Localized degradation of membrane-electrode assemblies by using in-situ reference electrode array fuel cell

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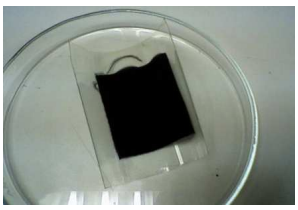
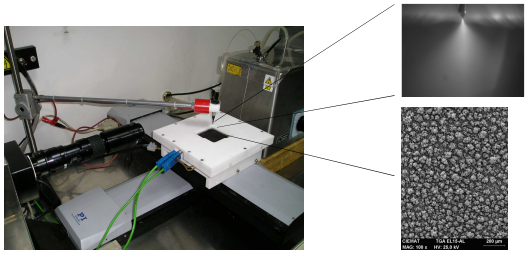
Degradation of a polymer electrolyte membrane fuel cell (PEMFC) with electrosprayed cathode catalyst layers (ECLs) is investigated during cyclic start-up and shut-down events. The study is carried out within a single cell incorporating an array of reference electrodes that enables measurement of cell current as a function of local cathode potential (localised polarization curves). The ECLs are characterised by a highly porous morphology that provides superhydrophobic character, which improves water transport in the cathode and homogeneity of cell response. Accelerated degradation of the cell by start-up/shut-down cycling gives rise to inhomogeneous performance loss as reflected by the localized polarization curves. Performance losses are more severe close to the gas outlet, and occur predominantly during start-up. The degradation consists primarily of loss of cathode catalyst activity and increase in cell internal resistance, which is attributed to carbon corrosion and Pt dissolution in both anode and cathode. Cells with electrosprayed cathode catalyst layers showed lower degradation rates during the first 150 cycles, compared with those with a conventional gas diffusion electrode. Afterwards, the degradation rate is dominated by the Pt/C ratio in the cathode catalyst layer.



Electrospray preparation of MEAs



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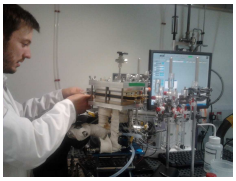
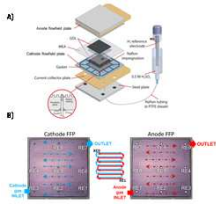
Catalyst layer deposition parameters

- Pt/C catalysts: 20, 40, 60 Pt wt%
- Suspension: Pt/C + ionomer (Nafion), in isopropanol (1 wt% solids)
- Substrate: Nafion 212R
- Catalyst layer: 0.25mg$_{Pt}$·cm^{-2}, 15 wt% ionomer
- Active area: 7x7 cm^2
- Electrospray: V_{DC}= 10kV, T_{subs}=50ºC, T_{susp}=22ºC, P_{susp}=0.1bar

PEMFC set-up for local cathode potential measurements





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PEMFC Mounting

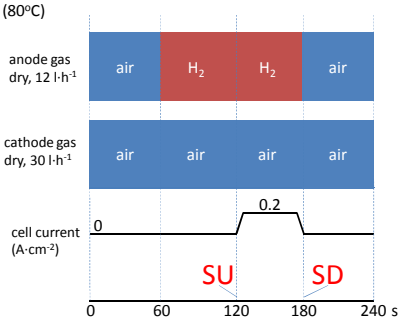
- CCM expansion in 0.5M H_2SO_4, 22ºC, 2h
- Cathode CL: electrosprayed Pt/C, 0.25 mg/cm^2
- Cathode GDL: ELAT GDL LT1200W (BASF)
- Anode: ELAT GDE LT250EWALTSI 30wt% Pt/C, 0.25 mg/cm^2 (BASF)
- **For the "standard" cell (GDE30):**

Membrane Nafion 212R
Anode and cathode: ELAT GDE LT250EWALTSI 30wt% Pt/C, 0.25 mg/cm^2 (BASF)

Test conditions

- Normal cell operation = 80 C, 100% RH, 2:2 stoichiometry, 2bar$_a$ backpressure
- Conditioning overnight at 200 mA/cm^2
- Polarisation curves obtained at (a) 2bar$_g$ and (b) 1bar$_g$ backpressures
- ECSA measured at 35 C, 100% RH, 1bar$_a$ backpressure.
- Start-stop cycling procedure: 80 C, 100%RH, atmospheric pressure, open circuit, anode gas was switched between H_2 and Air at 60 s intervals for 20 cycles.

Start-up and shut-down cycle

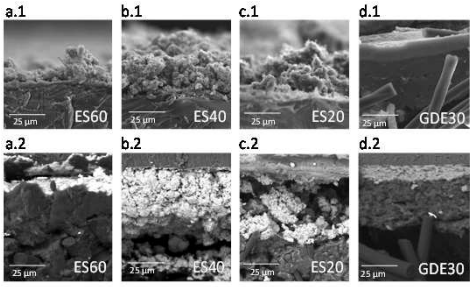


MEAs characteristics

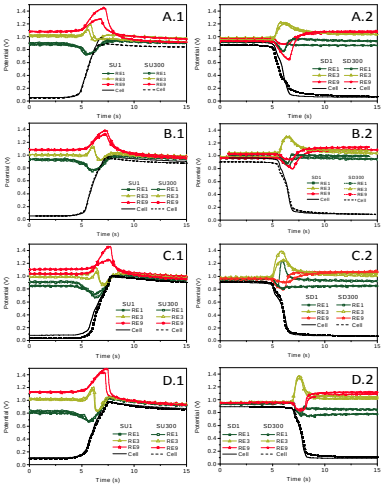
	MEA	Anode	Cathode	Cathode CL characteristics					
				Thickness µm	Pt load mg·cm^{-2}	Pt conc. mg·cm^{-3}	Pt/C	d_{Pt} (XRD)[a] nm	ECSA m^2·g$_{Pt}^{-1}$
A	ES60	GDE30	ES60 (Pt(60wt%)/HSAAC on NRE212) + GDL	10±5[b]	0.25	250	1.50	2.8	43
B	ES40	GDE30	ES40 (Pt(40wt%)/V-XC72 on NRE212) + GDL	45±10[b]	0.25	56	0.67	3.4	34
C	ES20	GDE30	ES20 (Pt(20wt%)/V-XC72 on NRE212) + GDL	40±10[b]	0.25	63	0.25	2.7	36
D	GDE30	GDE30	GDE30 (Pt(30wt%))/V-XC72)	12±1	0.25	21	0.43	5.0	42

[a] As measured by analysing the broadening of the X-ray diffraction line corresponding to the [2 0 0] plane of Pt crystallites at 2Θ = 67.5°.
[b] Due to the large porosity and complex internal structure of these layers this value is given as a rough estimation.

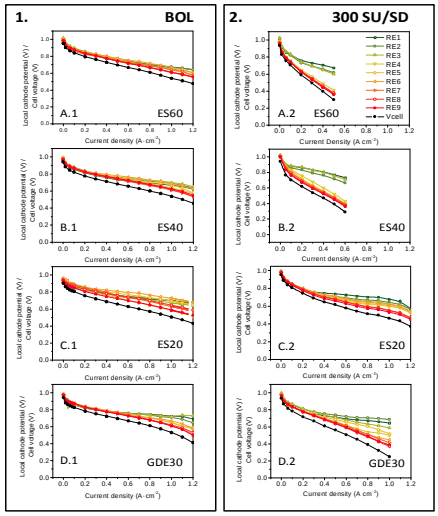
SEM cross sections BOL



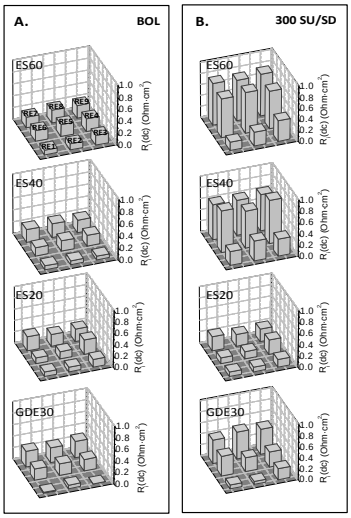
Transient voltage response



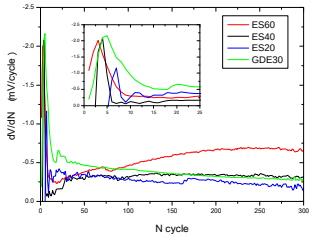
Polarization curves



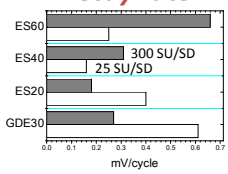
DC internal resistance



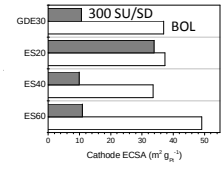
Cell voltage decay rate



Decay rate



Active area



Conclusions

- Degradation rate under SU/SD cycling is lower with electrosprayed cathodic CL until 75 cycles.
- After 300 cycles, degradation rate follows Pt/C ratio in the catalyst.
- Height and the length of the transient voltage during SU/SD show little relation with the degradation rate.
- Degradation is more accute in the MEA zones close to the gas outlet.