

Interfacial Phenomena of Polycrystalline Mg-Doped p-Type Iron(III) Oxide Photoelectrodes

A. H. A. Tinnemans*), T. P. M. Koster, A. Mackor

TNO Institute of Applied Chemistry, P. O. Box 5009, 3502 JA Utrecht, The Netherlands

J. Schoonman

Laboratory of Inorganic and Physical Chemistry, Delft University of Technology, P. O. Box 5045, 2600 GA Delft, The Netherlands

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The small-signal a.c. response of photoelectrochemical (PEC) cells with Mg-doped α -Fe₂O₃ photocathodes has been studied in the range 10⁻² to 10⁴ Hz. A non-linear least-squares analysis of the complex admittance/impedance data leads to a detailed equivalent circuit for the cell. The capacitance data have been employed to construct Mott-Schottky plots. For a p-type Fe₂O₃:Mg (1 at.%) electrode the flat-band potential V_{fb} in 0.1 M carbonate buffer (pH = 10) is +2.2 V vs. SCE.

Introduction

Important parameters in the study of semiconductor-electrolyte junctions are the flat-band potential V_{fb} , and the acceptor density N_A . V_{fb} defines the electrochemical characteristics of the system in the dark, and under illumination. In principle, V_{fb} and N_A can be determined from measurements of the space-charge capacitance C_{sc} at the semiconductor-electrolyte interface at a fixed frequency as a function of the electrode potential V , provided that the equivalent

circuit of the photoelectrochemical (PEC) cell comprises simply a series combination of a resistance, and the space charge capacitance. Recently, small-signal a.c. response measurements of PEC cells have been carried out in a wide frequency range [1–4]. A non-linear least-squares analysis of the admittance, and impedance data then provides an excellent means to obtain equivalent circuits for PEC cells, and to fully characterize the semiconductor-electrolyte interface.

In the depletion region the relation between the space-charge capacitance C_{SC} and the electrode potential V is given by the Mott-Schottky equation:

$$C_{SC}^{-2} = \frac{2}{\epsilon \epsilon_0 \cdot e \cdot N_A \cdot A^2} \left(|V - V_{fb}| - \frac{kT}{e} \right) \quad (1)$$

where ϵ is the relative dielectric constant, ϵ_0 the permittivity of free space, e the electronic charge, and A the interfacial area.

All other parameters have their usual meaning. An ideal Mott-Schottky plot is linear, the V -axis intercept yielding a value for V_{fb} , and the slope being a measure for the total acceptor density in the surface layer of the electrode [5, 6].

Using the plate parallel capacitance approach and applying Eq. (1), one finds for the width L_D of the depletion layer:

$$L_D = \left(\frac{2 \epsilon \epsilon_0}{e \cdot N_A} \right)^{1/2} \left(|V - V_{fb}| - \frac{kT}{e} \right)^{1/2} \quad (2)$$

Recently, Hendewerk et al. [7] have reported impedance measurements over the frequency range $3 \cdot 10^2$ to $3 \cdot 10^3$ Hz on n- and p-type Fe_2O_3 /aqueous electrolyte junctions. Analysis of the a.c. response data at 1500 Hz resulted in quasi-linear Mott-Schottky plots. For a 5 at.% Mg-doped iron oxide electrode the value of 2.3 V vs. RHE was obtained for V_{fb} , while the slope yielded $N_A = 5 \cdot 10^{22} m^{-3}$. While capacitance measurements performed over the narrow frequency range $3 \cdot 10^2 < f < 3 \cdot 10^3$ Hz revealed no shift in V_{fb} , in general, frequency dispersion effects often obscure the determination of V_{fb} and N_A as Mott-Schottky plots can show large variations with the measuring frequencies.

The present paper presents a study of the small-signal a.c. response of polycrystalline $\alpha-Fe_2O_3$:Mg/aqueous electrolyte junctions in the frequency range 10^{-2} to 10^4 Hz utilizing the non-linear least-squares analysis of the admittance and impedance spectra. These electrodes made p-type by doping with 0.1 and 1 at.% Mg [9], are of special interest, as it has been demonstrated that they can be used in a short-circuited polycrystalline iron oxide p/n assembly for the photoelectrolysis of water [7, 8].

Experimental Aspects

The preparation and characterization of the polycrystalline p-type Fe_2O_3 electrodes, doped with 0.1 and 1 at.% Mg, was described previously [9]. The electrodes were mounted in a standard three-electrode photoelectrochemical (PEC) cell made of Teflon [10]. The PEC cell consisted of the Fe_2O_3 cathode with an effective surface of $0.125 cm^2$, a Pt counter electrode, and a SCE reference electrode. As electrolyte 0.1 M carbonate buffer (pH = 10) was utilized.

The frequency dispersion of the small-signal a.c. response of this PEC cell was studied in the frequency range 10^{-2} to 10^4 Hz using a Solartron 1172 Frequency Response Analyzer. The a.c. signal amplitude was kept at 20 mV (rms). Representative admittance spectra were analyzed using a computer programme for non-linear least-squares fitting to complex data [3]. This procedure has been applied before to analyze admittance spectra of PEC cells with titanate [1, 2] and ferrite (photo)anodes [4].

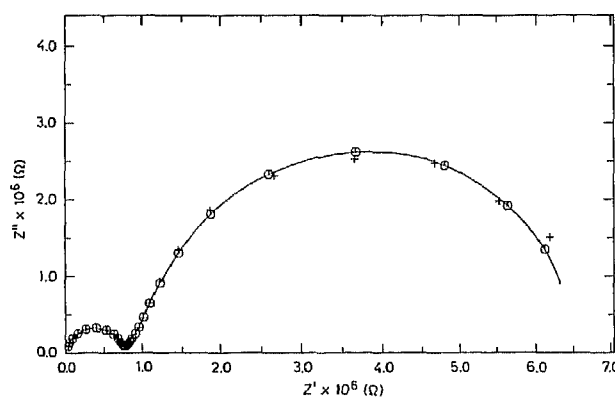
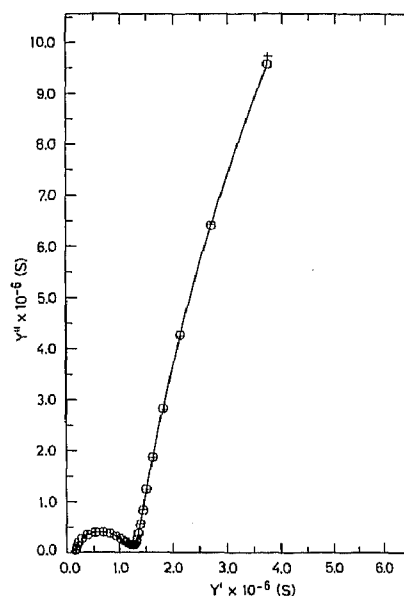


Fig. 1

- a) Admittance spectrum of a PEC cell with p- Fe_2O_3 :Mg (1 at.%) in 0.1 M carbonate buffer (pH = 10) at -1.5 V vs. SCE. Frequency range 10^{-2} to 10^4 Hz.
+ Experimental data; \circ fit to equivalent circuit in Fig. 2.
b) Conjunctional impedance spectrum

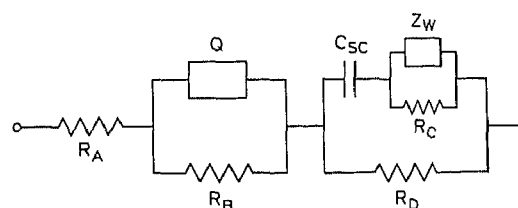


Fig. 2

Equivalent circuit used to model the small-signal a.c. response of a PEC cell with p- Fe_2O_3 :Mg (1 at.%) in 0.1 M carbonate buffer (pH = 10). See text

Experimental Results

The a.c. response data for the PEC cells can be presented in complex-plane admittance plots, and conjunctional complex-plane impedance plots. Fig. 1a shows a representative, experimental admittance spectrum of a PEC cell with p- Fe_2O_3 :Mg (1 at.%) with the electrode at -1.5 V vs. SCE. The conjunctional impedance spectrum is presented in Fig. 1b. The data can be adequately fitted

Table 1
Equivalent circuit parameter values from the non-linear complex least-squares analysis for p-Fe₂O₃:Mg (1 at.%) based PEC cell

Run ^{a)}	V vs. SCE (V)	C _{SC} (μF)	R _D (MΩ)	Z _w (μSs ²)	R _C (MΩ)	k _α (nSs ²)	α	R _B (MΩ)	R _A (kΩ)
1	0.10	0.59	61.7	0.71	1.21	0.46	0.91	0.76	8.1
	-0.50	0.55	34.0	0.64	1.10	0.44	0.91	0.74	8.5
	-1.00	0.48	11.3	0.74	1.03	0.47	0.91	0.74	8.1
	-1.50	0.44	5.7	0.67	0.80	0.45	0.91	0.72	8.8
2	-0.50	0.59	27.7	0.63	1.00	0.46	0.91	0.74	7.7
	-1.00	0.53	10.7	0.75	1.07	0.48	0.91	0.75	8.2
	-1.50	0.51	5.1	0.75	1.04	0.49	0.90	0.74	7.1
	-2.00	0.48	2.8	0.73	1.00	0.44	0.92	0.72	10.8
	-2.50	0.48	1.5	0.88	1.00	0.47	0.91	0.71	9.2
	-3.00	0.48	0.9	0.97	1.00	0.47	0.91	0.69	11.7
3	0.10	0.72	132.9	0.75	1.58	0.52	0.89	0.79	5.9
	0.50	0.83	42.3	0.68	1.20	0.51	0.89	0.77	6.2
	1.00	0.92	11.8	0.77	1.27	0.53	0.89	0.78	6.0
	1.50	1.12	6.0	0.82	1.13	0.49	0.90	0.76	7.1
	2.00	1.05	2.2	0.82	0.57	0.50	0.90	0.74	7.3
	2.50	0.96	1.3	0.82	0.61	0.51	0.90	0.74	6.9
4a	2.00	0.99	2.3	0.60	0.69	0.57	0.89	0.78	4.4
	1.00	0.96	22.2	0.53	0.73	0.52	0.90	0.72	6.0
	0.50	0.86	60.3	0.61	1.26	0.57	0.89	0.69	4.4
	0.25	0.82	49.8	0.64	1.75	0.60	0.89	0.67	4.1
	0.00	0.74	39.7	0.75	5.0	0.62	0.88	0.65	3.5
	-0.25	0.72	33.9	0.74	5.0	0.63	0.88	0.63	3.4
4b	2.00	0.98	2.2	0.58	0.62	0.54	0.89	0.75	5.1
	1.00	0.96	13.2	0.52	0.80	0.52	0.90	0.70	5.7
	0.50	1.24	23.4	0.55	0.80	0.55	0.89	0.66	4.9
	0.25	1.21	3.3	0.60	0.80	0.55	0.89	0.64	5.5
	0.00	0.97	0.78	0.68	0.80	0.56	0.89	0.62	5.2
	-0.25	0.95	0.43	0.72	1.00	0.54	0.89	0.59	6.1
5	-0.50	0.69							
	-1.00	0.57	8.7	0.39	1.09	0.63	0.88	0.69	1.6

^{a)} Run 1 to 4a under dark conditions; run 4b under irradiation at $\lambda = 390$ nm; electrolyte 0.1 M carbonate buffer (pH = 10). Run 5 under dark conditions; electrolyte 1 M carbonate buffer (pH = 10).

Table 2
Equivalent circuit parameter values from the non-linear complex least-squares analysis for p-Fe₂O₃:Mg (0.1 at.%) based PEC cell

V vs. SCE (V)	k _{SC} (μSs ²)	α _{SC}	R _{SC} (kΩ)	k _A (nSs ²)	α _A	R _A (MΩ)	k _B (nSs ²)	α _B
+0.60	0.463	0.83	57.9	16.7	0.95	0.24	109.0	0.82
+0.40	0.486	0.86	70.3	19.0	0.94	0.29	116.4	0.81
+0.20	0.454	0.85	72.4	19.5	0.93	0.28	109.2	0.83
0.00	0.439	0.87	64.6	18.9	0.93	0.15	90.9	0.85
-0.20	0.414	0.89	46.5	16.1	0.97	0.17	83.6	0.83
-0.40	0.389	0.89	43.2	16.7	0.96	0.16	83.7	0.83
-0.60	0.367	0.89	47.7	18.4	0.95	0.15	88.4	0.83
-1.00	0.373	0.88	30.6	14.8	0.99	0.15	70.3	0.83

to the equivalent circuit given in Fig. 2. This circuit can be represented by $Z_w R_D P C_{SC} S R_C P Q R_B P S R_A S$, following the notation presented in Refs. [1–3] (P stands for parallel and S for series). The Q element represents a constant-phase-angle (CPA) admittance. $Q_j = k_j (i\omega)^{\alpha_j}$. For $\alpha_j = 1$ a CPA admittance represents the admittance of a capacitor, for $\alpha_j = 1/2$ the admittance of a Warburg element, Z_w , while for $\alpha_j = 0$ this element reduces to a resistor. The Q element is usually attributed to current inhomogeneities.

The data for the p-Fe₂O₃:Mg (0.1 at.%) based PEC cell can be adequately fitted to the equivalent circuit $Q_{SC} R_{SC} P Q_A R_A P S Q_B S$

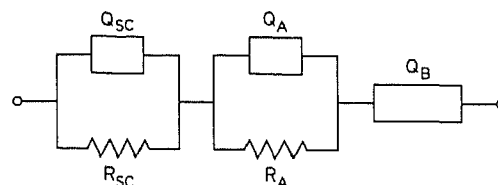


Fig. 3

Equivalent circuit used to model the small-signal a.c. response of a PEC cell with p-Fe₂O₃:Mg (0.1 at.%) in 0.1 M carbonate buffer (pH = 10). See text

which is given in Fig. 3. Fig. 4 presents the admittance and impedance plots along with the fit results for this PEC cell at 0.0 V vs SCE. Table 1 presents parameter values for the circuit elements: the case of the Fe₂O₃:Mg (1 at.%) based PEC cell, while the result for the Fe₂O₃:Mg (0.1 at.%) based PEC cell are given in Table 2. The run numbers refer to capacitance measurements of the sample on subsequent days.

The symmetrical cell Ag/p-Fe₂O₃:Mg (1 at.%) / Ag exhibits frequency dispersion. The admittance spectrum can be adequately fitted to the equivalent circuit $Q_B R_B P R_A S$, with $k_B = 0.71 \cdot 10^{-6}$ μSs², $\alpha = 0.86$, $R_A = 0.15$ kΩ, and $R_B = 4.53$ MΩ. The a.c. response data for the symmetrical cell Ag/p-Fe₂O₃:Mg (0.1 at.%) / Ag can be

reproduced by $Q_b R_b P Q_a R_a P S$. The numerical values of circuit elements involved are $k_b = 35.5 \cdot 10^{-3} \mu S s^\alpha$, $\alpha_b = 0.98$, $R_b = 31 k\Omega$, $k_a = 0.375 \mu S s^\alpha$, $\alpha_a = 0.88$ and $R_a = 33 k\Omega$.

Discussion

The equivalent circuit elements describing the admittance spectra of the $Fe_2O_3:Mg$ (1 at.%) based PEC cell can be divided into two main categories. The values of the elements in the part $Q R_b P R_a S$ of the equivalent circuit are independent of the applied potential. The branch $Q R_b P R_a S$ in which the Q element approaches the behaviour of a pure capacitance ($\alpha = 0.91$), can be related to processes in the bulk of the semiconductor and in the electrolyte. Resistance

R_A comprises contributions of the bulk of the Fe_2O_3 -grains, and of the electrolyte, whereas R_B and Q have been associated with the resistance and capacitance at the grain boundaries, respectively [9].

In comparison with the resistance R_a (0.15 k Ω) in the symmetrical cell, the resistance R_A (8.5 k Ω) in the PEC cell is dominated by the contributions of the electrical contact of the dark-site electrode, of the electrolyte, and of the Platinum counter-electrode.

From the capacitance data Q an apparent dielectric constant, ϵ , of our polycrystalline $\alpha-Fe_2O_3:Mg$ (1 at.%) was calculated according to the equation for a parallel plate capacitor.

$$C = \frac{\epsilon \epsilon_0 \cdot A}{d} \quad (3)$$

where d and A are the disk thickness and area. A dielectric constant value of approximately 1140 was obtained. This value is much higher than the one reported by Quinn [11] for the dielectric constant of $\alpha-Fe_2O_3$ for an unspecified single crystal face ($\epsilon = 120$), and the value reported by Kennedy [12] for a polycrystalline TiO_2 -doped $\alpha-Fe_2O_3$ ($\epsilon = 80$). The discrepancy is attributed to the fact that the capacitor effect is located at grain boundaries.

The subcircuit, $Z_w R_C P C_{SC} S R_D P$ must then be representative for processes at the semiconductor-electrolyte interface. The elements C_{SC} and R_D are the only elements which depend on the applied d.c. potential, hence they are to be related to processes at the semiconductor-electrolyte interface.

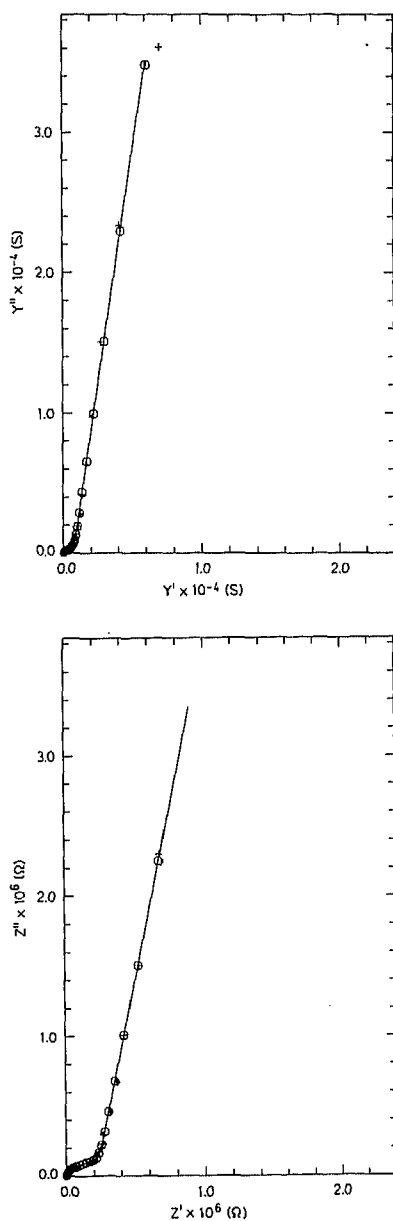


Fig. 4

- a) Admittance spectrum of a PEC cell with $p-Fe_2O_3:Mg$ (0.1 at.%) in 0.1 M carbonate buffer (pH = 10) at 0.0 V vs. SCE. Frequency range 10^{-2} to 10^4 Hz.
+ Experimental data; \circ fit to equivalent circuit in Fig. 3.
b) Conjunctive impedance spectrum

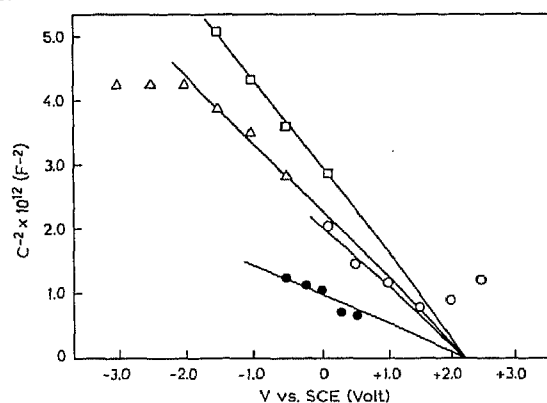


Fig. 5

Mott-Schottky plot of the C_{SC} data for a $p-Fe_2O_3:Mg$ (1 at.%) electrode in 0.1 M carbonate buffer. Open points (run 1–4a) in the dark; closed circles (run 4b) under 390 nm irradiation

Fig. 5 presents Mott-Schottky plots for the $p-Fe_2O_3:Mg$ (1 at.%) based PEC cell. From the V -axis intercept a value for the flat-band potential was obtained, viz. $V_{fb} = +2.2$ V vs. SCE. As for the pH dependence of V_{fb} of an oxidic semiconductor a theoretical shift of 59 mV per pH unit is expected, a V_{fb} at pH = 0 is calculated to be +3.0 V vs. NHE. This value is ~ 0.7 V more positive than the one reported by Hendewerk [7].

For comparison, the a.c. response data analysis of Dare-Edwards et al. [14] for n-type $\alpha-Fe_2O_3$ resulted in a non-linear Mott-Schottky plot. These authors limited the anal-

ysis to a five-component equivalent circuit and used only pure capacitances. Their plots could, however, be extrapolated to $V_{fb} = -0.5$ V vs. SSE (1 M KOH) (SSE = -0.02 V vs. SCE), i.e. $V_{fb} = +0.45$ V vs. NHE at pH = 0, designating approximately the location of the conduction band edge. A measured bandgap of 2.2 eV places the valence band edge of the n-type electrode at $E_{VB} = +2.65$ V vs. RHE.

From the slope of the Mott-Schottky plot of the first run a value for the acceptor density was derived, viz. $N_A = 5.7 \cdot 10^{24}$ m $^{-3}$. The decrease of the slopes of the Mott-Schottky plots from runs on subsequent days may be ascribed to a deterioration of the electrode surface.

For the 1 at. % Mg-doped material the acceptor densities is in reasonable agreement with the positive carriers determined from Seebeck measurements, i.e. $5.9 \cdot 10^{25}$ m $^{-3}$ [9].

The data for a p-Fe $_2$ O $_3$:Mg (0.1 at. %)-based PEC cell can be adequately fitted to the equivalent circuit which is given in Fig. 3. Since Q_{SC} and R_{SC} both depend on the electrode potential, as well as on the composition of the aqueous electrolyte they are related to the space-charge region. Because calculated k_{SC} values are close to actual C_{SC} values, the k_{SC} data have been employed to construct a Mott-Schottky plot which is shown in Fig. 6. From the V -axis intercept the V_{fb} was calculated to be +2.2 V vs. SCE. This is in good agreement with the V_{fb} value for a sample with 1 at. % Mg dopant content. In our previous report [9] we have shown that the grain size effect decreases and substantial porosity occurs with increasing Mg content. The circuit element Q parameter values for the 0.1 at. % and for the 1 at. % Mg-doped samples are fully in line with this effect, i.e. $35.5 \cdot 10^{-9}$ and $0.71 \cdot 10^{-9}$ S s $^{\alpha}$, respectively. However, we don't believe that the porosity differences are as great as indicated by the Q -values. It, therefore, appears that the apparent ϵ increases with decreasing Mg content.

According to the equation for a parallel plate capacitor the apparent ϵ of our polycrystalline α -Fe $_2$ O $_3$:Mg (0.1 at. %) is approximately 61500. Taking this value, the total acceptor density of the electrode surface from the slope of the Mott-Schottky plot of Fig. 6 is calculated to be $5.9 \cdot 10^{22}$ m $^{-3}$.

From Table 1 it is apparent that the resistance R_D of the space-charge region is relatively small for small, and large band bending in p-Fe $_2$ O $_3$:Mg. For intermediate voltages R_D

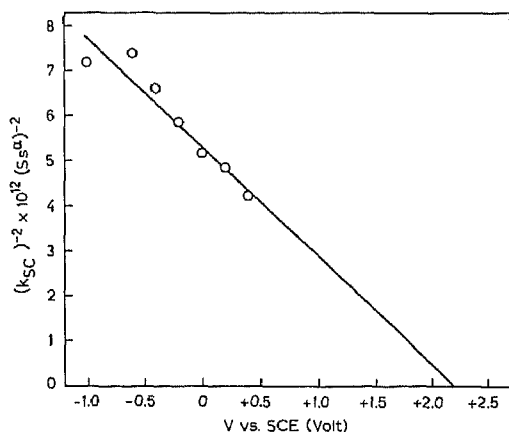


Fig. 6

Mott-Schottky plot of the k_{SC} data for a p-Fe $_2$ O $_3$:Mg (0.1 at. %)-electrode in 0.1 M carbonate buffer

becomes large. This has been reported before for titanate photoanodes [1,2]. At potentials near V_{fb} , the width of the space-charge layer L_D is relatively small, hence R_D is relatively small. At more negative potentials the space-charge region broadens and becomes more depleted in holes. Therefore, R_D increases. However, below a certain electrode potential holes are injected directly from the solution into the valence band of the semiconductor, giving rise to dark currents. This results in a decrease of R_D .

The data from Table 1 clearly illustrate that irradiation of the semiconductor (run 4b) gives rise to increased values of C_{SC} over the entire potential region employed. The increase is due to the generation of electron-hole pairs in the depletion layer: the presence of electrons near the electrode surface gives rise to an excess negative space-charge, thus increasing the space-charge capacitance [13]. As a result of the photoinduced generation of charge carriers the resistance R_D drastically decreases upon irradiation. However, at high positive potentials the photoeffect will be obscured by darkcurrent effects.

In conclusion we have shown that impedance spectroscopy of PEC cells in a wide range of frequencies yields reliable equivalent circuit parameter values. In the case of polycrystalline samples usually CPA elements are required in order to adequately fit the response data. They are often due to current inhomogeneities. The utilisation of a circuit with frequency independent circuit elements [14] will be of limited use in the case of polycrystalline Fe $_2$ O $_3$ electrodes.

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References

- [1] R. U. E. 't Lam, J. Schoonman, and G. Blasse, *Ber. Bunsenges. Phys. Chem.* **85**, 592 (1981).
- [2] R. U. E. 't Lam, L. H. J. M. Janssen, and J. Schoonman, *Ber. Bunsenges. Phys. Chem.* **88**, 163 (1984).
- [3] A. Roos, D. R. Franceschetti, and J. Schoonman, *J. Phys. Chem. Solids*, in press.
- [4] L. G. J. de Haart and G. Blasse, *J. Electrochem. Soc.*, submitted.
- [5] H. Gerischer, in: *Physical Chemistry*, Vol. IXa, pp. 468–473, eds. H. Eyring et al., Academic Press, New York 1970.
- [6] R. Memming, in: *Electroanal. Chemistry*, Vol. 11, p. 1, ed. A. J. Bard, Marcel Dekker Inc., New York 1979.
- [7] J. E. Turner, M. Hendewerk, J. Parmeter, D. Neiman, and G. A. Somorjai, *J. Electrochem. Soc.* **131**, 1777 (1984).
- [8] C. Leygraf, M. Hendewerk, and G. A. Somorjai, *J. Phys. Chem.* **86**, 4484 (1982).
- [9] A. H. A. Tinnemans, T. P. M. Koster, D. H. M. W. Thewissen, A. Mackor, and J. Schoonman, *Ber. Bunsenges. Phys. Chem.* **90**, 383 (1986).
- [10] R. U. E. 't Lam, L. G. J. de Haart, A. W. Wiersma, G. Blasse, A. H. A. Tinnemans, and A. Mackor, *Mat. Res. Bull.* **16**, 1593 (1981).
- [11] R. K. Quinn, R. D. Nasby, and R. J. Baughman, *Mat. Res. Bull.* **11**, 1011 (1976).
- [12] J. H. Kennedy and K. W. Frese, *J. Electrochem. Soc.* **125**, 723 (1978).
- [13] Ref. [5], pp. 481–483.
- [14] M. P. Dare-Edwards, J. B. Goodenough, A. Hamnett, and P. R. Trevellick, *J. Chem. Soc., Faraday Trans 1*, **79**, 2027 (1983).

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