Evaluation of Hematite as a Photo-Anode

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Presentation Outline

1. Theory
2. Fabrication
3. Photo-response with and without Dopants
4. Hematite | Liquid Interfacial Structure
5. Future Research
Pros and Cons of Hematite as a Photoanode

**Suitability of Fe\textsubscript{2}O\textsubscript{3}:**
- Absorption spectrum well matched to solar spectrum
- Easily fabricated on a large scale at low cost
- Stable to decomposition by $e^-$ and $h^+$ over wide potential range
- Valence band energy below that for decomposition of H\textsubscript{2}O to O\textsubscript{2}

**Limitations of Fe\textsubscript{2}O\textsubscript{3}:**
- Conduction band energy below decomposition potential for H\textsubscript{2}O to H\textsubscript{2}
- Stable only in neutral / alkaline pH
Pros and Cons of Hematite as a Photoanode

**Suitability of Fe₂O₃:**
- Absorption spectrum well matched to solar spectrum
- Easily fabricated on a large scale at low cost
- Stable to decomposition by $e^-$ and $h^+$ over wide potential range
- Valence band energy below that for decomposition of H₂O to O₂

**Limitations of Fe₂O₃:**
- Conduction band energy below decomposition potential for H₂O to H₂
- Stable only in neutral / alkaline pH

![Graph showing physical and electrochemical scales with Fe₂O₃'s CB and VB energies](image-url)
Hematite Photoanode Production

Fabrication of Fe$_2$O$_3$ and Sn$^{IV}$-Fe$_2$O$_3$ by Spray Pyrolysis

1. Compressed Air
2. Precursor reservoir
3. Syringe pump
4. Quartz nebuliser
5. CNC machine
6. Substrate
7. Clamping block
8. Hotplate

Fe$_2$O$_3$ coating produced by nebulising Fe$^{III}$Cl$_3$ and Sn$^{IV}$Cl$_4$ in solvent onto heated FTO glass

The Electrode

Photographic image

SEM image
Hematite: What is it and what do we want it to do? Why is it naturally an n-type material and hence only suitable as a photoanode? How would it function in a water splitting system? What is the ideal system? Is hematite a good absorber of solar radiation? How do we make it? What thicknesses do we achieve and how is that thickness measured? How does the thickness compare with absorption length? Why do we heat treat it – what do we think that achieves? Do we dope it? Why? How did we decide what to dope it with? And what is the effect? How do we analyse its performance and what are the main scientific considerations? Electrode polarisation – current density versus potential curve. Light current and dark current and light current. What is the world record current density on this material under solar illumination? Impedance spectroscopy – what is its purpose and what could it tell us? Impedance experiments – difference between light and dark – different O₂ evolution mechanism; different intermediates formed during photooxidation? What could these be? How do we know what is going on? What does the interface look like? Why is it important to have an accurate picture? How do we construct such a picture? How does drawing such a picture help to verify the parameters obtained using standard electrochemical procedures? What is next?

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**Hematite Photo-Response in Steady State**

- Effect of Potential (applied at 1mV s⁻¹) and White Light Illumination (49 W m⁻² Xe) on ca. 40 nm thick films on FTO | 1 M NaOH (pH 13.7)
- Illuminated area ≈ 0.15 cm²
- **Light (doped)** ca. 0.6 % Sn⁴⁺
- **Light (undoped)**
- **Dark (undoped and doped)**

**Current Density, j / A m⁻²**

- **V_{FB} = +0.022 V (HgO|Hg)** (undoped)

**Electrode Potential / V (HgO|Hg)**

- -0.2 -0.1 0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8

- 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
Flat Band and Charge Carrier Determination

Mott-Scottky Values

Electrode Potential / V (HgO|Hg)

\[ A^2 C^2 / m^4 F^2 \]

\[ V_{FB} = V_{x-intercept} - \frac{k_B T}{e_0} \]

Kennedy, J. Electrochem. Soc. 1978


Butler, J. Appl. Phys., 1977

100 kHz (Dark)

50 kHz (Dark)

25 kHz (Dark)

10 kHz (Dark)

5 kHz (Dark)

1 kHz (Dark)

100 Hz (Dark)
Evaluation of the Flat Band Potential from $j_2$ vs $V$

\[ y = 0.087x - 0.004 \quad \text{R}^2 = 0.998 \]

\[ y = 19.601x - 4.088 \quad \text{R}^2 = 0.998 \]

\[ V_{FB} = V_{x-intercept} \]

| Material                  | $V_{FB}$ (HgO|Hg) / V | $pH$ of zero charge |
|---------------------------|------------------------|---------------------|
| Undoped Fe$_2$O$_3$       | +0.02                  | 6.7 *               |
| Sn$^{IV}$ doped Fe$_2$O$_3$ | +0.18                 | < 6.7 (?)           |

Verification of the Solid|Liquid Energetic Alignment

\[ \Delta V_H = \frac{2.3RT}{F} \left\{ \log \left( \frac{[Fe-O^-]}{[Fe-OH_2^+]} \right) \right\}^{1/2} \]

For Fe\textsubscript{2}O\textsubscript{3} in alkaline solution

\[ \text{pH} \gg \text{pH}(\text{pzc}) \text{ and } \left[ \frac{Fe-O^-}{Fe-OH_2^+} \right] \gg 1 \]

Liquid Phase
(Electrochemical Scale / V)

Solid Phase
(Absolute Scale / eV)

\[ E_A + \Delta E = -(V_F (\text{measured}) - V_H + 4.44 + E^0(\text{RE vs SHE})) \]

Conduction Band
\( (E_{CB}) \)

\( -E / \text{eV} \)

Fermi Level
\( (E_F) \)

\( 0 \text{ eV} \)

Vacuum

Helmholtz Layer
Bulk Measurements
Vacuum

\( \Delta V_H < 0 \text{ V} \)

Fermi Level
\( (V_F) \)

\( +V / V \text{ (vs. RE)} \)

\( -V / V \text{ (vs. RE)} \)
**Modelling the Hematite | Liquid Interface**

**Constructing an Interfacial Model**

- Distribution of applied bias
  \[ \Delta V_{\text{Interface}} = \Delta V_{\text{SC}} + \Delta V_{\text{H}} \]

- Potential drop across the Helmholtz layer
  \[ \Delta V_{\text{H}} = \Delta V_{\text{H,0}} + \frac{Q_{\text{SC}}}{C_{\text{H}}} \]

- Electric charge in semiconductor depletion layer
  \[ Q_{\text{SC}} = (2\varepsilon_{0}e_{0}N_{D})^{\frac{1}{2}} \left( \Delta E_{\text{SC}} - \frac{k_{B}T}{e_{0}} \right)^{\frac{1}{2}} \]

- Total interfacial capacitance
  \[ C_{\text{Interface}} = \frac{1}{C_{\text{SC}}} + \frac{1}{C_{\text{H}}} \]

- Semiconductor capacitance
  \[ C_{\text{SC}} = \frac{2}{e_{0}\varepsilon_{0}N_{D}} \left( \Delta E_{\text{SC}} - \frac{k_{B}T}{e_{0}} \right)^{\frac{1}{2}} \]

- Depletion layer thickness
  \[ x_{\text{dl}} = 2L_{D} \left( \frac{e_{0}\Delta V_{\text{SC}}}{k_{B}T} - 1 \right)^{0.5} \]

- Tunnelling distance and probability
  \[ x_{\text{tunnelling}} = 2 \left( \frac{e_{0}\varepsilon_{0}}{2e_{0}N_{CB}} \right)^{\frac{1}{2}} \left[ \left( E_{\text{CB}}^{\text{Bulk}} - E_{\text{SC}}^{\text{Surface}} \right)^{\frac{1}{2}} - \left( E_{\text{CB}}^{\text{Bulk}} - E_{\text{rev, O}/\text{H}_{2}O} \right)^{\frac{1}{2}} \right] + x_{\text{dl}} \]

- Tunnelling probability
  \[ T(e_{0}\phi_{CB}, E_{D}) = \exp \left[ -K \left( \frac{e_{0}\phi_{CB} \times E_{D} - (e_{0}\phi_{CB} - E_{D}) \ln \left( \frac{\sqrt{e_{0}\phi_{CB} - E_{D}}}{\sqrt{e_{0}\phi_{CB} - E_{D}}} \right)}{4m^{*}e_{0}^{2}N_{D}} \right) \right] \]

- Tunnelling constant
  \[ K = \frac{4\pi e_{0}}{h} \sqrt{\frac{4m^{*}e_{0}}{N_{D}e_{0}^{2}}} \quad ; \quad E_{D} = E_{\text{CB}}^{\text{Surface}} - E_{\text{REDOX}} \]
Model Predictions for Interfacial Behaviour

\[ \Delta V_{\text{Tunnelling}} = V_{\text{Rev}} - V_{\text{CB, Surface}} \]

\[ \Delta V_{SC} \approx 0.2 \text{ V} \]
Interfacial Charge Transfer Prediction

\[ j_{\text{Total}} = \text{Anodic} & \text{ Cathodic currents through CB edge} + \text{Anodic tunnelling current into CB} \]

\[
j = j_{T,0} \exp \left\{ \frac{\alpha F}{RT} (E_p - E_{E_{\text{red}}}) \right\} T(x(E_p)) + C(OH^-) N_{CB} \left( \frac{k_B T}{\lambda \pi} \right)^{\frac{3}{2}} \exp \left\{ -\frac{e_0^2 (E_{E_{\text{edge}}} - E_{E_{\text{red}}} + \lambda)^2}{2 \lambda k_B T} \right\} \]

\[
1 + \frac{j_{T,0} \exp \left\{ \frac{\alpha F}{RT} (E_p - E_{E_{\text{red}}}) \right\} T(E_p) + C(OH^-) N_{CB} \left( \frac{k_B T}{\lambda \pi} \right)^{\frac{3}{2}} \exp \left\{ -\frac{e_0^2 (E_{E_{\text{edge}}} - E_{E_{\text{red}}} + \lambda)^2}{2 \lambda k_B T} \right\}}{4Fk_{n,OH} [OH^-]}
\]

\[
C(O_2(aq)) N_{CB} \exp \left\{ -\frac{e_0}{k_B T} (E_{E_{\text{edge}}} - E_p) \right\} \left( \frac{k_B T}{\lambda \pi} \right)^{\frac{3}{2}} \exp \left\{ -\frac{e_0^2 (E_{E_{\text{edge}}} - E_{E_{\text{red}}} - \lambda)^2}{2 \lambda k_B T} \right\} \exp \left\{ \frac{(1-\alpha F)}{RT} (E_p - E_{E_{\text{red}}}) \right\}
\]

Experimental data; 1 mV s\(^{-1}\)

Model (predominantly tunnelling current)

Equilibrium Potential

\[
O_2(aq) + 2H_2O + 4e^- \longleftrightarrow 4OH^- \]
The charge carrier densities are calculated from the slopes of Mott-Schottky plots, obtained at higher frequencies.

\[ N_D = \frac{2}{\varepsilon_0 \varepsilon_r \varepsilon_0} \frac{d(C^2 A^{-2})}{dV} \]

**Material** | **\( N_D / \text{m}^{-3} \)**
--- | ---
Undoped \( \text{Fe}_2\text{O}_3 \) | \( 2.80 \times 10^{25} \)
\( \text{Sn}^{IV} \) doped \( \text{Fe}_2\text{O}_3 \) | \( 2.75 \times 10^{25} \)

\( m_e^* = 1.5m_e^0 \), Peng H., Lany S. (2012) *Phys. Rev. B* **85**, 201202-1
Effect of Dopant of Recombination Kinetics

Analysis of typical Nyquist plots obtained under illumination

\[
\frac{k_{\text{recombination}}}{k_{\text{transfer}}} = \frac{(R_3 - R_1)}{(R_2 - R_1)} - 1
\]

Conclusions

- We have obtained a reasonably good understanding of interfacial behaviour of undoped Fe$_2$O$_3$ films in steady state
  - Photocurrent onset potential cannot be shifted further left as limited by flat band potential, obtained from $j^2$ vs. $V$ plots
  - To maximise the photocurrent, surface area should be increased and recombination rate minimised

- The influence of dopants must be better understood, particularly their effect on recombination rate

- The pH of zero charge must be experimentally determined for each film in order to improve model accuracy
END
Interfacial Characteristics of the Undoped Fe$_2$O$_3$

\[
E_A + (E_{CB} - E_F) = - (V_{F\text{ (measured)}} - \Delta V_H + 4.44 + E^0(\text{RE vs SHE}))
\]

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
<th>Unit</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>On the absolute scale</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta E$</td>
<td>-0.013</td>
<td>eV</td>
<td>Calculated using the charge carrier density, $n_{CB}$, obtained from Mott-Schottky plots</td>
</tr>
</tbody>
</table>

| **On the electrochemical scale** | | | |
| $V_{FB\ (measured)}$ | + 0.022 | V ($HgO|Hg$) | Determined from the intercept of $(j_{\text{photocurrent}})^2$ with the x-axis |
| $\Delta V_H$ | -0.15 | V | Calculated as the only unknown in the energy-potential balance |
| \([\text{Fe-O}^-] / [\text{Fe-OH}_2^+]\ (at\ surface)\) | 8.38×10$^8$ | 1 | |

**For the conversion between the two scales**

\[
E^0(\text{RE}) = E^0(\text{HgO|Hg}) + 0.12\ V\ (\text{SHE})\quad\text{Experimentally measured}
\]

\[
E^0(\text{SHE}) = 0\ V\ (\text{SHE})\quad\text{Standard value}
\]
Electrochemical Impedance of Hematite in the Dark

Circuit representation of the interfacial charge transfer

- $R_{\text{Faradaic}}$
- $C_{\text{Interface}}$
- $R_1$
- $C_2$
- $R_2$

$Z'' / \Omega$
$Z' / \Omega$

1\textsuperscript{st} semicircle
Charge transfer via conduction band

2\textsuperscript{nd} semicircle
Charge transfer by tunnelling & surface state formation

Capacitance, $C / \text{F m}^{-2}$

Predicted $C_{\text{Interface}}$
Evaluated $C_{\text{Interface}}$
Evaluated $C_{\text{surface state}}$

Applied Potential, $V (\text{HgO}|\text{Hg}) / \text{V}$