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Photogalvanic Effect in Alkylammonium Molybdate Solutions and Production of Hydrogen

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Introduction

We have reported the photochemical properties ($Mo^{6+} \rightarrow Mo^{5+}$) of the alkylammonium molybdates in solids and aqueous solutions [1–2]. The exposure of colorless solutions to UV light led to the formation of the blue species as a final product. We found that the solutions exhibited photogalvanic behavior based on the photoreduction of Mo^{6+} to Mo^{5+} and that H_2 formation at the counter electrode for the photogalvanic cell was possible. There have been a few studies of molybdenum photogalvanic systems, one of the best known examples being Mo^{4+} system based on the photo-induced disproportionation to Mo^{3+} and Mo^{5+} [3]. This letter describes the photogalvanic properties of the aqueous solution containing hexakis(isopropylammonium)heptamolybdate as the molybdate and the preliminary experiment for H_2 production.

Experimental

Hexakis(isopropylammonium)heptamolybdate trihydrate $[NH_3Pr^i]_6[Mo_7O_{24}]\cdot 3H_2O$ was prepared and recrystallized following our procedure [2] and its structure (P2/n, $Z = 4$) was determined by a single-crystal X-ray diffraction. The working electrode was a bright platinum circular plate (20 mm^2 area) placed parallel to the light beam. The potential (against SCE) of the electrode was measured by a Takeda Riken Co. electrometer TR-8651. Photocurrent measurements were performed under potentiostatic conditions with a home-made potentiostat. The solution in the electrochemical cell contained 13.6 m*M* $[NH_3Pr^i]_6[Mo_7O_{24}]\cdot 3H_2O$ and 1 *M* $NaClO_4$ electrolyte and was purged with nitrogen. The pH value for the solution was 5.2. A 500-W superhigh pressure mercury lamp was used as a light source. The measurement of the action spectrum of the photocurrent was done with a combination of a monochromator (Nikon G-250) and a 500-W xenon lamp and the signals obtained were corrected to constant photon flux at each wavelength.

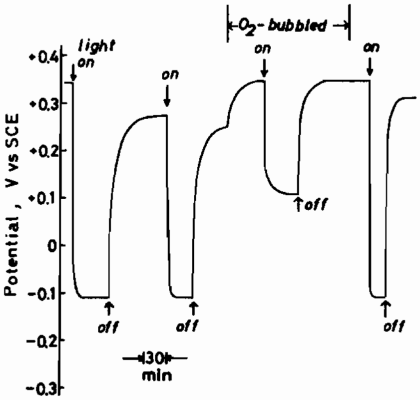

Fig. 1. Time course of the photopotential *vs.* SCE upon 365 nm light illumination.

The relaxation phenomena of the photocurrent were studied by measuring the change in current entering the electrode when chopped white light (nonfiltration) was incident on the sample, in order to have sufficient light intensities for this kind of experiments. The electrical signal was amplified by PAR 113 preamplifier and measured on an oscilloscope (Sony-Tektronix 475). With the use of a fast-response photodiode placed in front of the sample, it was determined that the chopped light reaching the sample was a good approximation to the square wave, with a rise time less than 10% of the total open time.

Results and Discussion

Figure 1 shows the typical photopotential responses of $[NH_3Pr^i]_6[Mo_7O_{24}]\cdot 3H_2O$ to illumination cycles. Upon illumination with 365 nm (3.6×10^{-7} E/l s), the photopotential decreases for a few minutes and then reaches a photostationary value (E_l) of ~–0.1 V. The signs of the quantity $E_{ld} = E_l - E_d$ (photostationary potential relative to the dark equilibrium potential) are always negative, indicating that the main electrochemically active species are photoreduced substances. The accumulation of the blue species (λ_{max} 730 nm, λ_{sh} 620 nm) [2] near the illuminated electrode did not bring about a perfect recovery of the original value of E_d. When oxygen was admitted into the solution it could be seen that E_d was restored to the original value (0.34 V *vs.* SCE) with an accompanying bleaching due to the oxidation of Mo^{5+} to Mo^{6+}. For solution saturated with oxygen by bubbling it through, E_{ld} was about half of that for the nitrogen-bubbling and the coloration to blue was little.

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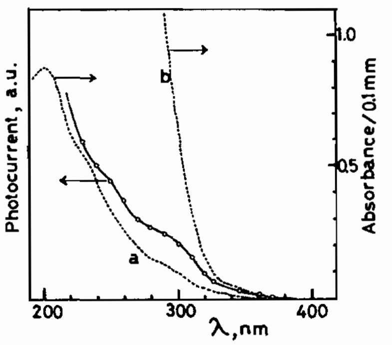

Fig. 2. Spectral distribution of photocurrent. (a) and (b) indicate absorption spectra of sample solutions for 1.75 m*M* and 13.6 m*M* $[NH_3Pr^i]_6[Mo_7O_{24}]\cdot 3H_2O$, respectively.

The time course of the photocurrent was similar to that of the photopotential. The cyclic voltammogram at Pt electrode did not show any significant current due to $[NH_3Pr^i]_6[Mo_7O_{24}]\cdot 3H_2O$ at $-0.1\ V \leqslant U_{SCE} \leqslant 1.0\ V$.

The action spectrum of the photocurrent at $U_{SCE} = 0.7$ V and the absorption spectrum of the aqueous solution are shown in Fig. 2. The peak responses occurring around 220, 250, and 290 nm coincide nearly with the peaks for the absorption spectrum, indicating that the photogalvanic effect is caused by the photo-excitation of $[NH_3Pr^i]_6[Mo_7O_{24}]\cdot 3H_2O$.

In order to estimate the life time and the redox potential for the electrochemically active species the relaxation behavior of the photocurrent was investigated using chopped light illumination (chopping frequency $\geqslant 8$ Hz). The time profile was approximately independent of the applied potential. The time dependence of the photocurrent signal at $U_{SCE} = 0.7$ V is shown in Fig. 3(A) where the photocurrent signal reaches a maximum value just before the light is turned off. The photocurrent changed exponentially with a time constant $\cong 20$ ms. The result indicates that the photochemical formation of the electrochemically active species leading to the photocurrent can be understood as a quasi first order process with $\tau \cong 20$ ms. Fig. 3(B) shows the maximum value at the end of each light pulse as a function of the applied potential. The signal increases with increasing U_{SCE} up to 1.0 V. At $U_{SCE} \geqslant 1.1$ V, water was oxidized to oxygen and the signal decreased drastically with increasing number of the illumination cycle, due to the oxygen-quenching of the electrochemically active species. The onset of the photocurrent at $U_{SCE} \cong -0.25$ V indicates that the standard redox potential ($E^0_{Mo^{6+} \rightleftharpoons Mo^{5+}}$) for the electrochemically active species at pH 5.2 is positioned around -0.25 V *vs.* SCE.

The estimated value of $E^0_{Mo^{6+} \rightleftharpoons Mo^{5+}}$ is very close to the standard redox potential (-0.244 V *vs.* SCE) of $2H^+/H_2$, suggesting that the photogalvanic cell of this system is capable of reducing hydronium ions without any applied potential. The photogalvanic cell proposed preliminarily for the hydrogen evolution consisted of two separate compartments connected by a KCl-agar salt bridge so that two Pt electrodes could be immersed in different electrolytes. The $[NH_3Pr^i]_6[Mo_7O_{24}]$ solution in the anode compartment was made 68 m*M* and purged with argon. The electrolyte in the cathode chamber was 5 *N* H_2SO_4. As irradiation to the Pt anode (20 mm^2 area) with the 500-W Hg lamp (nonfiltration proceeded, small gas bubbles at Pt wire cathode were continuously formed with a clearly visible rate. The H_2 gas was collected in an inverted buret and identified by gas chromatography (Hitachi 023 Chromatograph with a Carbosieve S column). The potential of the cathode at the stationary state was -0.255 V *vs.* SCE. During an irradiation time of 7 h a quantity of about 0.04 ml H_2 was produced. The results of quantitative measurement of integrated photocurrent (average photocurrent 15 μA) in the short circuit and H_2 production exhibited a stoichiometric ratio of 2:1 for mol of electrons to mol of H_2. It has been recently reported that the photoreduction to Mo^{5+} in $[NH_3Pr^i]_6[Mo_7O_{24}]$ solution is coupled with a water-oxidation to hydroxyl radical [4]:

$$Mo^{VI}{=}O + H_2O \xrightarrow{h\nu} Mo^{V}{-}OH + \cdot OH \qquad (1)$$

Therefore, the splitting pf water by alkylammonium molybdate in photogalvanic application may be given in terms of the half-reactions:

$$\text{Pt photoanode}: Mo^{V}{-}OH \rightarrow Mo^{VI}{=}O + H^+ + e \qquad (2)$$

$$\text{Pt cathode}: H^+ + e \rightarrow \tfrac{1}{2} H_2 \qquad (3)$$

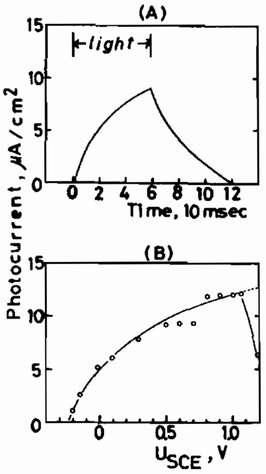

Fig. 3. Photocurrent transient (A) and maximum photocurrent–potential curve (B).

This represent the C2 category ($H_2O \rightarrow \frac{1}{2} H_2 + \cdot OH$) in the classification of methods for photochemical water decomposition [5].

References

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