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Behaviour of Titanium-based Fe_2O_3 Photo-Anodes in Photo-Electrochemical Reactors for Water Splitting

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ABSTRACT

The behaviour of titanium substrates was investigated as replacements for transparent fluorine-doped tin oxide-coated glass substrates, the low conductivity of which causes inhomogeneous spatial distributions of potential and current densities on scaling up photo-electrodes in photo-electrochemical reactors. Hence, Fe_2O_3 (ca. 23 nm thick) was deposited by spray pyrolysis onto the titanium surface at 450 °C in air, causing growth of (less photo-active) rutile by thermal oxidation, the thickness being measured as ca. 20 nm by secondary ion mass spectrometry. Anodising titanium in aqueous phosphoric acid enabled ca. 12 nm anatase TiO_2 to be grown prior to spray pyrolysis, limiting the subsequent thermal growth of rutile, so the overall TiO_2 thickness was ca. 16 nm. 23 nm thick Fe_2O_3 deposited on a 22 nm TiO_2 | Ti substrate after heat treatment at 500 °C for 1 hour was found to produced greater current densities than Fe_2O_3 deposited onto TEC-8 fluorine-doped tin oxide coated on glass; uv absorption by TiO_2 and reflection by the titanium substrate contributed to measured photo-current densities.

1. Introduction

Photo-electrochemical production of hydrogen [1] from water using solar energy and its subsequent use in fuel cells, could obviate the predicted consequences of CO_2 emissions from fossil-fuelled power stations. The feasibility of such solar-powered processes is well established; suitable semiconducting films in contact with water absorb photons with energies greater than their band gap energy, produce electron-hole pairs (excitons) by:

$$semiconductor + h\nu \underset{recombination}{\overset{absorption}{\rightleftarrows}} semiconductor(h^+_{vb} + e^-_{cb}) \quad (1)$$

Suitably energetic electron 'holes' in the semiconductor's valence band (vb) could then oxidise water to oxygen by reaction (2) if $E_{vb}/e^- > U_{O_2/H_2}$ and electrons in the semiconductor's conduction band (cb) could reduce water to hydrogen by reaction (3), if $E_{cb}/e^- < U_{H^+/H_2}$, where E represents energies of the band edges and U represent the corresponding (relative) electrode potentials:

$$2H_2O + 4h^+_{vb} \rightarrow O_2 + 4H^+ \quad (2)$$

$$2H^+ + 2e^-_{cb} \rightarrow H_2 \quad (3)$$

In the photo-electrochemical reactor described below, a n-type photo-anode was connected electronically to a platinized titanium cathode, with anolyte and catholyte separated by an ion-permeable membrane. This design was intended to maximise the effective charge yield of reaction (3), by minimising the rates of hydrogen-oxygen recombination (c.f. electron-hole recombination by the reverse of (1)) and/or the rates of the reverse of reactions (2) and (3) at the cathode and anode, respectively. Such reactors would enable photon energy harvesting and chemical energy storage, thereby compensating for their diurnal operation.

Most research on photo-electrochemical processes has been focussed on the properties and behaviour of semiconducting photon-absorbing phases, with little development of reactors [2,3] in which to deploy them. While relaxing the design constraints for achieving more homogeneous photon fluxes, the use of (transparent) fluorine-doped tin oxide (FTO) substrates was predicted to result in large spatial distributions of electrical potential and hence current densities [2].

The objective of the work reported below was to determine whether such effects can be mitigated by using metallic substrates, such as titanium, which would be subject to subsequent thermal oxidation, increasing interfacial resistance, during spray pyrolysis of semiconducting photon absorbing phases such as iron(III) oxide (α-Fe_2O_3). Fe_2O_3 was chosen as the photo-anode material because it absorbs visible light (ca. 560 nm ≡ 2.2 eV band gap energy), is stable under water oxidation conditions, is cheap to fabricate and abundant [4].

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Nomenclature

Symbol

A_i	Surface area of i (m^2)
C	Area specific capacitance ($F\ m^{-2}$)
e^-	Electronic charge, 1.602×10^{-19} (C)
E	Energy (J)
H	Characteristic length of electrochemical cell (m)
I	Current (A)
I_0	Incident light irradiance ($W\ m^{-2}$)
I''	Light intensity after absorption ($W\ m^{-2}$)
j_i	Current density of reaction i ($A\ m^{-2}$)
k_B	Boltzmann constant, 1.38×10^{-23} ($J\ K^{-1}$)
K	Ratio of light absorption for multiple and single passes through absorber (A.8) (1)
L	Distance between current collectors on the same electrode (m^2)
N	Number of passes through light absorbing semiconductor (1)
N_D	Donor density (m^{-3})
R_i	Area specific resistance of i ($\Omega\ m^2$)
t_i	Thickness of material i (m)
T	Temperature (K)
U	Electrode potential vs. reference electrode (V)
Wa	Wagner number (1)
X	Distance at which the light is absorbed into the semiconductor (m)
ε_0	Permittivity of vacuum, 8.854×10^{-12} ($F\ m^{-1}$)
ε_{sc}	Relative permittivity of semiconductor (Fe_2O_3), 26.4 (1)
η	Overpotential (E - E_{eqm}) (V)
κ_i	Electrical conductivity of phase i ($\Omega^{-1}\ m^{-1}$)
κ_λ	Absorption coefficient (m^{-1})

Subscript

A	Anode
Cb	Conduction band
E	Electrolyte
FTO	Fluorine-doped tin oxide substrate
Vb	Valence band

2. Potential and current density distributions

Electrochemical processes are highly sensitive to electrode potentials, the spatial distributions of which, together with the resulting current density distributions, are major design considerations in the scale up and optimisation of electrochemical systems in general, the objective being to minimise spatial inhomogeneities [5]. In photo-electrochemical water splitting research, optically transparent materials, such as fluorine-doped tin oxide (FTO) coated glass, are commonly used as substrates, onto which absorbing semiconductor photo-electrode materials are deposited. The thin (ca. 300 nm [6]) TEC-8 FTO coating has low in-plane electrical conductivity, so scale up simply by increasing the geometric photo-electrode area would result in large potential distributions between the current collectors. A simple photo-electrochemical reactor system consisting of two flat plate electrodes is illustrated in Fig. 1. Current is collected at the edges of the electrodes, of length L, height h_1 and distance apart h_2.

The equivalent circuit of the reactor system can be approximated as a resistance in series problem shown in Fig. 2. Since a metallic cathode was used, its resistance was neglected by comparison with the other resistances, so it was treated as an equipotential surface.

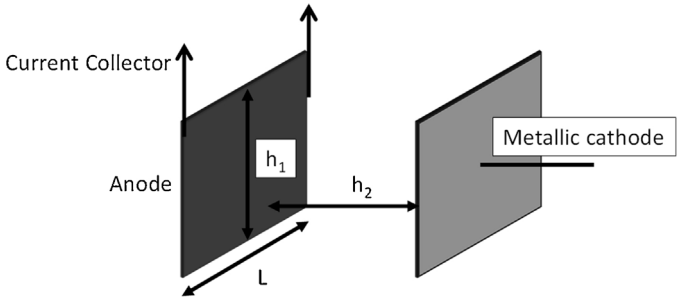

Fig. 1. Schematic of photo-electrochemical reactor system.

The current flowing through the mid-point of the anode, I_2 was smaller than the current I_1 flowing near the current collector at the edge:

$$\frac{I_1}{I_2} = \frac{R_2}{R_1} > 1 \tag{4}$$

If the ratio of I_1 and I_2 is unity, the potential and current distribution would be uniform. The Wagner number [7] can be defined by the ratio of area specific resistances R_a due to the faradaic reaction at the anode and that of the electrolyte R_e, for the case when the anode has metallic conductivity:

$$Wa = \frac{R_a}{R_e} = \frac{\left(\frac{A_a \cdot d\eta_a}{dI}\right)}{\left(h/\kappa_e\right)} \tag{5}$$

Where h is the characteristic length. If $h_1 \gg h_2$, then $h = h_2$. If $h_2 \gg h_1$, then $h = h_1$. κ_e is the conductivity of the electrolyte, while $R_a = A_a.d\eta_a/dI$. The larger Wa, the more uniform the current density distribution; $Wa = 0$ corresponds to the primary current distribution for which effects of electrode kinetics can be ignored. When the anode has finite conductivity, the Wagner number can be redefined as the ratio of polarisation resistance and the sum of resistance in the electrolyte and the resistance in the FTO at the mid-point between two current collectors (Fig. 1):

$$Wa' = \frac{R_a}{R_e + R_{FTO}} \tag{6}$$

Since R_e and R_{FTO} can be expressed as:

$$R_e = \frac{h}{\kappa_e} \tag{7}$$

$$R_{FTO} = \frac{L'}{\kappa_{FTO} \cdot t_{FTO} \cdot h_1} \cdot L' \cdot h_1 = \frac{L'^2}{\kappa_{FTO} \cdot t_{FTO}} \tag{8}$$

Where t_{FTO} is the thickness of the FTO layer, which usually is ca. 300 nm [6] and L' is the longest distance away from the current collector, in this case, $L' = \frac{1}{2} L$. Hence:

$$R_{FTO} + R_e = \frac{L'^2}{\kappa_{FTO} \cdot t_{FTO}} + \frac{h}{\kappa_e} = \frac{L'^2 \cdot \kappa_e + h \cdot \kappa_{FTO} \cdot t_{FTO}}{\kappa_e \cdot \kappa_{FTO} \cdot t_{FTO}} \tag{9}$$

On substituting equation (9) into equation (6), the modified Wagner number is given by:

$$Wa' = \left(\frac{A_a \cdot d\eta_a}{dI}\right) \cdot \frac{\kappa_e \cdot \kappa_{FTO} \cdot t_{FTO}}{\left(L'^2 \cdot \kappa_e + h \cdot \kappa_{FTO} \cdot t_{FTO}\right)} \tag{10}$$

So the ratio of the two Wagner numbers is:

$$\frac{Wa}{Wa'} = \left(1 + \frac{L'^2 \cdot \kappa_e}{h \cdot \kappa_{FTO} \cdot t_{FTO}}\right) \tag{11}$$

Hence, potential and current density distributions are predicted to be more uniform if: