Building the “perfect” PEFC fuel cell electrode

Innovative concepts from Electrodes to Stacks

Anthony R. J. Kucernak

Department of Chemistry
Imperial College London
London UK SW7 2AZ
anthony@imperial.ac.uk

H2FC Supergen, University of South Wales, 7-8 September
FLEXIBLE: Building the “perfect” PEFC fuel cell electrode

• One year Project (1 Apr 14 - 31 Mar 15)
• £92k (80% FEC)
• 12 Months PDRA time (Dr Matthew Markiewicz)

Achievements
• Successful transfer of technology to Johnson Matthey
• Three papers published so far (at least four more to come)
• Presentations at three conferences
  • ISE 2014, Lausanne Switzerland, September 2014
  • Summer school on Electrochemistry, Switzerland, August 2014
  • ECS meeting Chicago, April 2015
• Poster at Gordon conference on Fuel Cells, RI, August 2014
• Shown that approach can be utilised to build an low-cost electrolyser
Platinum all over again...

Advances in performance of polymer electrolyte fuel cells

W.L. Gore and Associates, GORE® PRIMEA® MEAs for Transportation (2003).  
How low can we go with Pt loading?

Calculated assuming H₂/Air, 50% RH, 1.5bar backpressure, 0.11/0.02 mg Pt cm⁻² cathode/anode loading. Mass transport losses are imposed on device performance by assuming 

\[ \frac{1}{j_{\text{observed}}} = \frac{1}{j_{\text{Kinetic}}} + \frac{1}{j_{\text{Limiting}}}, \]

and \[ j_{\text{Limiting}} = 2 \text{ A cm}^{-2}. \]
What would an ideal structure look like?

- **Substrate**: thin (< 10 μm), high electrical conductivity
- **Condensed phase**: Fast diffusion of reactants with no condensation
- **Pt/C agglomerate**: 0.5 μm
- **Gas phase**: Fast access of protons

**Diagram**: 200 μm
Use any catalyst

- E.g. 0.16 $\mu$g cm$^{-2}$ Pt (60wt% JM HiSPEC 9100)

10 $\mu$m thick GDL

400 nm diameter hydrophobic pores

Tortuosity = 1
Catalyst Loadings

Uniform homogeneous layer across the macro and micro scale

**ORR: Gaseous diffusion test**

**Catalyst:** 60% Pt/C catalyst, Alfa Aesar, HiSPEC 9100, 4.0 mol dm$^{-3}$ HClO$_4$, $O_2$, 298 K, 10 mV s$^{-1}$, 4.9 µg$_{Pt}$ cm$^{-2}$

220 $O_2$ molecules/Pt/s

$P[O_2]/P[total] = 0.21$

**Carrier gas:**
- Nitrogen
- Helium

Gradient = 1.29
Gradient = 1.04
Gradient = 1.02

$J$ at 0.9 V Vs. RHE
$J$ at 0.7 V vs. RHE
$J$ at 0.4 V vs. RHE

$\log(J_{Specific} / mA cm^{-2})$
$\log(p(O_2) / atm)$
**HOR/HER on Low Pt Loading Electrodes**

Catalyst: 60% Pt/C catalyst, Alfa Aesar, HiSPEC 9100, 4.0 mol dm\(^{-3}\) HClO\(_4\), O\(_2\), 298 K, 10 mV s\(^{-1}\), 2.2 µg\(_{Pt}\) cm\(^{-2}\)

- \(0.55 \text{ A cm}^2\)
- \(\approx 1300 \text{ H}_2 \text{ molecules s}^{-1}/\text{Pt site}\)
- \(8 \text{ A cm}^2 = 19,000 \text{ H}_2 \text{ molecules s}^{-1}/\text{Pt site}\)

\(\Rightarrow\) Limiting current due to adsorption rate limitation

\(\Rightarrow k_{ad} > 4.9 \text{ cm s}^{-1} \) (c.f. \(k_{MT} > 50 \text{ cm s}^{-1}\))
How little platinum can we get away with?

**Two goals**

- Understand performance of catalyst at low loading
  - By extension at high loading
  - Detailed kinetic model of hydrogen and oxygen reactions
- Produce a system which demonstrates the performance of low loading electrodes
  - We decided on an electrolyzer rather than a fuel cell
Hydrogen modelling

- Produced a detailed micro electrokinetic model
  - 4 Parameter fit ($E_a$, 2 kinetic rate constants, 1 kinetic ratio)
    \[ j = F \left( k_{1}^{eq} a_{H_2}^{surf} (1 - \theta_{H_{ad}}(\eta)) + k_{2}^{eq} \theta_{H_{ad}}(\eta) \right) e^{\alpha \eta} \]
    \[ - \left( k_{1}^{eq} a_{H_2}^{surf} \theta_{H_{ad}}(\eta) + \frac{k_{2}^{eq}}{K} (1 - \theta_{H_{ad}}(\eta)) \right) e^{-(1-\alpha)\eta} \]
    \[ \frac{-E_{a} e}{e^{R T} - 1} \]

- Used it to simultaneously fit 19 datasets under different conditions
  - $\eta$
  - pH effect from 0.1 to 4.0 M HClO$_4$
  - $p_{H_2}$ from 0.01-1 bar
  - $T$ from 273 to 333 K

The double trap model

Divergence at high overpotentials.

\[
\begin{align*}
\frac{1}{2} O_2 & \rightleftharpoons O_{ad} \\
\frac{1}{2} O_2 + H^+ + e^- & \rightleftharpoons OH_{ad} \\
O_{ad} + H^+ + e^- & \rightleftharpoons OH_{ad} \\
OH_{ad} + H^+ + e^- & \rightleftharpoons H_2O
\end{align*}
\]

There is more going on during the ORR than RDE would lead you to believe.

http://dx.doi.org/10.1016/j.electacta.2015.04.066
A simple blocking function for the ORR

\[ j(E) = j_{STP} e^{-E_a/R(1/T-1/298.15)} \left( \frac{c}{c^0} \right) (1 - \theta) e^{(E-E^0)/2RT} \]

\[ (1 - \theta) = \frac{1}{1 + e^{\Delta S_{ad}/R} e^{-\Delta H_{ad}/R} e^{-zFE/RT}} \]

\[ E^0_{(ad)} = 0.637 \text{ V vs RHE} \]

\[ O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2 \quad E^0 = 0.695 \text{ V} \]
Modified Kinetic Double Trap

**Double Trap**

\[
\begin{align*}
1/2 \text{O}_2 & \rightleftharpoons \text{O}_{\text{ad}} \\
1/2 \text{O}_2 + \text{H}^+ + \text{e}^- & \rightleftharpoons \text{OH}_{\text{ad}} \\
\text{O}_{\text{ad}} + \text{H}^+ + \text{e}^- & \rightleftharpoons \text{OH}_{\text{ad}} \\
\text{OH}_{\text{ad}} + \text{H}^+ + \text{e}^- & \rightleftharpoons \text{H}_2\text{O}
\end{align*}
\]

**Simplified Peroxoo Pathway**

\[
\begin{align*}
\text{O}_2 + \text{H}^+ + \text{e}^- & \rightleftharpoons \text{HO}_2(aq) \\
\text{HO}_2 + \text{H}^+ + \text{e}^- & \rightleftharpoons 2\text{OH}_{\text{ad}}
\end{align*}
\]

Agreement within 5% throughout potential range

Pt Surface Coverage

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E^0_{\text{fit}}$ / V</th>
<th>$E^0_{\text{lit}}$ / V</th>
</tr>
</thead>
<tbody>
<tr>
<td>RA1: $\frac{1}{2} \text{O}<em>2 + \text{H}^+ + e^- \rightleftharpoons \text{OH}</em>{(ad)}$</td>
<td>1.509</td>
<td>1.86$^a$</td>
</tr>
<tr>
<td>RA2: $\text{O}_2 + \text{H}^+ + e^- \rightleftharpoons \text{HO}_2(ad)$</td>
<td>0.459</td>
<td>0.46$^b$</td>
</tr>
<tr>
<td>RT1: $\text{O}<em>{(ad)} + \text{H}^+ + e^- \rightleftharpoons \text{OH}</em>{(ad)}$</td>
<td>0.899</td>
<td>0.83$^c$</td>
</tr>
<tr>
<td>RT2: $\text{HO}<em>2(ad) + \text{H}^+ + e^- \rightleftharpoons 2\text{OH}</em>{ad}$</td>
<td>2.559</td>
<td>3.26$^d$</td>
</tr>
<tr>
<td>RD: $\text{OH}_{(ad)} + \text{H}^+ + e^- \rightleftharpoons \text{H}_2\text{O}$</td>
<td>0.949</td>
<td>0.6$^c$</td>
</tr>
</tbody>
</table>

$^a$ Calculated using $E^0$ of the ORR, and RD.
$^d$ Calculated from RA1 and RA2.

Oxygen reduction results are intriguing as:

- Polymer Electrolyte Fuel cells appear to suffer from mass transport loses at high overpotential and also low loadings
- Our results show similar loses, but we know that mass transport losses are low
  - In fact the loses look to be electrokinetic in nature
- We may be looking in the wrong area to improve fuel cell performance
What does this mean to PEFC operation?

Calculated assuming $H_2$/Air, 50% RH, 1.5bar backpressure, 0.11/0.02 mg$_{Pt}$ cm$^{-2}$ cathode/anode loading. Mass transport losses are imposed on device performance by assuming $1/j_{observed} = 1/j_{Kinetic} + 1/j_{Limiting}$ and $j_{Limiting} = 2$ A cm$^{-2}$.

Only 78 ug cm$^{-2}$ Pt required for 1W cm$^{-2}$ at 55% efficiency (50% RH, H2/Air, 1.5 bar backpressure).
Pushing reduction of precious metal use in electrochemical devices

- Electrolysers use much higher loadings than PEFCs
  - $>1 \text{ mg}_{\text{PMG}} \text{ cm}^{-2}$
  - Electrolysers use much higher loadings than PEFCs

Prototype electrolyzer
OER Catalyst evaluation

IrO$_2$ (14 nm)
RuO$_2$ (70 nm)
IrRuO$_2$ (ND)
Baseline

20 $\mu$g$_{cat}$ cm$^{-2}$, 1M H$_2$SO$_4$, RT, 50 mV s$^{-1}$

Oxygen evolution
OER Catalyst evaluation
Prototype electrolyzer

Anode: 10 ug cm\(^{-2}\) Ir/C
Cathode: 10 ug cm\(^{-2}\) Pt/C
Electrolyte: 1M HClO\(_4\)
Temperature: RT
\(v: 2 \text{ mV/s}\)

\(~ 1500 \text{ mA mg}^{-1_{\text{cat (total)}}} \) at \(\eta = 0.4 \text{ V}\)
Prototype electrolyzer

Anode: 10 ug cm$^{-2}$ Ir/C
Cathode: 10 ug cm$^{-2}$ Pt/C
Electrolyte: 1M HClO$_4$
Temperature: RT
v: 2 mV/s

$\sim 1500$ mA mg$^{-1}$ cat (total) at $\eta = 0.4$ V

DOE Hydrogen and Fuel Cells Program
FY 2014 Annual Progress Report
Hui Xu (Primary Contact), Brian Rasimick, and Allison Stocks (Giner)
Bryan Pivovar, Shaun Alia, and K. C. Neyerlin (NREL)
Krzysztof Lewinski and Sean Luopa (3M)
Innovative Concepts from Electrodes to Stack

- Three year Project (1 Feb 15 - 31 Jan 18)
- £1M (80% FEC)
- UK: UCL (Prof. D Brett), Loughborough (Dr R. Chen), Imperial
- Korea: KIER (Prof. C.S. Kim); Hanbat (Dr K.Y. Kim); Soongsil (Dr K.W. Park)

Achievements

- Consortium agreement
- Kick-off meeting Imperial 24/7/2015
- Next meeting in Korea 1/11/2015
Innovative Concepts from Electrodes to Stack

- Johnson Matthey Analyst
- NPL
- Intelligent Energy Arcola
- Management (WP0)
  - UK: ICL
  - Korea: KIER

Electrodes (WP1): durability & performance
Bipolar Plate (WP2): enhanced transport and dynamics
Stack (WP3): improved dynamic performance
Roles of UK participants

- **Catalyst and Support**: Imperial College, Amalyst, Johnson Matthey
- **Transport layer**: Imperial College, NPL
- **MEA**: Imperial/UCL, Johnson Matthey
- **CFD of Heat and Mass Transport in Metal foam**: Loughborough
- **Metal Foam and Metal Bipolar Plate**: Imperial/UCL/NPL
- **Imaging and diagnostics**: UCL
- **Stack Construction**: Loughborough, Intelligent Energy
- **Evaluation of Stack and Analysis**: Loughborough/UCL, Arcola
Roles of Korean participants

- Catalyst and Support: Soongsil University
- Catalyst Mass Production: RTX
- MEA: KIER

- CFD of Heat and Mass Transport in Metal foam: Hanbat National Univ.
- Metal Foam and Metal Bipolar Plate: Hyundai Hysco
- Graphite Bipolar Plate: Hankook Tire

- Stack Clamping Method: KIER
- Stack Construction: KIER, Hyundai Hysco
- Evaluation of Stack and Analysis: KIER
Model system – Ag membrane

50 µm thick
5 µm pore size
52% open space

Corrosion and water contact angle

1 M Na$_2$SO$_4$, pH 3 at 80$^\circ$C
Thank you for listening