Kinetics of oxygen evolution at α-Fe₂O₃ photoelectrodes
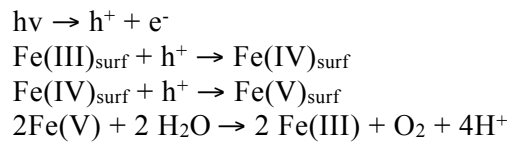
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Haematite (α-Fe₂O₃) is a n-type semiconductor that can be used as a photoanode in tandem water splitting cells, in which holes created by absorption of high energy photons by the Fe₂O₃ oxidize water, and lower energy photons transmitted through the oxide are harvested by a solar cell that applies the bias voltage required for hydrogen evolution at the cathode. However, the short hole diffusion length (L_p) and the high doping lead to poor collection of photogenerated holes. The problem has been addressed by fabricating nanostructured films, so that holes have more chance of reaching the surface, but even if holes reach the interface, electron transfer must compete with surface recombination. Remarkably little is known about the kinetics of these competing processes.

Photoelectrochemical oxygen evolution on α-Fe₂O₃ involves the transfer of 4 electrons per molecule of O₂ formed. The elementary steps in the reaction are likely to involve higher-valent states of iron formed at the surface by hole capture.

$$hv \rightarrow h^+ + e^-$$
$$Fe(III)_{surf} + h^+ \rightarrow Fe(IV)_{surf}$$
$$Fe(IV)_{surf} + h^+ \rightarrow Fe(V)_{surf}$$
$$2Fe(V) + 2\ H_2O \rightarrow 2\ Fe(III) + O_2 + 4H^+$$

The Fe(IV) and Fe(V) intermediates in this scheme can also act as electron acceptors so that surface recombination reactions of the following kind are likely to take place.

$$Fe(IV) + e^- \rightarrow Fe(III)$$
$$Fe(V) + e^- \rightarrow Fe(IV)$$
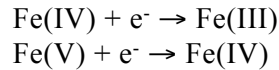
The Fe(IV) and Fe(V) states are effectively 'surface-trapped holes'. A simple phenomenological scheme describing charge transfer and recombination is illustrated in Fig.1. The rates of hole transfer and recombination (cm⁻² s⁻¹) are described using the rate constants k_t and k_r (s⁻¹) in Fig. 1 and the surface concentration of 'trapped holes' (cm⁻²). In the scheme above, surface trapped holes correspond to Fe(IV) and Fe(V) species and 'hole transfer' corresponds to the overall 4-electron oxidation process leading to the formation of oxygen and 'recombination' to electron capture by Fe (IV) and Fe(V) species. The rate of recombination depends on the electron capture cross sections and surface concentrations of Fe(IV) and Fe(V) species ('trapped holes') as well as on the concentration of free electrons available at the surface. It follows that k_r should depend on band bending q$\Delta\phi$, since the electron concentration at the surface is given by $n_{x=0} = n_{bulk}\exp(-q\Delta\phi/k_BT)$, where n_{bulk} is determined by the doping density
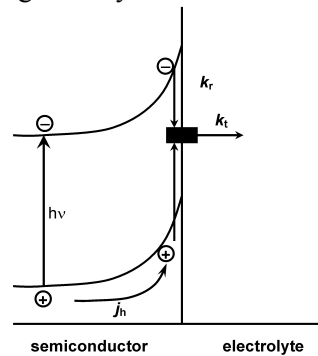

Fig 1 Phenomenological kinetic scheme for PEIS analysis

The impedance of the illuminated electrode is given by

$$Z = R_{ser} + \cfrac{1}{i\omega C_{sc} + \left(\dfrac{q}{k_BT}\right)j_h \dfrac{k_r}{k_t + k_r}\dfrac{k_t + i\omega}{k_t + k_r + i\omega}} \quad (1)$$

R_{ser} is the series resistance, C_{sc} is the space charge capacitance, j_h is the current density corresponding to the flux of holes reaching the interface. The impedance corresponds to two

semicircles in the complex plane. The low frequency semicircle tends towards a zero frequency intercept on the real axis given by

$$Z_1 = R_{ser} + \frac{k_t + k_r}{\left(\dfrac{q}{k_B T}\right) j_h k_r}\left(1 + \frac{k_r}{k_t}\right) \quad (2)$$

The radial frequency ω_{max}(LF) corresponding to the maximum imaginary component of the low frequency semicircle is equal to k_t. The high frequency limit of the low frequency semicircle is

$$Z_2 = R_{ser} + \frac{k_t + k_r}{\alpha\left(\dfrac{q}{k_B T}\right) j_h k_r} \quad (3)$$

It follows that

$$\frac{Z_1 - R_{ser}}{Z_2 - R_{ser}} = 1 + \frac{k_r}{k_t} \quad (4)$$

and

$$j_h = \frac{k_t + k_r}{\alpha\left(\dfrac{q}{k_B T}\right) k_r \left(Z_2 - R_{ser}\right)} \quad (5)$$

The radial frequency ω_{max}(HF) corresponding to the maximum imaginary component of the high frequency semicircle is given by $1/[C_{sc}(Z_2 - R_{ser})]$. It can be seen from this set of equations that k_t, k_r, C_{sc} and j_h can be determined experimentally from the PEIS response shown schematically in Fig. 2.

The α-Fe_2O_3 electrodes used in the study were relatively smooth polycrystalline films deposited by aerosol-assisted chemical vapour deposition (AACVD) on fluorine-doped tin oxide coated glass substrates using ferrocene as precursor.
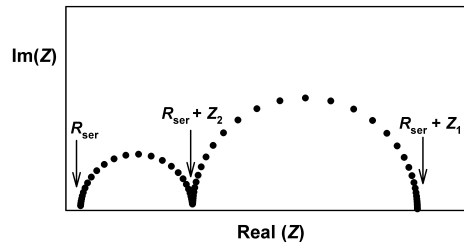

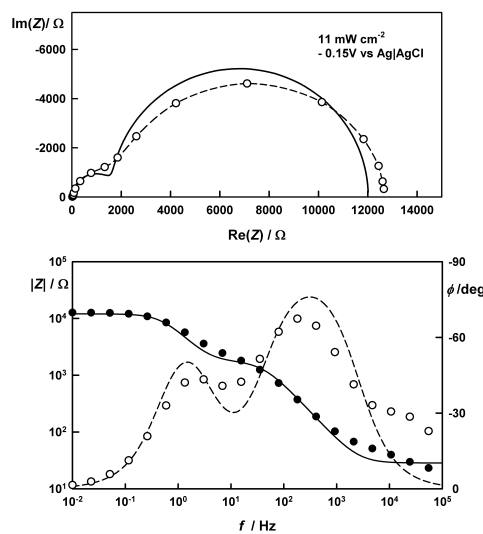**Fig 2** Typical PEIS response predicted by equation 1

Fig. 3 Typical experimental Nyquist and Bode plots of the PEIS response

PEIS spectra were fitted and analyzed to obtain k_t, k_r, C_{sc} and j_h as a function of potential at three light intensities. Fig. 4 illustrates a set of data obtained at 1.1 mW cm^{-2}.

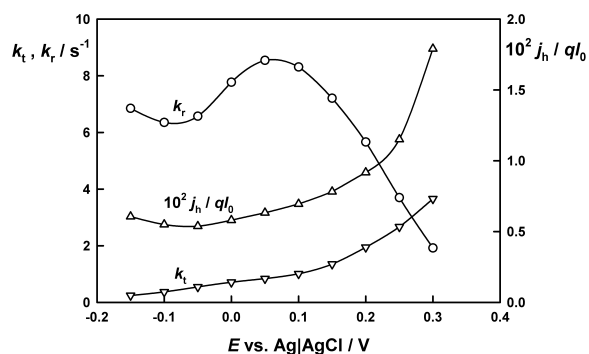**Fig. 4** Rate constants for charge transfer and recombination (k_t and k_r) and the normalised hole flux derived from the analysis of PEIS spectra. dc illumination intensity 1.1 mW cm^{-2}.

Fig. 5 contrasts the k_t and k_r values obtained from the analysis of PEIS spectra measured for three different illumination intensities.
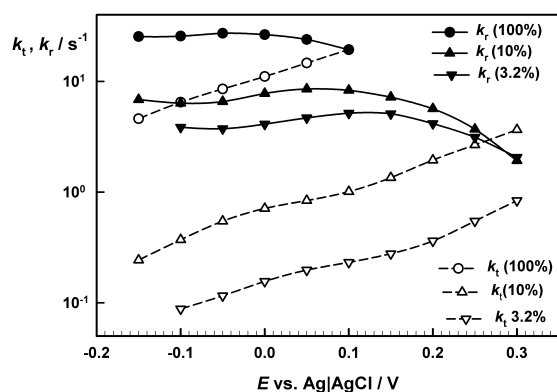

Fig. 5 Dependence of k_t and k_r on potential for three light intensities.

k_r varies with $I_0^{0.54}$, which is close to a square root dependence. By contrast k_t varies with $I_0^{1.2}$ which is close to a linear dependence.

The fraction of the hole flux that is consumed in the oxygen evolution reaction is given by the ratio $k_t/(k_t + k_r)$, which has been plotted as a function of potential in Fig. 6. The results demonstrate that the delayed photocurrent onset can be attributed to surface recombination and Fermi level pinning. .
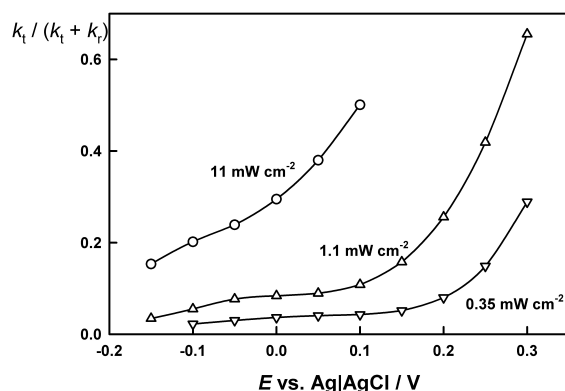

Fig. 6 The ratio $k_t / (k_t + k_r)$ as a function of potential for different light intensities**.**

This study has shown that electrochemical impedance spectroscopy can provide information about the phenomenological rate constants describing the competition between charge transfer and recombination during light driven oxidation of water at semiconductor electrodes.

Acknowledgments