Towards visible light activated porous photoanodes in conjunction with polymeric electrolyte photoelectrochemical cells with gaseous reactants

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Activities of my group: Electrochemical devices with solid electrolytes for energy storage.
- Light assisted processes
- Electrochemical activation of catalysis
- Plasma assisted electrocatalysis

Novel design of photoelectrochemical (PEC) cells for energy applications based on polymeric electrolyte membrane (PEM)

Inspiration of conventional PEM electrolyzers

Conventional PEC cells

Novel PEM-PEC cells with new modes of operation

Possible application in PEM FCs or ECs

Tools
**Motivation for photoelectrochemical (PEC) cell research**

**Theoretical efficiency** of PEC cells based on the photoelectrode bandgap under illumination on earth surface.

**PEM electrolyser coupled with PV for indirect SF production:**
Expensive noble metal (i.e. Pt, Ir-Ru) electrode materials → Not sustainable solution at the moment.

**PEC for direct SF production:**
- Cheap abundant electrode materials
- Ongoing research for materials
- Scaling up → design modification
- Novel operation modes

When a **semiconductor** catalyst absorbs photons whose energy is more than the semiconductor’s band gap, the electron in valence band (VB) can transit to the conduction band (CB).

- **Photogenerated electrons and holes are formed in the CB and VB**
- **Holes drive the oxygen evolution reaction**
- **Electrons (via external circuit) drive the hydrogen evolution reaction**

PEC design inspiration for PVs.
The ideal photoelectrode:

- Light adsorption - Small bandgap
- Correct band edge alignment
- Charge separation-transport
- Catalysis $\rightarrow$ HER, OER
- Stability and low cost

Trade-off solution

- Development of composite photoelectrodes $\rightarrow$ different materials fulfill different functionalities
- Nanostructuring
- Co-catalysts
- Z-scheme: Photoanode + photocathode

No semiconducting material meets these criteria.
Conventional PEC design: aqueous electrolytes

Photoelectrode for conventional PEC cells (liquid electrolytes):
Semiconducting layer deposited on a transparent glass substrate (with an electronically conducting layer).

- Challenges in scaling up
- Limited modes of operation
**Solid state PEC or PEM-PEC**

### Conventional PEC cells

- O₂ → V → H₂
- Aqueous electrolyte
- Photoanode → Diaphragm → Cathode

### PEM-PEC cells

- O₂ → V → H₂
- Polymeric membrane electrolyte
- Photoanode → Cathode

**PEM-PEC cells advantages:**
- New modes of operation
- Capturing H₂O from ambient air*
- CO₂ or N₂ fixation
- Operation in microgravity environment
- No need for replenishing the electrolyte
- Operation at elevated T, P
- Mechanistic studies: FTIR and Raman

**PEM-PEC modes of operations:**
- **Anode:** H₂O carried by He or air
- **Cathode:** N₂ or CO₂ reduction

**PEM-PEC challenges:**
- Porous photoelectrodes → new fabrication route
- Electrode electrolyte compatibility

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*J. Ronge et al, RSC Adv 4 (2014) 29286*
Solid state PEC with powder TiO$_2$ photoelectrode and gas phase operation

Cathode feed: H$_2$O

Cathode feed: H$_2$O, CH$_3$OH

PEM-PEC electrode design

**PEM technology** is based on **porous electrodes** that allows access to gas in the electrode electrolyte interface → gas diffusion electrodes.

Membrane electrode assembly for PEM electrolysis

Photoelectrodes based on semiconductors in the form of powders

Our approach for high surface area photoelectrodes
PEM-PEC cell design

- Operation with liquid and gaseous reactants
- Reference electrode
- Applicable also for alkaline and bipolar membranes
Fabrication: Photoelectrodes for PEM-PEC

Starting material Ti felt (3D web of microfibers):
(i) TiO$_2$ nanotube arrays → LaTiO$_2$N
(ii) Deposition of WO$_3$/BiVO$_4$ junction

**Photoanode**
LaTiO$_2$N

**Tandem cell**
BiVO$_4$  Cu$_2$O, CZTS

![Diagram showing electron and hole flow in photoanode and tandem cell](image-url)
TiO$_2$ nanotube arrays photoelectrodes

Anodization:
$30V$, $1h$ in Ethylene glycol + 0.3wt% NH$_4$F + 2vol% H$_2$O

BET measurement
$1300cm^2$
$2.7m^2/gr$

Fabrication: Steps of titania nanotube arrays formation

Oxidation

\[2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{e}^- + 4\text{H}^+\]  
(field assisted)

\[\text{Ti} + \text{O}_2 \rightarrow \text{TiO}_2\]  
(field assisted)

Dissolution (due to the presence of fluoride ion)

\[\text{TiO}_2 + 6\text{F}^- + 4\text{H}^+ \rightarrow \text{TiF}_6^{2-} + 2\text{H}_2\text{O}\]  
(field and chemical dissolution)
TiO$_2$ nanotube arrays photoelectrodes

**TiO$_2$ nanotubes** on a web of microfibers

**TiO$_2$ nanotubes**

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**PEM-PEC evaluation**

- He carrier + 2.5% H$_2$O $\rightarrow$ close to liquid phase operation in conventional PEC.
- Air carrier + 2.5% H$_2$O $\rightarrow$ $\sim$90% vs He carrier. “Water neutral” process.
- 2-10 times higher than the TiO$_2$ state-of-the-art

Light harvesting → BiVO₄/WO₃/TiO₂ photoelectrodes

- BiVO₄ is among the most promising materials for **visible light** induce photoelectrochemical water splitting thanks to appropriate band gap and band positions.
- Its relative **stability** in acidic and alkaline medium allows its use in a wide range of conditions.
- It exhibits synergic properties when interfaced with WO₃.

**The objectives is to fully cover the Ti felt with a first layer of WO₃ and then to form the junction with BiVO₄.**


Light harvesting → \( \text{BiVO}_4/\text{WO}_3/\text{TiO}_2 \) photoelectrodes

- **W-sputtering**
- **Anodization of W**
- **BiVO\(_4\) deposition via SILAR**

\( \text{BiVO}_4/\text{WO}_3 \)

*T. Stoll et al, Electrochem Commun in preparation*
Ammonia synthesis with plasma activation

Nitrogen fixation at the cathode:
\[ N_2 + 6H^+ + 6e^- \rightarrow 2NH_3 \text{ (NRR)} \]
\[ 6H^+ + 6e^- \rightarrow 3H_2 \text{ (HER)} \]
Kinetics of HER >> NRR

Plasmo-electrochemical nitrogen fixation: \( N_2 \) is activated by plasma \( \rightarrow \) HER vs NRR?

F. Fleming Crim, PNAS, 2008, 105, 12654
Proton exchange membrane fuel cells (PEMFCs) represent a source of efficient and sustainable technology for the generation of energy.

Conventional oxygen reduction reaction (ORR) catalyst is Pt deposited on a porous carbon support. Limitations → electrooxidation of C, agglomeration of Pt.

Utilization of alternative supports based on a porous 3D web of titanium microfibers for improving the performance via MSI.

![25 cycles Pt ALD](image1)
![50 cycles Pt ALD](image2)
![100 cycles Pt ALD](image3)

![Liquid phase PEC](graph1)
Cyclic voltammetry in H₂SO₄ without and with EtOH

Future plans Pt by ALD deposition on TiO₂ nanotube arrays for improving the surface area.

High specific area support

TiO₂ nanotube arrays
High ion flux He plasma treatment: 3D Ti-web nanostructuring

Unmodified

Tanyeli "Helium ion induced nanostructuring of metal surface", PhD thesis 2015
High ion flux He plasma treatment: 3D Ti-web nanostructuring

Unmodified

Modified by plasma treatment

1040°C

1200°C
Thank you for your attention