition; *i.e.*, some of the active materials stored during charging are still left on the A-electrode surface after discharge. We can also not overlook the possibility that the imperfect selectivity of on permeation of the separator(M) allows the self-discharge reaction to proceed to some extent during the prolonged discharge. According to a study of the electrochemical behavior of Ni in aqueous solutions,[7] it is likely that a passive film is formed in neutral and alkaline solutions under suitable conditions. However, judging from the fairly fine features, the formation of such a film seems not to be very likely in this battery. Nevertheless, it is possible that the electrode reaction of the $Ni(OH)_2/Ni,OH^-$ couple plays some role at the Ni electrode surface, resulting in a larger open-circuit voltage than that expected solely from the standard electrode potential of the Ni^{2+}/Ni couple. We may also note that the pH of the electrolyte solutions in this battery should be carefully controlled in view of two restrictions: the photodissolution of n-GaP and the passivity of Ni.

We could thus establish the photochemical charging of the storage battery with an n-GaP photoelectrode. An energy-level diagram of the battery during irradiation is shown in Fig. 6. In this battery, the storage of light energy is possible because of the existence of both the space-charge layer at the semiconductor surface and the separator between the cell compartments. The former assures the occurrence of charging reactions according to Eqs. 1—3, while the latter avoids the mixing of the $Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ in the compartment of the P- and C-electrodes and the Ni^{2+} in the compartment of the A-electrode. We could not dispense with the three-membrane system of the separator, as it was difficult to assemble a useful battery having only either an ACH-45T or CSV membrane. It seems that the existence of these three membranes has some effect upon the output voltage of the battery, as the open-circuit voltage was slightly dependent on the combination of the membranes. We may try to define the power efficiency of the storage battery, η, in the following way:

$$\eta = \Phi_i \Phi_m \frac{q|E(\mathrm{Ox/Red}) - E(\mathrm{N}^{n+}/\mathrm{N})|}{E_g}, \tag{4}$$

where Φ_i and Φ_m denote the apparent quantum efficiency of the charging current and the efficiency of conversion from Q_{ch} to Q_{dis} respectively. E_g is the band-gap energy of the photoelectrode; E(Ox/Red) and $E(\mathrm{N}^{n+}/\mathrm{N})$ are the standard electrode potentials of the redox couple and metal ion/metal respectively. q is the electron charge. As Φ_i and Φ_m are 13 and 55% respectively in this battery, η amounts to 1.9%. This value is considerably larger than the $\eta = 0.14\%$ evaluated for the storage battery with the n-$\mathrm{TiO_2}$ photoelectrode.[1]

Hodes *et al.*[2] and Ang and Sammells[3] have used n-CdSe, n-GaAs, and n-$\mathrm{MoSe_2}$ as the photoelectrodes of the photoelectrochemical systems with energy storage. In their cells, they have chosen various kinds of half-cells which demonstrate a good electrochemical cyclic performance in conventional batteries. However, the exact amount of light energy stored in the form of solid materials seems to be ambiguous in their cells, such as n-CdSe|S/$\mathrm{S^{2-}}$|$\mathrm{Ag_2S}$-Ag[2] and n-GaAs|Se/$\mathrm{Se^{2-}}$|Cd[3], because they have employed metal electrodes themselves as the storage electrodes, *i.e.*, the Ag electrode in the former cell and the Cd electrode in the latter cell.

Of all the photoelectrolysis cells which can store light energy as chemical energy, light-energy storage as solid materials on the electrode surface seems to have two striking features; it enables the cell size to be compact, and the electrical energy can easily by drawn out of the cell by switching the junction of the electrodes.

This work was carried out with financial support from the Ministry of Education, Science and Culture (Grant-in-Aid for Scientific Research, No. 57040014).

References

1) H. Hada, K. Takaoka, M. Saikawa, and Y. Yonezawa, *Bull. Chem. Soc. Jpn.*, **54**, 1640 (1981).

2) G. Hodes, J. Manassen, and D. Cahen, *Nature*, **261**, 403 (1976); J. Manassen, G. Hodes, and D. Cahen, *J. Electrochem. Soc.*, **124**, 532 (1977).

3) P. G. P. Ang and A. F. Sammells, *Faraday Discuss. Chem. Soc.*, **70**, 207 (1980).

4) R. Memming, *J. Electrochem. Soc.*, **125**, 117 (1978).

5) Y. Nakato, K. Abe, and H. Tsubomura, *Ber. Bunsenges. Phys. Chem.*, **80**, 1002 (1976).

6) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).

7) M. Pourbaix, "Atlas of Electrochemical Equilibria in Agueous Solutions," translated by J. A. Franklin, Pergamon Press, Oxford (1966), pp. 330—342.