Methods for investigations on fuel cell degradation processes at Fraunhofer ISE

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Abstract

One of the key aspects in developing optimised fuel cell systems is to identify the major processes that are responsible for the decrease of the fuel cell performance during life time. To figure out the interaction of deployed materials and degradation effects, we have the possibility to resort to different ex-situ and in-situ analytical techniques.
An overview of these tools used at Fraunhofer ISE is given below.

In-situ measurement

Spatially resolved current density and impedance

Figure 1 illustrates impedance spectra in selected sections of a high temperature PEM fuel cell for three stoichiometries. Close to the air outlet, the spectra show an increased low frequency arc caused by oxygen mass transport problems with low stoichiometries. A continuously insufficient oxygen supply can contribute to an accelerated aging of CCM.

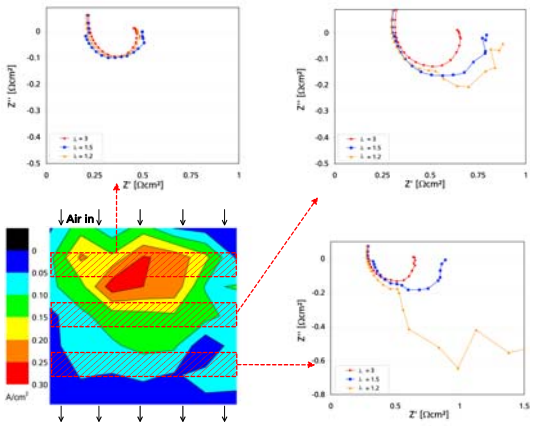
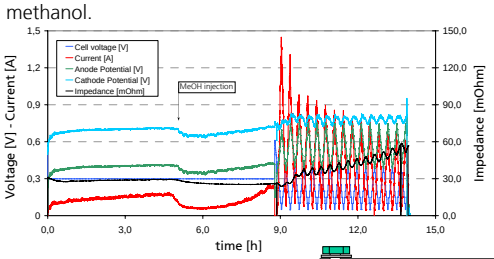


Figure 1: Spatially resolved current density and impedance of a segmented high temperature PEM fuel cell in dependence of various oxygen stoichiometries. The depicted current density distribution was recorded at 160°C, λ_{Oxygen} = 1.2 with a parallel flowfield.
The current density is decreasing from air inlet to outlet, due to oxygen depletion along the channels.

Reference cell analysis with impedance measurement

Reference electrode measurements can separate cell performance deterioration over time into cathode and anode degradation.
Figure 2 exemplifies a part of this test in a vapour-fed DMFC with pure methanol.



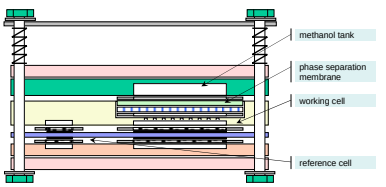


Figure 2: Characterisation plot of vapour-fed DMFC (above) and test cell scheme (left). After refilling methanol, the impedance decreases and the electrode potentials rise simultaneously due to the lower resistance of the CCM. With the methanol consumption after several hours test, the impedance increases and the cell performance declines.

Ex-situ measurement

Energy-dispersive X-Ray spectroscopy (EDX)

EDX technology is used to investigate CCM and GDL samples after long term tests (see Figure 3). The detected effects can explain a drop in power density caused by the aging of the used materials.

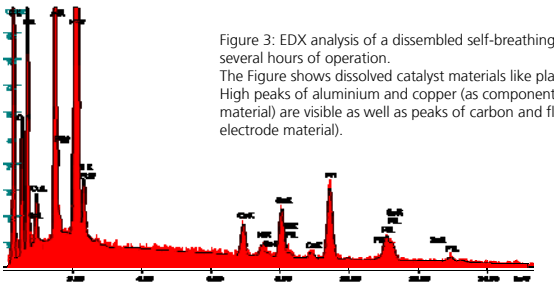


Figure 3: EDX analysis of a dissembled self-breathing DEFC cathode after several hours of operation.
The Figure shows dissolved catalyst materials like platinum or cobalt. High peaks of aluminium and copper (as component of the test cell material) are visible as well as peaks of carbon and fluorine (elements of electrode material).

Environmental Scanning Electron Microscopy (ESEM)

The local distribution of different elements can be detected and visualised by ESEM (shown in Figure 4). With this analytical instrument, degradation effects like platinum migration through the membrane, carbon corrosion or water in cross sections or top views of fuel cell samples can be visualised.

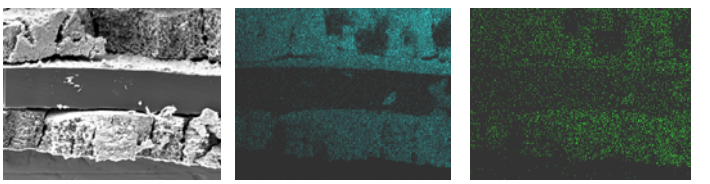


Figure 4: ESEM / EDX analysis of a cross-sectioned 5-Layer-MEA (grey) including element visualisation (Ru green, Pt blue).
The pictures show after long term tests no platinum migration but a complete ruthenium dissolution in GDL and CCM.

Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

By using ICP-MS (shown in Figure 5) cathode product water and anode methanol or ethanol solutions can be analysed. Contaminations from fuel cell system , e.g. bipolar plates, seals, screws, etc., can be detected (see Table 1).

			A	C	A	C	A	C	A	C	
Element / conc. [µg/l]	DI-H_2O fresh	Ref. DI-H_2O	Separator plate untreated in DI-H_2O		Separator plate plasma treated in DI-H_2O		Separator plate glass bead treated in DI-H_2O		Separator plate glass bead treated in DI-H_2O + HCl		DI-H_2O fresh
B	0	0.2	1	2	2	3	92	99	54	54	0.3
Na	0.6	4	15	11	44	16	2100	2300	2100	1800	1
Mg	0.2	5	54	11	27	96	620	630	1000	910	0.5
Si	11	16	110	63	100	150	7000	6400	31000	30000	6
K	5	6	6	5	17	8	98	100	110	100	5
As	0	0	0	0	0	0	22	20	15	13	0

Table 1: ICP-MS analysis of PPS separator plates (A: Anode plate, C: Cathode plate) for a DMFC inlaid in deionised water.
The analysis result shows that a glass bead treated conditioning is unsuitable due to higher amount of B, Na, Mg, Si, K, As ions, causing degradation.

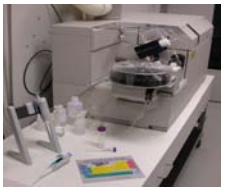


Figure 5: ICP-MS equipment.