ADVANCED DIAGNOSIS ON PROTON EXCHANGE MEMBRANE FUEL CELL STACKS

QUENTIN MEYER

SUPERVISORS: DANIEL J.L. BRETT
PAUL ADCOCK, TOBIAS REISCH, OLIVER CURNICK

Supergen, Birmingham, 16-18 December 2013
**INTRODUCTION**

**PROTON EXCHANGE MEMBRANE FUEL CELLS (PEMFC)**

PEM fuel cell operation, macro and micro structure.

GDL : Gas diffusion Layer
**PROJECT OUTLINE**

**THE AIR COOLED (AC), OPEN CATHODE 5 CELLS STACK**

**INTELLIGENT ENERGY AC64-5**

**SPECIFICATIONS:**

- Membrane active area of 60 cm²
- No external heating for the plates or the gases. Self heated fuel cell.
- Combined cooling and oxidant technology.
- Oxygen is supplied using fans blowing air through the channels. Over stoichiometry of 25
- Dry hydrogen

*Picture and simplified scheme of the fuel cell stack showing ‘active’ and ‘cooling’ channels.*

*MEA: membrane electrode assembly. GDL: gas diffusion layer*
FUEL CELL EFFICIENCY
AIR COOLED, OPEN CATHODE FUEL CELL
CURRENT AND TEMPERATURE INTERDEPENDENCE (K TYPE THERMOCOUPLE).

Polarisation and evolution of temperature of the fuel cell stack
FUEL CELL EFFICIENCY

AIR COOLED, OPEN CATHODE FUEL CELL

CURRENT AND TEMPERATURE INTERDEPENDENCE (THERMAL IMAGING).
**PROJECT OUTLINE**

**FUEL CELL TEST STATION FLOW DIAGRAM**

Illustration of the system test rig
Optimum Current Density
FUEL CELL OPERATION
WHERE SHOULD WE OPERATE THE FUEL CELL? AT WHAT CURRENT?

Optimum current density region

Cell voltage / V

Power density / A cm⁻²

Charge transfer

Ohmic

Mass transport

Optimum power density
1. Polarisation curve differentiation:

\[
\frac{\partial U}{\partial j}(j_n) = \frac{\Delta U}{\Delta j}(j_n) = \frac{E(j_{n+1}) - E(j_{n-1})}{j_{n+1} - j_{n-1}}
\]

2. Low frequency impedance:

\[
\frac{\partial U}{\partial j}(j_n) = \frac{\Delta U}{\Delta j}(j_n) = Z_n(\omega \to 0)
\]

\[R_{polarisation} = \frac{\partial E}{\partial j} = \lim_{\omega \to 0} Z(\omega) \quad [2]\]


POLARISATION CURVE DIFFERENTIATION
Polarisation and differentiated polarisation

\[ \frac{\Delta E}{\Delta I} = \frac{E(j_{n+1}) - E(j_{n-1})}{j_{n+1} - j_{n-1}} \]

Graph showing cell voltage and differentiated voltage against current density. The graph includes a linear regression line.

\[ \frac{\Delta E}{\Delta j}(j_n) = \frac{E(j_{n+1}) - E(j_{n-1})}{j_{n+1} - j_{n-1}} \]
**Polarisation Curve Differentiation**

**Low Resolution of the Voltage Readings**

<table>
<thead>
<tr>
<th>Current density / A cm(^2)</th>
<th>Voltage / V</th>
<th>$\Delta V$ / V</th>
<th>$\frac{\Delta E}{\Delta j}$ / $\Omega$ cm(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1E-5</td>
<td>0.95</td>
<td>0.15106</td>
<td>9.00238</td>
</tr>
<tr>
<td>0.00839</td>
<td>0.82575</td>
<td>0.04291</td>
<td>2.55569</td>
</tr>
<tr>
<td>0.01679</td>
<td>0.79894</td>
<td>0.02762</td>
<td>1.64503</td>
</tr>
<tr>
<td>0.02518</td>
<td>0.78284</td>
<td>0.01869</td>
<td>1.11316</td>
</tr>
<tr>
<td>0.03358</td>
<td>0.77132</td>
<td>0.01318</td>
<td>0.78499</td>
</tr>
<tr>
<td>0.04197</td>
<td>0.76415</td>
<td>0.01273</td>
<td>0.74032</td>
</tr>
<tr>
<td>0.05037</td>
<td>0.75814</td>
<td>0.01454</td>
<td>0.86599</td>
</tr>
<tr>
<td>0.05876</td>
<td>0.75172</td>
<td>0.01227</td>
<td>0.73079</td>
</tr>
<tr>
<td>0.06716</td>
<td>0.7436</td>
<td>0.00927</td>
<td>0.55152</td>
</tr>
<tr>
<td>0.07555</td>
<td>0.73945</td>
<td>0.02548</td>
<td>0.50586</td>
</tr>
<tr>
<td>0.08395</td>
<td>0.73434</td>
<td>0.03238</td>
<td>0.38571</td>
</tr>
<tr>
<td>0.12592</td>
<td>0.71397</td>
<td>0.02772</td>
<td>0.3302</td>
</tr>
<tr>
<td>0.1679</td>
<td>0.70196</td>
<td>0.027</td>
<td>0.30971</td>
</tr>
<tr>
<td>0.20987</td>
<td>0.68625</td>
<td>0.02018</td>
<td>0.27038</td>
</tr>
<tr>
<td>0.25185</td>
<td>0.67596</td>
<td>0.0186</td>
<td>0.22156</td>
</tr>
<tr>
<td>0.29382</td>
<td>0.66007</td>
<td>0.01876</td>
<td>0.22347</td>
</tr>
<tr>
<td>0.3358</td>
<td>0.65736</td>
<td>0.01835</td>
<td>0.21861</td>
</tr>
<tr>
<td>0.37777</td>
<td>0.64731</td>
<td>0.01644</td>
<td>0.19583</td>
</tr>
<tr>
<td>0.41974</td>
<td>0.63901</td>
<td>0.01845</td>
<td>0.21977</td>
</tr>
<tr>
<td>0.46172</td>
<td>0.63087</td>
<td>0.01768</td>
<td>0.2106</td>
</tr>
<tr>
<td>0.50369</td>
<td>0.62056</td>
<td>0.01304</td>
<td>0.15533</td>
</tr>
<tr>
<td>0.54567</td>
<td>0.61319</td>
<td>0.01107</td>
<td>0.13186</td>
</tr>
<tr>
<td>0.58764</td>
<td>0.60752</td>
<td>0.027</td>
<td>0.11983</td>
</tr>
<tr>
<td>0.62962</td>
<td>0.60212</td>
<td>0.01175</td>
<td>0.13996</td>
</tr>
<tr>
<td>0.67159</td>
<td>0.59746</td>
<td>0.01458</td>
<td>0.17367</td>
</tr>
<tr>
<td>0.71357</td>
<td>0.59037</td>
<td>0.01531</td>
<td>0.18237</td>
</tr>
<tr>
<td>0.75554</td>
<td>0.58288</td>
<td>0.01441</td>
<td>0.17165</td>
</tr>
<tr>
<td>0.79752</td>
<td>0.57506</td>
<td>0.01892</td>
<td>0.2254</td>
</tr>
<tr>
<td>0.83949</td>
<td>0.56847</td>
<td>0.02859</td>
<td>0.34056</td>
</tr>
<tr>
<td>0.88146</td>
<td>0.55614</td>
<td>0.03586</td>
<td>0.42716</td>
</tr>
<tr>
<td>0.92344</td>
<td>0.53988</td>
<td>0.04742</td>
<td>0.56486</td>
</tr>
<tr>
<td>0.96541</td>
<td>0.52028</td>
<td>0.12028</td>
<td>2.38793</td>
</tr>
<tr>
<td>1.00739</td>
<td>0.49276</td>
<td>0.10207</td>
<td>11.02027</td>
</tr>
</tbody>
</table>

$\Delta V$ is in the same range than the measurement noise

EIS provides a much higher sampling rate (150kHz) and therefore should provide a lower noise.
Low Frequency Impedance
Electrochemical Impedance Spectroscopy

General Principles

Oscillations of voltage and current

Voltage and Current

Relative amplitude

Phase shift

Decreasing frequency

Phase angle

Real Impedance

Imaginary Impedance

Oscillations of voltage and current
EIS allows the various losses in an electrochemical cell to be separated and quantified.
• Low frequency resistance corresponds to the slope of the I-V [1] (performed on methanol oxidation reaction).

• Possible to perform similar experiments in PEM fuel cells, in order to find the optimum resistance, and highlight the minimum in the V-I slope.

The polarisation resistance has been modelled, and the inductive arc is attributed to PtO formation [2], and/or adsorbed intermediate species in the oxygen oxidation reaction [3].

The low frequency intercept can be easily measured and used as an approximation of the polarisation gradient, for steady state conditions of 3 s.

**References**


Electrochemical Impedance Spectroscopy

Nyquist plots over the current density range: 0 to 1 A cm$^{-2}$
Frequency range: 3 kHz to 0.1 Hz
Low frequency intercept for the entire current range: 0 and 1 A cm\(^2\)
EIS provides a better accuracy than the differentiated polarisation curve in the determination of the overall resistance.

Indicates a minimum around 0.55 A cm$^{-2}$.

No need for entire Nyquist measurement, low frequency region is sufficient in order to study the intercept (1 Hz – 0.1 Hz).

Location of the minimum depends on the operating conditions.
APPLICATIONS TO DIFFERENT OPERATING CONDITIONS
Influence of the cathodic flow rate (Intelligent Energy Stack).

- Temperature management
- Membrane water management

Influence of the compression (Pragma System – Collaboration work with Erik Engebretsen- EIL).

- Contact resistance and mass transport limitations
APPLICATIONS: CHANGE OF FLOW RATE INFLUENCE ON THE VOLTAGE

Influence of the flow rate (1.05 m$^3$/min, 1.35 m$^3$/min, 1.65 m$^3$/min) on the voltage
APPLICATIONS:

CHANGE OF FLOW RATE

INFLUENCE ON TEMPERATURE

Influence of the cathode flow rate (1.05 m³/min, 1.35 m³/min, 1.65 m³/min) on the temperature
Applications: Change of Flow Rate

4 Dimensional Representation

I, V, Flow Rate and Temperature

Influence of the flow rate (1.05, 1.35, 1.65 m$^3$ min$^{-1}$ on the voltage and temperature)
APPLICATIONS:
CHANGE OF FLOW RATE
INFLUENCE ON THE CURRENT OF LOWEST RESISTANCE

Influence of the cathode flow rate (1.05 m$^3$/min, 1.35 m$^3$/min, 1.65 m$^3$/min) on the low frequency intercept
APPLICATIONS:
CHANGE OF FLOW RATE
I, V, LOW FREQUENCY RESISTANCE AND FLOW RATE

Influence of the cathode flow rate (1.05 m$^3$ min$^{-1}$, 1.35 m$^3$ min$^{-1}$, 1.65 m$^3$ min$^{-1}$) on the low frequency intercept and temperature
APPLICATIONS:

CHANGE OF FLOW RATE

INFLUENCE ON THE OHMIC RESISTANCE

Influence of the cathode flow rate (1.05 m$^3$/min$^{-1}$, 1.35 m$^3$/min$^{-1}$, 1.65 m$^3$/min$^{-1}$) on high frequency resistance
APPLICATIONS:
CHANGE OF FLOW RATE
I, OHMIC RESISTANCE, FLOW RATE AND TEMPERATURE

Similar results over 50 degrees also been reported on self breathing (no convection) systems [1]. Increase and decrease significantly more important here.

Influence of the cathode flow rate (1.05 m³ min⁻¹, 1.35 m³ min⁻¹, 1.65 m³ min⁻¹) on the high frequency resistance and temperature

APPLICATIONS:
CHANGE OF COMPRESSION LEVEL

- The applied compression can be varied (0 - 2.5 Mpa).
- Enables to study the effect of the compression on the membrane and GDL [1,2], and its influence on the hydration level [3].

APPLICATIONS:
CHANGE OF COMPRESSION LEVEL

Influence of the compression level (0.5 MPa, 1.5 MPa, 2.5 MPa) on the voltage and low frequency resistance.
CONCLUSION

• Low frequency intercept enables to find the optimum current density and the optimum operating conditions.

• Operating near the CLR should improve the durability of the fuel cell, as the effects of the charge transfer resistance and mass transport resistance are minimised.

• The optimum operating region is strongly depending on the operating conditions, and needs to be determined prior to long term endurance tests.
ACKNOWLEDGEMENT

Dan Brett, Paul Shearing, Simon Barrass, James Robinson, Krisztian Ronaszegi

Paul Adcock, Toby Reisch, Oliver Curnick, Sean Ashton
Questions