



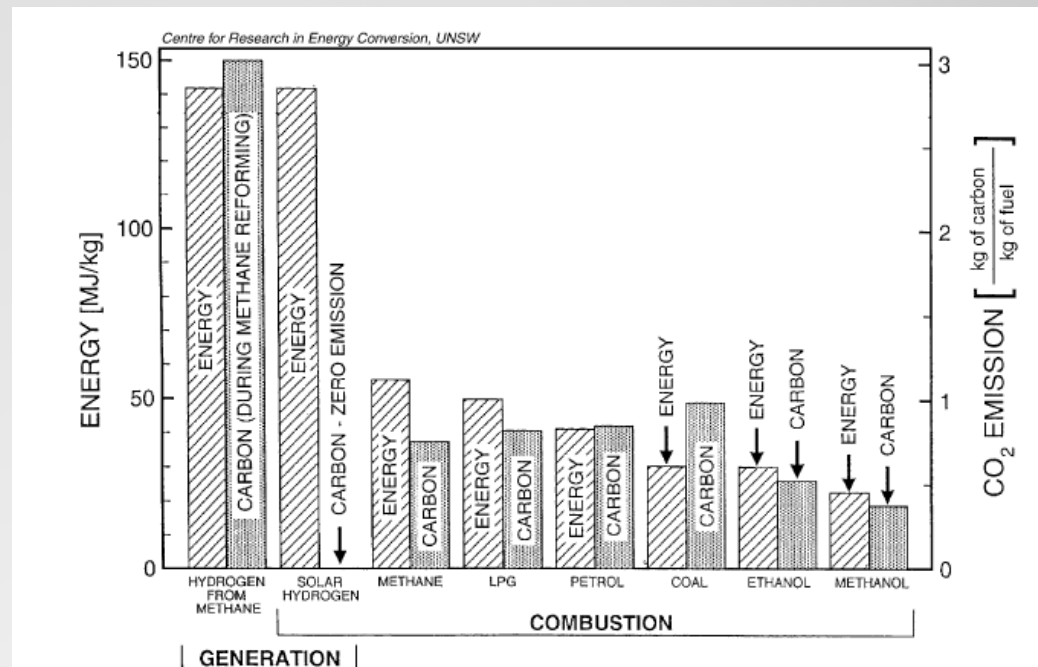
**Instituto de Química, Facultad de Ciencias
Laboratorio de Electroquímica**



PRODUCCIÓN FOTOELECTROQUÍMICA DE HIDRÓGENO

Ricardo Schrebler Guzmán

- Indice
- Dificultades actuales
- Algunas alternativas
- Producción
- Acumulación
- Uso



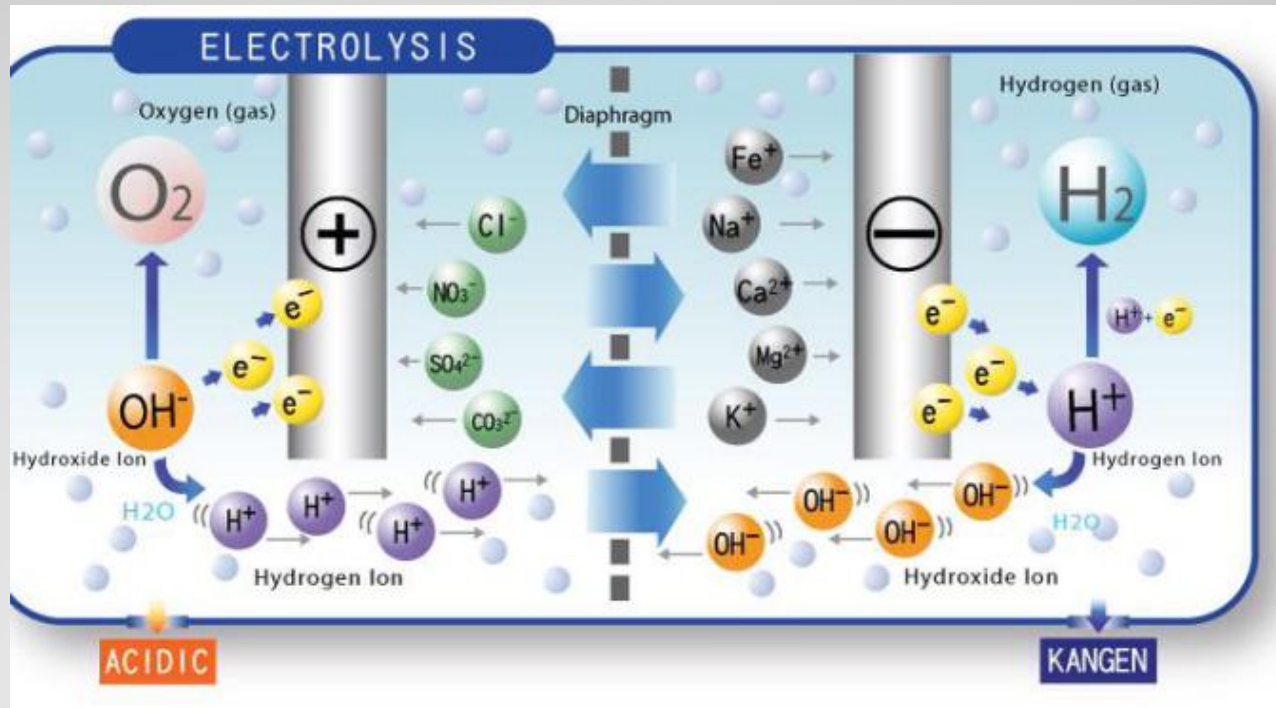
• Producción de hidrógeno

Se requiere de energía para disociar un compuesto que contiene hidrógeno, por ejemplo H_2O



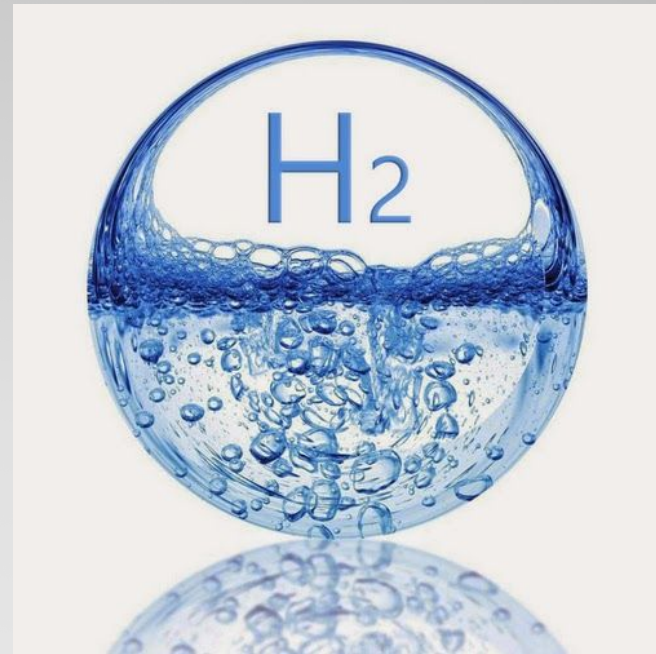
- Generación bioquímica
- Generación Térmica
Disociación de agua u otro compuesto, por ejemplo H_2O $\Delta H = 285.8 \frac{\text{kJ}}{\text{mol}}$ $\Delta S = 163.3 \text{ J/}^\circ\text{K}$
- Generación Electroquímica
Disociación de agua u otro compuesto mediante electricidad
- Generación Foelectroquímica
Disociación de agua u otro compuesto mediante radiación – electricidad

- La generación electroquímica





Acumulación y usos



¿Cómo funciona un vehículo eléctrico de hidrógeno?

1/PRODUCCIÓN

El hidrógeno líquido o en forma de gas se produce en plantas por distintos métodos



Es transportado mediante camiones a las estaciones de servicio H₂

2/TRANSPORTE



3/ESTACIÓN DE SERVICIO H₂

Estaciones de servicio con punto de repostado para vehículos de pila de combustible



Recarga en 3/5 minutos

4/VEHÍCULO

La carga del automóvil ofrece una autonomía de

500/600 km

CERO emisiones

TANQUE DE HIDRÓGENO

PILA DE COMBUSTIBLE

MOTOR ELÉCTRICO

Aire + H₂ = Electricidad
Emisión de agua pura



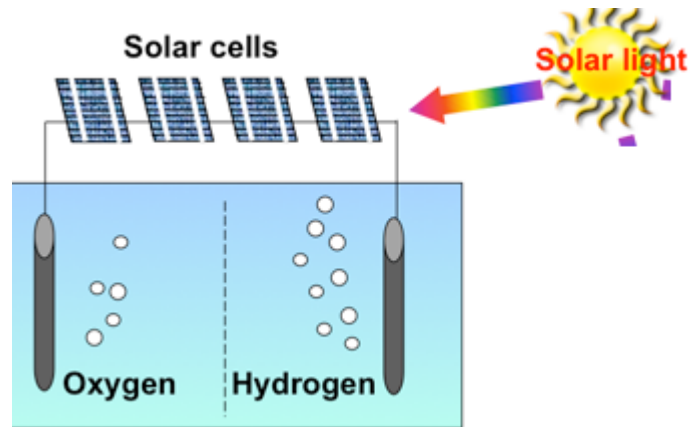
Congreso Mundial de Energía del Hidrógeno 2016 · www.whec2016.com

AeH₂
ASOCIACIÓN ESPAÑOLA
DEL HIDRÓGENO

whec
21th
Zaragoza
Spain
2016

Generación Fotoelectroquímica

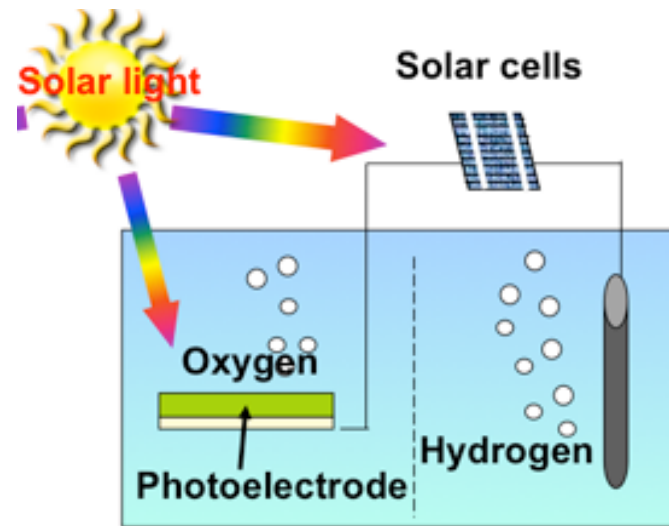
Una primera forma de emplear la energía solar ha correspondido al uso de celdas fotovoltaicas



Producción de hidrógeno por electrólisis normal de agua empleando celdas solares

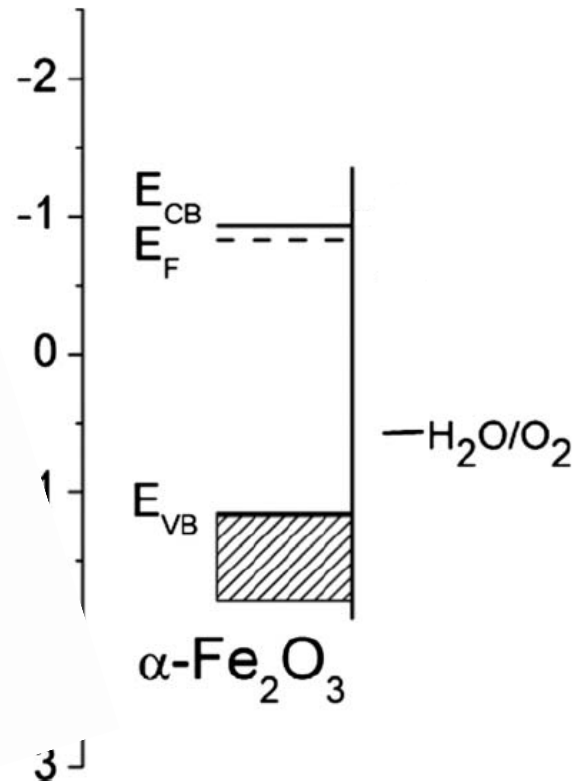
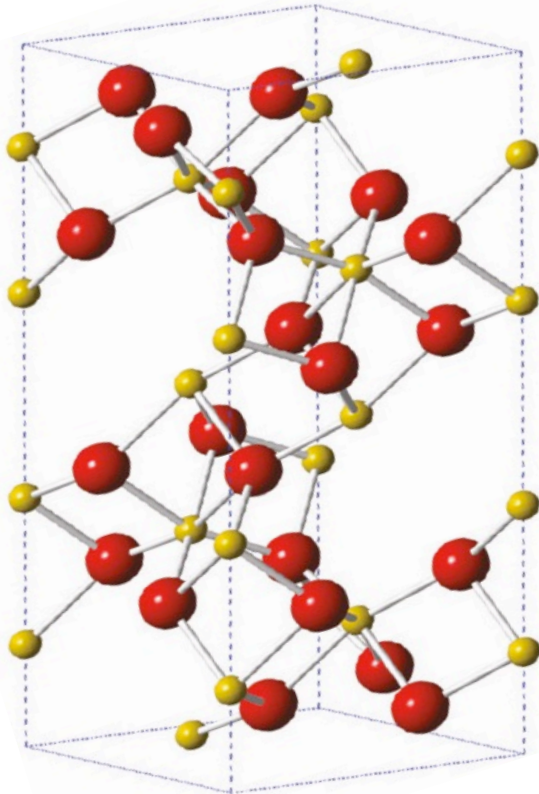
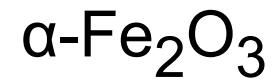
Incluyendo los sobrevoltajes (anódicos y catódicos) es necesario aplicar 1,6 V

Otra alternativa para reducir el número de celdas solares y con ello, disminuir el coste, consiste en emplear fotoelectrodos



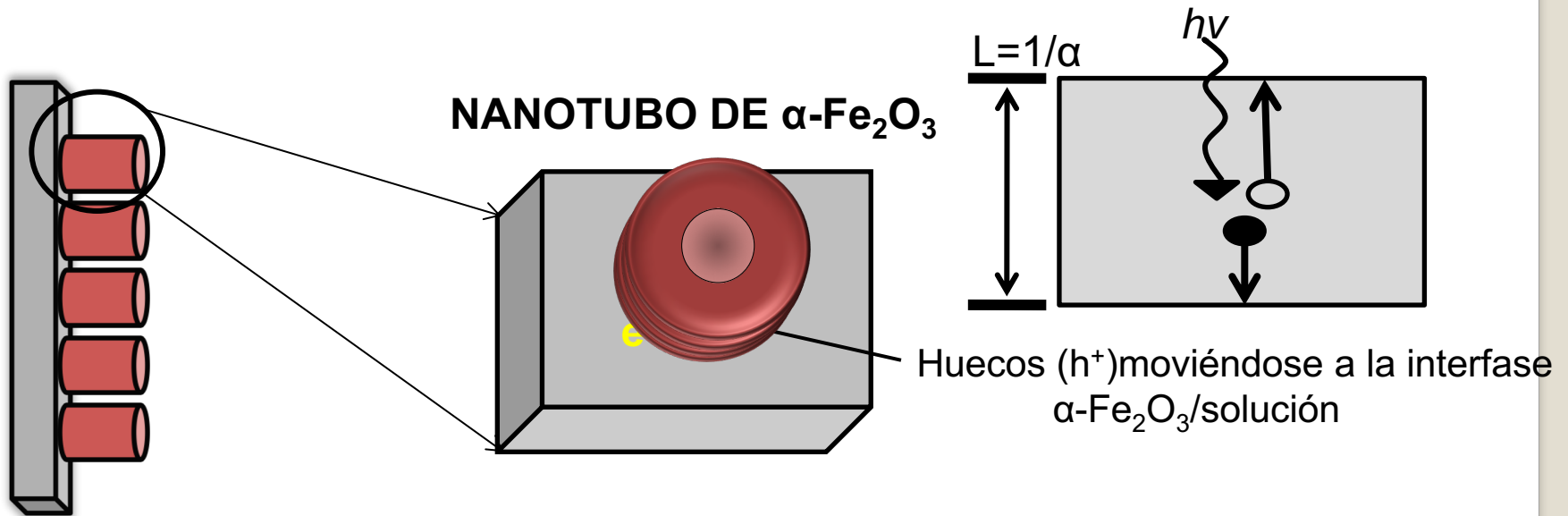
Las primeras celdas de electrólisis que han sido construidas han empleado fotoánodos constituidos por materiales semiconductores (TiO_2 ; $\alpha - Fe_2O_3$. entre otros)

HEMATITA



- Estrecho band gap (~ 2 eV)
- Buena estabilidad química
- Síntesis simple
- Compatibilidad ambiental
- Densidad de estados superficiales
- Velocidad de migración de los huecos

HIPOTESIS



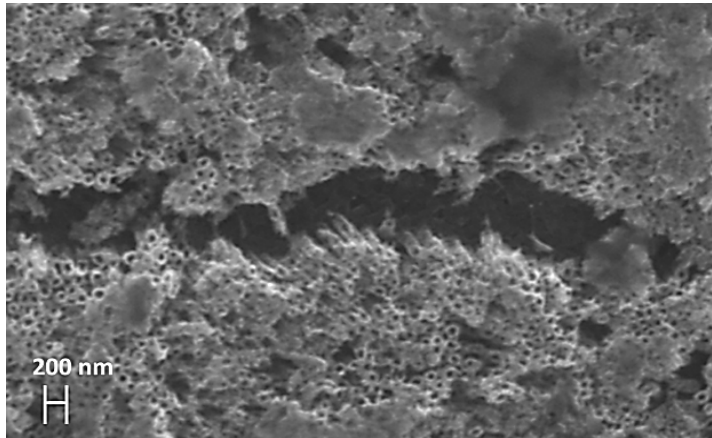
ELECTRODO DE Fe 99.99 %

PUREZA
1 cm²



CONTRAELECTRODO
DE GRAFITO 3,4 cm²

ELECTROLITO	VOLTAJE DE ANODIZACION
EG + (3 V %) H ₂ O + 0,5 % NH ₄ F	50 V , 13 MIN



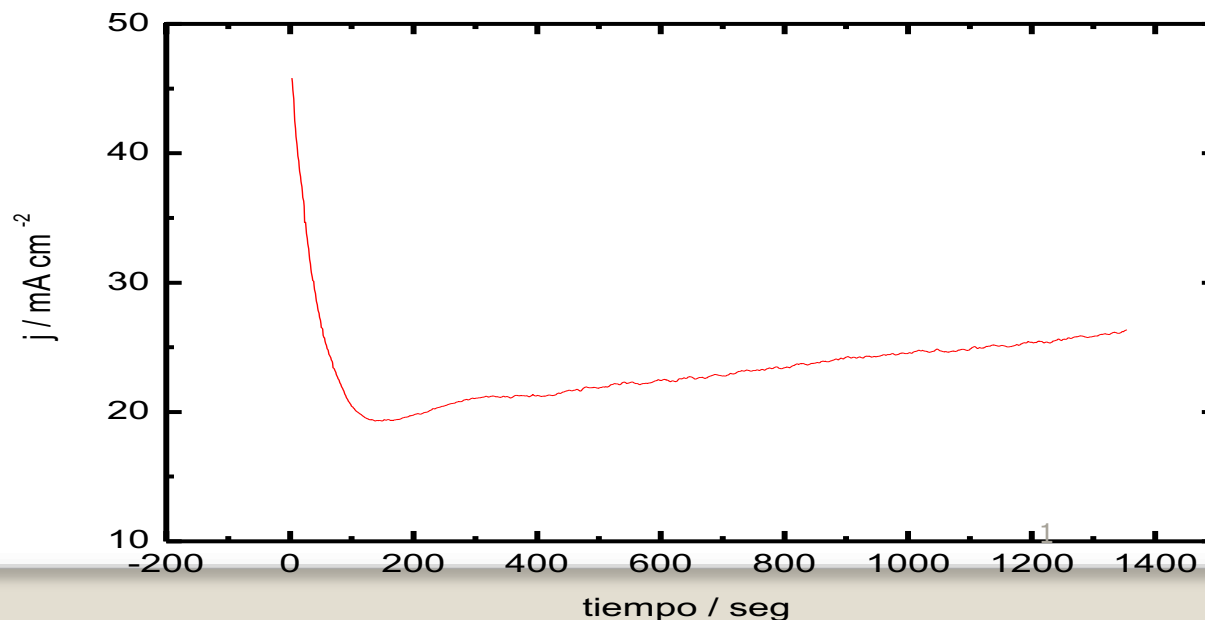
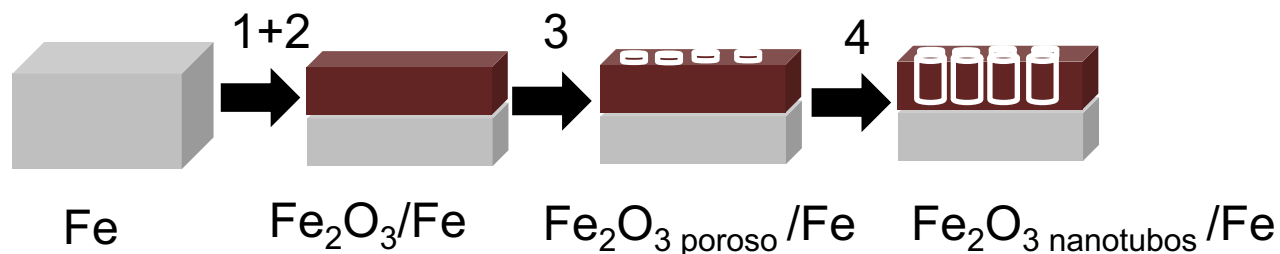
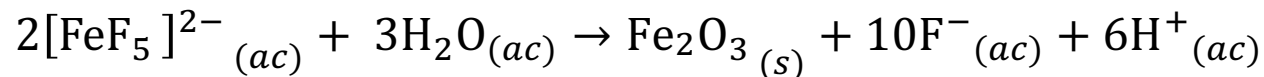
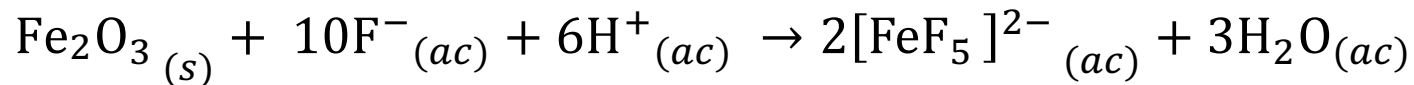
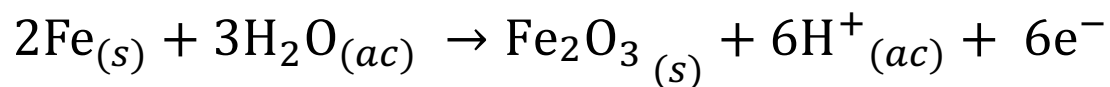
Journal of The Electrochemical Society, 161 (14) H903-H908 (2014)



Electrochemically Grown Self-Organized Hematite Nanotube Arrays for Photoelectrochemical Water Splitting

Ricardo Schrebler,^{a,z} Luis A. Ballesteros,^a Humberto Gómez,^a Paula Grez,^a Ricardo Córdova,^a Eduardo Muñoz,^a Rodrigo Schrebler,^b J. R. Ramos-Barrado,^c and Enrique A. Dalchiele^{d,*}

ESTUDIO DE LA FORMACION MEDIANTE ANODIZACION SONOELECTROQUÍMICA



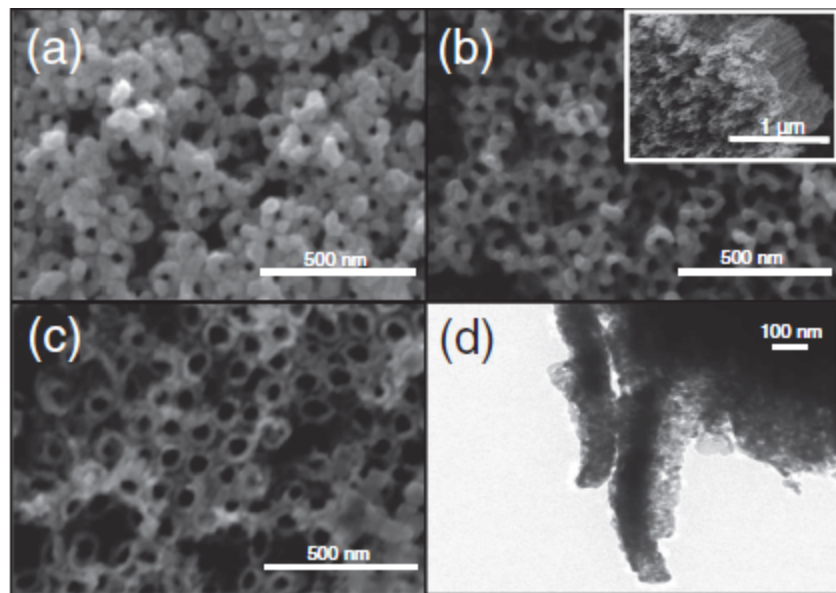


Figure 2. Top view FE-SEM images of nanostructured hematite samples: (a) HN(w/o), (b) HN(-0.8 V) and (c) HN(-1.0 V). The inset of Figure 2b shows a tilted FE-SEM micrograph view with of HN(-0.8 V) sample, tilt angle of 45°. (d) TEM micrograph of single hematite nanotubes extracted from sample HN(-0.8 V).

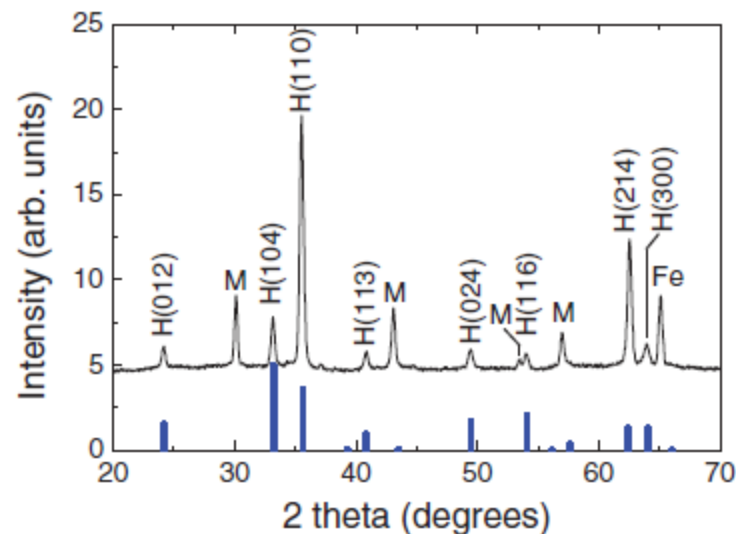


Figure 3. X-ray diffraction pattern of an annealed nanostructured iron oxide sample, electrochemically grown onto an iron substrate pretreated at -1.0 V (HN(-1.0 V)). JCPDS pattern of rhombohedrally centered hexagonal structure of Fe_2O_3 ($\alpha\text{-Fe}_2\text{O}_3$, hematite), is also shown for comparison at the bottom of the Figure. (Fe) and (M) indicate the diffraction peaks originated from the iron substrate and magnetite impurity phase, respectively.

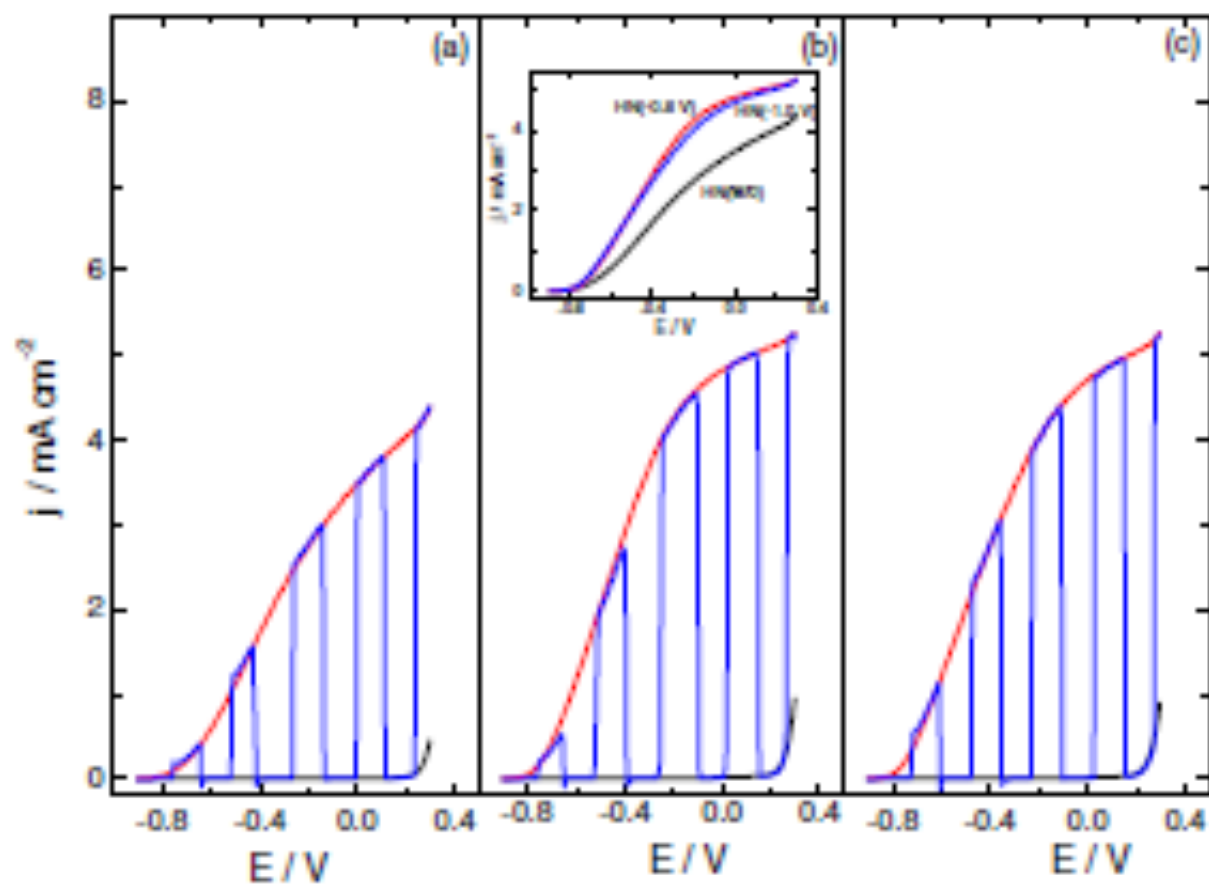


Figure 6. Linear scan voltammetry of hematite nanostructured electrodes: (a) HN(w/o); (b) HN(-1.0 V) and (c) HN(-0.8 V), in the dark (black line), with continuous light illumination (red line) and under chopped light illumination conditions (blue curve). These curves have been recorded at $v = 0.025 \text{ V s}^{-1}$ under white light solar simulator (0.5 sun). The inset of Fig. 6b shows the photocurrents under continuous white light illumination of Figures 6a, 6b and 6c re-plotted in a single plot for comparison.

Peter, L.M., *Journal of Solid State Electrochemistry*, 2012. 17(2): p. 315-326.

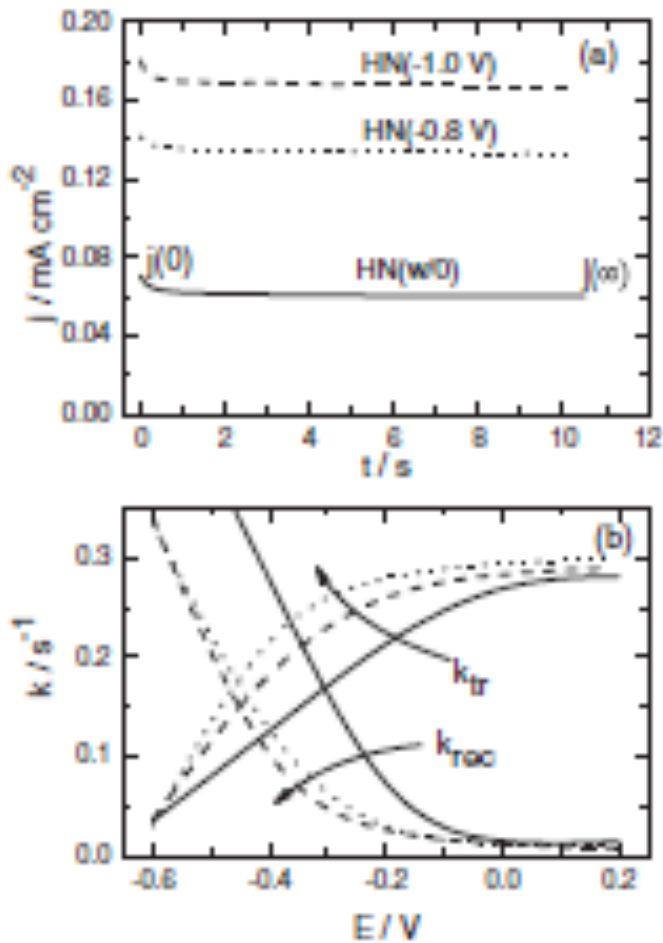
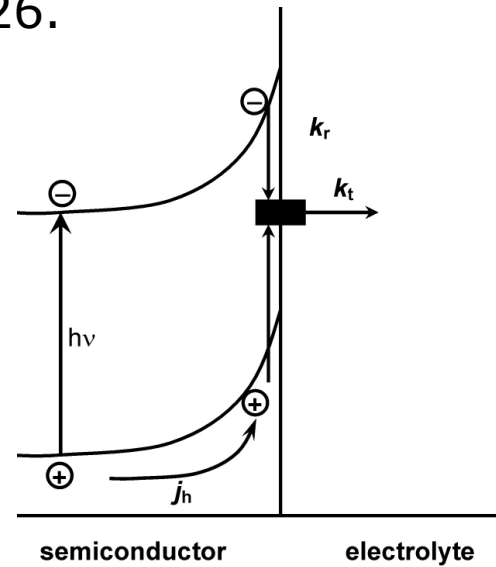


Figure 7. (a) Photocurrent pulses obtained at -0.185 V and (b) k_{tr} and k_{rec} values determined by fitting photocurrent transients obtained at different potentials for HN(w/o), HN(-1.0 V) and HN(-0.8 V) electrode systems. Photocurrent pulses were realized in 1.0 M NaOH using a LED 455 nm (20 mW cm^{-2}).



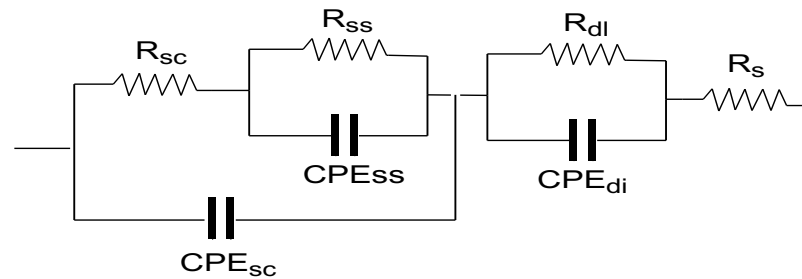
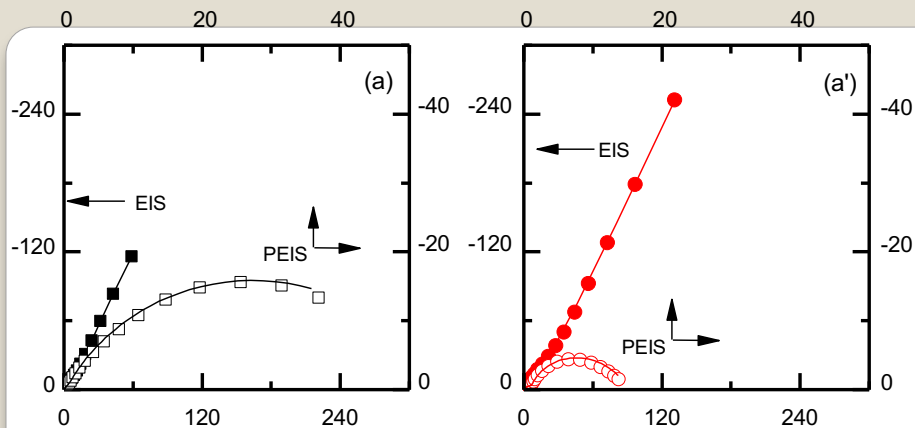
$$\frac{j(t) - j(\infty)}{j(0) - j(\infty)} = e^{-t/\tau}$$

$$\tau = (k_{tr} + k_{rec})^{-1}$$

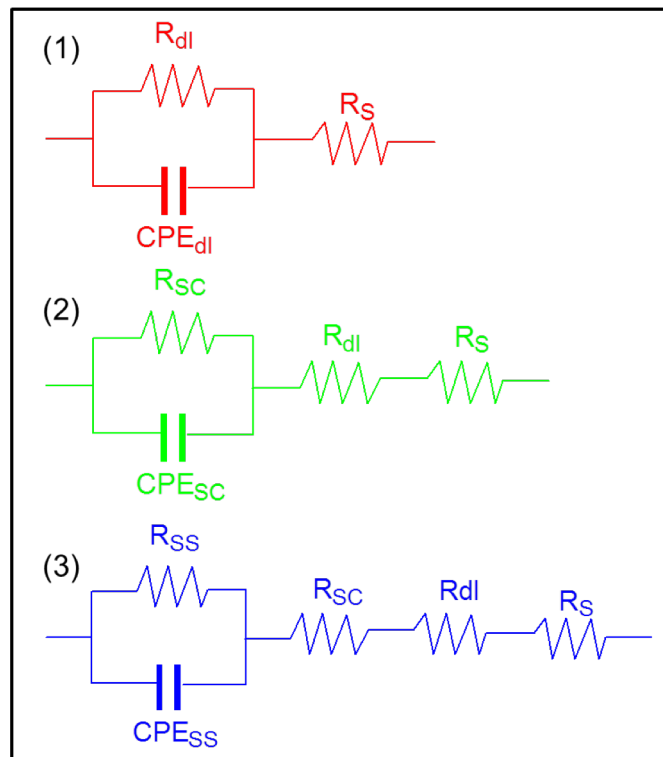
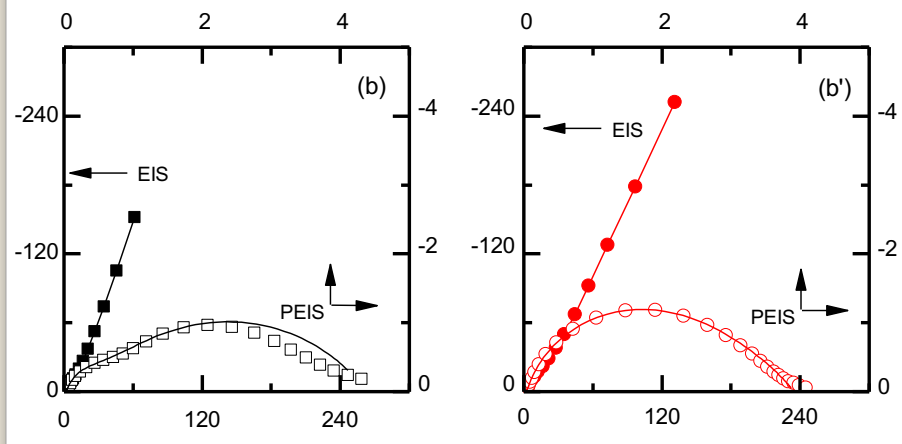
$$\frac{j(\infty)}{j(0)} = \frac{k_{tr}}{k_{rec} + k_{tr}}$$

1

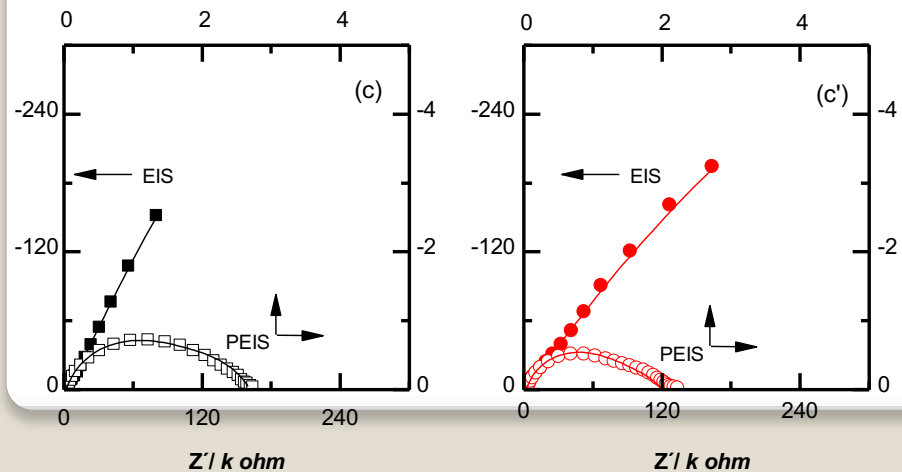
$Z'' / k \text{ ohm}$

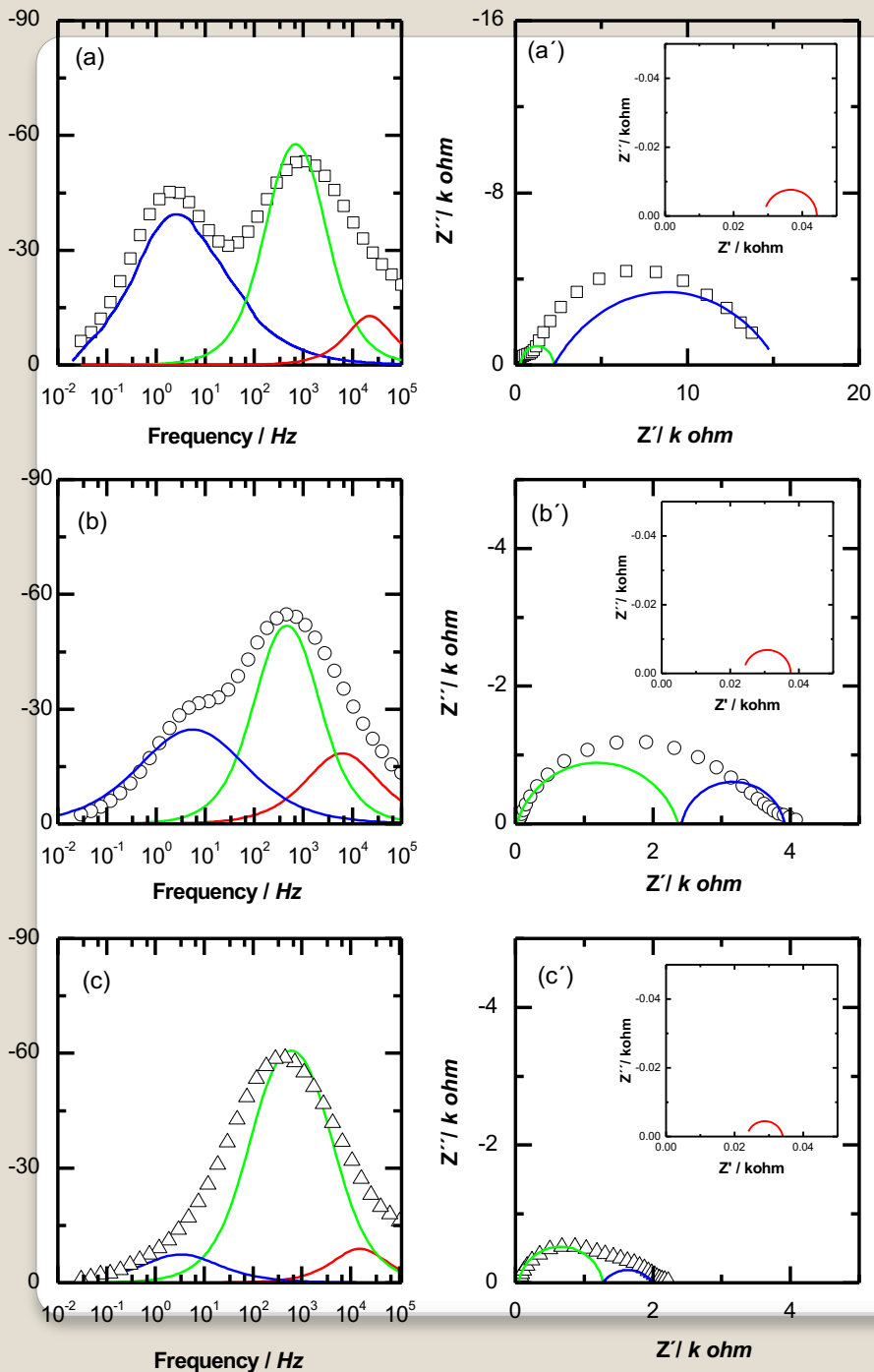


$Z'' / k \text{ ohm}$



$Z'' / k \text{ ohm}$





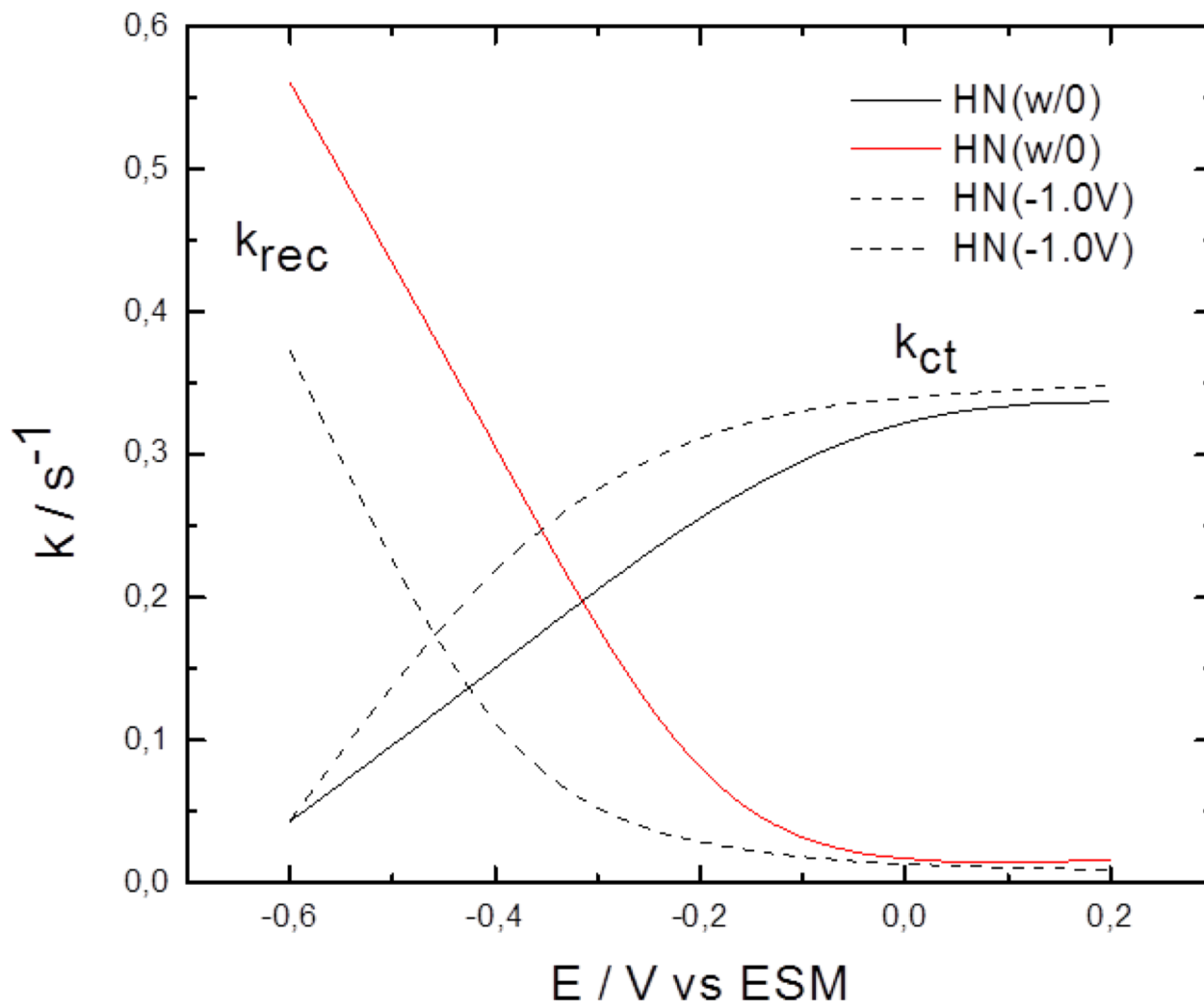
Espectros de impedancia PEIS para el electrodo NH(-1V) en las representaciones graficas de Bode y Nyquist a los potenciales de (a) – 0.6 V, (b) –0.4 V, (c) –0.185 V y de Nyquist (a') –0.6 V, (b') –0.4 V, (c') –0.185 V. Para las componentes del circuito (—) 1, (—) 2 y (—) 3. En el inserto de la Figura se muestra una ampliación de la simulación del circuito (—)

$$R_{LF} = \frac{k_B T}{q^2 J_h} \left(\frac{k_{tr} + k_{rec}}{k_{tr}} \right)$$

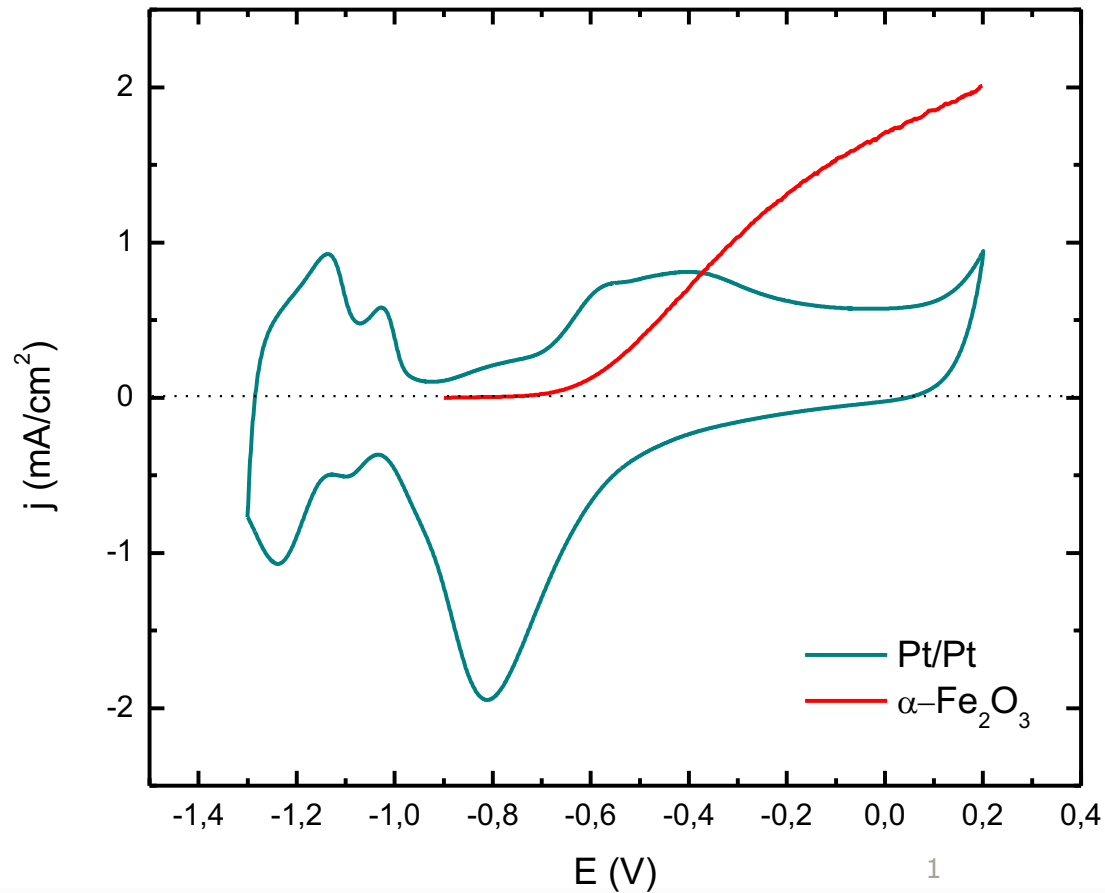
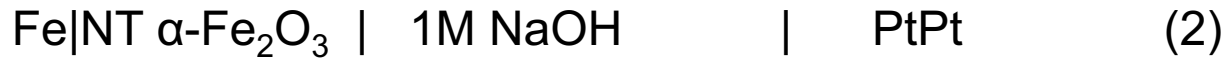
$$C_{LF} = \frac{q^2 J_h}{k_B T} \frac{1}{(k_{tr} + k_{rec})}$$

$$\omega_{max,LF} = \frac{1}{R_{LF} C_{LF}} = k_{tr}$$

Peter, L.M., *Journal of Solid State Electrochemistry*, 2012. 17(2): p. 315-326.



ESTUDIO EN CELDAS DE ELECTROLISIS



Para la celda (1):

$$\Delta E = 1.23 \text{ V}$$

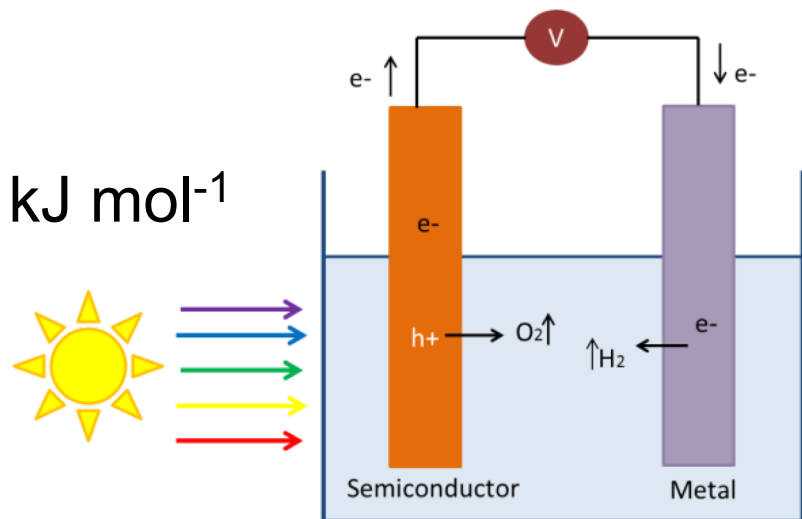
Considerando una densidad de corriente de 1 mA/cm²

$$\Delta V = 1.6 \text{ V}$$

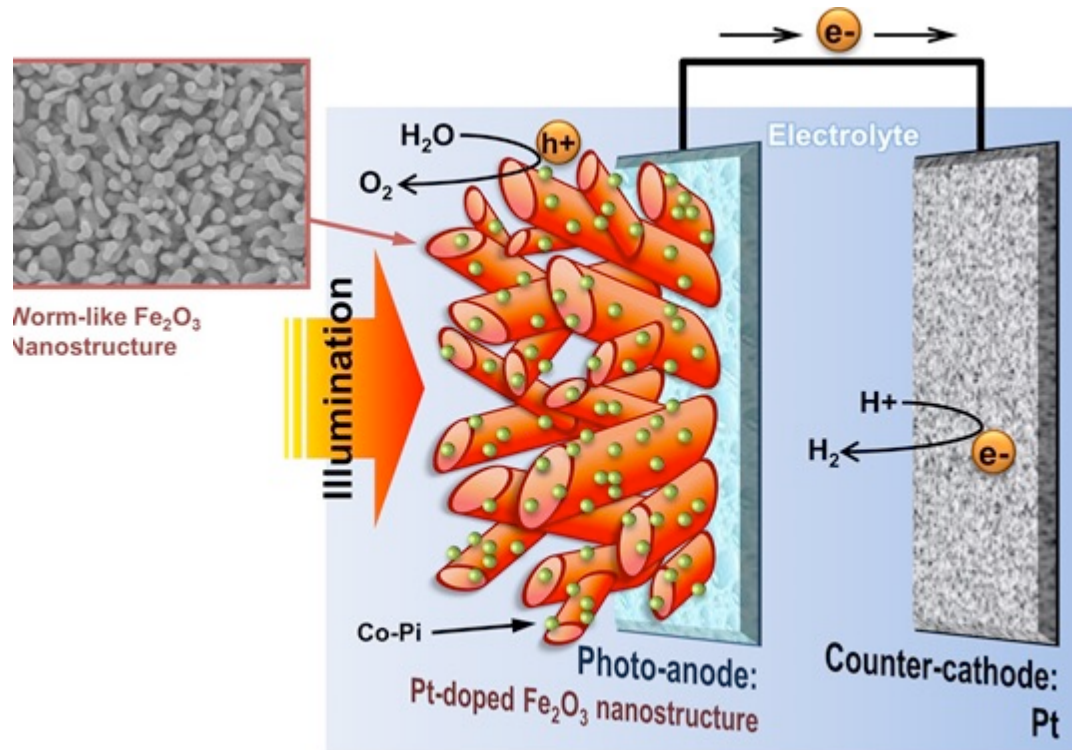
Para la celda (2)

$$\Delta V = 1.0 \text{ V}$$

Ahorro de Energía de 135,1 kJ mol⁻¹



Otras alternativas para mejorar el rendimiento de estos fotoelectrodos consiste en decorar las nano-estructuras con partículas que presenten una propiedad catalítica para la reacción de interés



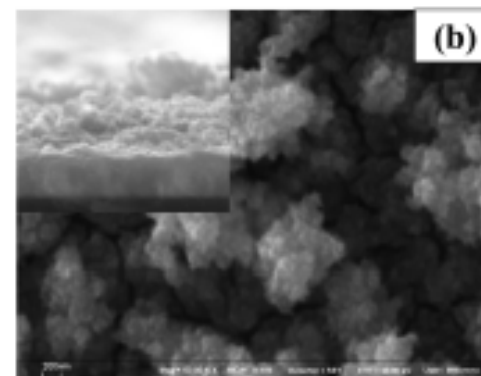
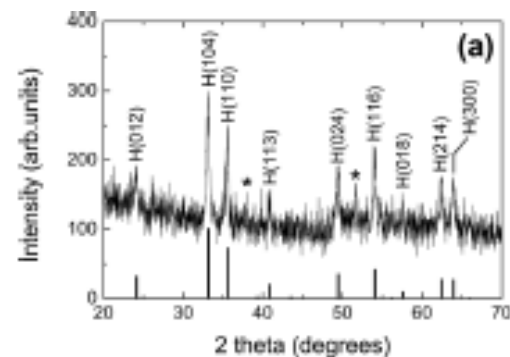
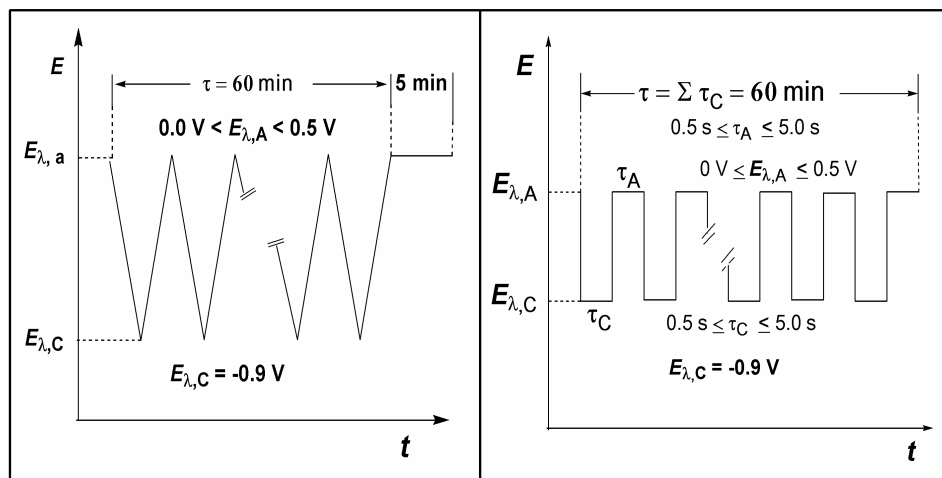


Figure 1. (a) Glancing-angle X-ray diffraction pattern of an electrodeposited α - Fe_2O_3 thin film onto SnO_2/F substrate obtained by the potential pulse procedure and after annealing at 500°C during 30 min (hematite peaks marked with H and with their respective plane indices). Hematite JCPDS pattern is also shown for comparison (black lines). (*, indicates the peaks originated from the SnO_2/F substrate). (b) Surface view SEM image of a typical α - Fe_2O_3 layer grown onto a PTCO coated glass obtained by the potential pulse procedure. Inset shows a cross sectional SEM micrograph of a typical electrodeposited hematite thin film. Scale bar applies to both panels.

Table I. V_{FB} and N_{D} values for the un-modified and Co-modified α - Fe_2O_3 films for different surface modification times with an aqueous solution of $10 \text{ mM Co}(\text{NO}_3)_2$.

Time (s)	V_{FB} (V)	$N_{\text{D}} \times 10^{-17} (\text{cm}^{-3})$
0	-0.950	3.15
30	-0.990	4.80
60	-1.010	8.53
90	-0.990	12.9
120	-0.996	10.1

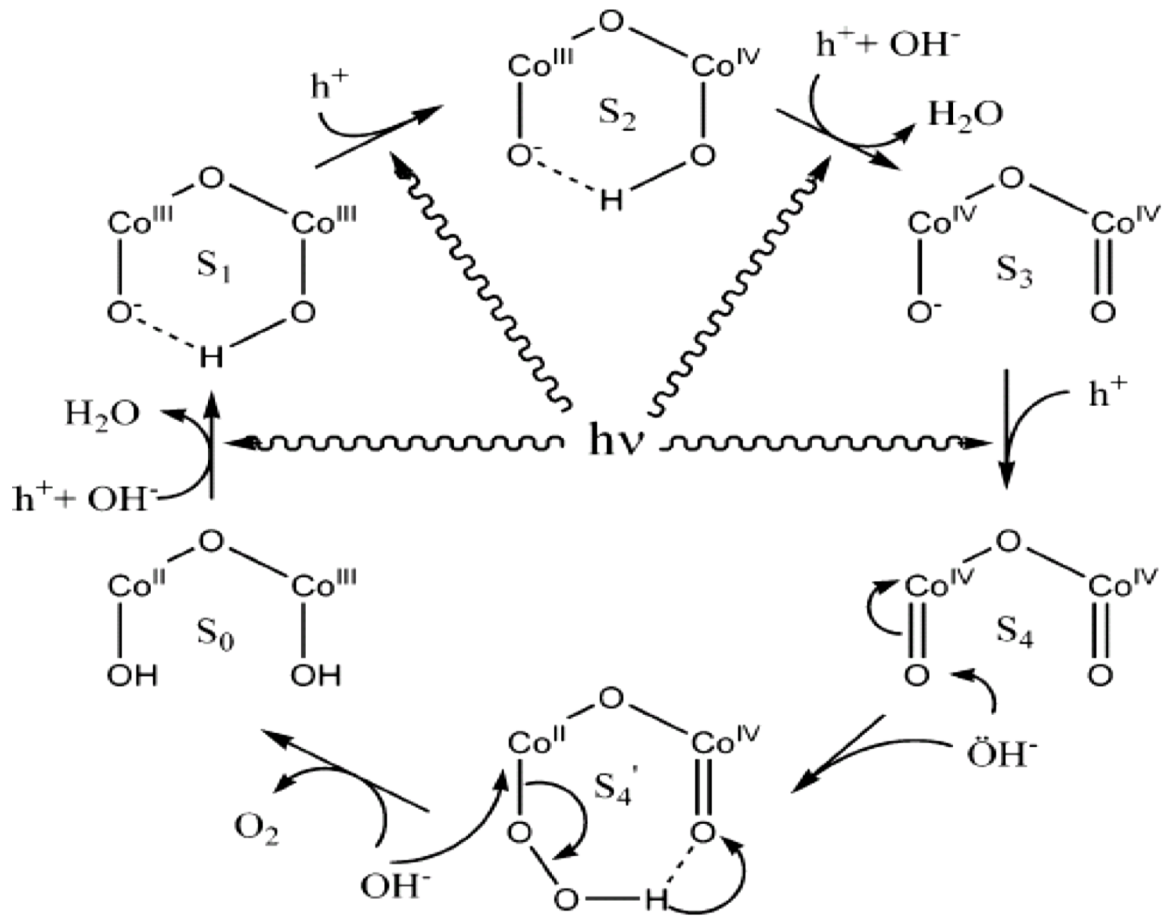
D500

Journal of The Electrochemical Society, 158 (8) D500-D505 (2011)
0013-4651/2011/158(8)/D500/6/\$28.00 © The Electrochemical Society

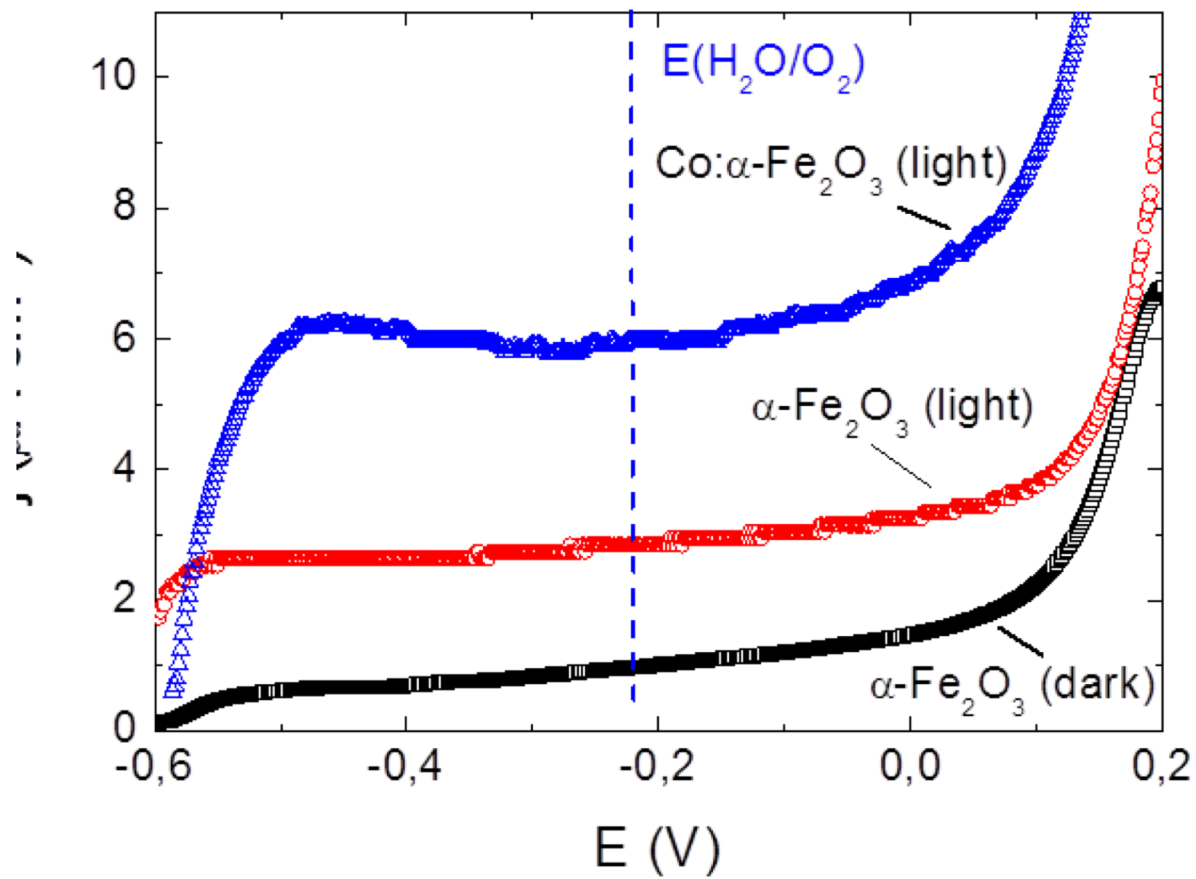


Electrodeposited Nanostructured α - Fe_2O_3 Photoanodes for Solar Water Splitting: Effect of Surface Co-Modification on Photoelectrochemical Performance

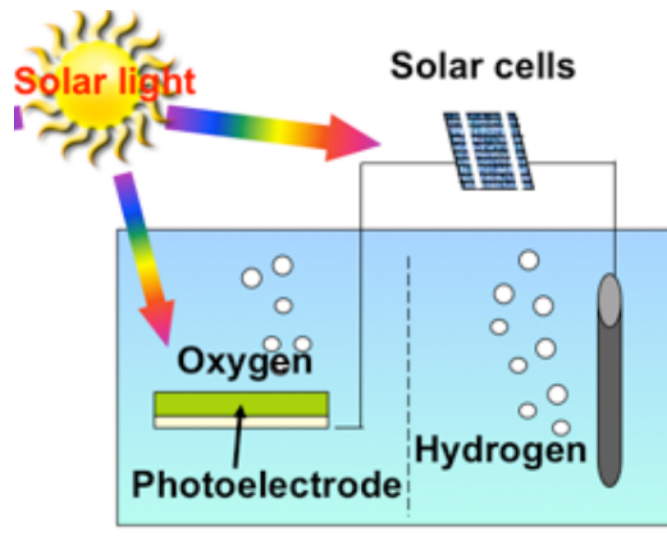
Ricardo S. Schrebler,^a Luis Ballesteros,^a Ana Burgos,^a Eduardo C. Muñoz,^a Paula Grez,^a Dietmar Leinen,^b Francisco Martín,^b José Ramón Ramos-Barrado,^{b,*} and Enrique A. Dalchiele^{c,*}



Rossmisl, J., A. Logadottir, and J.K. Nørskov,
Electrolysis of water on (oxidized) metal surfaces.
 Chemical Physics, 2005. **319**(1-3): p. 178-184.

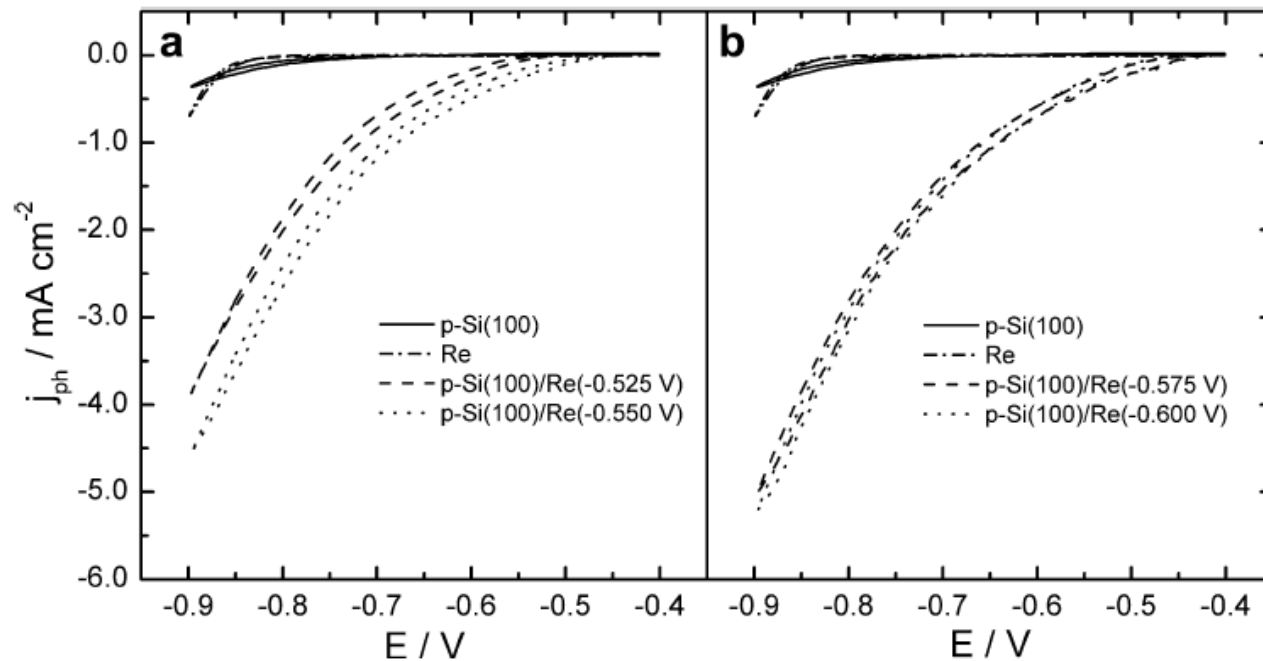


La siguiente etapa surge de emplear una celda electrolítica donde ambos electrodos estén constituidos por foto-electrodos



Por lo que los estudios han sido enfocados hacia la búsqueda de fotocátodos

INTERFASE p-Si/Re ELECTRODEPOSITADA: REH



Available online at www.sciencedirect.com
ScienceDirect

Journal of Electroanalytical Chemistry 611 (2007) 35–42

Journal of
Electroanalytical
Chemistry

www.elsevier.com/locate/jelechem

Rhenium electrodeposition process onto p-Si(100)
and electrochemical behaviour of the hydrogen evolution
reaction onto p-Si/Re/0.1 M H₂SO₄ interface

Eduardo C. Muñoz^{a,b,*}, Ricardo S. Schrebler^a, Marco A. Orellana^a, Ricardo Córdova^a

^a Instituto de Química, Facultad de Ciencias, Pontificia Universidad Católica de Valparaíso, Casilla 4059, Valparaíso, Chile

^b Departamento de Ciencias Básicas, Escuela de Educación, Universidad de Viña del Mar, Agua Santa 7255, Viña del Mar, Chile

Received 25 June 2007; received in revised form 30 July 2007; accepted 31 July 2007
Available online 10 August 2007

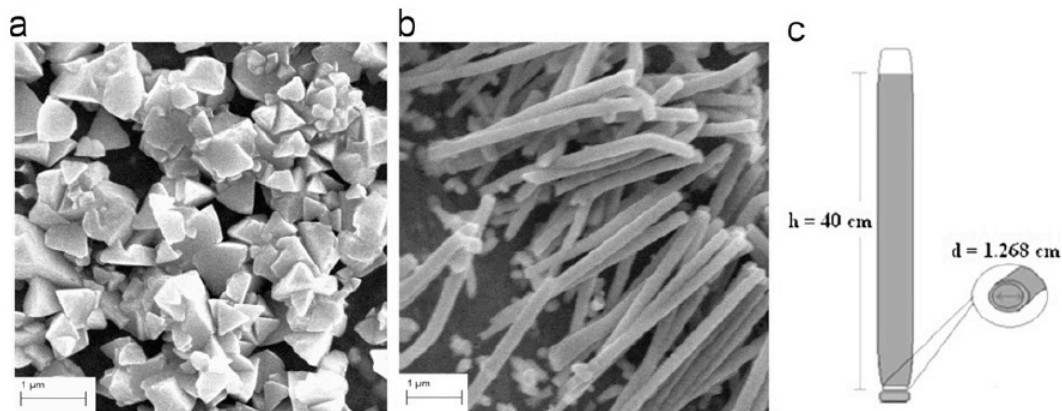


Fig. 1. SEM micrographs for Cu_2O nanowires grown by potential step at -0.575 V into PC membranes treated by the (a) Meth-1 and (b) Meth-2. (c) Diagram of system used for Meth 2.



Contents lists available at SciVerse ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

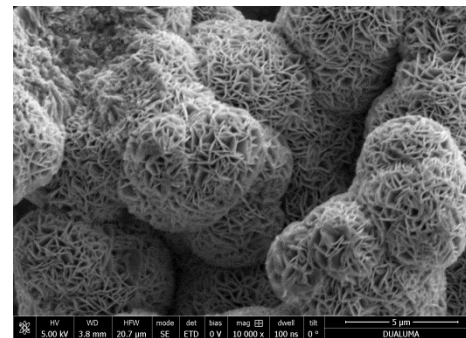
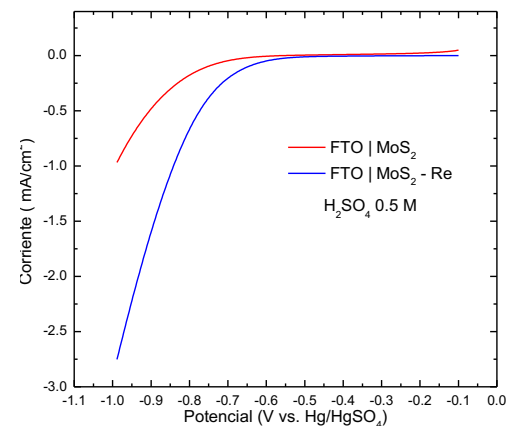
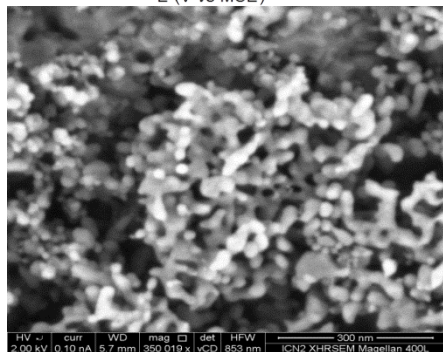
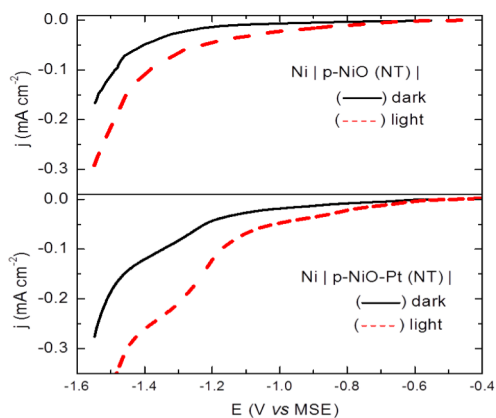


Synthesis and characterization of p- Cu_2O nanowires arrays

P. Grez^{a,*}, F. Herrera^b, G. Riveros^c, R. Henríquez^a, A. Ramírez^a, E. Muñoz^a,
E.A. Dalchiele^d, C. Celedón^e, R. Schrebler^a



Actualmente se trabaja con otros dos Semiconductores tipo- p NiO y MoS_2 modificados con Pt y Re, respectivamente



$Fe | \alpha - Fe_2O_3 NT | NaOH 1.0 M | | p - NiO | Ni$

$Ti | TiO_2 NT | H_2SO_4 1.0 M | | p - MoS_2 | FTO$



**FONDECYT
CHILE**