JOURNAL OF APPLIED ELECTROCHEMISTRY 10 (1980) 345–349

Photochemical properties of sintered iron(III) oxide

M. GORI, H. -R. GRÜNIGER, G. CALZAFERRI

Institute for Inorganic and Physical Chemistry, University of Bern, Freiestrasse 3, CH-3012, Bern, Switzerland

Received 21 May 1979

The photochemical properties of vacuum deposited films and of sintered and doped iron(III) oxide have been studied. From the wavelength dependence of the photopotentials we know that photo-activity of the electrochemical cell with the iodine/iodide redox couple starts at the same wavelength, 600–650 nm, as the absorption of light and the photoconductivity of vacuum deposited films. Open circuit potentials of about 400 mV have been observed with the visible radiation from a 150 W xenon lamp. In neutral solution photocorrosion was too small to be observed.

1. Introduction

Alpha-iron(III) oxide is antiferromagnetic and has semiconductor properties [1, 2]. Hardee and Bard [3] have found that Fe_2O_3 films prepared by chemical vapour deposition (CVD technique [4]) show photocurrents at wavelengths lower than about 550 nm. The authors estimate the band gap of these films at 2.2 eV. This value corresponds to the band gap of 2–2.2 eV observed in single crystals [5, 6]. Photo-assisted electrolysis of water with single crystal α-Fe_2O_3 as well as with sintered α-Fe_2O_3 has been discussed [5–8]. The flat band potential (− 4.7 eV) of sintered material seems to be approximately the same as that in single crystals [5–10].

The papers mentioned above do not show whether a large enough photopotential can be achieved by appropriate doping, so that iron(III) oxide might become a possible material for the production of electrochemical solar cells. In the past we have succeeded in producing an interesting electrode material by sintering doped tin dioxide [11–13]. Sintering is an easy method for preparing differently doped materials. We have examined a number of iron(III) oxide electrodes prepared this way. The main results can be summarized as follows:

(a) Photoconductivity of a thin film of Fe_2O_3 starts at 625 nm and is proportional to the applied voltage.

(b) From pure sintered Fe_2O_3 in neutral I_2/I^-, KCl solution we do not obtain a constant redox potential.

(c) After doping with 1% and 5% SnO_2 or 1% CaO, however, the redox potential becomes constant.

(d) Open circuit photopotentials of about 400 mV were observed with the visible radiation from a 150 W xenon lamp (approx. 0.21 W cm^{-2}, $350 nm < \lambda < 650 nm$).

(e) Absorption of light and photoconductivity of vacuum deposited films start at the same wavelength, 600–650 nm, as the photoresponse of sintered electrodes in iodine/iodide solutions.

(f) From X-ray data we know that the sintered iron(III) oxide is α-Fe_2O_3. The densities of the samples lie between 4.8 and 4.9 g cm^{-3}.

2. Absorption spectrum

Pure iron oxide (p.a. Merck) was vacuum deposited from a tungsten boat source onto tetrasil quartz [14]. These approximately 50 nm thick films were brown. Heating to 600° C for three hours changed their colour to red.* The absorption spectrum shows a shoulder at 19 kK and a first maximum at 25 kK. Because it is similar to the spectrum published by Gardner, Sweet and Tanner which was recorded by a different technique [15], it is not shown here.

---

* From X-ray data we know that impure α-Fe_2O_3 was obtained. Some tungsten contamination cannot be excluded.

0021–891X/80/030345–05$02.50/0

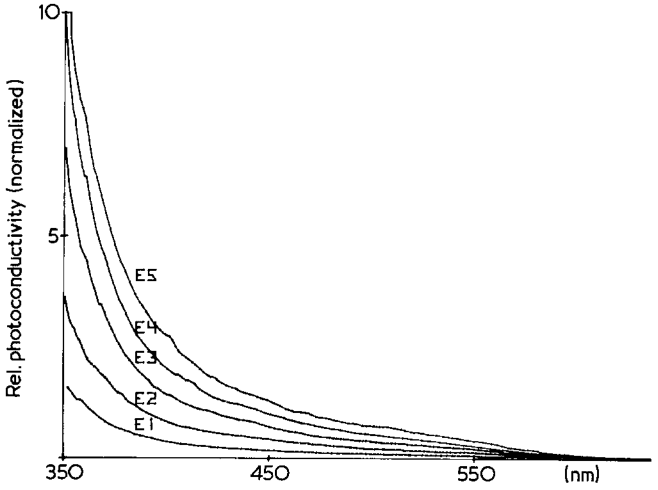

Fig. 1. Photoconductivity of vacuum deposited iron(III) oxide films normalized for constant photon flux. The following potential differences were applied: $E_1 = 50$ V, $E_2 = 100$ V, $E_3 = 150$ V, $E_4 = 200$ V, $E_5 = 250$ V.

3. Photoconductivity

As mentioned above, sintered α-Fe_2O_3 (p.a. Merck) does not show a constant potential in neutral I_2/I^-, KCl solution. We have therefore examined the photoconductivity of the undoped material to find out in which region of the absorption spectrum a photo-effect can be observed. Iron(III) oxide was vacuum deposited from a tungsten boat onto pyrex glass and heated to 600° C for three hours. Contact was made by applying silver epoxy resin. Photoconductivity was measured with monochromatic light of different wavelength, applying the following potential differences: $E_1 = 50$ V, $E_2 = 100$ V, $E_3 = 150$ V, $E_4 = 200$ V, $E_5 = 250$ V. In order to minimize the dark conductivity we worked with very thin layers. The room temperature resistivity of α-Fe_2O_3 is approximately 10^{13} Ω cm. This can be lowered to about 4 Ω cm by addition of titanium dioxide [19]. To eliminate the dark current, the light beam was chopped and the small photocurrents were measured with a PAR 186 lock-in amplifier.

The monochromatic light intensities used were low [$J_E(\lambda) \leqslant 13$ mW cm^{-2}], therefore the number of carriers produced is proportional to the number of photons absorbed and the observed photoconductivity can be normalized to a constant photon intensity (Fig. 1). The photoconductivity increases with increasing potential difference. The onset of photoconductivity is just below 600 nm. We know therefore that irradiation leads to a photo-effect over the entire absorption spectrum, except from the small portion at 15 kK.

4. Photopotentials and photocurrents

The photopotential η of a photo-electrochemical cell is defined as the difference between the potential ϕ_{dark} of an electrode in the dark and the poten-

Table 1. Composition of the electrolyte solutions

	Number				
Electrolyte	I	II	III	IV	V
I_2	10^{-2}	10^{-3}	10^{-4}	10^{-4}	10^{-3}
I^-	10^{-1}	10^{-1}	10^{-1}	1	1
KCl	1	1	1	1	1
Relative transmission for visible light $350 < \lambda < 650$ nm	43%	66.2%	100%	99.7%	67.8%

Table 2. Reversible redox potentials of the solutions ϕ_{rev} and dark potentials of the semiconductors ϕ_{sem} versus SCE; 25° C

Electrolyte	ϕ_{rev} (mV)	ϕ_{sem} (MV)*		
		1% SnO$_2$	*5% SnO$_2$*	*1% CaO*
I	337	314	310	322
II	300	215	237	305
III	274	174	120	128†
IV	186	50		105
V	216	107	124	210

* In all cases we obtained constant redox potentials which, however, in some cases are not completely reproducible.

† Dark current of 0.4 μA has been measured.

tial ϕ_{ill} of the same electrode under illumination:

$$\eta = \phi_{dark} - \phi_{ill}.$$

The magnitude of the photopotential is expected to depend on the electrolyte and on the doping [20–23]. Therefore we have examined three differently doped iron oxide electrodes (1% SnO_2, 5% SnO_2, 1% CaO) in the five solutions given in Table 1.

To prepare the electrodes, the iron oxide (Merck p.a.) was mixed with an appropriate amount of SnO_2 (Merck) or CaO (Merck p.a.). The ground material was pressed into tablets and sintered in air at 1350° C for 12 h. To avoid corrosion at the contact with a copper wire the tablet had to be protected by casting it in epoxy resin. Good results were obtained by pressing the tablet very strongly to the bottom of a graphite cylinder to which a little Araldite had been applied. The electrode was then centered in a teflon mould which was carefully filled with Araldite. Photopotentials were measured against the SCE using monochromatic light and white light (350 nm $< \lambda <$ 650 nm) of different intensities. The experimental set-up is shown in Fig. 2. Table 2 shows the reversible redox potentials of the solutions as well as the dark potentials of the semi-conductor electrodes in these solutions.

In Fig. 3 the observed photopotentials are plotted versus the logarithm of the relative light intensities for an electrode with 1% SnO_2 and 1% CaO. 100% relative light intensity corresponds

Table 3. Slopes $d\eta/dI_{rel}$. Theoretical value [20–23] 25.52 mV

Electrode	*Electrolyte*				
	I	*II*	*III*	*IV*	λ
1% SnO$_2$	24.7	19.1	17.8	24.2	white light
5% SnO$_2$	22.6	19.6	20.8		white light
1% CaO	34.5	30.6	22.9		white light
			39.1		360 nm
			35.2		400 nm
			36.6		450 nm
			40.8		500 nm
			38.7		550 nm
			31.7		600 nm

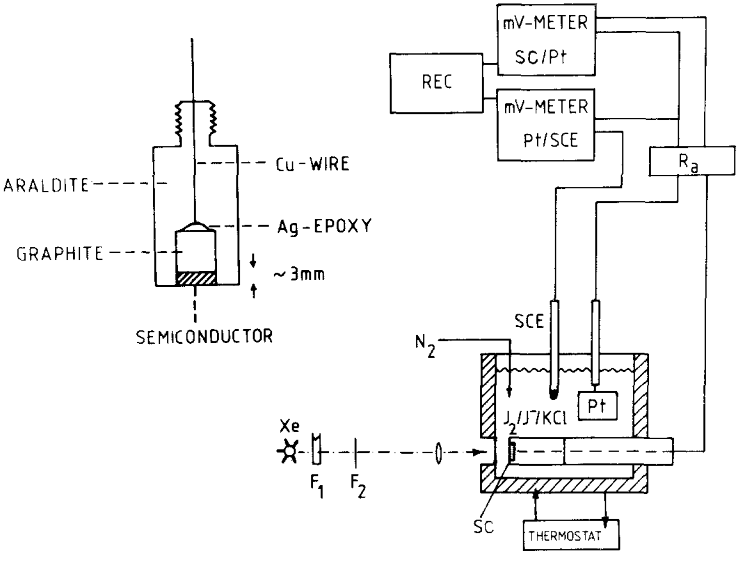

Fig. 2. Electrode and experimental set-up for the observation of photopotentials and photocurrents. Xe = 150 W or 300 W high pressure xenon lamp; F_1, F_2 = filters; SC = semiconductor electrode; Ra = variable resistor; REC = two channel recorder.

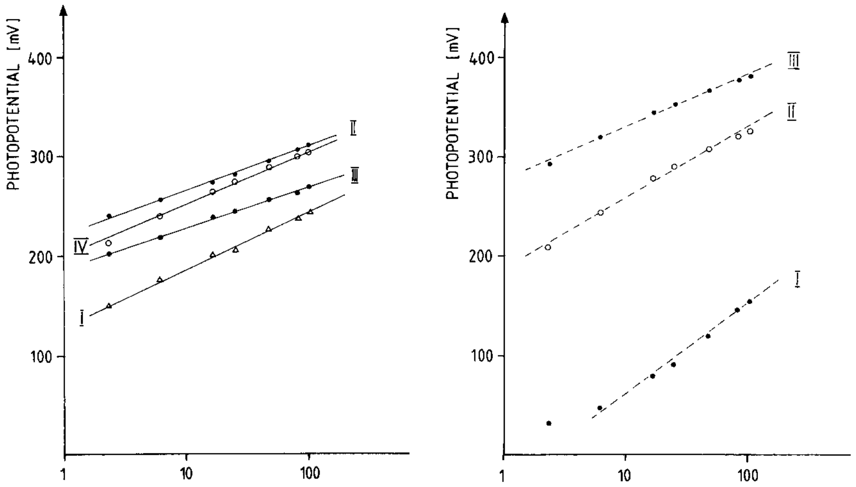

Fig. 3. Photopotentials of sintered iron(III) oxide in different electrolytes versus the relative light intensity. Left, 1% SnO_2; right 1% CaO.

to about 0.163–0.251 W cm^{-2}. The data for the tin-doped electrodes can be accurately described by the linear relationship [24, 25, 28]:

$$\eta = a \ln I_{\mathrm{rel}} + b$$

Some of the data obtained from the electrodes doped with 1% CaO show significant deviation from this linearity. We are not yet able to interpret this deviation [26]. The slopes of the different curves are given in Table 3. They lie between 19 mV and 41 mV. The theoretical value is 25.5 mV. The redox potentials of solutions I to V are between −4.9 and −5.1 eV, relative to vacuum potential, if that of the normal hydrogen electrode is assumed to be −4.5 eV [27]. Comparing this data to the flatband potential reported for pure α-Fe_2O_3 [3, 7, 8] we cannot explain the observed photopotentials. It seems that the flatband potential of our doped material is less negative than −4.7 eV. From the wavelength dependence of the photopotential plotted in Fig. 4 we know that photo-activity of the electrochemical cell starts at the same wavelength as the absorption of light and the photoconductivity of vacuum deposited films. Although our system has not been optimized for the observation of photocurrents, we wish to point out the remarkable dependence of these currents on the composition of the electro-

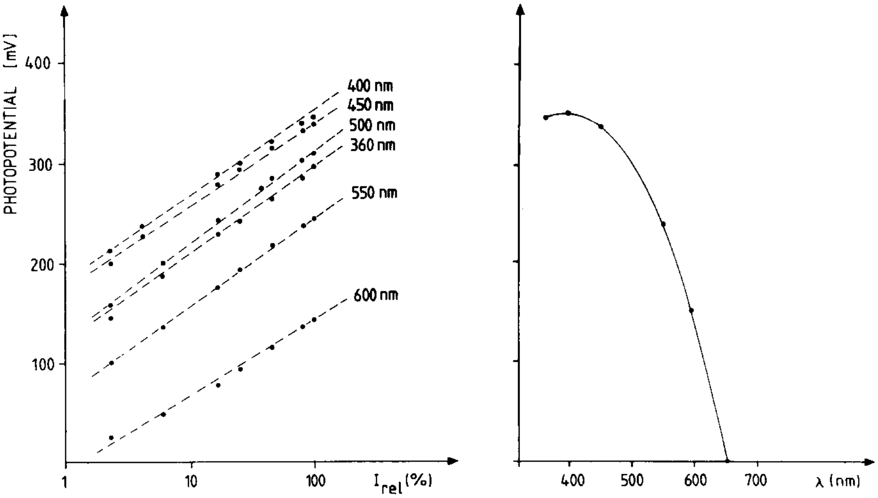

Fig. 4. Photopotentials of sintered iron(III) oxide observed with monochromatic light of a 150 W xenon lamp. Doping: 1% Cao; electrolyte III (Table 1).

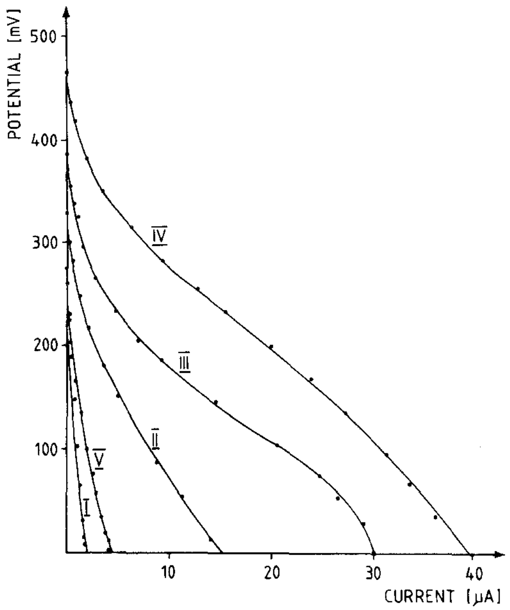

Fig. 5. Current–voltage characteristics for the different electrolytes given in Table 1. Doping: 1% CaO. I and II with a 300 W xenon lamp. III, IV, V with a 150 W xenon lamp.

lyte solution. For the 1% CaO case some data are given in Fig. 5.

Acknowledgements

We thank Professor E. Schumacher for support of this work. This paper is part of project no. 4.099–0.76.04 of the Swiss National Science Foundation.

References

[1] F. M. Morin, in 'Semiconductors' (edited by N. B. Hannay) Reynold Publishing Corp., New York (1959) p. 600.

[2] R. F. Gardner, F. Sweet and D. W. Tanner, *J. Phys. Chem. Solids* **24** (1963) 1175.

[3] K. L. Hardee and A. J. Bard, *J. Electrochem. Soc.* **123** (1976) 1024.

[4] *Idem, ibid* **122** (1975) 739.

[5] R. K. Quinn, R. D. Nasby and R. J. Bangham, *Mat. Res. Bull.* **11** (1976) 1011.

[6] H. H. Kunz, H. S. Jarrett, A. W. Sleight and A. Fenti, *J. Appl. Phys.* **48** (1977) 2463.

[7] J. H. Kennedy and K. W. Frese, *J. Electrochem. Soc.* **125** (1978) 709.

[8] *Idem, Proceedings of the Symposium on Electrode Materials and Processes for Energy Conversion and Storage*, The Electrochemical Society, Princeton 77–6 (1977) p. 77.

[9] *Idem, J. Electrochem Soc.* **125** (1978) 723.

[10] M. A. Butler and D. S. Ginley, *ibid* **125** (1978) 228.

[11] G. Calzaferri and H. R. Grüniger, *Helv.* **61** (1978) 950.

[12] H. R. Grüniger, J. Baumann and G. Calzaferri, *Report 2nd Int. Conference on the Photochemical Conversion and Storage of Solar Energy*, Cambridge (1978) p. 53.

[13] J. Baumann, diploma thesis, Institute for Inorganic Chemistry, University of Bern (1979).

[14] L. Holland, 'Vacuum Deposition of Thin Films', Chapman and Hall (1958).

[15] R. F. Gardner, F. Sweet and D. W. Tanner, *J. Phys. Chem.* **24** (1963) 1183.

[16] O. Madelung, 'Grundlagen der Halbleiterphysik', Springer-Verlag (1970).

[17] C. Kittel, 'Einführung in die Festkörperphysik', John Wiley, New York (1973).

[18] R. H. Bube, in 'Physical Chemistry, An Advanced Treatise', Vol. X, Academic Press (1970) p. 515.

[19] J. T. Law, in 'Semiconductors' (edited by N. B. Hannay) Reynold Publishing Corp., New York (1959) p. 676.

[20] H. Gerischer, *Z. physik. Chem. NF* 26 (1960) 223.

[21] *Idem, ibid* 26 (1960) 325.

[22] *Idem, ibid* 27 (1961) 48.

[23] H. Gerischer, in 'Physical Chemistry, An advanced Treatise', Vol. IXA, Academic Press, New York (1970).

[24] H. Gerischer, *Electroanalyt. Chem. Inter. Chem.* 58 (1975) 263.

[25] H. R. Grüniger, Ph.D thesis, University of Bern (1979).

[26] H. Reiss, *J. Electrochem. Soc.* **125** (1978) 937.

[27] F. Lohmann, *Z. Naturforsch.* **22a** (1967) 813.

[28] F. M. Delnick and N. Hackerman, *J. Elecktrochem. Soc.* **126** (1979) 732.