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ARTICLE TYPE

Kinetics and Mechanism of Light-Driven Oxygen Evolution at Thin Film α-Fe$_2$O$_3$ electrodes[§]

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Rate constants for recombination and hole transfer during oxygen evolution at illuminated α-Fe$_2$O$_3$ electrodes were measured by intensity-modulated photocurrent spectroscopy and found to be remarkably low. Treatment of the electrode
10 **with a Co(II) solution suppressed surface recombination but did not catalyse hole transfer. Intermediates in the reaction were detected spectroscopically.**

Light-driven water splitting at α-Fe$_2$O$_3$ (hematite) electrodes has been investigated extensively since the material is stable in
15 alkaline solutions and has a band gap (2.0 eV) suitable for efficient light harvesting.[1] However, there have been remarkably few quantitative studies of the kinetics and mechanisms of the light-driven oxygen evolution reaction (OER) at α-Fe$_2$O$_3$ (or at other n-type semiconductor photoanodes). In a study of single
20 crystal hematite electrodes, Dare-Edwards et al.[2] concluded that the light driven OER was a slow process, and a recent study of hematite thin film electrodes by photoelectrochemical impedance spectroscopy (PEIS) reached a similar conclusion.[3]

The performance of α-Fe$_2$O$_3$ photoanodes is limited by bulk
25 and surface electron-hole recombination. Nanostructuring of electrodes[4] enhances performance by reducing the distance that holes need to travel to reach the interface, but the problem of surface recombination remains. The competition between surface recombination (first order rate constant k_{rec}) and hole transfer
30 (first order rate constant k_{tr}) determines the fraction $\eta_{trans} = k_{tr}/(k_{tr} + k_{rec})$ of the hole flux into the surface that is consumed in the OER. The remaining fraction $1-\eta_{trans}$ corresponds to holes lost by surface recombination.[3,5]

The effects of surface recombination are evident in the
35 transient photocurrent response of a compact α-Fe$_2$O$_3$ film (prepared by aerosol-assisted CVD[6]) shown in Fig. 1 (Electrolyte 1.0 M NaOH). The instantaneous current when the light is switched on is a measure of the flux of holes into the surface. The subsequent decay towards the steady state current results
40 from the capture of build-up holes in surface states inducing an electron flux associated with recombination. The cathodic current overshoot observed when the light is switched off is due to the continuing flux of electrons into the surface as holes remaining in the surface states recombine.

45 The rate constants k_{tr} and k_{rec} can be obtained by analysing the transient photocurrents response,[7,8] but a more powerful method is intensity-modulated photocurrent spectroscopy (IMPS), which involves modulating the intensity of the illumination and

measuring the magnitude and phase of the photocurrent response
50 as a function of frequency.[9-11] An example of the characteristic IMPS response of an α-Fe$_2$O$_3$ electrode in the complex plane is shown in Fig. 2 for a cobalt-treated electrode (see below).
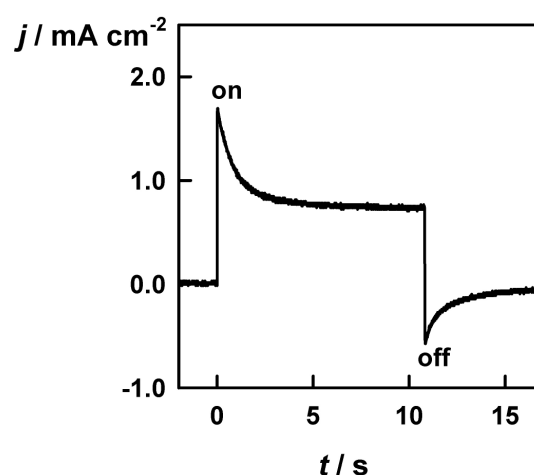

Fig. 1. Transient photocurrent response of thin film α-Fe$_2$O$_3$ electrode at
55 0 V vs. Ag|AgCl showing the decay and overshoot characteristic of surface electron-hole recombination.
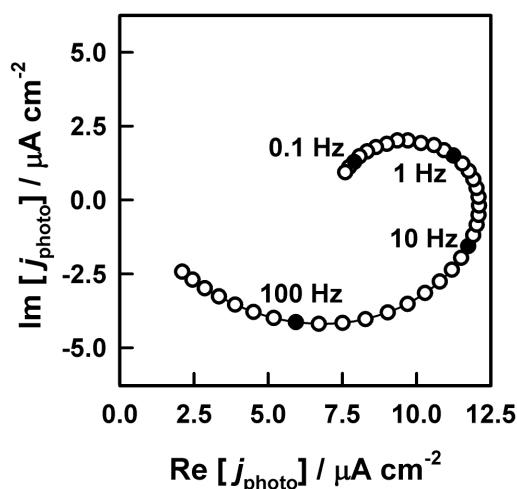

Fig. 2. IMPS response of a Co(II) treated film α-Fe$_2$O$_3$ electrode., -0.3 V vs. Ag|AgCl. The low frequency semicircle in the upper quadrant is due
60 to electron-hole recombination. Electrolyte 1.0 M NaOH. The flattened semicircle in the lower quadrant is due to attenuation by the series resistance and space charge capacitance.

The first order rate constants $k_{tr} + k_{rec}$ are obtained by analysing the low frequency upper semicircle in Fig. 2 (the high frequency semicircle arises from RC attenuation by the series resistance and space charge capacitance. The radial frequency corresponding to the maximum in the semicircle is equal to $k_{tr} + k_{rec}$, and the ratio of the low and high frequency intercepts is equal to $k_{tr}/(k_{rec} + k_{tr})$.[10]

It has been suggested that treatment of α-Fe$_2$O$_3$ electrodes with a solution of cobalt nitrate catalyses hole transfer and shifts the photocurrent onset potential to more negative values.[12] The improvement in performance was confirmed in the present study, and IMPS was used to relate the observed enhancement to changes in k_{tr} and k_{rec}. The results are illustrated in Fig. 3 and 4, which compare the potential dependencies of the two rate constants on potential before and after the cobalt treatment.
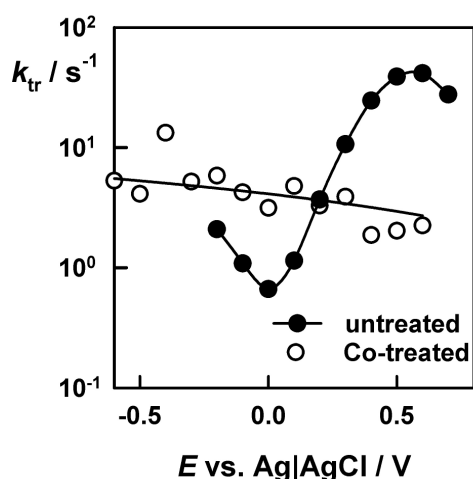

Fig 3. Charge transfer rate constant k_{tr} as a function of potential for untreated and Co(II)-treated α-Fe$_2$O$_3$ electrodes.
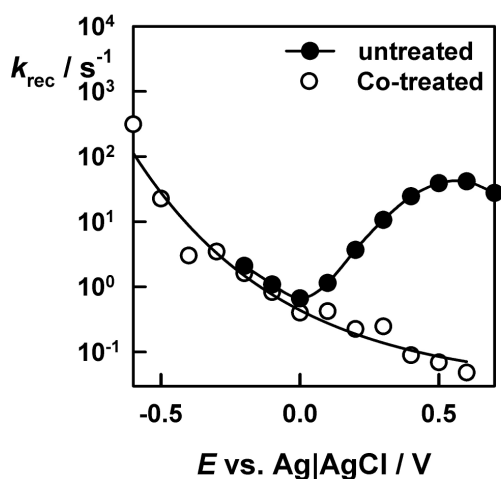

Fig. 4. Recombination rate constant k_{rec} as a function of potential for untreated and Co(II)-treated α-Fe$_2$O$_3$ electrodes.

For an ideal semiconductor (low doped) /electrolyte junction, under depletion conditions, the potential difference across the Helmholtz layer remains almost constant when the electrode potential is changed, so the charge transfer rate constant (for a single hole transfer step) should be independent of potential. This is evidently the case for the Co(II)-treated electrode, but not for the untreated electrode. The highly non-ideal behaviour of the untreated electrode indicates that a substantial fraction of the change in applied potential appears across the Helmholtz layer, enhancing the rate constant for charge transfer. This is consistent with a high density of surface electronic states that can store charge and alter the potential drop across the Helmholtz layer. The S-shape of the k_{tr} plot suggests that the band bending may be modulated by the time-dependent concentration of surface-trapped holes as discussed by Fermin et al..[13]

For an ideal n-type semiconductor/electrolyte junction, the potential dependence of the recombination rate constant depends on the electron concentration at the surface, $n_{x=0}$, which is determined by the band bending, i.e. on the difference between the applied potential E and the flat band potential E_{fb}:

$$k_{rec} = \sigma_n \nu_n n_{x=0} = \sigma_n \nu_n N_d e^{-q\left(\frac{E-E_{fb}}{k_B T}\right)} \quad (1)$$

where σ_n is the electron capture cross section, ν_n is the thermal velocity of electrons and N_d is the doping density. For $T = 298$K, it follows that k_{rec} should decrease by a factor of 10 for every 59 meV increase in band bending. The recombination behaviour of the untreated electrode is clearly highly non-ideal, mirroring the non-ideal variation of k_{tr} with potential seen in Fig. 3. Again this is consistent with substantial changes in the potential drop across the Helmholtz layer arising from charging of surface states. The increase in both k_{tr} and k_{rec} over the potential range 0 to 0.5 V suggests a broad Gaussian distribution of surface states that become positively charged as the voltage is increased. By contrast, the Co(II)-treated electrode shows a monotonic decrease of k_{rec} with potential that is more gradual than predicted by equation 1. This suggests that even in the case of the Co(II)-treated electrode, the classical model of the semiconductor/electrolyte junction may not be applicable due to the build-up of charge associated with surface-bound intermediates in the OER as a consequence of slow charge transfer. The surface hole concentration p_{surf} is given by

$$p_{surf} = \frac{j_h}{q\left(k_{tr} + k_{rec}\right)} \quad (2)$$

where j_h is the hole current into the surface. It follows from the low values of k_{tr} that the surface hole concentration could approach 10^{14} cm^{-2} under solar illumination. This large accumulated charge will reduce band bending substantially.

The most remarkable feature of the rate constants measured in this study is that both k_{tr} *and* k_{rec} are so small. The low rate constant for charge transfer is not surprising since the OER is an inner-sphere reaction involving - nominally at least - 4 holes. One might expect that this kinetic 'bottleneck' would make it difficult for charge transfer to compete with more rapid electron hole recombination at the surface. The fact that recombination is also very slow (i.e. the capture cross section σ_n is anomalously small) indicates that the recombination step involves a thermally activated step. This conclusion highlights the limitations of using conventional 'solid state' descriptions of the redox processes taking place at the electrode surface.

The kinetic results raise the question – what are the surface

species (i.e. the 'surface trapped holes) involved in the OER and in recombination? In order to address this question we have used light-modulated absorbance spectroscopy (LMAS) to detect species generated under illumination. LMAS relies on lock-in detection to achieve high-sensitivity. A 365 nm light-emitting diode modulated at 2.7 Hz was used to illuminate a thin (40 nm) α-Fe$_2$O$_3$ electrode deposited on a conducting glass substrate, and the changes in transmission were measured in the range 450 – 1100 nm. Measurements were made in the same potential range used for IMPS. Potential-modulated absorption spectroscopy (PMAS) was also used to characterize the same electrode at (more positive) potentials close to the onset of oxygen evolution in the dark. In this case the potential was modulated using a 100 mV sine wave at 2.7 Hz. Fig. 5 illustrates the LMAS and PMAS spectra obtained. Although the LMAS response is more than two orders of magnitude smaller than the PMAS response, it is clear that the same species is detected by two methods. The spectra are similar to those reported by Pendlelbury et al.[14] for 'surface trapped holes' produced by pulsed laser excitation of α-Fe$_2$O$_3$ electrodes. (Further details of the LMAS and PMAS measurements are given in the Electronic Supplementary Information and elsewhere.[15])
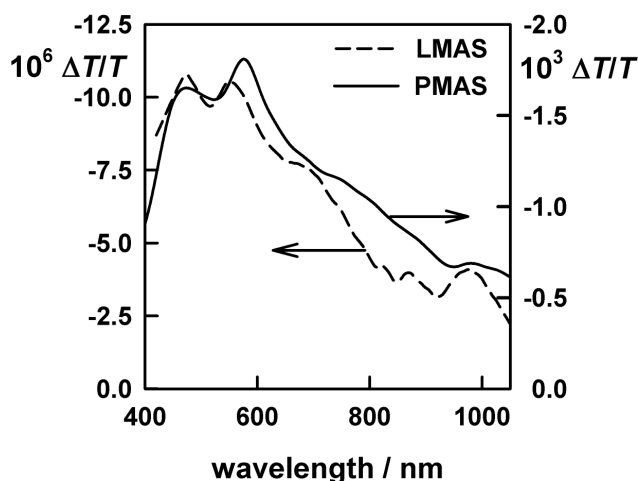

Fig. 5. Comparison of LMAS and PMAS spectra. Film thickness 40 nm. Electrolyte 0.1 M NaOH.

The photo-induced states seen in the LMAS spectra are evidently long-lived since the signal attenuates rapidly when the modulation frequency is increased above 10 Hz. An order of magnitude estimation of the lifetime from the attenuation gave a value of 100 ms, which is consistent with the slow decay of the photocurrent transient in Fig. 1 and the values of k_{tr} and k_{rec} in Fig. 4 and 5. We therefore conclude that the absorption spectra in Figure 5 arise from surface-bound iron species with a higher valence state (e.g. Fe(IV)). This higher valent state is clearly identical to the 'surface trapped hole' discussed in other work.[14] The LMAS and PMAS spectra do not match those of Fe(IV), Fe(V) and Fe(VI) in solution[16], and further experiments are needed to identify the exact chemical nature of the surface species that are formed during OER.

Conclusions

The results reported in this communication indicate that light-driven oxygen evolution on α-Fe$_2$O$_3$ electrodes involves remarkably slow charge transfer, pointing to a kinetic bottleneck in the 4-hole oxidation of water. Fortunately, recombination is also slow, so that the efficiency for hole transfer can approach unity for electrodes that have been treated with Co(II) to reduce surface recombination. In this case, the overall efficiency is limited by bulk recombination outside the space charge region. The results also show that the apparent 'catalytic' effect of surface treatment with Co(II) is in fact due to suppression of surface recombination and not to acceleration of charge transfer by lowering the activation barrier. Control of surface and bulk recombination as well as the identification of catalysts for the OER will be essential elements of any new strategy to optimize photoanodes for light driven water splitting.

Notes and references

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