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# Sintered Iron (III) Oxide Photoanode Doped with Molybdenum

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**Synopsis.** Sintered iron(III) oxide electrodes which contained about 0.01 atomic% of molybdenum showed considerable improvement in generating anodic photocurrent, particularly, in a cathodic potential region. 0.01 Atomic% doping level was found to be attained by sintering at 1200 °C for 12 h using 0.2 atomic% of $MoO_2$ or 1.0 atomic% of $MoO_3$.

The photoelectrochemistry of sintered iron(III) oxide has received considerable attention in recent years, because of prospects of an efficient and low-cost photoanode in the direct photoassisted electrolysis of water using visible light.[1–8] In order to make iron(III) oxide conductive by increasing negative carriers, doping with group IVB elements has been intensively investigated, and among them silicon doped iron(III) oxide has appeared to have good properties in producing photocurrent and stability against photodissolution.[2] We report here the photoelectrochemical behavior of sintered iron(III) oxide doped with molybdenum.

## Experimental

Electrodes were prepared from α-$Fe_2O_3$ (99.999%, Alfa Co.) by mixing with 0.02—2 atomic% of $MoO_2$ (99%, Mitsuwa Co.) or $MoO_3$ (99.999%, Aldrich Co.), pressing into pellets, sintering at 1150—1300 °C for 6—24 h in air, followed by quenching to room temperature. Dimensions of the pellets were 1.1 cm (diameter)×0.1 cm (thickness). New surfaces were obtained by polishing with emery, washed with water using ultrasonic wave, and etched with concentrated hydrochloric acid. A copper lead was attached to the back surface by ultrasonic soldering. Resistances measured across the thickness were 3—50 Ω. The electrodes were mounted into appropriate glass holders with epoxy resin.

Current-potential curves were obtained with a potentiostat HA-104 (Hokuto Denko Co.) and a regular three-electrode arrangement, in which a platinum wire as a counter electrode and a saturated calomel electrode(SCE) as a reference electrode were used. Iron(III) oxide electrodes were illuminated with a 1 kW xenon lamp through a Pyrex optical system, and a series of interference filter was employed for the measurement of spectral response.

The concentrations of molybdenum in sintered iron(III) oxide were photometrically determined by the use of 3,4-toluenedithiol.[9]

## Results and Discussion

An alumina mortar was used for mixing ferric oxide with dopants because it was found that the use of an agate mortar, the chemical compornent of which is none other than silica, brought about contamination with silicon which concealed any effects caused by other dopants.

Figures 1, 2, and 3 show the dependencies of photocurrent upon sintering temperature, sintering time, and amounts of dopants, respectively. Sintering at 1200 °C for 12 h gave the best result. At these conditions, the concentration of molybdenum at the boundary of each grain of iron(III) oxide may be most suitable for the flow of photocurrent. In the case of electrode sintered at a higher temperature and/or for a longer time, where dopant may diffuse into the grains of iron(III) oxide, photocurrent was rather small. Attempts to know the actual concentration of molybdenum at the electrode surface by means of fluorescence X-ray analysis and ESCA were unsuccessful because of low concentration. Chemical analysis for molybdenum, however, revealed that iron(III) oxide pellets sintered at 1200 °C for 12 h contained

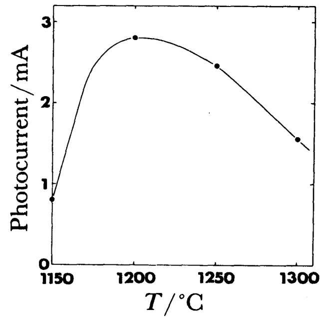

Fig. 1. The dependence of anodic photocurrent upon sintering temperature measured at 0.1 V (*vs.* SCE) in pH 10 borate buffer (0.1 M). Iron(III) oxide pellets containing 0.2 atomic% of $MoO_2$ were sintered for 6 h.

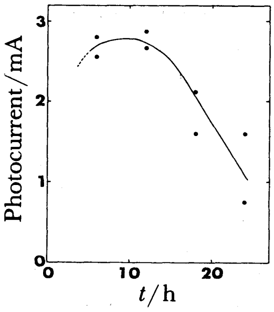

Fig. 2. The dependence of anodic photocurrent upon sintering time measured at the same conditions as Fig. 1. Iron(III) oxide pellets containing 0.2 atomic% of $MoO_2$ were sintered at 1200 °C.

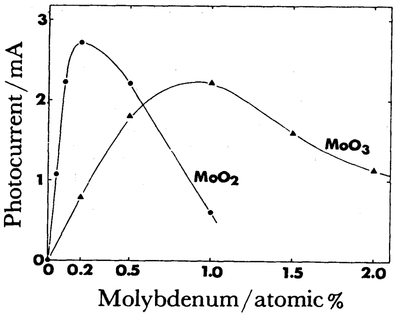

Fig. 3. The dependence of anodic photocurrent upon the amounts of dopants used, measured at the same conditions as Fig. 1. Sintering was conducted at 1200 °C for 6 h.

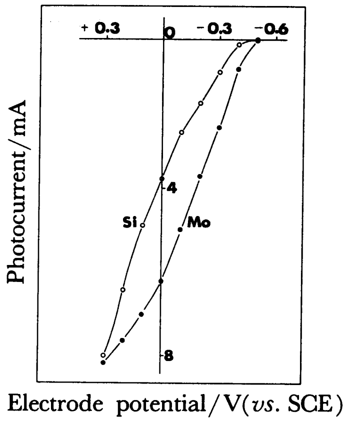

Fig. 4. Photocurrent-electrode potential curves for 0.01 atomic% of molybdenum and 2 atomic% of silicon doped iron(III) oxide electrode, measured in pH 10 borate buffer (0.1 M).

about 1/20 and 1/100 of the original amount of molybdenum when $MoO_2$ and $MoO_3$ were used as dopants, respectively. Therefore, in Fig. 3, the best results for anodic photocurrent generation are considered to be obtained at around 0.01 atomic% of doping level based on the actual concentration of molybdenum. The decrease in concentration of molybdenum is due to the oxidation of $MoO_2$ to volatile $MoO_3$.[10] Then, it can be concluded that the optimum conditions for sintering are corresponding to those in which 0.01 atomic% of doping level was attained when the sintering of iron(III) oxide was completed.

The surface of the effective electrode was revealed to be porous by means of a scanning electron microscope; one hole (around 20 μm in diameter) per $4\times10^3$ μm$^2$. Similar microstructure of electrode surface could be observed even in the case of electrodes not containing molybdenum, but they were not effective. The presence of molybdenum is essential for producing photocurrent.

A typical polarization curve for 0.01 atomic% Mo doped iron(III) oxide is shown in Fig. 4. A considerable improvement in the cathodic potential region can be noticed as compared with the case of the best 2% Si doped iron(III) oxide electrode[2] which we could prepare. This advance is important considering the reduction at the counter electrode in the electrolysis cell.

Visible light up to around 570 nm were effective in generating photocurrent and this is in accord with the fact that a band gap of iron(III) oxide is 2.2 eV.[1]

Photodissolution of the electrode was inspected by means of bathophenanthroline photometry using hydroxylamine as a reducing agent of iron(III) to iron(II) ion. The electrode is so stable against photodisolution that detectable amount of iron(II) ion was not found in 10 cm$^3$ of anolyte(1 mol/dm$^3$ aq NaOH) when 42 coulomb of photocurrent flowed at 0.3 V (*vs.* SCE).

The electrode is also stable in generating photocurrent, indeed, about 4 mA of steady photocurrent was flowing for 6 h in a two-electrode system divided by agar–agar using a platinum wire as a counter electrode, where 1 mol/dm$^3$ aqueous sodium hydroxide 0.5 mol/dm$^3$ sulfuric acid were used as an anolyte and a catholyte, respectively. Moreover, in this case, oxygen and hydrogen could be collected in 92% current efficiency.

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