



DEVELOPMENT OF AN OXYGEN ELECTRODE FOR A UNITIZED REGENERATIVE PEM FUEL CELL

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1 Introduction

Regenerative fuel cell systems are used to store energy from renewable sources such as solar energy or wind energy. Such systems consist of a separate electrolyser and a fuel cell. In a unitised regenerative PEM fuel cell both functions are combined in one stack allowing a significant cost and volume reduction. The technology will open new markets in rapidly growing sectors. The hydrogen storage system will replace batteries in UPS and diesel generators in autonomous power supplies. The aim is to achieve a roundtrip efficiency of at least 40%. In order to achieve this roundtrip efficiency the current densities in both the electrolyser as well as in the fuel cell mode must be limited to 100 mA/cm².

The activities for stack development for reversible fuel cells have focused on the examination of various electrode compositions. A bifunctional catalyst is required; unsupported platinum can be used as a catalyst during the fuel cell mode and iridium and ruthenium are suitable as a catalyst when operating under electrolyser conditions. Since carbon compounds are not stable under electrolysing conditions, ECN has focused on the development of a novel titanium gas diffusion layer and support of the oxygen side of the cell.

2 Experimental

2.1 Electrode development

Mixtures of catalysts (platinum black (Chempur), iridium (Agussa)) and Nafion have been evaluated as well as platinum deposited on iridium, by hydrolysis of platinum acid, followed by fixation and reduction on iridium. Electrode optimisation was initially done using Etek and SGL gas diffusion layers on single cells of 8 cm². The structure of the catalyst layer, made with the optimum composition, has been examined with SEM/EDX and Hg-porosimetry.

2.2 Gas diffusion layer

The gas diffusion layer consists of a porous support structure with a thin and dense layer on top of it. The support structures examined are:

- ECN made porous titanium, made of sintered titanium powder, see figure 1
- Porvair titanium foam
- Bekinit sintered and unsintered titanium felt

Titanium foam of Porvair was too brittle for Membrane Electrode Assembly (MEA) fabrication and was not used as a suitable gas diffusion support structure.

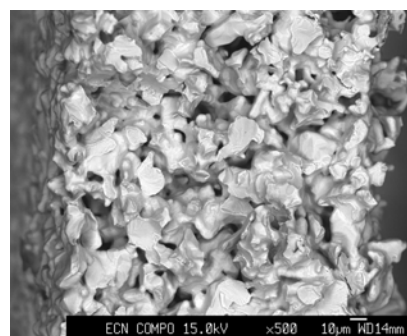


Figure 1. SEM cross section of ECN porous titanium

Titanium is hydrophilic by nature and in order to have a proper water and gas management during both electrolyser and fuel cell operation modes, the gas diffusion layer needs to be made hydrophobic to a certain extent. Several methods were examined to render the porous titanium gas diffusion support structure hydrophobic:

- Impregnation (Dyneon TF 5032 PTFE, 3M Novec ECG-1700)
- Plasma coating (C_3F_6)

The morphology of the gas diffusion layer has been examined with SEM/EDX and Hg-porosimetry. *In situ* Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy measurements (EIS) have been conducted for further characterisation of the interaction between the gas diffusion layer and the electrode.

2.3 MEA testing

The MEA of a reversible fuel cell may comprise of a standard fuel cell anode (SGL, Pt on C), Nafion electrolyte and the specific titanium gas diffusion layer with a Pt/Ir electrode. The electrode is applied directly to the titanium structure. After drying, a hot press step is required to bond the electrode plus gas diffusion support structure to the electrolyte and a standard PEMFC anode. The MEA (7 cm^2) is subsequently built in a test station for both electrolyser and fuel cell mode tests. An example of test conditions is shown in table 1.

Table 1. Test conditions

Fuel cell mode		Electrolyser mode	
Cell temperature	70°C	Cell temperature	80°C
Gases humidified	yes	Water flow	10 g/hr
Stoichiometry O_2	3	Pressure	4 barg
Stoichiometry H_2	2	Constant current	100 mA/cm ²
Pressure	1 barg		
Constant current	100 mA/cm ²		

3 Results

3.1 Electrode development

Various MEA's have been tested with varying Pt and Ir ratios as well as different Nafion concentrations in the ink, see figure 2. The tests indicate that a combination of platinum powder and iridium powder with a ratio of 1:2 and a Nafion content of 30% is the optimal combination.

Platinum on iridium combinations all shows a relatively low performance. Decreasing the platinum to iridium ratio results in an improved but still relatively low performance. At a ratio of 1:25 the platinum still forms a layer around the iridium powder. For the iridium supported platinum approach it can be concluded that the specific area (m^2/g) of the substrate is too low when being used as a bifunctional catalyst.

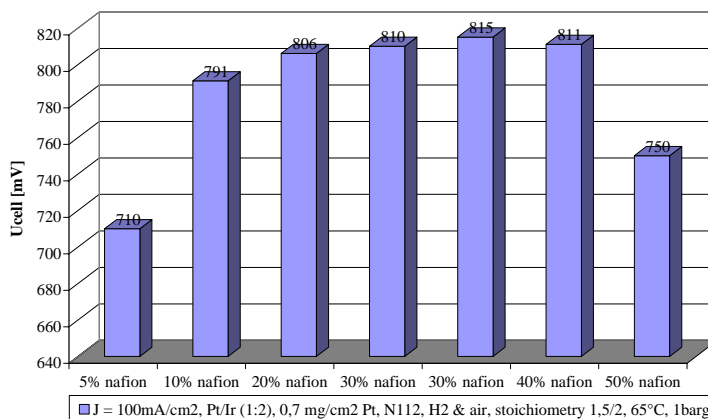


Figure 2. Cell performance of different Nafion contents in electrodes

3.2 Gas diffusion layer

SEM/EDX analysis showed that platinum particles on porous titanium structures were not homogeneously dispersed and due to the morphology of the titanium gas diffusion structure the electrode could sink into the gas diffusion layer. This could result in higher activation energies, diffusion limitations and a lower effective electrocatalytic surface area. CV measurements confirm that a non ideally dispersed ink that sinks into the gas diffusion layer results in a lower Effective Electrocatalytic Surface Area (EESA) at the 3-phase boundary, as can be seen in table 2 for the measurements of ink type I. Improved ink compositions (type II) using a different solvent mixture and additives enhance the surface area.

Table 2. Results of CV coulometric determined Pt surface areas

	Ink type	EESA [m^2/g]		Ink type	EESA [m^2/g]
SGL31BC	I	5.04	SGL31BC	II	14.63
ECN Ti	I	0.80	Bekinit sintered Ti felt	II	8.24

The difference in surface area for ink type I is reflected in the EIS measurements (figure 3). It is expected that for ink type II the impedance (figure 4) for all three GDL's should be the same. The difference in impedance is most likely due to a reduced surface area due to water retention.

Impregnation of the titanium gas diffusion support structure, in order to render its ex- and internal surface hydrophobic, with a PTFE solution was partially successful. Promising results have been obtained with low-pressure plasma deposition and impregnation with a fluoroacrylate solution. Fluor is found throughout the complete porous structure (SEM/EDX). A thin microporous gas diffusion layer on top of the gas diffusion support may be required and can be prepared with different metals like titanium and iridium. This thin layer can improve the cell performance in both modes because of a higher

Effective electrocatalytical surface area at the 3-phase boundary, better gas diffusion and improved reactant removal. This thin gas diffusion layer needs to have both hydrophobic as well as hydrophilic sites in order to have proper gas and water management in both operation modes. A polymer binds metallic powders. This polymer can render the thin layer partly hydrophobic. Different combinations of these metals and polymer binders are under evaluation at this moment. An example of such a microporous layer is shown in figure 5.

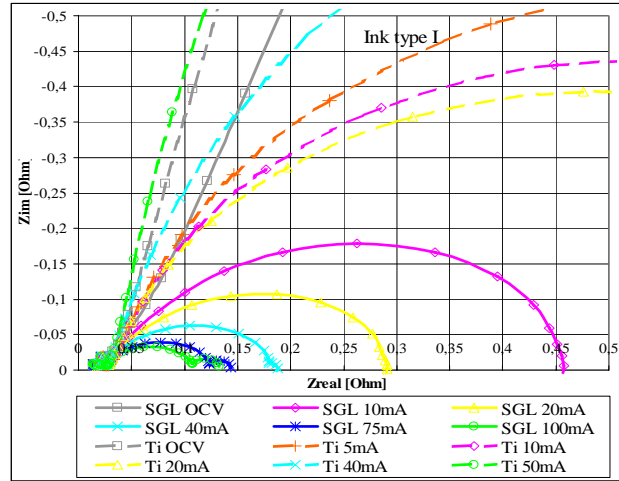


Figure 3. EIS measurements ink type I

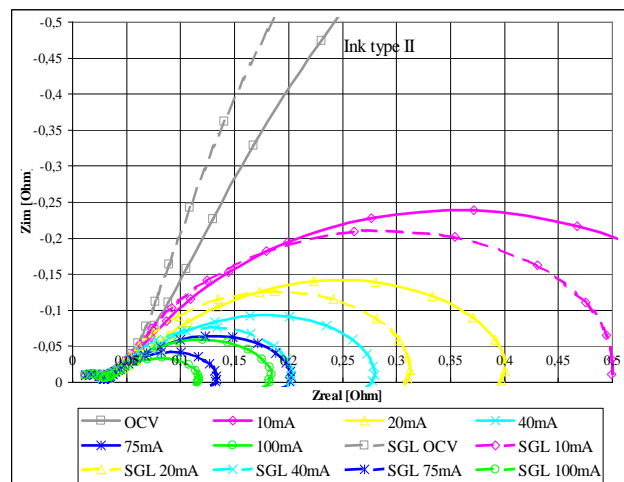


Figure 4. EIS measurements ink type II

3.3 MEA testing

Test data shown in figure 6 show that stable operation in both fuel cell and electrolyser mode is possible. This means that the cell does not flood during fuel cell operation, yet enough water can diffuse through the gas diffusion support during the electrolysis mode. The roundtrip efficiency in this case is $0.8V/1.8V = 44\%$.

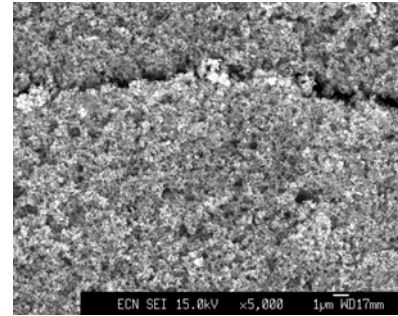


Figure 5. SEM photo of microporous layer

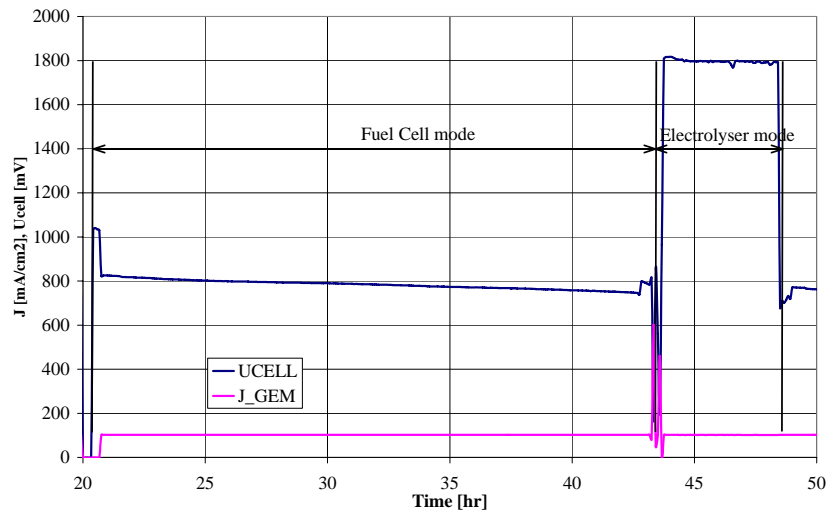


Figure 6. MEA testing in fuel cell and electrolyser mode

4 Acknowledgements

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Development of an oxygen electrode for a unitized regenerative PEM fuel cell

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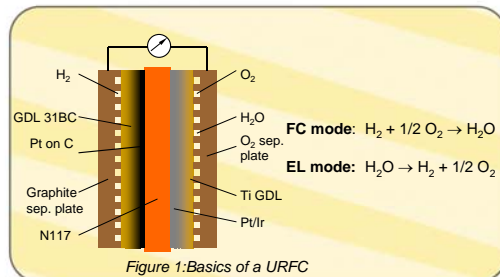
Introduction:

Regenerative fuel cell systems can be used to store energy from renewable sources such as solar energy or wind energy. Such systems consist of a separate electrolyzer and a fuel cell. In a Unitized Regenerative PEM Fuel Cell (URFC) both functions are combined in one stack, allowing a cost and volume reduction.

The URFC system can replace batteries in UPS systems and diesel generators in autonomous power supplies. Advantages are less maintenance and a longer life time. A disadvantage is the energy efficiency. The aim of the project is to achieve a roundtrip efficiency of at least 40%.

Basics of a unitized regenerative PEM fuel cell:

URFCs can store and produce energy using a reversible electrochemical process: In electrolysis (EL) mode water is split into hydrogen and oxygen by electricity, in fuel cell (FC) mode hydrogen and oxygen is combined to water with the production of electricity.



Experimental:

Mixtures of catalysts (platinum black (Chempur), iridium (Agussa)) and Nafion have been evaluated. Electrode optimization was initially done using GDL 31BC gas diffusion layers (SGL Technologies GmbH) on single cells of 8 cm². A Nafion membrane was hot pressed in order to bond the electrodes plus gas diffusion supports.

Fuel cell mode		Electrolyser mode	
Cell temperature	70°C	Cell temperature	80°C
Gases humidified	yes	Water flow	10 g/hr
Stoichiometry O ₂	3	Pressure	9 bara
Stoichiometry H ₂	2	Constant current	100 mA/cm ²
Pressure	2 bara		
Constant current	100 mA/cm ²		

Table 1: URFC test parameters

Development of an oxygen electrode for a unitized regenerative PEM fuel cell



The optimized electrode ink was combined with various porous titanium structures, like:

- ECN made porous titanium
- Porvair titanium foam
- Bekinit sintered and unsintered Ti felt

These GDLs were made hydrophobic using a (C_3F_6) plasma or by impregnation of PTFE.

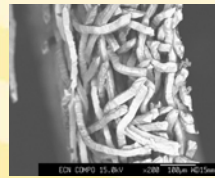


Figure 2: Bekinit Ti felt

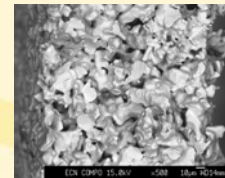


Figure 3: ECN Ti foam

Results:

- Optimized ink: 1:2 Pt:Ir, 1,5 mg/cm² Pt
- Bekinit is selected as GDL, Porvair is too brittle, ECN Ti foam has low porosity

The interaction between the GDL and the electrode ink is important. An oxygen electrode with a GDL 31BC performs better than with Bekinit.

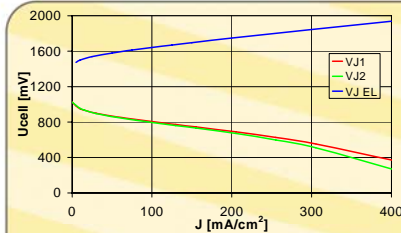


Figure 4: Performance of MEA Bekinit / Pt-Ir / N117 / Pt on C / GDL 31BC

Electrochemical Impedance Spectroscopy (EIS) indicate that titanium GDLs plus electrodes have higher activation energies. *In situ* Cyclic Voltametry (CV) measurements show for electrodes on Ti GDLs a lower effective electrocatalytical surface area, compared to electrodes on GDL 31 BC. SEM analyses show that part of the electrode penetrated the Ti structure, which might be an explanation of the lower performance.

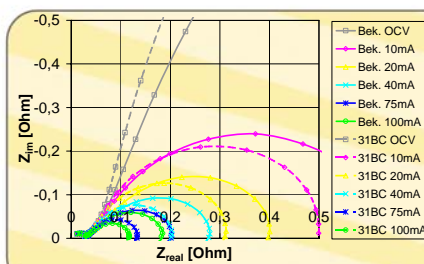


Figure 5: EIS measurements

Development of an oxygen electrode for a unitized regenerative PEM fuel cell



Test data show that stable operation in both fuel cell and electrolyzer mode is possible. This means that the cell does not flood during fuel cell operation, yet enough water can diffuse through the gas diffusion layer during the electrolysis mode.

The roundtrip efficiency of the MEA in this case is $0.8V/1.7V = 47\%$.

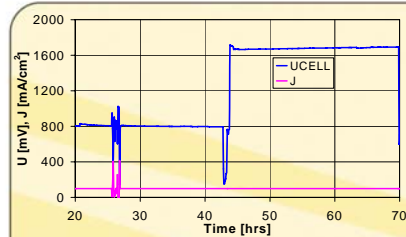


Figure 6: EL & FC modes test, MEA Bekinit / Pt-Ir / N117 / Pt on C / GDL 31BC

The oxygen electrode performance can be further improved by preventing the electrode from penetrating the GDL. This could be achieved by having an intermediate layer between the catalyst layer and the GDL.

Stack development:

At this moment a 250W URFC stack is being developed. The stack will consist of 20 cells of 156cm^2 .



Figure 7: URFC sub stack

Conclusion:

- Pt/Ir/Nafion electrode at the oxygen side and Pt on C at the hydrogen side is used as EL + FC mode catalysts.
- Treating the Bekinit titanium gas diffusion layer with a plasma in order to render its surface hydrophobic results in stable operation conditions in both modes.
- Roundtrip efficiency of at least 40% is possible with a URFC.
- Further improvement of the oxygen electrode is possible with the addition of an intermediate layer

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