FUTURE & VESI DISSEMINATION SEMINAR – EPSRC (IDP5)

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14 January 2014

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Loughborough University

Low Carbon Research



AAE FC Research Areas

- Tom Fletcher <u>T.P.Fletcher@lboro.ac.uk</u> is working to reduce the energy consumption of Fuel Cell Hybrid Electric vehicles by the application of dynamic programming and model predictive control.
- Michael Whiteley <u>M.Whiteley@lboro.ac.uk</u> is working on reliability of PEMFC using computational simulation and experimental methods
- Andrey Vasilyev <u>A.Vasilyev@lboro.ac.uk</u> Fuel Cell 'Health Monitoring' for Extended Lifetime Performance
- Ben Davies <u>B.Davies2@lboro.ac.uk</u> Enhancing fuel cell lifetime performance through effective health monitoring and decision support
- Simon Howroyd <u>S.Howroyd@lboro.ac.uk</u> Using a practical methods to design, test and verify a custom fuel cell controller to enable quick and easy hybridisation of a commercial, 'off the shelf', remote controlled plane or UAV.
- Ash Fly <u>a.fly@lboro.ac.uk</u> is studying evaporative cooling of FC stacks for automotive applications
- Manoj Ranaweera <u>R.A.M.P.Ranaweera@lboro.ac.uk</u> Developing a sensor array to assemble a 3D temperature map of a SOFC stack while assuring minimum disturbance to the normal operation of it.
- Indea Choi <u>i.choi@lboro.ac.uk</u> In-situ investigation of curvature change induced by stress in multilayer structure during co-sintering for new design SOFC



Todays Topics

- Introduction to Fuel Cells (FCs)
- Degradation in FCs
 - Mechanisms, Load Cycles & Scaling
- Cathode 'Gas diffusion layer' (GDL) degradation
- Optimising Catalyst layer distribution and its impact on degradation



Fuel cells, and why GDLs?



Typical FC schematic



Polarisation Curves (.cm-²)

(e.g. Woven Vs. Non-woven Cathodes form the same manufacturer)





Peak Power

(e.g. density difference in Cathode GDLs from same manufacturer)





FC Degradation

- With the possible exception of whiskey, all systems degrade over time
- Degradation can be characterised as a decrease in the peak power of the system over time
- Despite the relative simplicity of FCs, there are a huge number of factors involved in their degradation



- <u>Chemical attack (catalyst poisoning, corrosion)</u>
- <u>Chemical blocking (G-II metal ions, Ammonia, sulphonic side chains</u> in Nafion reduced)
- <u>Mechanical stress (excess clamping, abnormal loading, Volume changes in Nafion/gaskets)</u>
- Thermo-Mechanical attack (thermal cycling)
- <u>Direct pathways for reactants through the membrane (Pinholes, cracks etc. lead to run-away O2 / H2 reactions)</u>
- <u>Hydration cycling</u> (flooding of reactant pathways, drying of membranes)
- <u>Short circuit between conductive layers</u> (creep, fibre penetration, membrane thinning)
- Catalyst site reduction (poisoning, ACSA loss)
- <u>GDL</u> (wetting changes, structural changes)



Degradation and Load Cycles

Different load cycles can impact the speed and type of degradation, and this is of critical importance for FCs in automotive applications



IEC/FC testnet & FCTT (wet) Duty Cycles





[1]



DST & NEDC (squared pulses) cycles





[1]



Drive cycles and hybridisation

- The above drive cycles for fuel cell stack testing all assume a '100%' Fuel Cell drive train
- Many in the field of FC research would argue that a FC hybrid (battery / capacitor) system is likely to be preferable
- Assessment of the FC : battery/capacitor ratio needs to be undertaken
 - This would then enable an optimised Drive cycle test regime for the hybrid power train



Alternate Degradation Criteria

- Duty cycles give us a new way to consider the aging of FCs
 - Time at Open Circuit
 - Time at Low Voltage Load
 - Steady State Midrange Load
 - Rapid cycling frequency duty cycle dependant
 - Time at High voltage
 - Air Quality
 - Fuel quality
- Hybridisation can give us a degree of control on the time spent at certain voltage loads





Degradation Mechanisms and Experimentation

- Several authors have attempted to model and verify degradation in FCs, often with some success, but there are difficulties in identifying the contribution of each mechanism
 - Multiple basic factors
 - Different environmental conditions
 - Different duty cycles



Stack - Degradation Mechanisms

40-Cell 2.89 kW 1800 - a, b [45] 5-Cell, 600W 550 8% - 32 10-Cell 7863 11 μV h ⁻¹ - 32 9-Cell, 5kW 1000 5-10 μV h ⁻¹ - 30 40-Cell, 5kW 1000 40 μV h ⁻¹ - 104 15-Cell 2000 20 μV h ⁻¹ c 85 15-Cell 2000 20 μV h ⁻¹ c [49] 2-Cell, 10 kW 400 - 40 [71] 8-Cell 3000 - [72] [71] 2-Cell 1000 0.5 μV h ⁻¹ - [72] 10-Cell 100 - None [72] 12-Cell 100 - None [73] 32-Cell 320 93.36 10 μV h ⁻¹ - [74] 32-Cell 1000 - - [86] [75] 32-Cell 500 2.5 μV h ⁻¹ - [86] <	Stack description	Test length (h)	Voltage decay	Causes of performance loss or failure	Ref.
$\begin{array}{cccc} -5-cell, 600 W & 550 & 8% & - & & & & & & & & & & & & & & & & & $	40-Cell, 2.89 kW	1800	-	a, b	[45]
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	5-Cell, 600 W	550	8%	-	[32]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	10-Cell	7863	11 μV h ⁻¹	-	[97]
$\begin{array}{cccc} 40 \ cell, 5 \ kW & 1000 & 40 \ \mu^1 h^{-1} & - & [104] \\ 15 \ cell & 2000 & 20 \ \mu V h^{-1} & c & [85] \\ 5 \ cell & 2000 & 25 \ \mu^V h^{-1} & c & [87] \\ 60 \ cell, 10 \ kW & 400 & - & d & [49] \\ 2 \ cell & 2000 + & 10 \ \mu^V h^{-1} & c & [71] \\ 8 \ cell & 3000 & - & e & [72] \\ 10 \ cell & 100 & 0 \ p^V h^{-1} & - & None & [72] \\ 10 \ cell & 1100 & - & & None & [72] \\ 10 \ cell & 1300 & 0 \ 5 \ \mu^V h^{-1} & - & [105] \\ 32 \ cell & 3239, 3836 & 10 \ \mu^V h^{-1} & - & [105] \\ 32 \ cell & 668 & 17 \ -36 \ \mu^V h^{-1} & - & [105] \\ 32 \ cell & 668 & 17 \ -36 \ \mu^V h^{-1} & - & [106] \\ 30 \ cell, 5 \ kW & 640 & 72 \ 5 \ \mu^V h^{-1} & - & [38] \\ 30 \ cell, 5 \ kW & 640 & 72 \ 5 \ \mu^V h^{-1} & - & [38] \\ 30 \ cell, 5 \ kW & 640 & 72 \ 5 \ \mu^V h^{-1} & - & [38] \\ 32 \ cell \ 500 \ W \ H^-PEMFC & 658 & 200 \ -520 \ \mu^V h^{-1} & - & [50] \\ 24 \ cell \ 500 \ W \ H^-PEMFC & 658 & 7.6\% & - & [51] \\ 100 \ cell & 500 & - & & f \ g \ 1461 \\ 1 \ W \ Uinit \ A) & 1875 & - & e \ ex \ 800 \ h \ at \ 1178 \ h \ 1001] \\ 1 \ W \ Uinit \ A) & 1875 & - & e \ ex \ 800 \ h \ at \ 1178 \ h \ 1001] \\ 1 \ W \ Stack \ (Unit \ B) & 163 & - & e \ ex \ 800 \ h \ at \ 1178 \ h \ 1001] \\ 1 \ W \ Stack \ (Unit \ B) & 163 & - & e \ ex \ 800 \ h \ at \ 1178 \ h \ 1001] \\ 1 \ W \ Cell \ 500 \ M \ 1000 \ 10 \ W^{h^{-1}} \ den \ 521 \ - & - \ (102) \ 3 \ - & (102) \ - & (102) \ 3 \ - & (102) \ - & (102) \ 3 \ - & (102) \ - & (102) \ 3 \ - & (102) \ 3 \$	9-Cell	1000	5-10 µV h-1	-	[30]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	40-Cell, 5 kW	1000	40 µV h-1	-	[104]
$\begin{array}{ccccc} 15-\text{Cell} & 2000 & 25\mu\text{V}\text{h}^{-1} & \text{c} & \text{d} & [49] \\ 60-\text{Cell}, 10\mu\text{W} & 400 & - & \text{d} & [72] \\ 8-\text{Cell} & 2000+ & 10\mu\text{V}\text{h}^{-1} & - & \text{e} & [72] \\ 8-\text{Cell} & 3000 & - & \text{e} & [72] \\ 10-\text{Cell} & 1100 & - & & \text{None} & [72] \\ 11-\text{Cell} & 13,000 & 0.5\mu\text{V}\text{h}^{-1} & - & & [105] \\ 32-\text{Cell} & 3239, 3836 & 10\mu\text{V}\text{h}^{-1} & - & & [105] \\ 32-\text{Cell} & 2239, 3836 & 10\mu\text{V}\text{h}^{-1} & - & & [105] \\ 32-\text{Cell} & 668 & 17-36\mu\text{V}\text{h}^{-1} & - & & [98] \\ 80-\text{Cell}, 5\text{W} & 640 & 72.5\mu\text{V}\text{h}^{-1} & - & & [98] \\ 80-\text{Cell}, 5\text{W} & 640 & 72.5\mu\text{V}\text{h}^{-1} & - & & [98] \\ 10-\text{Cell} & 200 & - & & & & & [84] \\ 24-\text{Cell}, 500\text{W}\text{HT-PEMFC} & 658 & 200-520\mu\text{V}\text{h}^{-1} & - & & & & [50] \\ 24-\text{Cell}, 500\text{W}\text{HT-PEMFC} & 658 & 7.6\% & - & & & & [50] \\ 10-\text{Cell} & 500 & - & & & & & & & & & & & & & & & & \\ 100-\text{Cell} & 500 & - & & & & & & & & & & & & & & & & &$	15-Cell	2000	20 µV h-1	c	[85]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	15-Cell	2000	25 µV h-1	c	
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8-Cell 3000 - e [72] 10-Cell 1100 - None [72] 17-Cell 13,000 $0.5 \mu V h^{-1}$ - [105] 32-Cell 3209,3836 10 $\mu V h^{-1}$ e [100] 32-Cell 668 17-36 $\mu V h^{-1}$ - [98] 80-Cell,5kW 640 72.5 $\mu V h^{-1}$ - [84] 10-Cell 200 - a [87] 24-Cell,500W HT-PEMFC 658 200-520 $\mu V h^{-1}$ - [50] 24-Cell 500W HT-PEMFC 658 7.6% - [51] 100-Cell 500 - e at 800h, h at 1178 h [10] 11W (Unit A) 1875 - e at 800h, h at 1178 h [10] 11W stack (Unit B) 1653 - e at 800h, h at 1178 h [10] 3-Cell 800 60 $\mu V h^{-1}$ - - [46] 8-Cell 5800 1 $\mu V h^{-1}$ - - [102] 3-Cell, 100 kW 1000 20 $\mu V h^{-1}$ - - [102]	2-Cell	2000+	10 μV h ⁻¹	-	[71]
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$\begin{array}{cccccccccccccccccccccccccccccccccccc$	10-Cell	1100	-	None	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	17-Cell	13,000	0,5 μV h ⁻¹	-	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	64-Cell, 1 kW	500	27 µV h ⁻¹	-	[105]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	32-Cell	3239, 3836	10 µV h-1	e	[100]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	36-Cell	668	17-36 µV h-1	-	[98]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	80-Cell, 5 kW	640	72,5 μV h ⁻¹	-	[84]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	10-Cell	200	-	a	[87]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	24-Cell, 500 W HT-PEMFC	658	200–520 μV h ⁻¹	-	[50]
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	24-Cell 500 W HT-PEMFC	658	7.6%	-	[51]
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	100-Cell	500	-	f, g	[46]
1 kW stack (Unit B) 1653 - e at 1460 h, no h 3-Cell 800 $60 \mu V h^{-1}$ d [52] 50-Cell 2500 $20 \mu V h^{-1}$ - - 8-Cell 5800 $1 \mu V h^{-1}$ - [19] 8-Cell, 20 kW 11,000 $2 \mu V h^{-1}$ - [102] 3-Cell, 100 kW 1000 $10 m V h^{-1}$ after 350 h, 0.22 m V h^{-1} after 400 h - [67] 3-Cell, 100 kW 1000 $10 m V h^{-1}$ after 350 h, 0.22 m V h^{-1} after 400 h - [67] 3-Cell, 100 kW 700 $1 m V h^{-1}$ after 350 h, 0.22 m V h^{-1} after 400 h - [67] 3-Cell, 100 kW 700 $1 m V h^{-1}$ after 350 h, 0.22 m V h^{-1} after 400 h - [67] 3-Cell, 100 kW 700 $1 m V h^{-1}$ after 350 h - - [67] 3-Cell 1000 - h at 450 h [68] [68] 6-Cell 1200 $0.128 m V h^{-1}$ - - [106] 20-Cell, 0.4 kW 5000 $1.5 \mu V h^{-1}$ - - [106] 4-Cell 10	1 kW (Unit A)	1875	-	e at 800 h, h at 1178 h	[101]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1 kW stack (Unit B)	1653	-	e at 1460 h, no h	
	3-Cell	800	60 μV h ⁻¹	d	[52]
8-Cell 5800 $1\mu V h^{-1}$ - [19] 8-Cell, 20 kW 11,000 $2\mu V h^{-1}$ - [102] 3-Cell, 20 kW 1000 $2\mu V h^{-1}$ - [102] 3-Cell, 100 kW 1000 $10 m V h^{-1}$ after 350 h, 0.22 m V h^{-1} after 400 h - [67] 3-Cell, 100 kW 700 $1m V h^{-1}$ in first 500 h - - 3-Cell 1000 - h at 450 h [68] 6-Cell 1200 0.128 m V h^{-1} a, then h at 800 h [86] 20-Cell, 0.4 kW 5000 $1.5 \mu V h^{-1}$ - [106] 4-Cell 1000 $0.8 - 0.26 m V h^{-1}$ thinner membranes a, e [88]	50-Cell	2500	$20 \mu V h^{-1}$	-	
8-Cell, 20 kW 11,000 $2\mu V h^{-1}$ - [102] 3-Cell, 100 kW 1000 $10 m V h^{-1}$ after 350 h, 0.22 m V h^{-1} after 400 h - [67] 3-Cell, 100 kW 700 $1m V h^{-1}$ in first 500 h - - 3-Cell 1000 - h at 450 h [68] 6-Cell 1200 0.128 m V h^{-1} a, then h at 800 h [86] 20-Cell, 0.4 kW 5000 1.5 $\mu V h^{-1}$ - [106] 4-Cell 1000 0.026 m V h^{-1} thinner membranes a, e [88]	8-Cell	5800	1 µVh-1	-	[19]
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3-Cell, 100 kW 700 1 mV h ⁻¹ in first 500 h - 3-Cell 1000 - h at 450 h [68] 6-Cell 1200 0.128 mV h ⁻¹ a, then h at 800 h [86] 20-Cell, 0.4 kW 5000 1.5 μV h ⁻¹ - [106] 4-Cell 1000 0.18-0.26 mV h ⁻¹ thinker membranes a, e [88]	3-Cell, 100 kW	1000	10 mV h ⁻¹ after 350 h, 0.22 mV h ⁻¹ after 400 h	-	[67]
3-Cell 1000 - h at 450 h [68] 6-Cell 1200 0,128 mV h^{-1} a, then h at 800 h [86] 20-Cell, 0,4 kW 5000 1.5 μ V h^{-1} - [106] 4-Cell 1000 0,18 - 0.26 mV h^{-1} thinner membranes a, e [88]	3-Cell, 100 kW	700	1 mV h ⁻¹ in first 500 h	-	
6-Cell 1200 $0.128 \text{mV} \text{h}^{-1}$ a, then h at 800 h [86] 20-Cell, 0.4kW 5000 $1.5 \mu V \text{h}^{-1}$ - [106] 4-Cell 1000 $0.8 - 0.26 \text{mV} \text{h}^{-1}$ thinner membranes a, e [88]	3-Cell	1000	-	h at 450 h	[68]
20-Cell, 0.4 kW 5000 $1.5 \mu V h^{-1}$ - [106] 4-Cell 1000 $0.18-0.26 m V h^{-1}$ thinner membranes a, e [88] 0.09 m V h^{-1} thicker membranes a, e [88]	6-Cell	1200	0,128 mV h ⁻¹	a, then h at 800 h	[86]
4-Cell 1000 $0.18-0.26 \text{ mV}\text{h}^{-1}$ thinner membranes a, e [88] $0.09 \text{ mV}\text{h}^{-1}$ thicker membranes	20-Cell, 0.4 kW	5000	1.5 μV h ⁻¹	-	[106]
	4-Cell	1000	0.18–0.26 mV h ⁻¹ thinner membranes 0.09 mV h ⁻¹ thicker membranes	a, e	[88]

a - catalyst degradation.

b - MEA contamination.

c – Pt surface area loss,

d - insufficient water removal,

e – crossover leak,

f - increased internal resistance,

g – decreased active area, h – membrane or cell failure,

PEMFC stack Durability [2]



Degradation Mechanisms and Experimentation

- Degradation mechanisms do not scale uniformly
 - Fundamental scale (e.g. Micron and smaller scale effects – Note pm, nm & µm scale models have issues informing each other)
 - E-chem lab scale (e.g. 1cm⁻² rotating disc electrode)
 - Small Test bench scale (e.g 25cm⁻² single cell)
 - Large Test bench scale (e.g 25cm⁻² stack of 5 cells)
 - Stack scale (e.g. 'real life' scale for most automotive applications with 200 cells or more)



Standardising New Test and Characterisation Procedures for PEMFCs in Support of Longer Life and Improved Reliability

Poster(s) Introduction



Focus on Cathode GDL - Matrix plot



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ANOVAR Model (Wmax.cm⁻²) from 'R'®

Coefficients:					
	Estimate	Std. Error	t value	Pr(> t)	
(Intercept)	0.4922468	0.0527059	9.339	5.55E-14	***
H ₂ Oangle	-0.0003779	0.0002174	-1.739	0.08644	
MPL Mod'	0.0398119	0.0103118	3.861	0.000247	***
PTFE wt%	-0.2254306	0.0731867	-3.08	0.002942	**
RH%	-0.0011252	0.0004949	-2.274	0.026019	*
Structure Mod	-0.0141882	0.0083572	-1.698	0.093942	
% pores	-0.0014299	0.0003463	-4.129	9.81E-05	***



Theoretical Distributed catalyst layers



Jain (2009), and other authors, have put forward both 2D and 3D catalyst distribution models as a method for optimising the performance of fuel cells and reducing their fabrication costs



Actual Distributed Catalyst Layers





100µm



References

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- MILLER, M. and BAZYLAK, A., 2011. A review of polymer electrolyte membrane fuel cell stack testing. *Journal of Power Sources*, **196**(2), pp. 601-613.

With thanks to

Ahmad El-kharouf (UoB), Ash Fly (LU) & Billy Wu (ICL)



Thank you for listening

QUESTIONS?

