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New Insights into Water Splitting at Mesoporous α -Fe₂O₃ Films : A Study by Modulated Transmittance and Impedance Spectroscopies

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ABSTRACT. Thin mesoporous films of α -Fe₂O₃ have been prepared on conducting glass substrates using layer by layer self-assembly of ca. 4 nm hydrous oxide nanoparticles followed by calcining. The electrodes were used to study the oxygen evolution reaction (OER) in the dark and under illumination using *in situ* potential-modulated absorption spectroscopy (PMAS) and light-modulated absorption spectroscopy (LMAS) combined with impedance spectroscopy. Formation of surface-bound higher-valent iron species (or ‘surface trapped holes’) was deduced from the PMAS spectra measured in the OER onset region. Similar LMAS spectra were obtained at more negative potentials in the onset region of photoelectrochemical OER, indicating involvement of the same intermediates. The impedance response of the mesoporous α -Fe₂O₃ electrodes exhibits characteristic transmission line behavior that is attributed to slow hopping of holes, probably between surface iron species. Frequency-resolved PMAS and LMAS measurements revealed slow relaxation behavior that can be related to the impedance response and which indicates that the lifetime of the intermediates (or trapped holes) involved in the OER is remarkably long.

KEYWORDS α -Fe₂O₃, hematite, oxygen evolution reaction, photoanode, photoelectrolysis, water splitting.

Introduction

α -Fe₂O₃ (hematite) has been investigated extensively as a potential photoanode material for water splitting cells.¹⁻⁶ Although its band gap (~2.0 eV) is suitable for harvesting visible light and its valence band is low enough in energy for holes to oxidize water, an external bias is needed to raise the free energy of electrons in the conduction band sufficiently to drive the hydrogen evolution reaction at the counter-electrode in order to split water. The necessary external voltage bias can be provided by a solar cell in a tandem cell configuration.⁷ Performance limitations imposed by high doping and short hole diffusion lengths in hematite films have been addressed by nanostructuring the electrode in order to enhance the chances of holes reaching the oxide/electrolyte interface.^{8,9} However, surface and bulk recombination losses still limit performance, and in order to make progress towards the ultimate goal of efficient water splitting, it is essential to understand these processes.

Recent work in our laboratory^{10,11} confirms that the light-driven oxygen evolution reaction (OER) at hematite involves very slow electron transfer, as suggested originally by Dare-Edwards et al.¹ At the same time, surface recombination of electrons and holes shifts the photocurrent onset away from the flatband potential, degrading the efficiency of the water splitting process. It has been shown that this loss process can be minimized by treatment of the surface of the hematite layer with a cobalt solution⁴, but we have shown that the improvement arises from suppression of surface recombination rather than from catalysis of the electron transfer process, which remains remarkably slow, implying substantial build-up of intermediate species.¹¹ These intermediates can be considered either as surface trapped holes or as higher-valent iron species formed at the surface by hole capture.

Recent studies of hematite films using pulsed laser excitation have identified a long-lived transient absorption that has been attributed to surface trapped holes.^{12,13} The reported decay time of this transient absorption (seconds) is very similar to the slow decay seen in photocurrent transients¹¹. The competition between electron transfer and recombination that determines the transient photocurrent response and the external quantum efficiency has been characterized quantitatively in our laboratories

using photoelectrochemical impedance spectroscopy (PEIS) and intensity-modulated photocurrent spectroscopy (IMPS).^{10,11} These experiments showed that electron transfer and surface recombination processes at hematite photoelectrodes are both unusually slow, with estimates of surface intermediate concentrations approaching monolayer levels at solar intensities.^{10,11} The present study used *in situ* absorbance spectroscopy to detect and compare surface intermediate species formed during the OER in the dark and under illumination. The required sensitivity was obtained either by modulating the electrode potential in the case of the dark OER (potential-modulated absorbance spectroscopy: PMAS) or by modulating the intensity of illumination in the case of the light-driven OER (light-modulated absorbance spectroscopy: LMAS). In both cases, well-resolved normalized absorbance spectra were obtained that suggest that the ‘surface trapped holes’^{12,13} are in fact long-lived higher-valent Fe species formed as intermediates in the OER. A parallel study of the system using impedance spectroscopy led to a clear understanding of the frequency dependence of the modulated absorbance response and allowed deconvolution of the total impedance. Analysis of the transmission line behavior observed in the high frequency part of the impedance showed that hole transport is slow and probably occurs via hopping between adjacent surface Fe sites. The long lifetimes of the ‘trapped hole’ states derived from these measurements are similar to the values obtained in our previous work on compact hematite layers by photoelectrochemical impedance spectroscopy (PEIS)¹⁰ and by intensity-modulated photocurrent spectroscopy (IMPS)¹¹.

Experimental Methods

NaOH, FeCl₃, HClO₄ and carboxymethylcellulose (sodium salt) were obtained in analytical reagent grade from Sigma-Aldrich. Solutions were prepared with deionised and filtered water from a Thermo Scientific water purification system (Barnstead Nanopure) with 18.2 MΩ cm resistivity. Films of mesoporous iron oxide were fabricated by a layer-by-layer technique developed in our laboratory^{14, 15,16}. A stable colloidal solution of hydrous iron oxide nanoparticles (ca. 4 nm in diameter by TEM and SAXS¹⁶) was prepared by hydrolysis of ferric chloride in boiling water followed by dialysis against

aqueous HClO_4 (pH 3.5)¹⁷. A conducting glass slide (fluorine-doped tin oxide coating: TEC 8, Libbey Owens Ford) was immersed into the 2 mM colloidal solution for one minute to bind a monolayer of oxide particles. After rinsing and drying, the film was immersed for one minute into a solution containing 1.5 %w/w carboxymethylcellulose (sodium salt). Rinsing and drying completed one deposition cycle. This process was repeated until the desired number of layers was obtained. The multilayer films were calcined in a tube furnace at 500° C in air for 30 minutes to remove the organic components, leaving an orange-brown mesoporous iron oxide (hematite) film. The electrode area exposed to the electrolyte was 1 cm². Figure 1 illustrates the effect of the number of layers deposited on the color of the films. Further details of film characterization have been given elsewhere.^{15,16}

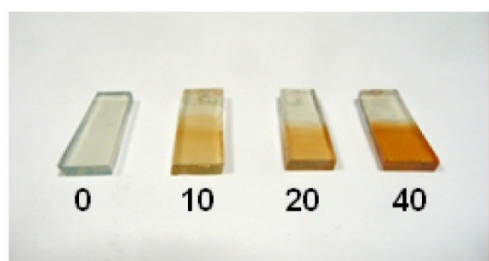


Figure 1. Mesoporous $\alpha\text{-Fe}_2\text{O}_3$ films prepared by layer by layer dip coating of conducting glass. The numbers shown indicate the number of dip cycles.

The electrolyte used in all the measurements was 0.1 M NaOH. A MicroAutolab III potentiostat system (EcoChemie, NL) was used for cyclic voltammetry and a low noise battery-powered potentiostat for PMAS and LMAS. The optical cell incorporated a platinum wire counter electrode and a KCl saturated calomel reference electrode (SCE, Radiometer). Impedance measurements were made using a Solartron 1250 frequency response analyzer with a Solartron 1286 electrochemical interface. PMAS measurements were performed using monochromatic light provided by a Xe lamp light source and monochromator (Bentham Instruments). Transmitted light was detected with a silicon photodiode connected to a lock-in amplifier (Stanford Research SR 830) via a low noise current amplifier. The sinusoidal potential modulation (100 mV p-p, 35.4 mV rms) was provided by the lock-in amplifier. Spectra were recorded at a frequency of 2.7 Hz and at 90° phase shift with respect to the sinusoidal

potential modulation in order to eliminate the small background signal arising from electroreflectance effects from the FTO substrate. LMAS measurements were performed using a tungsten optical fiber illuminator and a monochromator (Bentham Instruments). The modulated illumination (80% depth) was provided by a 370 nm light emitting diode (LED: Thorlabs) coupled via a LED driver (Thorlabs) to the signal output of the lock-in amplifier. A 2 mm GG400 nm filter (Schott) was used in front of the silicon photodiode detector to minimise light throughput from the UV LED. The frequency response of the PMAS and LMAS signals at constant wavelength (460 nm) were measured using the Solartron 1250 frequency-response analyser.

Theoretical Basis

If a surface species is formed by reversible oxidation of a surface site, e.g.



modulation of the potential close to the standard potential of the redox couple leads to a corresponding periodic change in the number densities (concentrations) of oxidized and reduced species (Δn_O , Δn_R – referred to the geometric area) that depends on the Faradaic charge passed, i.e. on the integral of the Faradaic component of the total ac current.

$$\tilde{Q}_F = zq\Delta n_O = -zq\Delta n_R = \int j_F(\omega t) dt \quad (2)$$

where z is the number of electrons transferred and q is the elementary charge. The corresponding normalized change in absorbance depends on the difference in (wavelength dependent) optical absorption cross sections, $\sigma_O(\lambda)$ and $\sigma_R(\lambda)$ of the two species.^{18,19}

$$\frac{\Delta T}{T} = \Delta n [\sigma_O(\lambda) - \sigma_R(\lambda)] = \frac{\tilde{Q}_F}{zq} [\sigma_O(\lambda) - \sigma_R(\lambda)] \quad (3)$$

In order to derive the frequency dependence of the PMAS response, it is necessary to consider the total impedance of the system, which in the present case is a mesoporous film. The theory of impedance of finite porous electrodes has been reviewed and generalized by Bisquert.²⁰ Electron transport and

electron transfer can be represented in a transmission line model as shown in Figure 2a (the additional series resistance, R_{ser} , arising mainly from the FTO substrate and contacts, is not shown). The model describes charge transport in the electrode material as well as the transfer and storage of charge at the electrode/electrolyte interface. r_{trans} is the distributed transport resistance, r_{ct} is the charge transfer resistance and C_{surf} is the capacitance of the $\alpha\text{-Fe}_2\text{O}_3$ /electrolyte interface. We assume that the dominant contribution to the capacitance comes from pseudocapacitance associated with the surface redox reaction. The particle size is sufficiently small (4nm) that band bending is likely to be negligible, which means that the contribution of the space charge capacitance can be neglected, and also the redox pseudocapacitance is expected to be larger than the double layer capacitance. Since the $\alpha\text{-Fe}_2\text{O}_3$ film is mesoporous, it is reasonable to assume that electron (or hole) transport is driven by diffusion, because charges in the particles will be shielded effectively by the electrolyte so that any macroscopic electrical field will be negligible. At low frequencies, the transmission line reduces to the parallel RC circuit shown in Figure 2b, which is in series with the resistance of the FTO substrate electrode. The time constant $R_{\text{ct}}C$ corresponding to the discharge of the pseudocapacitance through the Faradaic resistance effectively represents the lifetime of the surface-bound redox species.

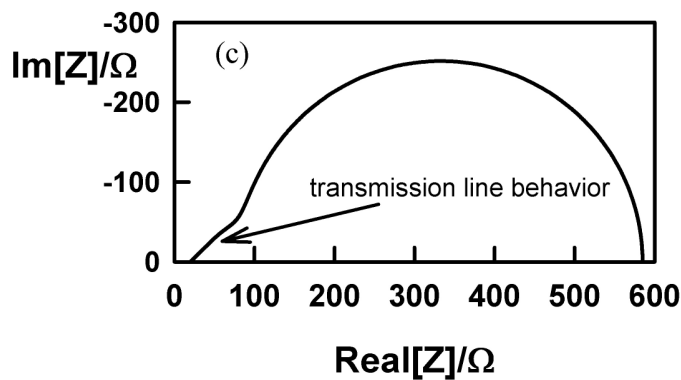
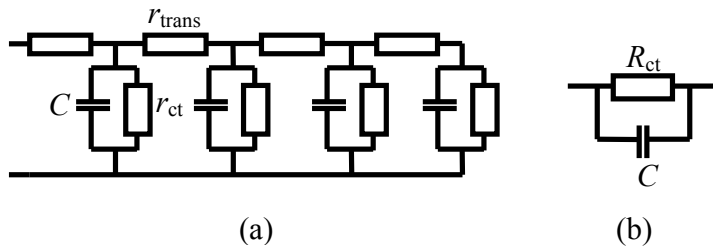


Figure 2. (a) Finite transmission line representing the impedance of the porous $\alpha\text{-Fe}_2\text{O}_3$ electrodes. (b) equivalent circuit in the low frequency limit. The additional series resistance is not shown in either circuit. (c) Typical impedance response for the transmission line circuit including a series resistance. Note the linear region at high frequencies, which is characteristic of transmission line behavior.

As shown in the Supporting Information, the periodic component of the charge stored by the pseudocapacitance can be expressed in terms of a complex capacitance C_c

$$\tilde{Q}_F = C_c \tilde{V} \quad (5)$$

where \tilde{V} is the voltage modulation. An example of the calculated frequency dependence of the modulated charge stored in the pseudocapacitance is shown in Figure 3. In the case where $R_{\text{ser}} < R_{\text{ct}}$, the characteristic time constant corresponding to the minimum of the semicircular response is determined by the series combination of the series resistance and the capacitance. In the case where $R_{\text{ct}} < R_{\text{ser}}$, the time constant is determined by the decay of charge through the Faradaic resistance, i.e. it is a measure of the lifetime of the surface-bound species. Since the modulation of the absorbance is linearly dependent on the modulation of stored charge, the PMAS response should mirror the charge response, showing the same characteristic relaxation frequency. As mentioned above, in the case where $R_{\text{ser}} < R_{\text{ct}}$, the relaxation frequency does not reflect the ‘lifetime’ of the surface intermediate – this must be obtained from analysis of the electrode impedance as shown below.

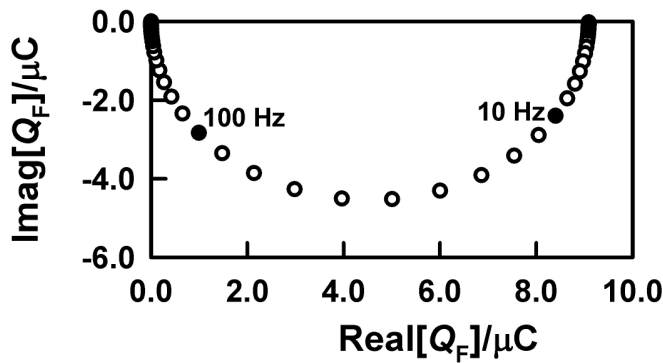


Figure 3. Frequency dependence of the modulated charge Q_F on the pseudocapacitance in Figure 2b

calculated for a series resistance of $50\ \Omega$, $R_{ct} = 500\ \Omega$, $C = 10^{-4}\ \text{F}$ and a modulation amplitude of 100 mV. The potential-modulated absorbance response should exhibit an identical frequency response.

Results and Discussion

OER in the dark

A typical cyclic voltammogram of the mesoporous $\alpha\text{-Fe}_2\text{O}_3$ films is shown in Figure 4. The quasi-reversible behavior at the onset of oxygen evolution suggests the formation of a higher valent Fe species. In previous work, it has been shown that this surface species (tentatively identified as Fe(IV)) is active in the oxidation of glucose.¹⁶ The figure also shows the deconvoluted voltammogram obtained by subtraction of the steady state OER current (which was fitted to a Tafel slope of 93 mV/decade) and of the background charging current from the FTO substrate. The anodic and cathodic charge associated with the quasi-reversible couple is of the order of $25\ \mu\text{C cm}^{-2}$ for an anodic limit of 0.8 V.

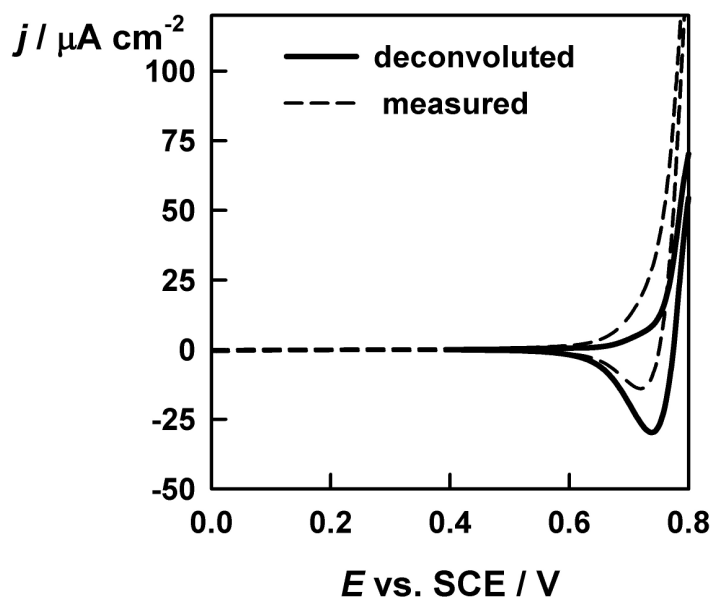


Figure 4. Broken line - cyclic voltammogram of 20 layer film. Sweep rate $100\ \text{mV s}^{-1}$. Full line current after correction for steady state OER current and substrate charging current.

PMAS spectra recorded at different dc potentials in the range 0.65 V to 0.85 V vs. SCE are illustrated in Figure 5 for a 20 layer film. The spectra exhibit two well-defined peaks (460 nm and 560 nm) and a shoulder at around 770 nm. Similar spectra with two clear peaks were measured for the 10 layer film, whereas the peaks, although still evident, were not so pronounced as for the 40 layer film. The PMAS response increases with voltage, peaking at 0.725 V before falling at higher dc voltages. The shapes of the spectra appear to be independent of dc potential, suggesting that only one surface-bound redox couple is involved.

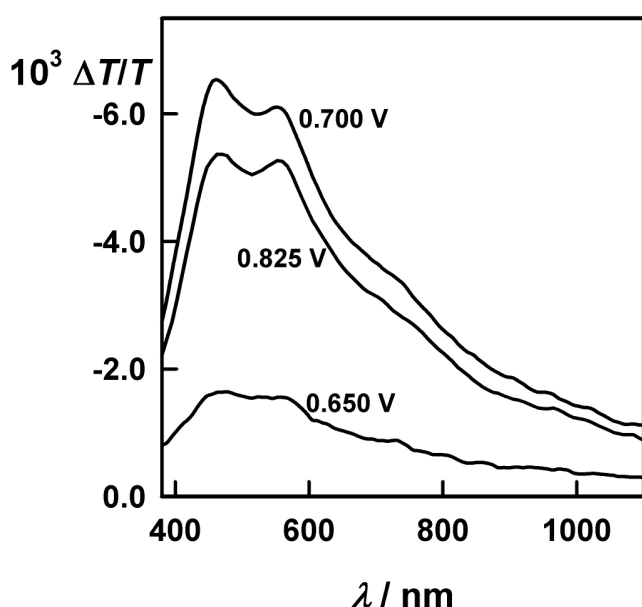


Figure 5. PMAS spectra for a 20 layer mesoporous α -Fe₂O₃ layer measured at the dc potentials shown. Modulation 2.7 Hz, 100 mV peak-peak.

PMAS measures the difference in absorbance brought about by potential modulation (cf. equation 3). The well-defined spectra in Figure 6 correspond to a decrease in transmittance when the potential is made more positive, i.e. when oxidation takes place. Impedance measurements (see below) showed that the pseudocapacitance associated with surface oxidation is of the order of 0.5 mF cm⁻² (geometric) at 0.7 V for a 20 layer film. It follows that the modulated charge (rms) in the PMS experiments is ca. 20 μ C cm⁻², corresponding to $\Delta n_O \sim 10^{14}$ cm⁻² (geometric). This is consistent with the charge under the

reduction peak in the voltammogram shown Fig 1 (ca. $25 \mu\text{C cm}^{-2}$). Assuming a nanoparticle packing fraction = 0.5, the internal surface area of the 20 layer film (ignoring necking during sintering) should be $\sim 30 \text{ cm}^2$. It follows that the surface concentration of oxidized species (or ‘surface trapped holes’) is $\sim 4 \times 10^{12} \text{ cm}^{-2}$, i.e. around 1% of a monolayer. The $\Delta T/T$ value at the peak in the PMAS spectrum (460 nm) measured at 0.7 V can be used to calculate the difference in absorption cross sections as $6 \times 10^{-17} \text{ cm}^2$, corresponding to a difference in molar absorption coefficient $\epsilon = 3.6 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.

The PMAS spectra and molar absorption coefficients of surface species can be compared with known absorption spectra of higher valent Fe species. The absorption spectra reported for Fe(IV), Fe(V) and Fe(VI) species in solution in the region 400-700 nm have been reviewed recently by Sharma and Virender²¹. Fe(IV) shows a broad peak at 420 nm ($\epsilon = 1200 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). Fe(VI) has a broad peak at 510 nm ($\epsilon = 1100 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). Fe(V) has a main peak at 400 nm ($\epsilon = 900 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and a second peak at 500 nm ($\epsilon = 650 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). Clearly none of these solution species correspond to the observed PMAS spectra. The most striking difference is that the molar absorption coefficient of the surface species appears to be more than an order of magnitude higher than that of the ferrate ions. Other possibilities that can be considered are low spin and high spin iron peroxo species which show charge transfer bands in the visible at around 550 nm^{22,23}, but these complexes (with organic ligands) also have absorption coefficients in the region of $10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, i.e. lower than those estimated for the surface-bound species detected by PMAS.

Light-driven OER

The photoelectrochemical OER takes place at much less positive potentials than the dark OER as can be seen from the voltammogram shown in Figure 6 which was recorded in the potential range where LMAS spectra were measured. The anodic photocurrents observed with the mesoporous $\alpha\text{-Fe}_2\text{O}_3$ films used in the present study are considerably smaller than those measured with at films of similar thickness

prepared in our laboratories by aerosol-assisted CVD^{10,11} (possibly as a consequence of the absence of a space charge region), and the substantial losses due to surface recombination are evident in the spiked response. The photocurrent onset potential could not be determined for these mesoporous films since reduction takes place at more negative potentials.¹⁶

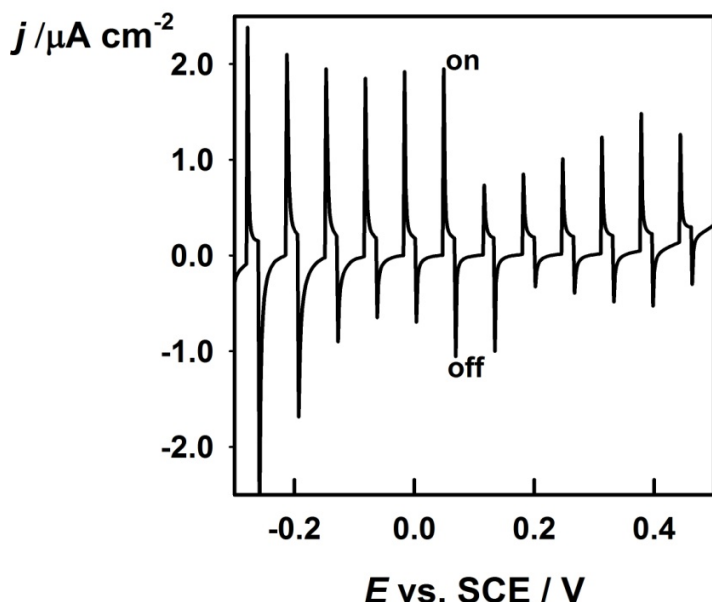


Figure 6. Voltammogram of 40 layer α -Fe₂O₃ film under chopped monochromatic illumination. Sweep rate 10 mV s⁻¹. Illumination 365 nm, 10 mW cm⁻². The apparent variation in the height of the current spikes is an artifact arising from the digital signal sampling.

Light-driven OER at α -Fe₂O₃ involves holes that are formed by excitation of electrons from the valence band to the conduction band. By contrast, holes required for the OER in the dark must be created by another mechanism. In the case of bulk thin films of highly-doped α -Fe₂O₃ under inversion conditions, holes can be created at the oxide/electrolyte interface via electron tunneling from the valence band to the conduction band across the narrow space charge region. This mechanism seems unlikely for the mesoporous films in which band bending is expected to be minimal. An alternative mechanism involves oxidation of surface Fe sites at the substrate/Fe₂O₃ contact followed by progressive oxidation of the internal surface of the mesoporous layer by hole hopping (or equivalent electron hopping)

between adjacent surface sites. This process is analogous to the hole hopping process that takes place between dye molecules adsorbed on mesoporous TiO_2 .^{24,25} In both light driven and dark OER, we may expect to form higher valent iron species at the surface. In the case of the photoelectrochemical OER on $\alpha\text{-Fe}_2\text{O}_3$, our previous work suggests that a substantial concentration of ‘trapped holes’ will accumulate at the surface because OER involves very slow electron transfer. This conclusion is supported by recent work by Pendlebury et al.^{12,13}, who observed a long lived transient absorbance following pulsed laser excitation of $\alpha\text{-Fe}_2\text{O}_3$ electrodes. The spectra reported by Pendlebury et al., which are broadly similar to those in Figure 7, were attributed to ‘surface trapped holes’. In the present study, LMAS was used to investigate optical changes brought about by illumination of mesoporous $\alpha\text{-Fe}_2\text{O}_3$ electrodes with a near UV LED. The electrode potentials were chosen to lie in the region where photocurrents corresponding to photoelectrochemical OER are observed. Figure 7 illustrates the LMAS spectra obtained. Although the spectra were noisier than the PMAS spectra, their structure is very similar (the data in Figure 7 have been smoothed to allow better comparison with Figure 6). The LMAS response is nearly two orders of magnitude lower than in the PMAS spectra, reflecting the fact that the internal quantum efficiency for the photoelectrochemical OER is small, because the majority of holes formed by illumination are lost by recombination.

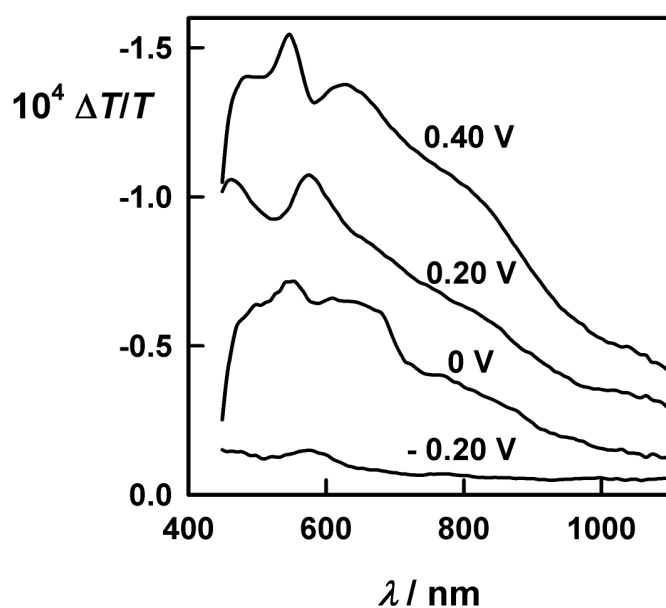


Figure 7. LMAS spectra recorded for a 20 layer α -Fe₂O₃ film at the potentials (vs. SCE) shown.

As we have shown elsewhere^{10,11}, the photoinduced concentration of intermediates (trapped holes) at the surface of α -Fe₂O₃ electrodes is determined by the hole flux into the surface and the first order rate constants for recombination and interfacial charge transfer. The fact that the intermediates can be detected spectroscopically indicates that the rate constants are small (for bulk thin films of the order of 10 s⁻¹ or less^{10,11}). In the present case, the surface concentration of intermediate states (referred to the internal surface area) can be estimated by comparing the magnitude of the largest LMAS and PMAS responses to be $\sim 10^{11}$ cm⁻². Since the measured photocurrent density ($\sim 1 \mu\text{A cm}^{-2}$; cf. Figure 6) corresponds to a flux of holes into the internal surface equal to 2×10^{11} cm⁻² s⁻¹, the lifetime of the intermediate should be of the order of 0.5s, which is consistent with the photocurrent decay seen in the transient photocurrent response as a consequence of surface recombination. This calculation highlights the very long lifetimes of the ‘surface trapped hole’ intermediates involved in the photoelectrochemical OER.

Frequency-dependence of the PMAS and LMAS responses

It was found that the PMAS and LMAS responses of the α -Fe₂O₃ films are attenuated at high frequencies, so that a low frequency (2.7 Hz) was used for all the measurements of spectra. In order to understand the frequency dependence of the PMAS response of the α -Fe₂O₃ films, impedance measurements were carried out (in the dark) in the potential range where PMAS spectra were recorded. Figure 8 illustrates a typical impedance response which exhibits transmission line behavior in the high frequency region of the complex plane plot. The fit to the data to the model shown in Figure 2 is excellent, as can be seen more easily in the phase angle part of the Bode plot.

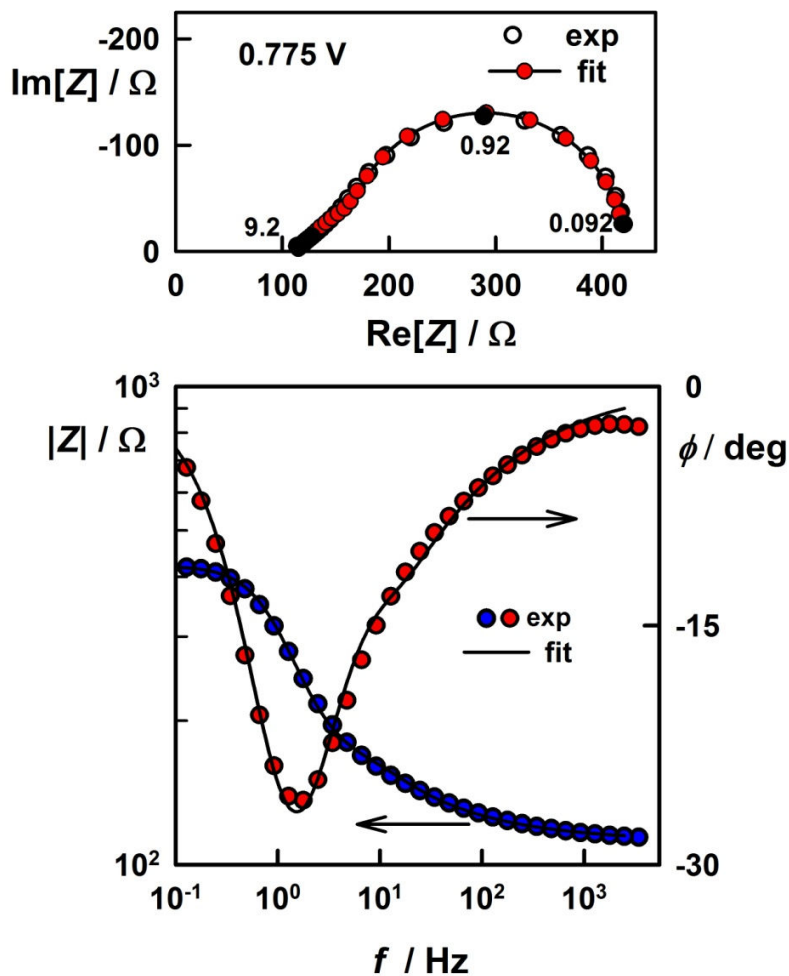


Figure 8. Impedance of 40 layer α -Fe₂O₃ film measured in the dark at 0.775 V vs. SCE showing the fit of the data to the transmission line model (cf. Figure 2a). The frequencies in Hz are labeled on the complex plane plot. Fit values $R_{ct} = 275 \Omega$, $R_{trans} = 161 \Omega$, $C = 0.68$ mF.

The variation of R_{ct} , R_{trans} and C with electrode potential was recorded for 10, 20 and 40 layer α -Fe₂O₃ films. Figure 9 illustrates the trends with the example of the 40 layer film. It can be seen that the time constant $R_{ct}C$ corresponding to the ‘lifetime’ of the oxidized Fe states decreases from 0.1 s to 10 ms as the potential is increased from 0.7 to 0.8V, reflecting the increasing rate of electron transfer in the OER.

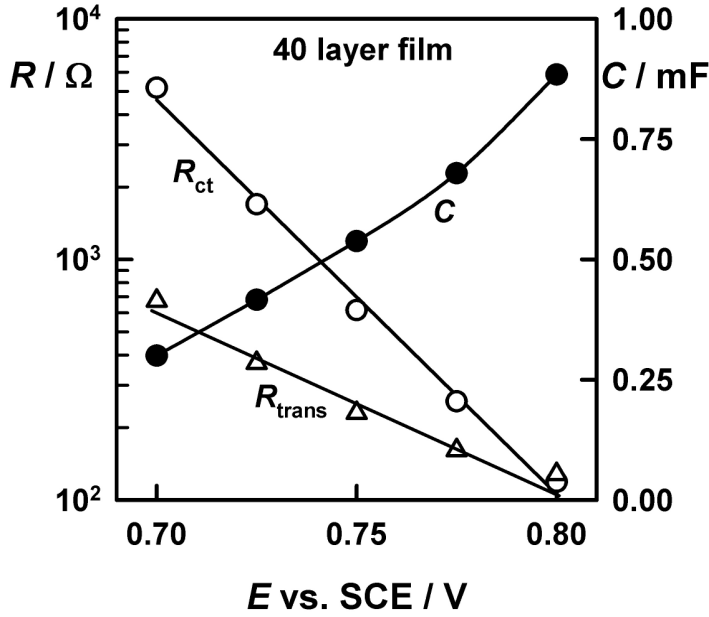


Figure 9. Potential dependence of transport resistance, R_{trans} , charge transfer resistance R_{ct} and capacitance C for a 40 layer α -Fe₂O₃ film. Values derived from the fitting to the equivalent circuit shown in Figure 2a with inclusion of the series resistance.

The transmission line behavior seen in the impedance response suggests slow transport of charge in the mesoporous α -Fe₂O₃ film. Hole transport in α -Fe₂O₃ is known to be slow and to depend strongly on direction in the crystal lattice. In a recent theoretical study, Iordanova et al.²⁶ have modeled electron and hole transport in α -Fe₂O₃ using Marcus theory and obtained hole mobilities of $3.6 \times 10^{-7} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $1.7 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for transport in the (001) plane and along the [001]axis respectively. The transport resistance measured by impedance spectroscopy is related to the hole concentration by

$$R_{tr} = \frac{d_{film}}{\sigma} = \frac{d_{film}}{qp\mu_p} \quad (6)$$

where d_{film} is the film thickness and the conductivity σ is determined by the product of the hole mobility, μ_p and the hole concentration p . So that the decrease in R_{trans} observed in the semi-logarithmic plot in Figure 9 can be interpreted as an exponential increase of hole concentration with potential. If we take

the lower value of mobility and consider a 80 nm film with $R_{tr} = 100 \Omega$ (cf. Figure 9) at 0.8V, the free hole concentration would be $1.4 \times 10^{18} \text{ cm}^{-3}$, corresponding to charge of $1.8 \mu\text{C cm}^{-2}$ (geometric). This is an order of magnitude lower than the charge (ca. $20 \mu\text{C cm}^{-2}$) estimated from the pseudocapacitance. If the mean mobility is higher, the hole concentration will be correspondingly lower still. We therefore consider the possibility that hole transport in the mesoporous film is even slower than in the bulk because holes are localized at the surface of the $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles, with transport occurring via a hole hopping mechanism involving the higher valent Fe species observed in the PMAS spectra. In order to examine this model semi-quantitatively, we need to establish a correspondence between the electrical and optical properties of the film. In other words, we need to relate the impedance of the films to the frequency dependent PMAS response. Figure 10 shows that there is indeed a one to one correspondence between the frequency dependence of the modulated transmission and the modulated charge on the pseudocapacitance, validating the model given in theoretical section (in the present case, the frequency attenuation arises predominantly from the combination of series resistance and pseudocapacitance).

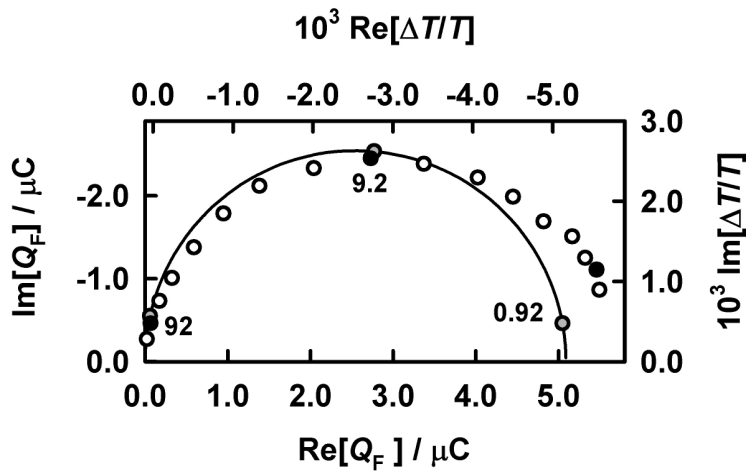


Figure 10. Comparison of frequency dependence of the PMAS response of 20 layer mesoporous $\alpha\text{-Fe}_2\text{O}_3$ film at 0.775 V vs. SCE with the rms modulated charge calculated from the complex capacitance obtained using values of R_{ct} , C and R_{ser} derived from the impedance analysis. Line fit. Frequencies in

Hz as shown: black experimental $\Delta T/T$, grey fit.

As discussed above, the surface concentration of higher valent iron species ('surface trapped holes') in the potential range where a large PMAS response is observed is estimated to be of the order of $4 \times 10^{12} \text{ cm}^{-2}$, which corresponds to a volume concentration of around 10^{19} cm^{-3} . Therefore if we interpret the transport resistance as arising from hopping of surface trapped holes between sites, the mobility would be an order of magnitude lower than the values for the bulk, i.e. ca. $4 \times 10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which corresponds to a diffusion coefficient of $10^{-9} \text{ cm}^2 \text{ s}^{-1}$. This low diffusion coefficient is consistent with thermally activated electron transfer between adjacent Fe sites on the surface. A crude estimate based on an average hopping distance of 0.5 nm and an attempt frequency of 10^{13} s^{-1} gives an activation energy of around 0.4 eV, which corresponds to the depth of the hole trap.

The LMAS response is also attenuated at high frequencies, as can be seen from the results in Figure 11. The relaxation in this case can be related to the corresponding slow relaxation seen in the transient photocurrent (cf. Figure 6). The lifetime of the surface trapped hole intermediate derived from the frequency of the maximum in Figure 11 is about 50 ms.

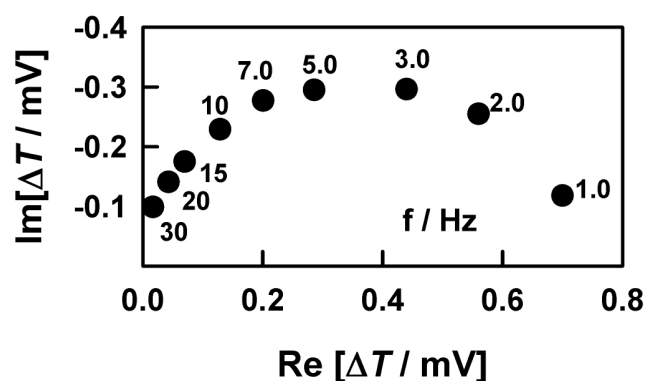


Figure 11. Frequency response of the LMAS response at 600 nm, 0.40 V vs . SCE.

We have recently reported the determination of rate constants for hole transfer and recombination at compact $\alpha\text{-Fe}_2\text{O}_3$ electrodes using intensity modulated photocurrent spectroscopy (IMPS).¹¹ The results were fitted using a model in which holes are trapped at surface states and can then either react to form

oxygen or recombine with conduction band electrons. The characteristic relaxation frequency in this case corresponds to the sum of the rate constants for hole transfer, k_{tr} and recombination k_{rec} , and the lifetime is the reciprocal of the sum of ($k_{tr} + k_{rec}$). The time constant derived from Figure 11 is consistent with the values measured by IMPS on compact α -Fe₂O₃ films, and we can therefore conclude that we are seeing the decay of the higher valent Fe species ('trapped holes') as they are consumed either by the OER or by capture of electrons from the conduction band of the Fe₂O₃. It follows that the LMAS and PMAS spectra provide a spectroscopic footprint of the 'trapped hole' intermediate in the OER.

Conclusions

The combination of spectroscopic and impedance techniques has given a deeper insight into the mechanism and kinetics of oxygen evolution at α -Fe₂O₃. The same species is detected in potential-modulated and light-modulated transmittance measurements, suggesting that the mechanisms of oxygen evolution involve the same intermediate in the dark and under illumination. The slow relaxation seen in light-modulated experiments and in impedance measurements confirms the existence of a kinetic bottleneck in the OER at α -Fe₂O₃. The chemical identity of the intermediate detected by modulated spectroscopy has not been established, but if we consider it as a 'surface-trapped hole', higher order reactions are required for the four electron oxidation of water. An elementary step involving 4-holes can be discounted, so that it is reasonable to assume that hole capture leads to Fe states with valencies higher than +4. As we have suggested elsewhere, the OER could involve adjacent surface sites corresponding nominally to Fe(V) or to Fe(IV) and Fe(VI). This would mean more than one hole must be captured at each site before oxygen evolution can proceed. In this context, the mobility of surface holes becomes important, and the low hole mobilities inferred from the impedance analysis suggest that the sluggishness of the OER may be due, at least in part, to slow surface diffusion, i.e. to deep trapping of holes in addition to the activation energy associated with O-O bond rupture.

Supporting Information

Derivation of the complex capacitance of the circuit in Figure 2. This information is available free of charge at <http://pubs.ac.org>

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