Production of Hydrogen by Photogalvanic Cell. Part 4 [1]. Photoelectrochemistry of Alkylammonium Tungstate
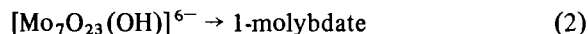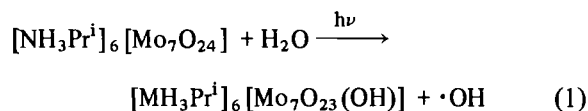
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Fig. 1. Schematic representation of the H_2 generation process by the photogalvanic cell with the $[NH_3Pr^i]_6[Mo_7O_{24}]$ system. NH_3Pr^i cations are omitted for clarity.

Introduction

In previous papers we reported the photogalvanic effect based on the photoreduction of Mo^{VI} to Mo^V for an aqueous solution of an alkylammonium polymolybdate [2–5]: Using $[NH_3Pr^i]_6[Mo_7O_{24}]$ as the polymolybdate, the overall reaction scheme for the initial step of the photoreduction is given by eqn. (1) and the produced $[Mo_7O_{23}(OH)]^{6-}$ was subsequently decomposed to 1-molybdate (eqn. (2)) [2].

$$[NH_3Pr^i]_6[Mo_7O_{24}] + H_2O \xrightarrow{h\nu}$$

$$[MH_3Pr^i]_6[Mo_7O_{23}(OH)] + \cdot OH \quad (1)$$

$$[Mo_7O_{23}(OH)]^{6-} \rightarrow \text{1-molybdate} \quad (2)$$

The electrochemically active species exhibiting the photogalvanic effect has been considered to be formed in the pathway to the decondensation of $[Mo_7O_{23}(OH)]^{6-}$. The photoelectrolysis of water can be achieved with the cell consisting of the neutral anodic solution of the polymolybdate and the acidic cathodic solution of 5 N H_2SO_4, Pt | 5 N H_2SO_4 || $[NH_3Pr^i]_6[Mo_7O_{24}]$ | Pt, although in this case the resulting pH gradient across the KCl-agar salt bridge supplies a voltage of approximately 0.47 V [4]. Schematic representation of the water-splitting process by the photogalvanic cell with the $[NH_3-Pr^i]_6[Mo_7O_{24}]$ system is shown in Fig. 1 where the recovery of $[Mo_7O_{24}]^{6-}$ from the photoproduced 1-molybdate is proposed on the basis of the well-known equilibrium reaction between 1- and 7-molybdates, $7MoO_4^{2-} + 8 H^+ \rightleftharpoons [Mo_7O_{24}]^{6-} + 4H_2O$ (log $K_f = 52.4$) [2, 6].

In extending the photogalvanic electrolysis of water to the polytungstate [4], we found two distinct polytungstates which exhibited photogalvanic effects. This paper described photoelectrochemical studies for the isopropylammonium polytungstate as an alkylammonium polytungstate.
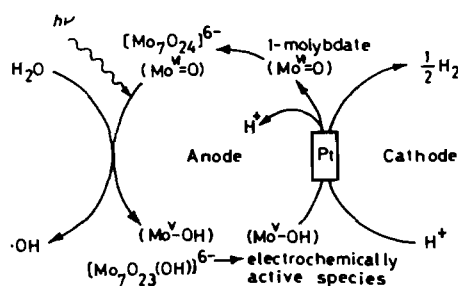
Experimental

Isopropylammonium polytungstate solutions were prepared by mixing 0.16 M Na_2WO_4 and 0.64 M $[NH_3Pr^i][ClO_4]$. Solution pH was adjusted by $HClO_4$ or NaOH. Sample solutions were flushed with argon to exclude oxygen. The working electrode was a bright platinum circular plate (18 mm^2 area) placed parallel to the light beam. Potentiostatic photocurrent-voltage curves were measured using a customary potentiostatic arrangement and each data point on curves was for the maximum value for the anodic photocurrent which was measured with the lock-in (NF Model L1-574) technique using a modulation of the light beam with 8 Hz. It was ascertained that the relaxation time of the photocurrent was short enough to use this technique. A Xe 500 W lamp was employed as a light source and a monochromator (Nikon G-250) with a grating of the blaze wavelength of 300 nm was used for wavelength selection. The action spectrum of the photocurrent was normalized on constant photon density. The experimental photogalvanic cell for H_2 production is the same as for the polymolybdate system [4].

Results and Discussion

Anodic photocurrent was observed for the polytungstate solution at various pH levels. This indicates that W^V produced as a result of the W^{VI}-photoreduction is oxidized at Pt electrode*. Action spectra of the photocurrents at $U_{SCE} = +0.5$ V are shown in Fig. 2(A). The photocurrent for the solutions at pH $\geq$ 4, which increases at shorter wavelength of

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*UV-induced formation of W^V was also suggested by an appearance of ESR signal at $g = 1.921$ for the photolyte at pH < 4.
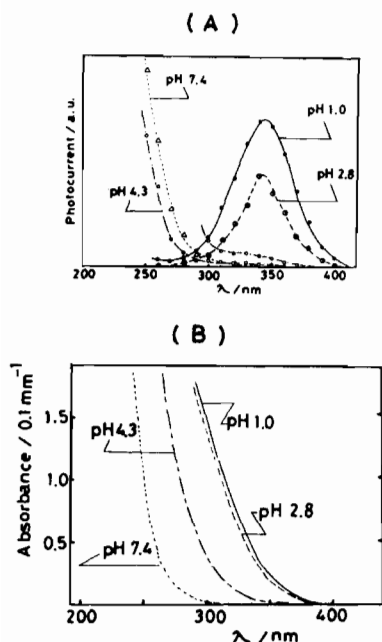
Fig. 2. Spectral distributions of the photocurrent (A) at U_{SCE} = 0.5 V and absorption spectra (B) of sample solutions for different pH-values.

λ < 350 nm, results from the light absorption by the polytungstate solution, since the spectral distribution of the photocurrent is nearly identical with the absorption spectrum of the solution as shown in Fig. 2(B). The spectral response of the photocurrent for the solutions at pH $\leqslant$ 3 exhibits a maximum at 345 nm and reveals a mismatch with the absorption spectrum of the solution. The linear dependence between the photocurrent and the light intensity was observed, when the solutions at pH 7.4 and 1.0 were irradiated with 313 nm- and 365 nm-light respectively**. This suggests that the formation of the electrochemically active species is a one-photon process irrespective of solution pH.

The photocurrent-applied potential behavior at given pH was measured. Typical results are shown in Fig. 3(A). Each curve showed a maximum in the photocurrent near the redox potential for the water oxidation to oxygen, as a result of the oxygen-quenching of the electrochemically active species at an anodic polarization higher than $E^{o}_{O_2/H_2O}$. Furthermore, a photocurrent onset for each of the curves, which corresponded to the standard redox potential ($E^{o}_{W^{VI}/W^{V}}$) for the electrochemically active species, showed approximately linear pH dependence with a slope of about 60 mV/pH. This indicates that the anode reaction of the electrochemically active

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**In this experiment, a 500 W Hg lamp as a light source was used to obtain high intensities of the monochromatic light at 313 and 365 nm.
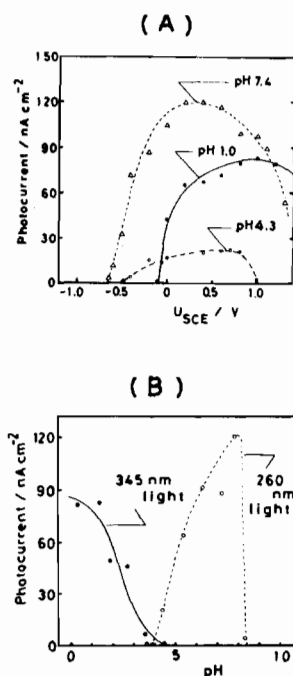

Fig. 3. Effect of applied potential on photocurrents for different pH-values (A) and plots of the maximum photocurrent for 260 nm (-- -o-- -) and 345 nm (—-•—-) light irradiations against pH (B). Curves for pH = 7.4 or 4.3 and 1.0 in (A) were obtained by 260 nm- and 345 nm-light irradiations, respectively.

species is given by a protonation—deprotonation process, $W^{V}-OH \rightarrow W^{VI} = O + H^{+} + e^{-}$. Similar behaviors were observed for the polymolybdate system [4]. The maximum photocurrent for each curve was plotted against solution pH. The results for 260 nm- and 345 nm-light irradiations are shown in Fig. 3(B). The photocurrent by the 260 nm-light irradiation increases with an increase in the solution pH at the range of 4 $\leqslant$ pH < 8, although the absorbance of the solution at 260 nm decreases with an increase in the solution pH (Fig. 2(B)). At pH levels exceeding 8, the photocurrent decreases drastically. On the other hand, the photocurrent by the 345 nm-light irradiation increases with the solution acidity.

In alkaline solution at pH > 8, tungstate(VI) is present as WO_4^{2-} and the acidification of the solution yields a paratungstate-A $[W_6O_{20}(OH)]^{5-}$ according to the equation, $6WO_4^{2-} + 7H^{+} \rightleftharpoons [W_6O_{20}(OH)]^{5-} + 3H_2O$ (log K = 57.5) [7]. In addition, $[W_6O_{20}(OH)]^{5-}$ changes to paratungstate-B $[W_{12}O_{36}(OH)_{10}]^{10-}$ according to the equation, $2[W_6O_{20}(OH)]^{5-} + 4H_2O \rightleftharpoons [W_{12}O_{36}(OH)_{10}]^{10-}$ [7]. These behaviors are reflected by the red shift of the absorption edge with an acidification of solutions (Fig. 2(B)). The maximum of the photocurrent around pH 7 for the 260 nm-light irradiation, therefore, implies that the photogalvanic effect results from the photo-

absorption of $[W_6O_{20}(OH)]^{5-}$ and that WO_4^{2-} is not photosensitive. The mismatch between action and absorption spectra at pH $\leqslant$ 3 indicates that the predominant species in solutions at pH $\leqslant$ 3, such as polytungstate-Y $[W_{12}O_x(OH)_y]^{(2x+y-72)-}$, ψ-metatungstate $[W_{24}O_{72}(OH)_{12}]^{12-}$, and metatungstate $[W_{12}O_{38}(OH)_2]^{6-}$ are not photosensitive, since the absorption spectra of these species show no maximum at 345 nm, may therefore be attributed to found at pH $\leqslant$ 3, which would exhibit its absorption maximum at 345 nm, may therefore attributed to be minor species in solutions and its concentration seems to increase with an increase in the solution acidity, judging from the fact that the 345 nm-photocurrent increased with increasing acidity (Fig. 3(B)). From above results, however it is very difficult to identify the photosensitive species in acidic medium, although we may regard this species as another 12-tungstate. The maximum at 345 nm in the spectral distribution of the photocurrent for an acidic medium is characteristic of the polytungstate solution, since the action spectra of the photocurrent for the polymolybdate solutions at various pH levels exhibit a weak tail at near ultraviolet wavelength region [4, 5]. This suggests that the application of the polytungstate system (especially for the acidic solution) to the solar energy-storage reaction is promising compared with the case of the polymolybdate system.

H_2 production by the photogalvanic cell, Pt$|5$ N $H_2SO_4\|$ polytungstate$|$Pt, was readily observed for the polytungstate solution at pH 3–8 where the onset potential for the photocurrent (Fig. 3(A)) was more negative than the standard redox potential of H^+/H_2 (-0.22 V $vs.$ SCE) in 5 N H_2SO_4, when the Pt anode was irradiated with a 500 W Hg lamp (nonfiltration). For the anode solution at pH $\leqslant$ 2, amount of observable H_2-bubbles at the cathode was very much smaller, probably due to the dominant quenching of the injected electrons (or electrochemically active species) by H^+ at the Pt anode. Studies of the different metal anode (W or Ti), of which the overpotential for H_2-evolution reaction is more negative than that of Pt, are in progress, in order to obtain higher optical energy conversion efficiency [4].

References

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