Electrochemistry for Fuel Cells and Electrolysers

Professor Bruno G. Pollet FRSC

HySA Systems, University of the Western Cape, South Africa
HySA Systems is a Systems Integration and Technology Validation Competence Centre on HFCT established in 2007, hosted at the University of the Western Cape (UWC) and located at the SAIAMC.

HySA Systems is an industry, technology and product development oriented Competence Centre, which has successfully demonstrated on many occasions its ability to develop, build, commission and validate prototype systems for Industry.
HySA Systems
What we do

HySA Systems

Combined Heat & Power
- HT-MEA
- System Integration
- System Validation
- System/Stack Modelling

Hydrogen Fuelled Vehicles
- HT-MEA
- HT-PEMFC Stacks
- System Integration
- System Validation
- System/Stack Modelling

Key Technologies
- High Temperature PEM Fuel Cell Stacks (>120°C)
- HT-Catalyst
- MEAs for HT-PEMFCs
- Solid State Hydrogen Storage
- Li-ion Batteries
- Pd-membranes
HySA Systems
Where we are

A novel 2,000 m² R&D building on the UWC campus hosting world-class and state-of-the-art equipment within the SAIAMC Innovation Centre
Learning Objectives – Today’s lecture

Electrochemistry for Fuel Cells & Electrolysers

By the end of this lecture, you should be able to:

Have an understanding of:

- Membrane Electrode Assembly (MEA)
- Bipolar plate (BPP)
- Gas Diffusion Layer (GDL)
- Electrocatalysts & Catalyst Layers (CL)
- Electrocatalysis
<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>Proton Exchange Membrane (PEM)</td>
<td>solid polymer membrane</td>
<td>hydrogen</td>
<td>pure or atmospheric oxygen</td>
<td>75°C (180°F)</td>
<td>35 – 60%</td>
</tr>
<tr>
<td>Alkaline (AFC)</td>
<td>potassium hydroxide</td>
<td>hydrogen</td>
<td>pure oxygen</td>
<td>below 80°C</td>
<td>50 – 70%</td>
</tr>
<tr>
<td>Direct Methanol (DMFC)</td>
<td>solid polymer membrane</td>
<td>methanol solution in water</td>
<td>atmospheric oxygen</td>
<td>75°C (180°F)</td>
<td>35 – 40%</td>
</tr>
<tr>
<td>Phosphoric Acid (PAFC)</td>
<td>Phosphorous</td>
<td>hydrogen</td>
<td>atmospheric oxygen</td>
<td>210°C (400°F)</td>
<td>35 – 50%</td>
</tr>
<tr>
<td>Molten Carbonate (MCFC)</td>
<td>Alkali-Carbonates</td>
<td>hydrogen, methane</td>
<td>atmospheric oxygen</td>
<td>650°C (1200°F)</td>
<td>40 – 55%</td>
</tr>
<tr>
<td>Solid Oxide (SOFC)</td>
<td>Ceramic Oxide</td>
<td>hydrogen, methane</td>
<td>atmospheric oxygen</td>
<td>800–1000°C (1500–1800°F)</td>
<td>45 – 60%</td>
</tr>
</tbody>
</table>
Copyright Dr Bruno G Pollet

AFC – 100°C
H₂, H₂O → OH⁻ → O₂

MFC – < 80°C
C₆H₁₂O₆, CO₂ → H₂O, CO₂ → H₂O

PEMFC – < 150°C
H₂ → H₂O → H₂O

DMFC – 80°C
CH₃OH, CO₂ → H₂O, CO₂ → H₂O

PAFC – 200°C
H₂ → H₂O → H₂O

MCFC – 650°C
H₂, H₂O & CO₂ → H₂O, CO₂ → H₂O

SOFC – 1,000°C
H₂, H₂O → O²⁻ → O₂
# Energy Storage Technologies:
## A Comparison

<table>
<thead>
<tr>
<th>Property</th>
<th>CAP-XX Supercapacitors</th>
<th>Capacitors</th>
<th>Fuel Cells</th>
<th>Batteries</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Charge/Discharge Time</strong></td>
<td>Milliseconds -Seconds</td>
<td>Picoseconds ((10^{-12})) – Milliseconds</td>
<td>Typically 1 to 300 hrs Instant charge (refuel)</td>
<td>1 to 10 hrs</td>
</tr>
<tr>
<td><strong>Operating Temperature</strong></td>
<td>-40 to +85 °C</td>
<td>-20 to +100 °C</td>
<td>+25 to +1000 °C</td>
<td>-20 to +65 °C</td>
</tr>
<tr>
<td><strong>Operating Voltage</strong></td>
<td>2.3V - 2.75V/cell</td>
<td>6 to 800 V</td>
<td>0.6 V - 1.0 V (max) / cell</td>
<td>1.25 to 4.2 V / cell</td>
</tr>
<tr>
<td><strong>Capacitance</strong></td>
<td>100 mF to &gt; 2F</td>
<td>10 pF to 2.2 mF</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td><strong>Life</strong></td>
<td>30,000+ hrs average</td>
<td>&gt;100,000 cycles</td>
<td>1,500 to 10,000 hrs</td>
<td>150 to 1500 cycles</td>
</tr>
<tr>
<td><strong>Weight</strong></td>
<td>1 g to 2 kg</td>
<td>1 g to 10 kg</td>
<td>20 g to over 5 kg</td>
<td>1 g to over 10 kg</td>
</tr>
<tr>
<td><strong>Power Density</strong></td>
<td>10 to 100 kW/kg</td>
<td>0.25 to 10,000 kW/kg</td>
<td>0.001 to 0.1 kW/kg</td>
<td>0.005 to 0.4 kW/kg</td>
</tr>
<tr>
<td><strong>Energy Density</strong></td>
<td>1 to 5 Wh/kg</td>
<td>0.01 to 0.05 Wh/kg</td>
<td>300 to 3,000 Wh/kg</td>
<td>8 to 600 Wh/kg</td>
</tr>
</tbody>
</table>
What is a PEFC?

- PEFC transforms the chemical energy liberated during the electrochemical reaction of hydrogen and oxygen to electrical energy, heat and water.

- PEFC relies upon the oxidation of hydrogen or methanol to form protons and the reduction of oxygen in catalyst layers.

- Protons ($H^+$) are transported across the electrolyte to the cathode where they react with oxygen to produce water.

- Electrons ($e^-$) are transported via an external circuit from the anode to the cathode side providing power to the external devices.

The half-reactions are:

**Anode:** $H_2 \rightarrow 2H^+ + 2e^-$  

**Cathode:** $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

**Net reaction:** $O_2 + 2H_2 \rightarrow 2H_2O$
PEM Fuel Cells

100 W to 500 kW
In the PEMFC, the combination of anode and cathode electrodes with a solid polymer electrolyte is called:

Membrane Electrode Assembly (MEA)
Membrane Electrode Assembly (MEA)

\[ \text{MEA} = \text{Heart of a PEMFC consisting of:} \]
- 2 Gas Diffusion Layers (GDLs)
- 2 Catalyst Layers (A&C CLs)
- Proton Exchange Membrane (PEM)
What is an MEA?

Flow Field Plate (FFP)

Gas diffusion layer (GDL) and catalyst layer (CL) [Pt/C ‘ink’]

Proton exchange Membrane (PEM) e.g. Nafion

MEA thickness 1 mm max.;
GDL 330um;
PEM 50um;
CL 10-30um
Bipolar Plate (BPP) with Seals

Bipolar plates have a number of functions within the PEMFC:

- Separating gases between single cells (reaction gases & water exhaust)
- Providing a conductive medium between the anode and cathode
- Providing a flow field channel for the reaction gases
- A solid structure for the stack
- Transferring heat out of the cell

Bipolar plates require the following characteristics:

- Impermeable to hydrogen and oxygen
- Very good electrical conductivity
- A balance between conductivity, strength, size and weight
- Resistance to corrosion
- Easy to manufacture in large quantities
- The flow field (FF) must provide uniform distribution of the reaction gases over the MEA to ensure even & efficient power production
Bipolar Plates (BPPs)

Bipolar plates have numerous functions to perform which have dramatic impact on PEM fuel cell performance.

- Separation of gases between cells
- A solid structure for the stack
- Current collection
- Uniform distribution of reaction gases
- Water and heat management out of the cell

Flow field plates make up a significant proportion of the cost, weight and volume of a PEMFC stack.
# Commercial Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Considerations</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Graphite</strong></td>
<td>• Bulk Conductivity</td>
</tr>
<tr>
<td></td>
<td>• Contact Resistance</td>
</tr>
<tr>
<td></td>
<td>• Permeability</td>
</tr>
<tr>
<td>Poco AXF-5Q (Pyrolytically sealed)</td>
<td>• Corrosion Resistance</td>
</tr>
<tr>
<td>Toyo Tanso IG-11 (Phenolic impregnation)</td>
<td>• Strength</td>
</tr>
<tr>
<td><strong>Carbon/Polymer Composite</strong></td>
<td>• Processability</td>
</tr>
<tr>
<td>Bac2 1106 &amp; 1109 (Electrophen)</td>
<td>• Cost</td>
</tr>
<tr>
<td>BMCI 940 (Vinyl ester)</td>
<td>• Density</td>
</tr>
<tr>
<td>ZBT Compound*</td>
<td></td>
</tr>
<tr>
<td>GrafTech*</td>
<td></td>
</tr>
<tr>
<td>Schunk*</td>
<td></td>
</tr>
<tr>
<td><strong>Metal</strong></td>
<td></td>
</tr>
<tr>
<td>316L SS</td>
<td></td>
</tr>
<tr>
<td>316L SS (TiN coated)</td>
<td></td>
</tr>
<tr>
<td>316L SS (Carbon coated)*</td>
<td></td>
</tr>
</tbody>
</table>
Conductivity

![Conductivity Graph](image)

Through-plane conductivity (S/cm)

- AXF-5Q
- IG-11
- BMCI 8649
- EP1109
- EP1106
- SS 316L
Requirement to Develop Coating Materials
Development and characterisation of conductive polymer, carbon and metallic coatings to avoid Corrosion.

Application to stamped/hydroformed metal bipolar plates. Characterisation of durability in test station

Polymer Electrolyte Membrane Fuel Cell (PEMFC) Flow Field Plate: Design, Materials and Characterisation

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Received February 16, 2010; accepted March 18, 2010

Abstract
This review describes some recent developments in the area of flow field plates (FFPs) for proton exchange membrane fuel cells (PEMFCs). The function, parameters and design of FFPs in PEM fuel cells are outlined and considered in light of their performance. FFP materials and manufacturing methods are discussed and current in situ and ex situ characterisation techniques are described.

Keywords: Bipolar Plate, Design; Materials, Flow Field Plate, PEMFC

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Hydrogen South Africa
Gas Diffusion Layer (GDL)

- A complex fibrous three-dimensional structure with variable wettability
- Either as a carbon cloth or carbon paper
- Porous materials which allow gases to pass through
- Since carbon is conductive, it facilitates the transport of electrons
- Can hold water produced at the cathode side
# GDLs used and their Properties

<table>
<thead>
<tr>
<th>GDL Material</th>
<th>Freudenberg</th>
<th>E-Tek</th>
<th>Sigracet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product</td>
<td>H2315 C1</td>
<td>Elat LT 1200 - W</td>
<td>10BC</td>
</tr>
<tr>
<td>Type</td>
<td>Paper</td>
<td>Woven Cloth</td>
<td>Paper</td>
</tr>
<tr>
<td>Thickness</td>
<td>252µm</td>
<td>275µm</td>
<td>415µm</td>
</tr>
<tr>
<td>Area Weight</td>
<td>132 g/m²</td>
<td>200 g/m²</td>
<td>135 g/m²</td>
</tr>
</tbody>
</table>
Effect of GDL on MEA Performance

(a) Polarisation curves: Ultrasonic-sprayed GDEs (Sigracet: SGL 10BC, Sigracet: SGL 24BC, Sigracet: SGL 34BC; Freudenberg: H2315 C2; E-TEK: Elat LT 1200W) of cathode loadings of 0.40 mg cm$^{-2}$ at A = 50%; C = 50%; (b) Power density curves. The anode loading for all experiments was 0.40 mg cm$^{-2}$. (JMFC).
Proton Exchange Membrane (PEM)

- A semi-permeable membrane
- Designed to conduct protons while being impermeable to oxygen or hydrogen
- Made from either pure polymer or from composite membranes where other materials are embedded in a polymer matrix
- One of the most common and commercially available PEM materials is Nafion® (a DuPont product)
- Nafion is a fluorinated polymer.
- PEMs are mainly characterized by proton conductivity, methanol permeability and thermal stability.
Polymer Membrane: A Proton Conductor

Molecular structure of Nafion®
Low Temperature (LT) PEMs

Nafion® - DuPont
- Excellent FC performance
- 80 °C, 100 % RH

Short side chain PFSAs (e.g. Dow, 3M, Flemion etc.)
- Improved conductivity
- Mechanical strength

High Temperature (HT) Membranes
Why High Temperature?

Improved FC Performance

- Increased reaction kinetics
- Higher CO tolerance (3%)
- Simplified heat and water management
- Non-fluorinated polymers (cost & environment)

# Membrane Materials – Considerations

<table>
<thead>
<tr>
<th>Polymer / Structure</th>
<th>Proton carrier</th>
<th>Manufacturing process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion®</td>
<td>Water</td>
<td>Extrusion/Casting</td>
</tr>
<tr>
<td>PFSA (Dow Membrane)</td>
<td>Phosphoric Acid</td>
<td>Acidification</td>
</tr>
<tr>
<td>Hydrocarbon (PEEK-WC)</td>
<td>Ionic Liquid</td>
<td>Solvents</td>
</tr>
<tr>
<td>PBI</td>
<td></td>
<td>Thermal post-treatment</td>
</tr>
</tbody>
</table>

**Polymer / Structure**

- **Nafion®**: A perfluorinated polymer, known for its high proton conductivity.
- **PFSA (Dow Membrane)**: Fluorinated polymer with sulfuric acid groups.
- **Hydrocarbon (PEEK-WC)**: A carbon-based polymer with fluorinated side chains.
- **PBI** (Polybenzimidazole): A high-temperature resistant polymer.

**Proton Carrier**

- Water
- Phosphoric Acid
- Ionic Liquid

**Manufacturing Process**

- Extrusion/Casting
- Acidification
- Solvents
- Thermal post-treatment
High Temperature PEMs

- Sulfonated Aromatic (water required)
- PBI/H$_3$PO$_4$
- Ionic liquids
- Inorganic-organic composites


## High Temperature PEM Materials

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Benefit</th>
<th>Best Performance</th>
<th>Challenge</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBI/H₃PO₄</td>
<td>HT/Anhydrous</td>
<td>0.16 S.cm⁻¹, 180°C</td>
<td>Poor LT conductivity &amp; acid leaching</td>
</tr>
<tr>
<td>Imidazole doped poly(ether ketone)</td>
<td>HT/Anhydrous</td>
<td>0.02 S.cm⁻¹, 120-200°C</td>
<td>Poor LT conductivity &amp; acid leaching</td>
</tr>
<tr>
<td>Composites (PBI or Aromatics (SPEEK,SPSU))</td>
<td>Increased H₂O uptake and retention</td>
<td>0.03 – 0.003 S.cm⁻¹, 135-185°C</td>
<td>Increased conductivity required</td>
</tr>
</tbody>
</table>


Catalyst Layers (CLs) (PEM)

- Where the electrochemical reaction takes place
- Mixture of carbon powder, Nafion and electrocatalyst such as Pt
- They are spread either on one surface of the GDL or the PEM
Anode Reaction: An Oxidation Process

© JMFC
Cathode Reaction: A Reduction Process

© JMFC
Most common MEA Fabrication Methods

- Screen printing
- Spraying

- Hot press all the layers together
- MEA obtained and ready to be tested
Performance of an **ideal** PEMFC

**Electrode Potential / Cell Voltage**

- **Cell Voltage** = 1.23V
- **Efficiency** = 100%
- **Power at 1A/cm²** = 1.23W/cm²

**Current (Amps)**

- **Cell Voltage** = 1.18V
- **Efficiency** = 100%
- **Power at 1A/cm²** = 1.18W/cm²

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Hydrogen South Africa
Performance of a real PEMFC

- Efficiency Loss
- Cell Voltage = 0.7V
  Efficiency = 57%
  Power = 0.7W/cm²

- Observed Cell Voltage
- Cell Voltage = 0.3V
  Efficiency = 25%
  Power = 0.3W/cm²
Issues related to PEMFC Performance

- An increase in CL thickness, for a given Pt catalyst loading ➞ a decrease in reactants diffusion rate towards Pt catalytic sites

- An increase in the amount of Pt catalyst in the CL ➞ an increase in the particle size of the catalysts, thus decreasing the fuel cell efficiency
Objectives for Improved PEMFC Performance

- Decrease in Pt loading due to high cost of Pt down to 0.05 mg.cm$^{-2}$ (A&C) for a 50kW stack
- Smaller active layer for better diffusion & less ohmic drop
- Increase in catalyst surface area i.e. decrease Pt size e.g. $< 10$nm (2 – 4nm)
Generating the Power by Stacking MEAs

Source: www.excellsis.com
The Proton Exchange Membrane (PEM) Fuel Cell consists of a Membrane Electrode Assembly (MEA) and a bipolar gas flow plate. Air and H2 are supplied to the flow distribution plates where they are distributed across either side of the MEA. Fuel Cells are combined in a stack to produce the required power output.

© JMFC
Working Prototypes

- Ballard 1.2kW Nexa stack
  Source: Ballard

- 1kW Capacity
  Source: Ballard

- 5kW Capacity
  Source: UTC

- Smart FC Power
  40W DMFC
  8hr lifetime @ 20W
  Source: Fuel Cells Today

- MTI MicroFuelCells
  Mobile phone recharger
  Source: Fuel Cells Today

- Casio notebook
  DMFC power source
  Source: Fuel Cells Today

© JMFC

Courtesy: JMFC Ltd

HySA Systems
Hydrogen South Africa
Daimler Chrysler Citaro bus
30 buses produced
Compressed H₂

Source: Ballard
Daimler Chrysler
F-cell
Compressed H₂
80 kW Ballard Stacks

UTC/Thor
‘ThunderPower’ bus
75 kW UTC stack
1st bus in commercial service, USA

Source: UTC

Nissan X-Trail
Compressed H₂
75kW UTC stacks

Source: UTC

Courtesy: JMFC Ltd
Market Forecasts

The overall fuel cell market is segmented on the basis of the power output categories into three different markets:

- **< 50 kW** – PEMFC/SOFC/AFC/DMFC for portable & micro/mini CHP systems
- **50 kW - 300 kW** – MCFC/SOFC for residential & commercial – PEMFC for transportation
- **> 300 kW** – MCFC/SOFC larger CHP systems

Revenues by Technology Forecast (2010) for Fuel Cells Market in Europe
Main Issues with PEMFC

- Expensive due to the use of Pt & Nafion - £2,000-£4,000/kW
  PEMFC stack, the catalyst accounts for 55% of the total cost, membrane (7%), bipolar plate (10%) and gas diffusion layers (10%) the average price of platinum has risen more than five times between June 1998 and June 2008, from $370 to $2100 per troy ounce

- Scarce of Pt

- Problem with water – Water management

- Durability (max. 10,000 hours of operation)

- Chemical Degradation of materials

- Alternative catalyst materials to Platinum

- Lower cost membranes

- Low cost MEA manufacturing

- Higher conductivity Bi-Polar plates

- Demonstrated repeatability/reliability/durability
Direct Methanol Fuel Cell (DMFC)
Electrochemistry

- **At the Anode**
  \[ \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \]

- **At the cathode**
  \[ \frac{3}{2} \text{O}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2\text{O} \]

- **Overall**
  \[ \text{CH}_3\text{OH} + \frac{3}{2} \text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{CO}_2 \]
Role of the catalyst in Methanol oxidation (MOR)

- Methanol oxidation is structure sensitive reaction and depends upon:
  - Dispersion of catalyst on support
  - Crystallographic orientation of catalyst
  - Catalyst size
  - Surface roughness
  - Operating temperature

- Platinum works best!....why??
CH$_3$OH + H$_2$O $\rightarrow$ CO$_2$ + 6H$^+$ + 6e$^-$

Three important steps

- Dehydrogenation of methanol to CO

  $\begin{align*}
  &\text{CH}_3\text{OH} &\rightarrow &\text{CO} \\
  \end{align*}$

- Dehydrogenation of water to oxygen

  $\begin{align*}
  &\text{OH}_2 &\rightarrow &\text{O} \\
  \end{align*}$

- Oxidative recombination: forming the C-O bond, and desorption of products.
Reaction pathways for ORR

Path A – direct pathway, involves four-electron reduction

\[ \text{O}_2 + 4 \text{H}^+ + 4 e^- \rightarrow 2 \text{H}_2\text{O} ; \quad E^\circ = 1.229 \text{ V vs. SHE} \]

Path B – indirect pathway, involves two-electron reduction followed by further two-electron reduction

\[ \text{O}_2 + 2 \text{H}^+ + 2 e^- \rightarrow \text{H}_2\text{O}_2 ; \quad E^\circ = 0.695 \text{ V vs. SHE} \]

\[ \text{H}_2\text{O}_2 + 2 \text{H}^+ + 2 e^- \rightarrow 2 \text{H}_2\text{O} ; \quad E^\circ = 1.77 \text{ V vs. SHE} \]
Role of the catalyst in ORR

- Catalyst favors formation of H$_2$O than H$_2$O$_2$.
- However, Pt alone is sluggish due to formation of OH @ +0.8 V

\[
\begin{align*}
O_2 + 2 \text{Pt} & \rightarrow \text{Pt}_2\text{O}_2 \\
\text{Pt}_2\text{O}_2 + H^+ + e^- & \rightarrow \text{Pt}_2\text{-O}_2\text{H} \\
\text{Pt}_2\text{-O}_2\text{H} & \rightarrow \text{Pt-OH} + \text{Pt-O} \\
\text{Pt-OH} + \text{Pt-O} + H^+ + e^- & \rightarrow \text{Pt-OH} + \text{Pt-OH} \\
\text{Pt-OH} + \text{Pt-OH} + 2 H^+ + 2 e^- & \rightarrow 2 \text{Pt} + 2 H_2O
\end{align*}
\]

- Need to alloy it with other metals such as Ru, Ni, Fe, Co etc.

Role of the catalyst in ORR

Loose grip. All-platinum electrodes (left) grab hydroxides (OH) tightly, preventing oxygen (O₂) from getting access to the catalyst. Adding nickel (right) softens this grip, speeding the desired oxygen-splitting reaction.

http://www.sciencemag.org/content/315/5809/220
# PEMFC vs. DMFC

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>PEMFC (Proton Exchange Membrane Fuel Cells)</th>
<th>DMFC (Direct Methanol Fuel Cells)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating temp (°C)</td>
<td>25– 80</td>
<td>25 – 80</td>
</tr>
<tr>
<td>Fuel</td>
<td>H₂ (pure or reformed)</td>
<td>CH₃OH</td>
</tr>
<tr>
<td>Charge carrier in the electrolyte</td>
<td>H⁺</td>
<td>H⁺</td>
</tr>
<tr>
<td>Poison</td>
<td>CO&gt;10 ppm</td>
<td>Adsorbed intermediates (CO)</td>
</tr>
<tr>
<td>Applications</td>
<td>Transportation, Portable</td>
<td></td>
</tr>
</tbody>
</table>
Conclusions

- DMFC use Methanol as a fuel
- Variety of applications.
- Use transition metals and their alloys as catalysts.
- Carbon based nanomaterials for EC support.
- Platinum is the best catalyst.
- Different pathways for oxygen reduction reaction (ORR).
- Pt is alloyed with other transition metals to increase rate of ORR.
PEM Electrolysers
**PEM Electrolysers**

- By addressing the questions around Hydrogen generation, electrolysers are smoothing and paving the way for fuel cell deployment.

- Electrolysers fit into three main areas within the Hydrogen economy: (i) Fuel Cell Electric Vehicles (FCEV); (ii) grid energy storage and grid integration of variable Renewable Energy sources; and (iii) autonomous energy systems allowing complete independence from the grid and from fossil fuels.

- Problems with Electrolysers: Too expensive and issues with the OER (Oxygen Evolution Reaction).
Catalysts for PEM Electrolysers

Summary of literature PEM water electrolysis performances

<table>
<thead>
<tr>
<th>$E_{\text{cell}}^{\text{act}}$ (V)</th>
<th>Anode, cathode</th>
<th>$E_{\text{cell}}^{\text{est}}$ (V)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.660</td>
<td>Ir, 40% Pd/C</td>
<td>1.697</td>
<td>[2]</td>
</tr>
<tr>
<td>1.590</td>
<td>Ir–Ru (70:30) oxide, 20% Pt/C</td>
<td>1.623</td>
<td>[15]</td>
</tr>
<tr>
<td>1.645</td>
<td>Ir oxide, 10% Pt/C</td>
<td>1.645</td>
<td>[15]</td>
</tr>
<tr>
<td>1.780</td>
<td>Ir–Ta oxide, 10% Pt/C</td>
<td>1.572</td>
<td>[15]</td>
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<tr>
<td>1.725</td>
<td>Ru oxide, Pt</td>
<td>1.675</td>
<td>[16]</td>
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<tr>
<td>1.720</td>
<td>Ir, Pt</td>
<td>1.620</td>
<td>[17]</td>
</tr>
<tr>
<td>1.533</td>
<td>Ir oxide, Pt black</td>
<td>1.620</td>
<td>[19]</td>
</tr>
<tr>
<td>1.750</td>
<td>Pt–Ir, Pt</td>
<td>1.750</td>
<td>[20]</td>
</tr>
<tr>
<td>1.590</td>
<td>Ir oxide, Pt black</td>
<td>1.680</td>
<td>[21]</td>
</tr>
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</table>

$E_{\text{cell}}^{\text{act}}$ = Actual $E_{\text{cell}}$ at 1 A cm$^{-2}$, $E_{\text{cell}}^{\text{est}}$ = Estimated $E_{\text{cell}}$ at 1 A cm$^{-2}$, 80 °C, Nafion 115

Electrocatalysis

## Contents

1. Introduction to electrocatalysis
2. Equilibrium: the Nernst potential
3. Electrode kinetics
4. The problems with Pt
5. Improved Pt catalysts for oxygen reduction
6. Practical evaluation of catalyst performance
Electrocatalysis

1. **Introduction to electrocatalysis**
   Catalysis of electrochemical reactions

   A catalyst is a material which modifies the rate of chemical reactions without being consumed in the process. (Wikipedia)

   **Heterogeneous catalysis**
   Reactions occur at the surface of metals or metal oxides

   All electrodes on which reactions occur by means of adsorbed intermediates can be considered **electrocatalysts**

   → Can achieve acceleration (or suppression) of reactions
   → Often involves modification of the electrode surface
1. Introduction to electrocatalysis

Applications of electrocatalysis

- You (enzymes)
  - Glucose oxidation, oxygen reduction
  - Photosynthesis

- Sensors

- Materials synthesis
  - Electrolysis

- Energy
  - Fuel Cells
  - Batteries
1. Introduction to electrocatalysis
   Properties of an electrocatalyst

**Activity (rate of reaction)**
- Exchange current density \( j_0 \) [A.m\(^{-2}\)]
- Rate constant \( k \) [mol.cm\(^{-2}\).s\(^{-1}\)]
- Turnover frequency \( f \) [s\(^{-1}\)]

**Selectivity**
- Quantified in terms of reaction yield
  e.g. for oxygen reduction, the % yield of H\(_2\)O vs. H\(_2\)O\(_2\)
  \[
  \begin{align*}
  O_2 + 4H^+ + 4e^- & \rightarrow 2H_2O \\
  O_2 + 2H^+ + 2e^- & \rightarrow H_2O_2
  \end{align*}
  \]

**Durability**
- Rate of reaction vs. time (long-term)
Electrocatalysis

2. Equilibrium: the Nernst potential
What can be done with a catalyst? (And what can’t.)

Consider the reaction

\[ \text{O} + e^- \rightleftharpoons \text{R} \]

\[ \Delta G^0 \, [\text{J.mol}^{-1}] \]

The standard change in Gibbs free energy \( \Delta G^0 \) represents the **maximum useful work** that can be done when one mole of the reaction products is formed from the reactants (at 25ºC, 100kPa)

E.g. Combustion of \( \text{H}_2 \)

\[ \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} \, (l) \]

\[ \Delta G^0 = -56.69 \, \text{kJ.mol}^{-1} \]

\( \Delta G^0 \) is a property of a particular reaction, and is unaffected by the rate or mechanism of the reaction.
2. **Equilibrium: the Nernst potential**

What can be done with a catalyst? (And what can’t.)

However, $\Delta G$ does vary with concentration & temperature:

$$\Delta G = \Delta G^0 + RT \ln \left[ \frac{R}{O} \right]$$

For an electrochemical reaction, the Gibbs free energy represents the maximum electrical work that can be done by the reaction

$$\Delta G = -nFE$$

Which gives rise to the **Nernst equation**:

$$E = E^0 - \frac{RT}{nF} \ln \left[ \frac{R}{O} \right]$$

Tells us how the electrode potential under equilibrium conditions (no net current flow) varies with temperature and reactant concentrations.
3. **Electrode kinetics**

**Butler-Volmer kinetics**

Nernst equation gives the electrode potential at equilibrium. Now need to explore what happens when we deviate from equilibrium...

\[ E_{\text{equilibrium}}^{m} = E^{0} - \frac{RT}{nF} \ln \left( \frac{[R]}{[O]} \right) \]

The forward and reverse reaction rates can be expressed as:

\[ i = i_{0} e^{-\frac{\alpha F \eta}{RT}} \quad \text{and} \quad \bar{i} = i_{0} e^{-\frac{(1-\alpha) F \eta}{RT}} \]

\[ i, \bar{i} \] are the current densities for the forward and reverse reactions measured at an overpotential \( \eta = E - E_{\text{equilibrium}} \) where \( E \) is the applied potential.

\( i_{0} \) [A.m\(^{-2}\)] is the exchange current density

\( \alpha \) is the symmetry factor for the reaction \((0 < \alpha < 1)\)

F is the Faraday constant \((96,485 \text{ C.mol}^{-1})\), R is the gas constant \((8.314 \text{ J.K}^{-1}.\text{mol}^{-1})\) and T is the absolute temperature at which the reaction is occurring (K).
3. **Electrode kinetics**

**Butler-Volmer kinetics**

\[ O + e^- \rightleftharpoons R \]

The **net rate of reaction** (net current) can be obtained by subtracting the backward reaction from the forward reaction:

\[ i = i_0 e^{-\alpha F \eta} \quad \text{forward reaction} \]

\[ i = i_0 e^{\frac{(1-\alpha) F \eta}{RT}} \quad \text{backward reaction} \]

\[ i = i - i = i_0 \left( e^{\frac{\alpha F \eta}{RT}} - e^{-\frac{(1-\alpha) F \eta}{RT}} \right) \]

**The Butler-Volmer equation**

for a single-electron transfer reaction
Electrocatalysis

3. Electrode kinetics

The exchange current density

\[ i = i_0 \left( e^{\frac{\alpha nF \eta}{RT}} - e^{\frac{(1-\alpha)nF \eta}{RT}} \right) \]

The exchange current density, \( i_0 \) [A.m\(^{-2}\)] is an intrinsic property of the electrode material or electrocatalyst

Large exchange current \( \rightarrow \) large current for a small applied overpotential
3. **Electrode kinetics**

* e.g. HOR/ORR on Pt

The **exchange current density**, $i_0$ [A.m$^{-2}$] is also different for different reactions on the same material.

**Anode:** Hydrogen Oxidation Reaction (HOR)

$$2H_2(g) \rightarrow 4H^+(aq) + 4e^- \quad E^\circ = 0V$$

Exchange current density $i_0 \approx 1$ mA.cm$^{-2}$

**Cathode:** Oxygen Reduction Reaction (ORR)

$$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l) \quad E^\circ = 1.229V$$

$i_0 \approx 10^{-3}$ mA.cm$^{-2}$ Pt

---

3. Electrode kinetics

The Volcano plot in catalysis

The exchange current density, $i_0$ [A.m$^{-2}$] is an intrinsic property of the electrode material or electrocatalyst.

$$i = i_0 \left( e^{\frac{\alpha nF \eta}{RT}} - e^{\frac{(1-\alpha) nF \eta}{RT}} \right)$$

e.g. Oxygen reduction reaction (ORR)

O$_2$ + 4H$^+$ + 4e$^-$ $\leftrightarrow$ 2H$_2$O  \( E^0 = 1.23 \) V

Pt is the most effective elemental catalyst for ORR.

Electrocatalysis

3. Electrode kinetics
The Sabatier Principle – interpreting the volcano plot

“A catalyst must bind reactants and intermediates with sufficient strength to allow electron transfer, but still allow desorption of reaction products”

e.g. Oxygen reduction reaction (ORR)

Au does not bind $O_2$ strongly enough to allow electron transfer (+ ve change in free energy)

Ni binds $O^-$, $OH^-$ very strongly, such that an irreversible surface oxide is formed (large –ve free energy change)

Pt balances $O_2$ adsorption strength to allow e- transfer, and intermediates are sufficiently unstable for the reaction to complete

3. Electrode kinetics

Why is Pt a good catalyst?

Requirements for effective catalysis of ORR:

- \(d\)-type orbitals with a large radial extent \(\rightarrow\) strengthens interaction
- Partially-filled outer \(d\) shell
- 5d levels above \(O_2\) \(2\pi\) \(\rightarrow\) favourable for \(e^-\) transfer
- Symmetry of \(O_2\) and Pt orbitals should match

- Ru [Kr] 5s\(^1\) 4d\(^7\)
- Rh [Kr] 5s\(^1\) 4d\(^8\)
- Pd [Kr] 5s\(^0\) 4d\(^{10}\) filled d
- Ag [Kr] 5s\(^1\) 4d\(^{10}\) filled d
- Ir [Xe] 4f\(^{14}\) 5d\(^7\) 6s\(^2\)
- Pt [Xe] 4f\(^{14}\) 5d\(^9\) 6s\(^1\) filled d
- Au [Xe] 4f\(^{14}\) 5d\(^{10}\) 6s\(^1\) filled d
4. The problems with Platinum

**Cost** - £33.38/g  
(Source: Kitco 18/11/2010)

For 75kW stack with 0.3mg$_{Pt}$/cm$^2$ and 1W/cm$^2$, require

22.5g of Pt = £750

**Availability**

Worldwide Pt reserves ~ 76,000 Mg

Annual production rate ~ 30 tons / year

**Durability**

- Pt dissolution
- Aggregation & sintering
- Carbon corrosion

Pt/C electrocatalyst
Hydrogen in transport – where are we now?

With the growing volatility of oil prices, Fleet News looks at one possible fuel of the future.

By Dr Bruno G Pollet, head of the Proton Exchange Membrane Fuel Cell Research Group, Centre for Hydrogen and Fuel Cell Research, University of Birmingham

Decarbonising transport is proving to be one of the largest research and development projects of the early 21st century. Motor vehicles are one of the greatest purchases that a person will make, with around 800 million vehicles in use worldwide. The motor industry is therefore one of the largest global forces, employing millions of people and generating a value chain in excess of £2.5 trillion per year. A consequence of this colossal industry is that road transport emits 4.6 billion tonnes of CO2 per year, approximately 17% of mankind’s greenhouse gas emissions.

The ever-increasing demand for personal mobility and near total dependence on liquid hydrocarbons means that emissions reductions from this sector will be particularly difficult.

The development of alternative fuels to petrol and diesel has been ongoing since the 1970s, initially in response to the oil shocks and concerns over urban air pollution. Efforts have gained momentum more recently as the volatility of oil prices and stability of supplies, not to mention the consequences of global climate change have risen up political agendas the world over.

‘The platinum industry has the potential to meet a scenario where HFCVs achieve 50% market penetration by 2050, while an 80% scenario could exceed the expansion capabilities of the industry. Recycled platinum from the transportation sector will be an increasingly critical source of supply.

Hydrogen fuel cell vehicles (HFCV)

Major global automotive manufacturers such as Honda (FCX Clarity – below), Nissan (FCV X-trail) and Daimler-Chrysler have invested significant amounts on R&D for fuel cell vehicles. Some prototypes using a proton exchange membrane fuel cells stack up to 100kW at a cost of £230,000 have ended up having a total vehicle cost of up to £1.7 million.

However, recently Toyota has announced a price tag of £30,000 for its first hydrogen fuel cell vehicle.

Nevertheless, there are three main problems associated with fuel cell vehicles:

- There are insufficient demonstration vehicles in the field to give adequate statistics on performance and cost in ‘real-world’ situations
- Vehicles are custom made and too costly for the consumer who typically only wishes to spend around £10,000 for a ‘green’ vehicle
- Difficulty meeting existing legislation

Another major obstacle to the widespread deployment of fuel cell vehicles is the availability of component materials. For example, if 600 million fuel cell vehicles running at 100kW were produced worldwide, around 40,000 tons of platinum would be required, which is far more than the estimated global resources. In other words, the platinum industry has the potential to meet a scenario where fuel cell vehicles achieve 50% market penetration by 2050, while 80% could exceed the expansion capabilities of the industry based on a US Department of Energy research R&D target of 0.6g/kW with a goal of 0.2g/kW by 2015.

‘Hydrogen is regarded as a sustainable fuel of the future’
Problem with Platinum: *Routes to reduce cost*

Cost breakdown for an 80kW PEMFC stack, assuming Pt cost of approx. £25/g and overall Pt loading 0.25mg.cm\(^{-2}\).\(^1\)

- **Final Assembly**: 12%
- **Membrane**: 5%
- **Bipolar Plates**: 9%
- **Cell**: 7%
- **Electrode**: 51%

---

**Problem with Platinum:**

1. Reduce platinum loading at cathode (g\(_{\text{Pt}}\).cm\(^{-2}\))
   - Target = 0.15mg.cm\(^{-2}\)
2. Increase specific catalytic activity towards reactions (mA.cm\(^{-2}\_\text{Pt}\))
3. Increase Pt surface area at electrodes (cm\(^2\).g\(_{\text{Pt}}\)^{-1})

---

\[1\] Sinha, Lasher *et al* – “Direct Hydrogen PEMFC Cost Estimation for Automotive applications” - TIAX LLC 2008
4. The problems with Platinum

**Cost**
- Pt loading: 0.2 mg.cm\(^{-2}\)
- Pt loading: 0.2 g.kW\(^{-1}\)

**Durability**
- 5000 hours
- <40% loss of catalyst surface area

US Dept. Of Energy targets

**Improve catalyst activity**
- Mass activity: mA.mg\(_{Pt}\)^{-1}
- Specific activity: µA.cm\(_{Pt}\)^{-2}

**Improve catalyst utilisation**
- \(N_{active}/N_{total}\)
- \(N=\) no. of catalyst particles

**Inhibit degradation mechanisms**
5. Improved Pt catalysts for ORR

Reactions occur only at triple-phase boundaries...

...extended throughout catalyst layer by adding Nafion dispersion

Catalyst layers have a complex, composite structure providing:
- Ionic conductivity (H⁺)
- Electrical conductivity (e⁻)
- Active Pt catalyst sites
- Empty space (pore network)
5. Improved Pt catalysts for ORR

Limitations on catalyst utilisation

Nafion cannot penetrate micropores (<2 nm) within the carbon support\(^1\)

Pt particles residing within micropores are inactive

\[ U = \frac{A_{ECSA}}{A_{physical}} \]

1 (Esparbé, Brillas et al. 2009)
2 (Wang, Zuo et al. 2008)
3 (Wikander, Ekström et al. 2007)
4 (Prabhuram, Wang et al. 2003)
5 (Salgado, Antolini et al. 2004)
6 (Janssen, Sitters 2007)
7 (Janssen, Sitters 2007)

Typically 25-60% catalyst utilisation

5. Improved Pt catalysts for ORR – Nafion-Pt/C

Standard catalyst preparation

Pt/C supported catalyst + Nafion dispersion

Nafion-Pt/C catalyst

Nafion-stabilised colloidal Pt + Carbon support
Electrocatalysis

5. Improved Pt catalysts for ORR - Nafion-Pt/C

- Effective distribution of ionomer within Pt agglomerates
- Ionomer network reaches all Pt particles

~100% catalyst utilisation
5. Improved Pt catalysts for ORR
Optimal ionomer content

Standard catalyst preparation
Optimal Nafion content at ~ 33 wt %

Low Nafion loading:
Ionomer network does not extend to all Pt particles

High Nafion loadings:
Poor electrical conductivity
Poor mass transport

5. Improved Pt catalysts for ORR - Nafion-Pt/C

- Optimum Nafion loading

- As-prepared

Optimal connectivity between agglomerates @ 20 wt % Nafion

- Nafion-Pt/C
- E-Tek Pt/C

20 wt % Nafion

33 wt % Nafion

Lower optimum Nafion loading

→ More efficient percolation of ionomer

→ Improved CL porosity?

HySA Systems
Hydrogen South Africa
5. Improved Pt catalysts for ORR
Improving utilisation – nanostructured thin-film (NSTF) catalysts

- NSTF catalyst developed by 3M Corporation
  - Organic whiskers sputter-coated with Pt
  - < 1um thick
  - Thin film of water provides H+ conduction
Electrocatalysis

5. Improved Pt catalysts for ORR

Particle size
Collapse in crystalline structure for Pt particles <1nm → reduced mass-specific activity

Particle shape
Activity varies for different crystal faces e.g. Pt(111) >> Pt(100)


5. Improved Pt catalysts for ORR

- Pt binds O2 and reaction intermediates ~ 0.2 eV too strongly → alloying with another metal can reduce this binding energy (electronic or ligand effect)
- Also get change in Pt lattice parameter (geometric effect)

5. Improved Pt catalysts for ORR

- More stable Pt-M alloys

Nature Chemistry 1, 552-556 (2009)
6. Practical evaluation of electrocatalysts

- Model thin-film catalysed electrode
  - Thin-film catalysed glassy carbon disc electrode (GCE)
  - Standard 3-electrode cell
  - In N₂-purged 0.1M HClO₄

- Electrochemical Surface Area (ECSA) \([m^2_{Pt} \cdot g^{-1}_{Pt}]\)
  - measured using hydrogen underpotential deposition (H\textsubscript{upd})

- Particle size distribution
  - from TEM microscopy

- Pt/C-catalysed GCE working electrode

Electrolyte (0.1M HClO₄)

Reference electrode

Pt wire

Counter electrode

N₂ gas bubbler

Water jacket @ 25°C
Electrocatalysis

6. Practical evaluation of electrocatalysts
Measurement of ECSA
  Cyclic voltammetry on Pt

25mV/s HClO4 0.1M vs SCE
N2 purge CV

$H_{\text{upd}}$ desorption
Pt oxidation
Double layer charging

$H^+$ adsorption
Oxygen reduction

HySA Systems
Hydrogen South Africa
6. Practical evaluation of electrocatalysts

**Electrochemical Surface Area**

- **Pt + H⁺ + e⁻ ⇌ Pt-H<sub>upd</sub>**
- Hydrogen Underpotential Deposition (H<sub>upd</sub>) (1 monolayer)

- Integrate CV to obtain charges \( Q_{\text{H}_{\text{ad}}} \), \( Q_{\text{H}_{\text{des}}} \)

- Charge \( Q_{\text{H}_{\text{ad}}} = Q_{\text{H}_{\text{des}}} = 210 \ \mu\text{C.cm} \text{Pt}^{-2} \)
6. Practical evaluation of electrocatalysts

**Electrochemical Surface Area**

[\text{m}^2_{Pt}.\text{g}^{-1}_{Pt}]

**Assumptions:**

- Pure Pt
- Perfectly crystalline
- 1:1 stoichiometry Pt:H\text{_{upd}}
- Pt surface atomic density, \( \Gamma = 3.48 \times 10^{14} \) atoms/cm\(^{-2} \)

- Faraday constant = 96485 C.mol\(^{-1} \)

\( \Rightarrow \text{H}_{\text{upd}} \) charge = 210\( \mu \)C.cm\(^{-2} \)
6. Practical evaluation of electrocatalysts

**Electrochemical Surface Area**

- ECSA, $A_{ec}$

$$A_{ec} = \frac{Q_{Hupd}}{(210 \cdot 10^4 \cdot L_{Pt} \cdot A_{geo})}$$

e.g.

- $Q_{Hupd} = Q_{Had} + Q_{Hdes}/2$ [µC]
  - $= (150 + 155)/2 = 152.5$ µC

- $L_{Pt} = $ Pt loading [g_{Pt}cm$^{-2}$]
  - $20$ µg_{Pt}cm$^{-2} = 2 \times 10^{-5}$ g_{Pt}cm$^{-2}$

- $A_{geo} = $ GCE geometric area [cm$^2$]
  - $= \pi r^2 = \pi(0.15)^2 = 0.0707$ cm$^2$

- $A_{ec} = 51.4$ m$^2$/g_{Pt}
6. Practical evaluation of electrocatalysts

Durability

- Accelerated stress test
  - Square-wave potential cycling between 0.6 – 1.2 V vs RHE
  - Pt surface repeatedly oxidised (1.2 V) & reduced (0.6 V)
  - 9600 cycles

- Measure ECSA every 1200 cycles

- TEM imaging of catalyst post-degradation gives physical surface area from particle size distribution

![Graph showing potential vs time with labels Pt, Pt-O, Pt-OH, Pt^{2+}](image)
6. Practical evaluation of electrocatalysts

- E-Tek commercial Pt/C

Graph showing cyclic voltammetry data with varying cycle counts and images of physical and ECSA measurements.
6. Practical evaluation of electrocatalysts

- Model thin-film catalysed electrode
  - Thin-film catalysed glassy carbon disc electrode (GCE)
  - Standard 3-electrode cell
  - In O\textsubscript{2}-purged high-purity 0.1M HClO\textsubscript{4}
  - N.B. Not H\textsubscript{2}SO\textsubscript{4} → SO\textsubscript{4}\textsuperscript{2-} anion undergoes specific adsorption on Pt → blocks reaction sites

![Electrode setup diagram]
6. Practical evaluation of electrocatalysts

The Rotating Disc Electrode

- Allows kinetic component of current to be separated from diffusion effects

At a given rotation rate \( \omega \), the diffusion-limited current \( i_D \) is given by the **Levich equation**

\[
i_D = 0.620 \ nFAD \ \frac{2}{3} \ \omega^{1/2} \ \nu^{-1/6} \ C
\]

where
- \( n \) is the no. of electrons transferred per mole of reactant,
- \( F \) is the Faraday constant \( (F = 96485 \ \text{C.mol}^{-1}) \)
- \( A \) is the area of the electrode
- \( D \) is the diffusion coefficient for the electroactive species (eg. \( O_2 \))
- \( \nu \) is the kinematic viscosity of the electrolyte
- \( C \) is the concentration of the electroactive species
6. Practical evaluation of electrocatalysts
Measuring reaction kinetics

- The Levich equation

\[ i_D = 0.620 \times nFAD^{2/3} \omega^{1/2} \nu^{-1/6} C \]
6. Practical evaluation of electrocatalysts

- The Koutecky-Levich equation
  - Relates the measured current $i$ to the diffusion-limited current $i_D$ and the kinetically-controlled component of current, $i_k$

$$\frac{1}{i} = \frac{1}{i_D} + \frac{1}{i_k}$$

$$i_D = 0.620 \cdot n \cdot F \cdot A \cdot D \cdot \frac{2/3}{\omega^{1/2}} \cdot \nu^{-1/6} \cdot C$$

Mixed kinetic/diffusion limited regime

Electrocatalysis

6. Practical evaluation of electrocatalysts

- Extracting $i_k$ from RDE data
  - Method #1: The Koutecky-Levich plot

\[
\frac{1}{i} = \frac{1}{i_k} + \frac{1}{0.620 \cdot nFAD \cdot 2^{1/3} \cdot \omega^{1/2} \cdot V^{-1/6} \cdot C}
\]

\[
i^{-1} = i_k^{-1} + A \cdot \omega^{-1/2}
\]

- Choose several potentials in the mixed kinetic/diffusion region
- Plot $i^{-1}$ vs $\omega^{-1/2}$ (K-L plot)
- Intercept at $\omega^{-1/2} = 0$ corresponds to an infinite mass transport rate

→ No diffusion component

\[i_D \rightarrow 0 \quad \rightarrow i^{-1} = i_k^{-1}\]
6. Practical evaluation of electrocatalysts

- Extracting $i_k$ from RDE data
  - Method #2: Directly from the Koutecky-Levich equation

\[
\frac{1}{i} = \frac{1}{i_k} + \frac{1}{0.620 \ \text{nFAD} \ \sqrt[3]{\omega} \ \sqrt{A} \ \nu^{-1/6} \ \text{C}}
\]

\[
i_k = \frac{i \cdot i_D}{i_D - i}
\]

- Plot $E$ vs $i_k$
Electrocatalysis

6. Practical evaluation of electrocatalysts

- Extracting $i_0$ from $i_k$ data

$$i_k = i_0 e^{\frac{\alpha nF \eta}{RT}}$$

- At high $-ve$ overpotentials, the butler-Volmer equation simplifies to

$$i_k = i_0 e^{\frac{\alpha nF \eta}{RT}}$$

$$\ln i_k = \ln i_0 + \ln e^{\frac{\alpha nF \eta}{RT}}$$

$$\ln i_k = \ln i_0 + \frac{\alpha nF \eta}{RT}$$

$$\eta = \frac{RT}{\alpha nF} \ln i_k - \frac{RT}{\alpha nF} \ln i_0$$

$$\eta = \frac{2.303 \ RT}{\alpha nF} \log i_0 - \frac{2.303 \ RT}{\alpha nF} \log i_k$$
6. Practical evaluation of electrocatalysts

Extracting $i_0$ from $i_k$ data

- The Tafel plot - kinetic current $i_k$ vs. overpotential $\eta$ (or just potential, $E$)

Intercept at $\eta=0$ gives exchange current density $i_0$

The Tafel slope, $b$ [mV/decade]

$$b = \frac{2.303 \ RT}{\alpha n F}$$

$\alpha =$ symmetry factor for rate-determining step

$n =$ no. of electrons in RDS
4. Measuring reaction kinetics

- Extracting $i_0$ from $i_k$ data
- The Tafel plot for ORR on Pt

For ORR on Pt, usually get 2 linear regions in Tafel plot
→ 2 exchange current densities, 2 Tafel slopes
6. Practical evaluation of electrocatalysts

- **2 Tafel slopes for ORR on Pt**

  **On bare Pt surface**

  RDS involves single e—transfer
  → Tafel slope = 120mV/dec

  **Surface oxides** form on Pt around 0.8 V

  \[
  \text{Pt} + \frac{1}{2}\text{O}_2 \rightarrow \text{Pt-O} + e^- \quad E^0=0.88V
  \]

  → Modifies ORR reaction mechanism

  → RDS involves a pseudo 2-electron transfer procedure

  → Tafel slope → ~ 60mV/dec

\[
b = \frac{2.303 \ RT}{\alpha nF}
\]
6. Practical evaluation of electrocatalysts

Rotating Ring-Disc Electrode
- e.g. Measuring peroxide production during ORR
- $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2 \text{H}_2\text{O} \quad E^0=1.23 \text{ V}$
- $\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2 \quad E^0=0.70 \text{ V}$

- Set potential at Pt ring = 1.2 V
- $\text{H}_2\text{O}_2$ generated on disc is oxidised at ring
  $\rightarrow$ Ring current gives measure of $\text{H}_2\text{O}_2$ yield
**Electrocatalysis**

**Summary**

- Electrocatalysts modify the rate of electrochemical reactions occurring at the surface of electrodes.

- The exchange current density, \( i_0 \), for a given reaction is an important intrinsic property of an electrocatalyst, and provides a quantitative measure of catalytic activity.

- Catalytic activity of Pt-based catalysts can be enhanced by modifying composition and morphology.

- For Pt-based catalysts, \( i_0 \), ECSA, durability and selectivity can be measured experimentally using a rotating disc electrode.
A BIG thank you to:

Dr Oliver J. Curnick
Dr Shangfeng Du
Dr Surbhi Sharma
Phil Hamilton
Mariska Hattenberger
James Courtney
and any other members of the UoB Centre for HFCR
who contributed to this presentation!
Thank you

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