Incorporation of CIGS Cells into Photo-Electrochemical Reactors...

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Principles of electrochemical reactions

Solid Phase
  e.g. metal

Liquid Phase
  e.g. H$_2$O + ions

$E_F$ (Fermi Level)

$E_{O/R}$ (Equilibrium energy of redox couple)

e.g. $2H^+ + 2e^- \leftrightarrow H_2$
Principles of electrochemical reactions

Liquid Phase
- e.g. $\text{H}_2\text{O} + \text{ions}$

Solid Phase
- e.g. metal

Fermi Level ($E_F$)

Equilibrium energy of redox couple ($E_{O/R}$)

- e.g. $2\text{H}^+ + 2e^- \Leftrightarrow \text{H}_2$

$\eta$
Kinetics

Good catalyst

Poor catalyst
Principles of electrochemical reactions

- **Solid Phase**: e.g. metal
- **Liquid Phase**: e.g. H₂O + ions

Fermi Level \( (E_F) \)

Equilibrium energy of redox couple \( (E_{O/R}) \)

E.g. \( O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O \)

**OXIDATION**
Principles of electrochemical reactors

Solid Phase
  e.g. metal

Liquid Phase
  e.g. H₂O + ions

Solid Phase
  e.g. metal

Fermi Level

**REDUCTION**

\[ 2H^+ + 2e^- \rightleftharpoons H_2 \]

**OXIDATION**

\[ O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O \]

Source?!
Electrochemical to Photo-Electrochemical

Solid Phase
Semiconductor

Liquid Phase
e.g. H₂O + ions

Solid Phase
Semiconductor

Conduction band

Valence band

Conduction band

Valence band

Source?!

$2H^+ + 2e^- \Leftrightarrow H_2$

$O_2 + 4H^+ + 4e^- \Leftrightarrow 2H_2O$
Electrode Design

Principal requirements for a photo-electrode:

• Good photo-absorber
• Suitable conduction and valence band energies
• Suitable direction of internal bias
• Chemically robust
• Cheap
Hematite Photo-Anode Production

Spray Pyrolysis Setup

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$_3$ coatings produced by nebulising Fe$^{III}$Cl$_3$ in solvent onto heated substrate**

Ti $|$ Fe$_2$O$_3$-$SnO_2$

Variables:

- **Dopants → Sn$^{IV}$ (0.6 %)** (increase photocurrent)
- **Substrate → Ti, FTO** (flexibility with illumination)

Photographic image  SEM image
The Mo | CIGS | CdS | ZnO | Ti system

-4 eV

\( \text{CB}_{\text{CIGS}} \quad -4 \text{ eV} \)

\( \phi_e^{\text{CIGS}} = ? \)

\( \text{CB}_{\text{CdS}} \quad -3.98 \text{ eV} \)

\( \phi_e^{\text{CdS}} = ? \)

\( \text{CB}_{\text{ZnO}} \quad -4.2 \text{ eV} \)

\( \phi_e^{\text{ZnO}} = ? \)

-5 eV

\( \phi_e^{\text{Mo}} \quad -4.6 \text{ eV} \)

\( \text{VB}_{\text{CIGS}} \quad -5 \text{ eV} \)

-6 eV

-7 eV

\( \text{VB}_{\text{CdS}} \quad -6.4 \text{ eV} \)

\( \text{VB}_{\text{ZnO}} \quad -7.4 \text{ eV} \)

\( \phi_e^{\text{Ti}} \quad -4.63 \text{ eV} \)
The Mo | CIGS | CdS | ZnO | Ti system

Moly | CIGS p-type | CdS n-type | ZnO n-type | Ti

Vacuum level

$\phi_e^\text{Net}$

$\text{CB}_{\text{CIGS}}$ $\text{CB}_{\text{CdS}}$ $\text{CB}_{\text{ZnO}}$

$\text{VB}_{\text{CIGS}}$ $\text{VB}_{\text{CdS}}$ $\text{VB}_{\text{ZnO}}$

$e^-$ $h^+$
To replicate the effect of illumination on energy levels within the photo-cathode, the photo-cathode (when studied in the air) must be biased in this way:

For the physicists:
This is ‘reverse bias’?

For the electrochemists:
Dark current and photo-current refer to the flow of electrons in this direction.
Performance of Al coated CIGS Cells

Current was measured in response to an applied cell bias.
Device & System Development

- **Photo-cathode fabrication**
  - Substrate
  - Electrical contact

- **Photo-anode fabrication**
  - Substrate
  - Electrical contact

- **Reactor body**
  - Geometry
  - Materials

- **Illumination**
  - Mirrors
  - Concentrators

- **Membrane**

- **External bias**

- **Electrolyte flow circuit**
  - Pumps
  - Reservoirs
  - Dosing

- **Product harvesting & storage**

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Diagram showing the flow of electrons (e^-) and various components involved in the device & system development process.
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