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« NEXPEL Project »
**Next-generation PEM electrolyzer for sustainable hydrogen
production**

WP3 “New binary/ternary catalyst systems”
D3.1 “Defined electrochemical test procedures for screening of catalyst activity”

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Preface

This document was produced as part of work package 3 (WP3) of the NEXPEL project (Next generation PEM electrolyzers for sustainable hydrogen production), funded by the European community’s Seventh Framework Programme (FP7/2007-2013) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement no. 245262. WP3, “New binary/ternary catalyst systems”, which is coordinated by SINTEF, is dedicated to the development of new catalysts for oxygen and hydrogen evolution during water electrolysis. Standardised test procedures have to be defined for electrochemical testing of the catalysts developed in order to have comparable results from different partners.

Key Words

**WATER ELECTROLYSIS, PEM ELECTROLYSER, NEXPEL, CATALYST, TEST
PROTOCOL**

**ÉLECTROLYSE DE L’EAU, ELECTROLYSE PEM, NEXPEL, CATALYSEUR, PROTOCOLE DE
TEST**



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I. Introduction

This document was produced as part of WP3 of the NEXPEL project (Next generation PEM electrolyser for sustainable hydrogen production), funded by European community (SP1-JTI-FCH). WP3, coordinated by SINTEF, is dedicated to the development of new catalysts for oxygen and hydrogen evolution during water electrolysis.

Standardised test procedures have to be defined for electrochemical testing of the catalysts developed in order to have comparable results from different partners.

- The reaction occurring at the cathodic side of a PEM water electrolyser is expected to be the reduction of protons (H^+):



Catalysts used for this electrode are mainly composed of platinum (Pt) on a support material. Platinum black or carbon supported platinum nanoparticles can be used. Platinum loading on the support material is generally between 0.4 and 5mg Pt cm^{-2} .

- At the anodic side, the water oxidation reaction is expected to be:



Due to the high potential and low pH conditions of the proton exchange membrane, only a few metal oxides are stable enough to be used as catalysts at the anodic side of the reaction. Iridium (Ir) and Ir based metal alloy oxides (with Ru, Ta, Sn...) are usually utilized with loadings comprised of between 1 and 6mg IrO₂ cm^{-2} .

Due to the different conditions, devices and techniques used to evaluate the electrocatalytic performance of the anodic and cathodic catalysts are not exactly the same. For example on the anodic side, catalysts would have to be deposited on a support which does not oxidize at high potentials, which could reach 1.5V vs. RHE or at high temperatures up to 80°C.



1.1 Standardised data and state of the art comparison of water electrolysers

Generally when comparing catalysts for water electrolysis a number of parameters are considered including the catalyst activity in relation to surface area, the noble metal loading, stability and durability over a range of applied electrical potentials and temperatures. The testing of these parameters is usually carried out using a series of electrochemical experiments which are complimented by physical characterisation techniques such as transmission electron microscopy (TEM), Scanning electron microscopy (SEM) and X-ray diffraction (XRD) which examines the structure and composition of the catalysts.

Often, the efficiency of the catalyst is reported in terms of the potential recorded at a potential of 1 A cm⁻² or alternatively as the current density (A cm⁻²) obtained at a specific potential and operation temperature such as 1.8 V and 80°C.

1.2 Targeted results within NEXPEL project

- H₂ evolution catalysts: Despite the development of supported noble metal catalysts for PEM fuel cells little implementation of such catalysts has been seen for water electrolysis. Generally Platinum Black has been used with a loading of up to 2 mg cm⁻². Within the Nexpel project it is expected to reduce Pt loading to 0.2 mg cm⁻² by using Pt on a support material such as carbon black or carbon nanofibers.
- O₂ evolution catalysts: Nanocrystalline Ru or Ir metal / metal oxides in the form of agglomerates with sizes of about 50nm are commonly used. Hence the active material in its pure form is most probably not being used to its full potential. A relatively high loading of up to 6 mg cm⁻² of Ir or Ru eg Ir black is used. Supported Ir or Ir oxide provides a cheaper alternative and the targeted loading within the Nexpel project is 0.8 mg cm⁻².



II. Theory of Analytical Techniques

II.1 Cyclic Voltammetry

Cyclic voltammetry (CV) is one of the most useful analysis tools for investigating electrocatalysts. The voltammogram is a current response to a potential sweep and gives an electrochemical spectrum of the electrode surface, with information regarding the solid-state redox transitions, active area and the electrode capacitance found. Normally, cyclic voltammetry is performed by sweeping the potential between two potential limits at a constant sweep rate (linear cyclic voltammetry).

Often cyclic voltammetry is used to study electrode reactions involving electroactive species present in the electrolyte, but it is also extremely useful for following the adsorption of species on the electrode (e.g. H_{ads} or CO on Pt). Reversible adsorption processes are characterised by the anodic and cathodic peaks being sharp and symmetrical with no significant difference in the peak potentials. For irreversible adsorption processes, the forward peak (i.e. adsorption of soluble species onto the electrode) becomes non-symmetric and the reverse desorption peak does not occur. For quasi-reversible reactions, there will be both peaks, however they will not be symmetric and there will be some difference between the peak potentials.

II.1.1 Cyclic Voltammetry of noble metal based materials

Noble metals such as Pt, Pd and Au have well defined hydrogen adsorption and desorption peaks seen upon cycling between suitable potential limits using the cyclic voltammetry technique. Due to these defined peaks several values can be determined for the Pt based catalysts. By analysis of the oxidation peaks a determination of the electroactive surface area (EAS) of catalyst ($m^2 \cdot g_{catalyst}^{-1}$) can be determined.

The EAS areas can be calculated from the hydrogen desorption peak area and from the CO stripping peak area.

Figure 1 shows the cyclic voltammograms obtained in 1 M H_2SO_4 at 298 K and 20 $mV \cdot s^{-1}$ scan rate on Pt/C, PtPd/C and Pd/C catalysts ^[1].

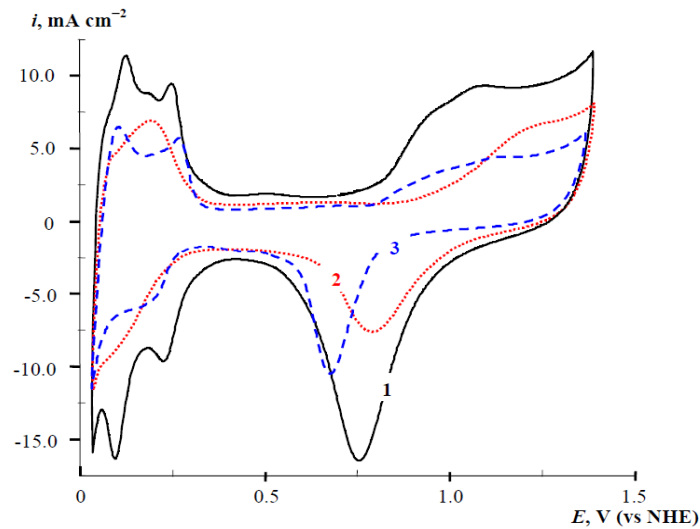


Figure 1: Cyclic voltammograms (20 mV s^{-1}) of electrodes based on synthesized catalyst. 1 – Pt40/Vulcan-XC72, 2 – Pt1Pd140/Vulcan-XC72 and 3 – Pd40/Vulcan-XC72. ^[1]

The EAS are calculated by measuring the peaks area in the voltammograms and using the following equations:

$$ECA_{H_{upd}} = \frac{Q_H (\mu C)}{210 (\mu C.cm^{-2})} = \frac{A_H / \nu}{210} \quad (1.1)$$

A_H is the hydrogen peak desorption area ($C.V.s^{-1}$), ν the scan rate (mVs^{-1}) and $210 \mu C/cm^2$ is an estimated value of the adsorption charge of an hydrogen monolayer on a smooth platinum electrode ^[2,3,4,5,6].

CO stripping

Additionally, to know and quantify the electrochemical active area in catalytic systems based on Pt, carbon monoxide is a useful probe in electrochemical platinum based catalysts characterization, blocking the Pt surface at low potentials (hydrogen region). The CO stripping procedure involves an electrochemical adsorption of carbon monoxide followed by electro-oxidation.

Figure 2 shows the first and the last voltammograms recorded on Pt/C catalyst in $0.5 \text{ M H}_2\text{SO}_4$ at 298 K and 20 mVs^{-1} scan rate after CO adsorption on catalyst and illustrates the charges corresponding to desorption of H_{upd} (Q_H) and CO (Q_{CO}).

The amount of CO adsorbed is estimated by stripping peak integration corrected to electric

double layer assuming that one CO monolayer its adsorbed linearly and the charge used for oxidise its $420 \mu\text{C.cm}^{-2}_{\text{Pt}}$. [7,3,8,9,10]

$$ECA_{\text{CO}} = \frac{Q_{\text{CO}}(\mu\text{C})}{420(\mu\text{C.cm}^{-2})} = \frac{A_{\text{CO}}/v}{420} \quad (1.2)$$

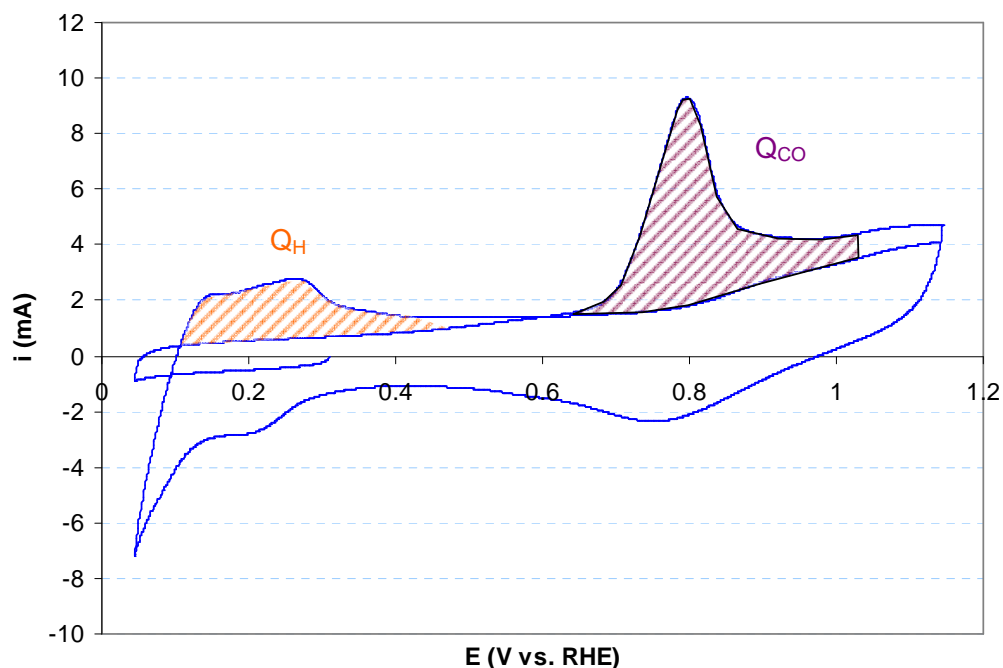


Figure 2: Cyclic voltammetry of a Pt/C catalyst – measurement of Q_{H} corresponding to H_{upd} desorption en Q_{CO} corresponding to CO oxidation

The shape of the CO stripping voltammogram in Pt catalyst is dependent on morphology, structure, size and chemical nature, and hence provides us with additional information about how the particles are dispersed on the support material, eg, if they are aggregated or homogeneously dispersed [10,11].

CO Stripping evaluate the tolerance towards carbon monoxide in electrocatalysts (H_2/CO supply from reformat), electrode activity in organic molecules electro-oxidation since CO is an intermediate produced during electrooxidation which pass through by successive deprotonation at room temperature [12].



II.1.2 Cyclic Voltammetry of oxides

Noble metal oxides such as IrO₂ and RuO₂ have quite characteristic voltammograms in acid electrolyte^[13] as shown in Figure 3.

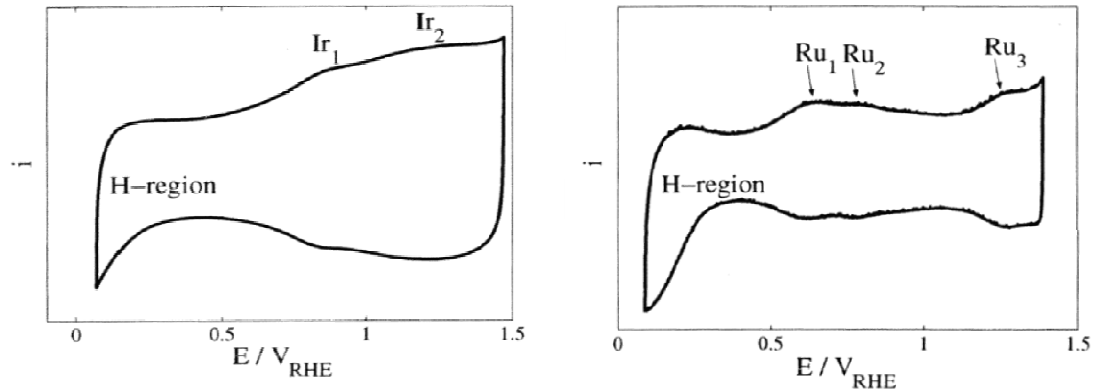
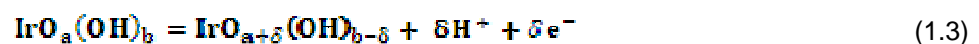


Figure 3: Cyclic voltammogram of IrO₂ and RuO₂ [Erreur ! Signet non défini.]

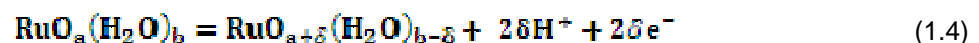
The voltammograms show the solid state redox transitions as peaks or broad waves. These redox transitions occur due to the adsorption and oxidation of oxygenated species from the electrolyte. These processes can be described as a pseudo capacitance, as the adsorbed species effectively store charge on the electrode surface. This differs from the double layer capacitance as this pseudo capacitance is a Faradaic process in which electrons cross the double layer region.

The charging / adsorption process for iridium oxide is given by the following equation (1.1):



Normally the peaks found on a voltammogram of iridium oxide in acid are located around 0.8-0.9 V and 1.25-1.35 V and correspond to the redox transitions of Ir³⁺/Ir⁴⁺ and Ir⁴⁺/Ir⁶⁺ respectively.

Similarly to IrO₂, the charging process for RuO₂ is given by (1.2):



This charging process is associated with three redox transitions, Ru²⁺/Ru³⁺, Ru³⁺/Ru⁴⁺ and Ru⁴⁺/Ru⁶⁺ resulting in three broad peaks in the oxide region of the voltammogram as seen in Figure 3. At higher potentials, ruthenium oxide electrodes can be further oxidised to Ru⁸⁺, which can result in formation of volatile RuO₄.

IrO₂ and RuO₂ are both covered by a hydroxide layer when placed in an electrolyte. This



hydroxide and lattice oxy groups enable the oxides to conduct protons via a “hopping” type mechanism. This implies that under some circumstances, protons can penetrate into the bulk of the oxide along crystal grain boundaries, pores, and defects, with the transport limited by the diffusion at these interfaces. This observation gives rise to the “inner” and “outer” surface area of the oxides

The ratio of Q_a/Q_c is used to examine the reversibility of the redox process. Q_a and Q_c are attained by calculating the ratio of the charge between 0.15 and 1.15 V_{SCE} of the forward sweep and the reverse sweep respectively ^[14,15,16,17]. These calculations could show changes in the reversibility during the charging process.

The voltamograms of noble metal oxides give vital information regarding the active area of these materials. It has been shown that the charge associated with the oxide region (normally 0.6-1.4 V) is directly proportional to the surface area or electrode roughness ^[18,20]. Furthermore, measuring the anodic charge (Q_a) as a function of sweep rate (v) can yield interesting information regarding the morphology of the active surface¹⁹. By plotting $1/Q_a$ vs. $v^{0.5}$ and Q_a vs. $v^{-0.5}$ and extrapolating the linear sections to the origin, the charge values at $v = \infty$ and $v=0$ are found. At high sweep rates only the outer surface of the oxide material takes part in the charging process, whereas at very low sweep rates the “inner” surface is also accessible due to diffusion of protons through pores, cracks and grain boundaries in the oxide material. The proton exchange between surface oxide-OH groups and the acid electrolyte is considered to be rapid at “easily accessible” regions, whereas this exchange has some diffusion limitations within the inner regions. Thus at $v=0$ the charge is said to be the total charge (Q_t) and at $v = \infty$ the charge gives the outer charge (Q_o). The total charge is the summation of the inner (Q_i) and outer charge. The outer charge (Q_o) is recognized as representing the surface available for the electrochemical reactions and is thus a measure of the active surface area of the catalyst under investigation.

Savinell et al. ^[20] found that the electrochemically accessible surface area was an apparent linear function of voltammetric charge for RuO_2 up to a loading of 14 mg cm^{-2} , giving a correlation of $2643 \pm 186 \text{ cm}^2 \text{ C}^{-1}$. Another correlation was found for IrO_2 films ($3260 \pm 174 \text{ cm}^2 \text{ C}^{-1}$) up to a loading of 2.66 mg cm^{-2} . However, some doubt about the validity of the latter correlation remains since its use in measuring kinetic rate constants of a simple redox reaction gives values that are an order of magnitude lower than expected.

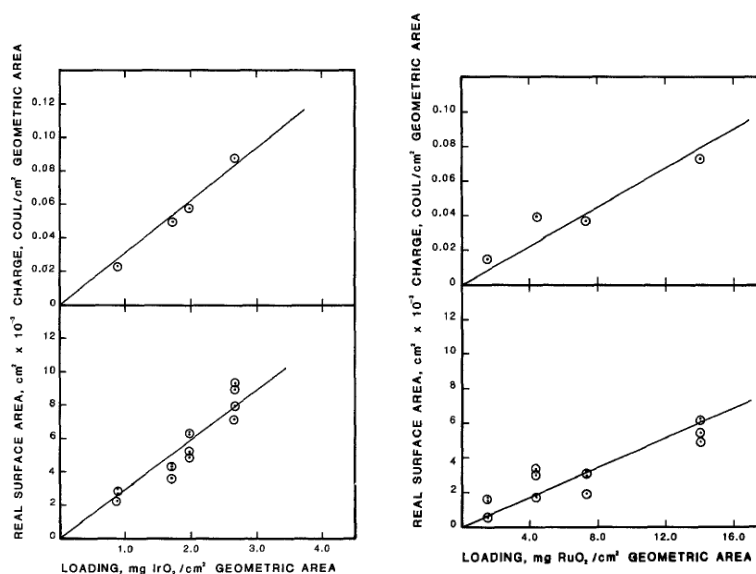


Figure 4: Voltammetric charge and electrochemically active (real) surface area correlated with loading for IrO₂ and RuO₂ on coated titanium electrodes. ^[20]

II.2 Linear Sweep Voltammetry - Polarisation curves

Linear Sweep Voltammetry examines the potential–current (E-I) relationship at the electrode surface and can be carried out under either potentiostatic (controlled potential) or galvanostatic (controlled current) conditions in which the response in the current or potential is monitored. In order to obtain a steady state the scan is usually run very slowly typically 1 – 5 mV/s. The analysis of the polarisation curve can provide information concerning the kinetics and the mechanism of the reaction at the catalyst in addition to providing a useful tool to compare catalyst activity.

II.3 Impedance Spectroscopy

AC Impedance is a method used to examine the stability, kinetics, double layer capacitance and other factors at the working electrode surface. Impedance measurements involve applying a small sinusoidal perturbation which is superimposed over a fixed DC potential or current at the electrode. The frequency of the sinusoidal perturbation is then varied over a range of frequency from about 10⁵ -10⁻¹ Hz and the AC response of the electrode recorded. AC Impedance in this work provides information concerning the ohmic resistance and the electrochemical activity at the electrode and in the cell.

Experimental results are expressed as a real and imaginary part from the shift in phase. These components are plotted on a vector diagram known as a "Nyquist" plot with the real component (Z') on the x-axis and the imaginary component (-Z'') on the y-axis at each measured frequency.



To interpret electrochemical impedance spectrums, the electrochemical systems are often represented as an equivalent electric circuit. These circuits are typically constructed of resistors, capacitors and inductors. In addition other more complex elements are used to interpret the theoretical and experimental data such as Warburg elements (which describe diffusion processes) and constant phase elements (which describe porous or rough electrodes).



III. Experimental

III.1 Sample preparation

III.1.1 Catalyst layer preparation

The catalyst layer is composed of a catalyst powder (eg. 2.0 mg) set in suspension (eg. 1000 μ l) in a solvent (eg. 20% isopropanol or ethanol in water). The catalyst may be dispersed by placing it in an ultrasonic bath for ~3min. This suspension can be sprayed or deposited on the flat electrode or the rotating disk electrode to fully cover it. In the case of the RDE electrode, 20 μ l of the catalyst dispersion is taken out with a pipette and put on a glassy carbon disk. After drying, a binder such as a dilute Nafion solution is then generally added on the catalyst to avoid delamination of the catalyst during experimental measurements. Alternatively the catalyst can also be set in suspension in a mixture of solvent and Nafion binder. The support is then coated with an appropriate amount of this mixture.

In most cases, the catalyst is mixed with deionised water, isopropanol and ionomer (Nafion or others). The amount of ionomer can vary: 16wt% to 30wt% ^[21,22]. After sonication and/or stirring, the obtained ink is dropped, painted or sprayed on a conductive substrate such as glass carbon or gold of a ring disk electrode or on to the MEA electrode preparation^[23,24]. Titanium-based substrates are typically used for anodic catalysts. They could be polished and etched in concentrated HCl at 80°C ^[20,25].

Catalyst layers are sometimes directly grown on the surface of a conductive substrate such as titanium foil or sinter, directly ^[26,27] or after sand-blasting and etching into boiling 10% oxalic acid ^[28], boiling 37% HCl ^[29] or both ^[30,31].

Catalyst can also be electrodeposited on the surface of a conductive electrode (glassy carbon, Au, Pt)^[32], ITO ^[33] or other conductive layers ^[34,35]



III.1.2 MEA preparation

Initially the Nafion membrane is prepared using a standardised procedure as follows.

- Pre clean Nafion 115 membrane in boiling water for 15 minutes
- Boil in 3% H₂O₂ for 30 minutes
- Wash with distilled water
- Boil in 0.5M H₂SO₄ for 30 minutes
- Wash with distilled water
- Boil in distilled water for 15 minutes (three times)
- Store in distilled water until use

The catalyst powder is usually mixed with the Nafion ionomer in alcoholic solution (5wt%^[36,37], 10wt%^[38,39], 15wt%^[40], 20wt%^[41], 25wt%^[42], 30wt%^[43,44], 33wt% Nafion^[45,46,47,48]), then sprayed or pipetted on to a point onto a Nafion (112 to 117) membrane by spray, decal^[38,37,49] or pipetting⁵⁰ technique.

Ma et al. ^[44] made an interesting study and found that the Nafion content in the catalyst layers has an obvious influence on the PEMWE performance. In particular, there is a significant decrease when the Nafion content is relatively high, such as 40wt%. It is ascribed to relatively thick Nafion film coating on catalyst surface that increases resistances of mass transportation, charge transfer and ionic transfer. The proton conductive resistance changed with operating conditions but it was clearly seen that the resistance enhances with the increasing of Nafion content. On the other hand, too low content of Nafion in catalyst layer can reduce three-phase interface and decrease the adhesive force between catalyst layer and membrane.

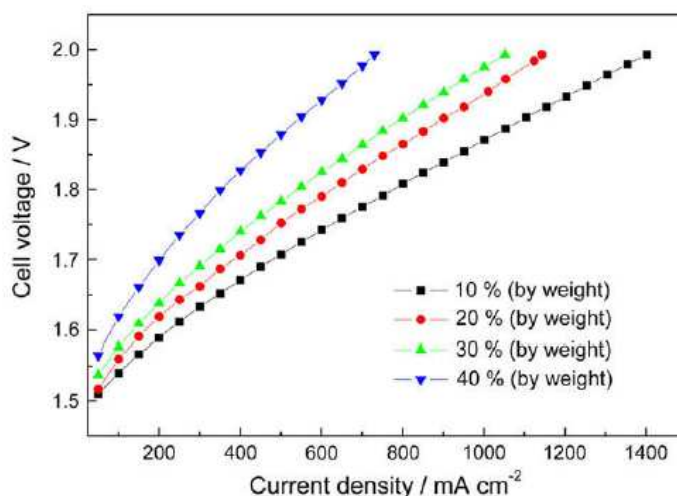


Figure 5: Effect of Nafion contents in catalyst layer of anodes on the PEMWE performance ^[44]



The low adhesive force will lead to an easy breaking away of the catalyst layers from the surface of membrane. In order to ensure the stability of MEA, the best content of Nafion in the anode was about 30wt%.

Pipetting method

- Make 2% Nafion solution using 1:1 nafion and iso-propanol
- Weigh out 12.5 mg of catalyst and add 250 μ l of 2% nafion solution
- Ultrasonicate for 1h and then stir for 1h at 2000 rpm
- Dry prepared-Nafion membrane at 70°C for 1h
- Place membrane on a Teflon sheet on the hotplate at 95°C
- Add 20 μ l of the catalyst ink to the membrane using pipette and leave to dry.
- Cure membrane in the oven at 80°C for 15 minutes
- Cut 5cm² square of the E-Tek
- Put the E-Tek on opposite side of nafion and place between two Teflon sheets
- Hot press at 130°C for 60 seconds using 50 kg force (10kg/cm²)



III.2 Three electrode cell setup

The three electrodes cell setup is the most common setup used in electrochemistry. It is composed of a working electrode (WE) counter electrode (CE) and reference electrode (REF) immersed in an electrolyte. The electrolyte is generally an aqueous solution of H_2SO_4 or HClO_4 . This type of cell is used for both the flat electrode experiments and with the rotating ring disk electrode as will be described in the following section.

III.2.1 Flat electrode

- Principle:

It is the simplest setup. Electrodes are prepared by immobilizing the catalyst on the surface of a flat metallic electrode as described previously. This electrode is then immersed in the electrolyte of a three electrodes electrochemical setup (working electrode WE, counter electrode CE and reference electrode REF). There are a host of reference electrodes which can be utilised but generally a standard hydrogen electrode (SHE) is chosen as this does not introduce any additional contamination as may be the case with Saturated Calomel electrodes which utilise KCl. As counter electrode a Pt wire attached to a Pt mesh are used. The electrolyte is generally an aqueous solution of 0,5M H_2SO_4 or HClO_4 . In addition the electrolyte maybe oxygenated or deoxygenated according to the experiment design by bubbling the relevant gas (O_2 , Ar or N_2)in to the electrolyte. The electrolyte of the cell may also be heated eg. 60°C in order to better mimic th e real conditions of the MEA in the cell but for this a specialised jacketed cell and heat resistant working electrode must be used.

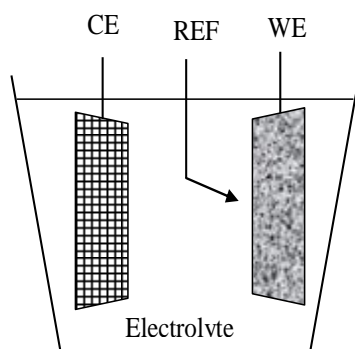


Figure 6 : Simple three electrode cell set up with a flat electrode

Table 1 : Characteristics of the flat electrode for catalyst testing



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Advantage	Disadvantage
<ul style="list-style-type: none">- easy to implement- small amount of catalyst needed (depend on the WE surface area)- In the case of RDE experiment measurement of the produced gas flow while cycling potential	<ul style="list-style-type: none">- The electrode has to be stable through the whole potential window of measurement (0 to 1.5V vs. RHE). Eg titanium or gold plate.- Evacuation of produced gas-Not necessarily representative of MEA behaviour

III.2.2 Rotating ring – disc electrode

- Principle:

The principle of rotating ring disc electrode is more or less the same as the flat electrode with the same type of reference and counter electrodes used. The catalyst is immobilized on the surface of a flat disk in the centre of the electrode. This electrode is immersed in the electrolyte of a three electrodes electrochemical setup. Glassy carbon or gold disks (Pine Instruments) are used as a substrate for the electrocatalysts.

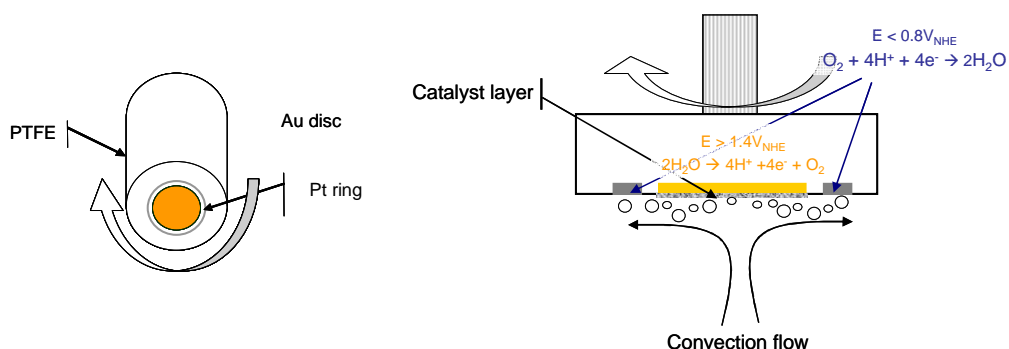


Figure 7 : Rotating ring disc electrode

The main difference in these experiments is that the electrode rotates at a define speed allowing a convection flow of electrolyte that evacuates gas by the electrode sides.

A part of the produced gases can be collected on the ring. When setting the potential of the ring at fixed value, the current measured is proportional to the produced gas flow.

Table 2 : Characteristics of the RDE for catalyst testing

Advantage	Disadvantage
<ul style="list-style-type: none"> - easy to implement - small amount of catalyst needed (depend on the WE surface area) - In the case of RDE experiment measurement of the produced gas flow while cycling potential 	<ul style="list-style-type: none"> - The electrode has to be stable through the whole potential window of measurement (0 to 1.5V vs. RHE). Eg titanium or gold plate. - Evacuation of produced gas -Not necessarily representative of MEA behaviour

III.3 MEA testing devices

Three different devices can be used to evaluate and compare the electrocatalytic performance of the catalyst. Each device has got its advantages and disadvantages which are presented and discussed below.

III.3.1 Half cell setup

- Principle:

The “half cell” device was developed to test the electrocatalytic activity of the catalysts layer assembled with a proton exchange membrane. The catalyst layer is set between a gas diffusion layer and the membrane; we obtain a membrane – electrode assembly. Only one catalytic layer is deposited on one side of the membrane. The other is left blank.

This assembly is put in a sample holder comprising a current collector (gold) and the membrane side is set in contact with the electrolyte of a three electrodes electrochemical setup. Evolved gases are evacuated through the gas diffusion layer.

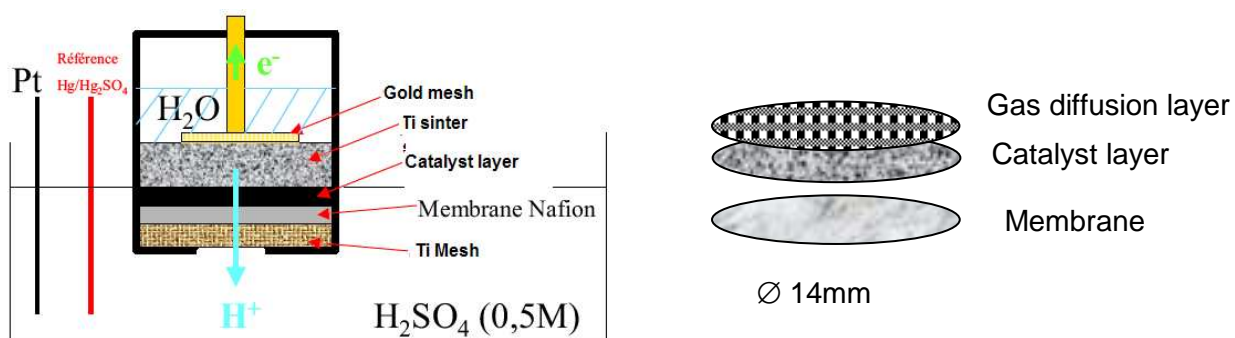


Figure 8 : half cell setup

- Sample preparation: see



MEA preparation, section III.1.1.

A suspension of catalyst in a mixture of solvent and binder is deposited on the membrane (spray, knife coating, screenprinting, decal ...) or on the gas diffusion layer. It is possible to evaluate the influence of catalyst layer composition (amount of Nafion) and differences relative to the deposition technique.

Table 3 : Characteristics of the half cell setup for catalyst testing

Advantage	Disadvantage
<ul style="list-style-type: none">- easy to implement- small amount of catalyst needed- representative of MEA behavior	<ul style="list-style-type: none">- High electrical resistance of electrolyte (few Ω cm^{-2}) leading to a limitation to low currents densities

III.3.2 Easy Test Cell

The easy test cell concept has been developed by Radev et al. [51]. It allows testing and optimizing single electrodes before coupling them to a working cell.

- Principle:

The counter electrode is used to pass a current through the working electrode. The EasyTest approach offers the possibility for carrying out electrochemical tests of MEA sealed in one gas compartment. Thus, instead of two different reactions proceeding on both electrodes, the reaction on the CE will be the same as that on the WE but will proceed in the opposite direction.

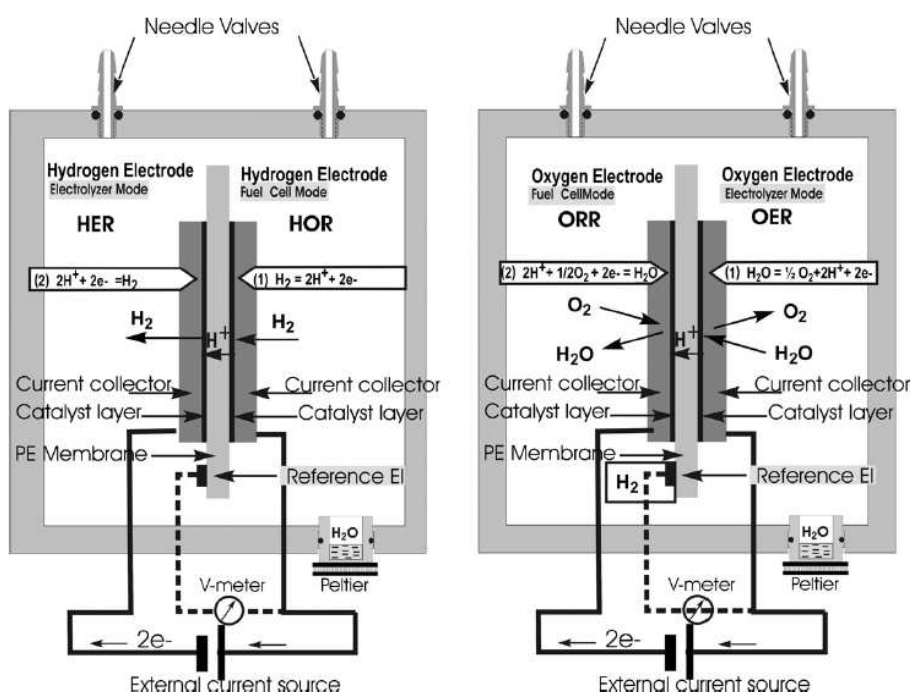


Figure 9: The EasyTest Cell principle – hydrogen version (left) and oxygen version (right). [51]

A counter electrode containing an active catalyst toward the opposite reaction is a prerequisite for this case.

- Example of results:

With such a device, it is possible to perform polarisation curves and cyclic voltammetry and compare them to those obtained on a PEMWE.

Experiments were performed on a MEA prepared by hot pressing of catalyzed gas diffusion layers on both sides of a Nafion117 membrane. The catalysts – Pt, IrOx, and a composite

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IrOx/Pt/IrOx – were deposited directly on the Toray paper gas diffusion sheets by dc magnetron sputtering. In order to improve the adherence of the catalytic layer to the substrate and, eventually, to prevent the oxidation of the carbon paper during oxygen evolution in the PEM WE, all films were deposited on a $7.5 \mu\text{g cm}^{-2}$ (50nm thick) Ti sublayer.

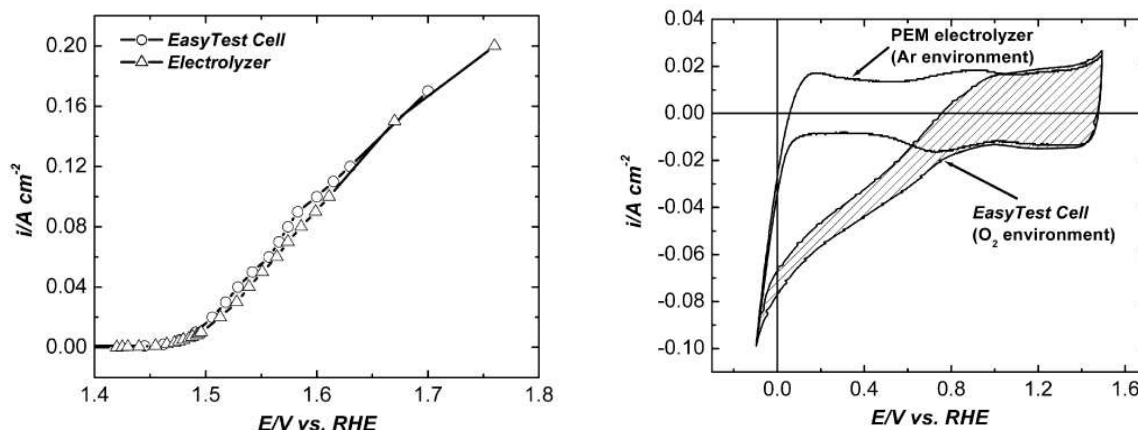


Figure 10: Comparison of the steady state polarization curves towards OER obtained in the EasyTest Cell and PEMWE at 20°C and 100% relative humidity (left) ; Cyclic voltammetry curves of the IrOx/Pt/IrOx electrode obtained in the EasyTest Cell and PEMWE at 20°C (right).^[40]

Results show a quite good correlation between polarization curves obtained on the Easy Test Cell and on PEMWE, however cyclic voltammetry is distorted because of oxygen reduction reaction.

Table 4 : Characteristics of the Easy Test Cell for catalyst testing

Advantage	Disadvantage
<ul style="list-style-type: none"> - one reaction (except reverse reaction) - low internal resistance - experiments in condition representative of real application (pressure, temperature) 	<ul style="list-style-type: none"> - MEA testing - CV impossible

III.3.3 Pipetting method

The preparation of the MEA using the pipetting technique in which a drop of catalyst is placed on a small area of the membrane is described below. The advantage of this method is an easy, fast and reproducible method of making catalyst coatings on Nafion membranes very similar to real MEA electrodes with very good control of the catalyst loading, even when using low amounts of catalyst.

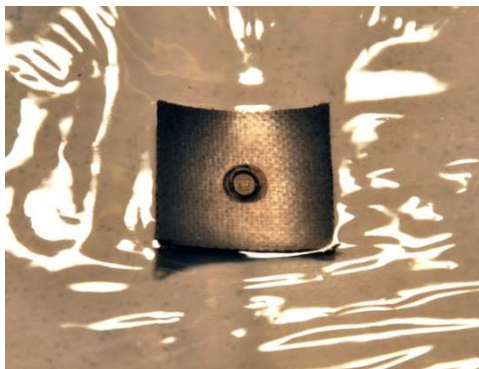
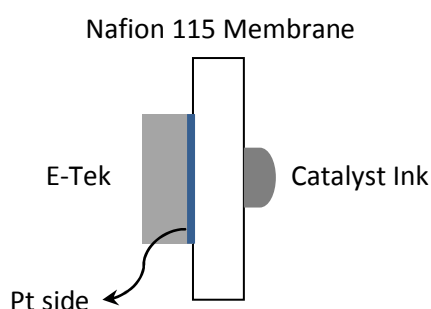


Figure 11 : Picture and Schematic of MEA assembly produced by pipette method to test small quantities of catalyst.

Table 5: Characteristics of the Pipetting method for catalyst testing

Advantage	Disadvantage
<ul style="list-style-type: none"> - Close to real MEA testing - Small amount of catalyst needed - Good control over total amount of catalyst - Relatively fast and easy method of making catalyst layer on Nafion membrane. 	<ul style="list-style-type: none"> - Less control of catalyst loading (mg/cm^2) than by ordinary MEA preparation methods.

III.3.4 Small size electrolysis cell

- Principle:

A small size electrolysis cell (typically 5 to 25cm²) can be used to evaluate the performance of the catalysts while using a small amount of catalyst. A full membrane – electrodes assembly has to be produced (including anodic and cathodic catalysts) although the catalyst to be tested can be deposited by the pipette technique or sprayed across a larger area, both sample preparation techniques are described earlier in section III.1.1.

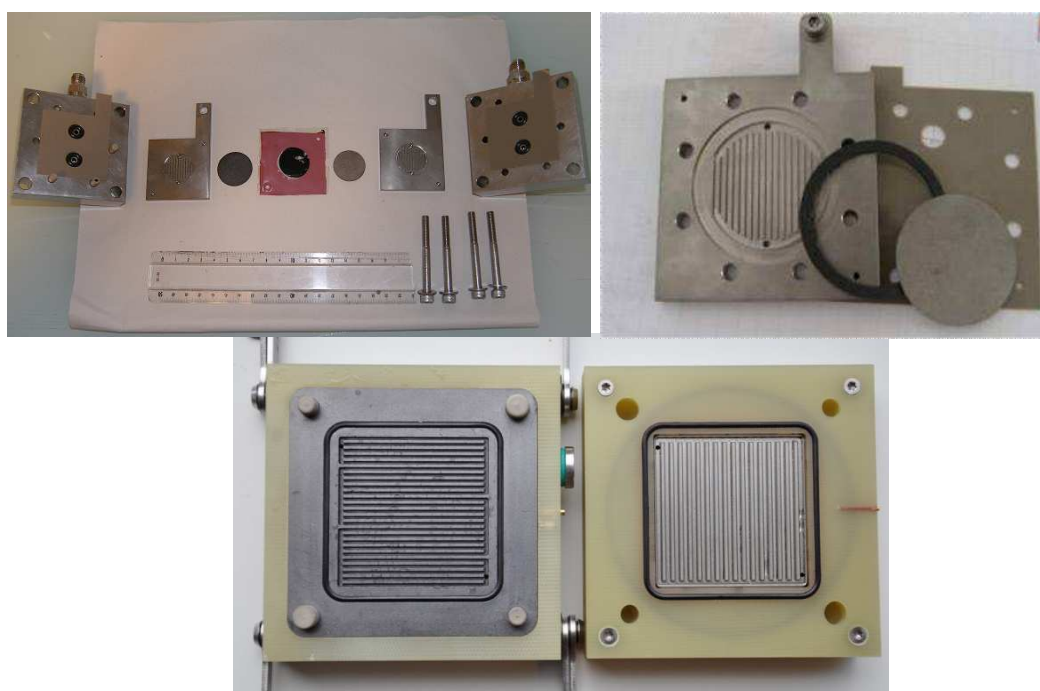


Figure 12 : 5 and 25 cm² single cells used for water electrolysis MEA testing

Table 6 : Characteristics of small size electrolysis cells for catalyst testing

Advantage	Disadvantage
<ul style="list-style-type: none"> - Real MEA testing - Small amount of catalyst needed 	<ul style="list-style-type: none"> - MEA preparation (numerous parameters to take into account during assembly processes).



IV. Testing protocols

To compare the results of tests conducted by NEXPEL partners on catalysts and MEA, it is necessary to harmonize the testing procedures and conditions under which these tests will be conducted. The aim of this paper is to describe the main tests and propose a detailed description of protocols.

IV.1 Three electrode cell setup

The standard conditions for three electrode cell measurements (flat or rotating electrode) to characterize the NEXPEL catalysts are given in the table below.

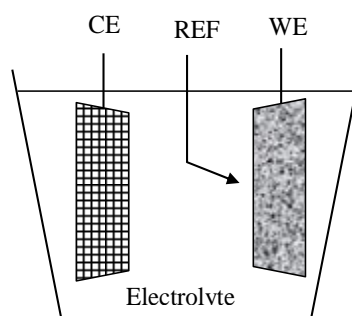


Table 7 : NEXPEL conditions for three electrode cell testing.

Reference electrode	Reversible hydrogen electrode
Counter electrode	Platinum mesh or foil
Electrolyte	Sulphuric acid, 0.5 M made from p.a grade conc. H ₂ SO ₄ and ion exchanged water (18.2 MΩ).
Temperature	Standard: Room temperature (20-25°C) Elevated temperatures (up to 60 °C) can sometimes be used.



IV.2 Sample preparation

IV.2.1 Deposition of catalyst suspension

Aqueous suspensions of the catalyst materials are produced by ultrasonically dispersing the appropriate amount of catalyst in a mixture of 20% isopropanol in water. The amount of catalyst added is dependent on the loading of active material and also the density and surface area of the support.

Typically a 20 μ l aliquot of the suspension is pipetted onto the substrate. After evaporation of the water under flowing nitrogen atmosphere, 20 μ l of a diluted Nafion solution (1/100 5wt% Nafion in pure water) is added on the top of the dried catalyst powder.

IV.2.2 Catalyst ink

The catalyst suspension is obtained, dispersing the catalyst powder with deionised water, isopropanol (20%) and Nafion (5wt% solution). Amount of ionomer for standard test is fixed at 30wt% for both anodic and cathodic catalysts.

IV.2.3 MEA

Ink is obtained as previously described. (The powder of catalyst is usually mixed with Nafion ionomer in alcohol solution. Standard electrodes are prepared by either pipetting or spraying the catalyst ink onto a PTFE support then decal on Nafion 117 membrane by hot pressing 135°C, 1Mpa for 3 minutes.



IV.3 Characterization techniques

IV.3.1 Cyclic voltammetry – Active surface Area

For anodic catalysts, cyclic voltammetry would be performed between 0 and 1.4 V/RHE at 20 mV.s⁻¹ under nitrogen bubbling.

The active surface area of the catalysts are evaluated by extrapolating the anodic charge (Q_a) to infinite sweep rate as described in section II.1.2.

IV.3.2 Cyclic Voltammetry - Polarisation curves

The electrode is assembled to the electrochemical cell and cyclic voltammetry is run. In total 16 steps of CV is performed. In all steps the potential is scanned to a vertex potential E₁ = 1.350V before it is reversed to E₂ = 0.400V. All potentials are referred to as vs. SHE. The cycling is repeated n_C times. The scan rate dE/dt is varied from each step. The set-up for the CV is described in Table 8

Table 8: Set-up for cyclic voltammetry

CV-1 dE/dt = 20 mV.s ⁻¹ , n _C = 19	CV 9 dE/dt = 40 mV.s ⁻¹ , n _C = 4
CV 2 dE/dt = 2 mV.s ⁻¹ , n _C = 1	CV 10 dE/dt = 60 mV.s ⁻¹ , n _C = 4
CV 3 dE/dt = 3 mV.s ⁻¹ , n _C = 2	CV 11 dE/dt = 80 mV.s ⁻¹ , n _C = 4
CV 4 dE/dt = 5 mV.s ⁻¹ , n _C = 2	CV 12 dE/dt = 100 mV.s ⁻¹ , n _C = 4
CV 5 dE/dt = 7 mV.s ⁻¹ , n _C = 2	CV 13 dE/dt = 150 mV.s ⁻¹ , n _C = 4
CV 6 dE/dt = 10 mV.s ⁻¹ , n _C = 4	CV 14 dE/dt = 200 mV.s ⁻¹ , n _C = 4
CV 7 dE/dt = 20 mV.s ⁻¹ , n _C = 4	CV 15 dE/dt = 250 mV.s ⁻¹ , n _C = 4
CV 8 dE/dt = 30 mV.s ⁻¹ , n _C = 4	CV 16 dE/dt = 300 mV.s ⁻¹ , n _C = 4

After the CV the gas is turned off, and the electrolyte is left to settle to a “normal” state before the linear sweep (polarization) is started. During the polarization there is no gas bubbling through the electrolyte. The electrode is set to rotate at a rate of 1000rpm. The set-up of the polarization is given in Table 9.

Table 9 Set-up for linear sweep.

Scan E _{WE} with dE/dt = 0.167 mV.s ⁻¹ from E _i = 1.100 V vs. SHE to E _f = 1.600 V vs. SHE
--



For anodic catalysts, cyclic voltammetry can be performed between 1.2 and 1.5 V vs. RHE on rotating disk electrode and between 1.2 and 1.7 V vs. RHE on half-cell. Slow scanning speeds (typically $1 \text{ mV}\cdot\text{s}^{-1}$ or $5 \text{ mV}\cdot\text{s}^{-1}$) are preferred to limit the effects related to capacitive phenomena.

On rotating ring disc electrodes and half cells, the faradaic currents (I_f) are relatively low and the contribution of capacitive current (I_c) cannot be neglected. One way to reduce the capacitive effect is to reduce the scan speed to approach the steady state and limit the effects related to phenomenon of "charge / discharge the double layer" and pseudo capacitance. Figure 13 show the general shape of the voltammograms obtained for the water electro oxidation when tested in rotating disk electrode.

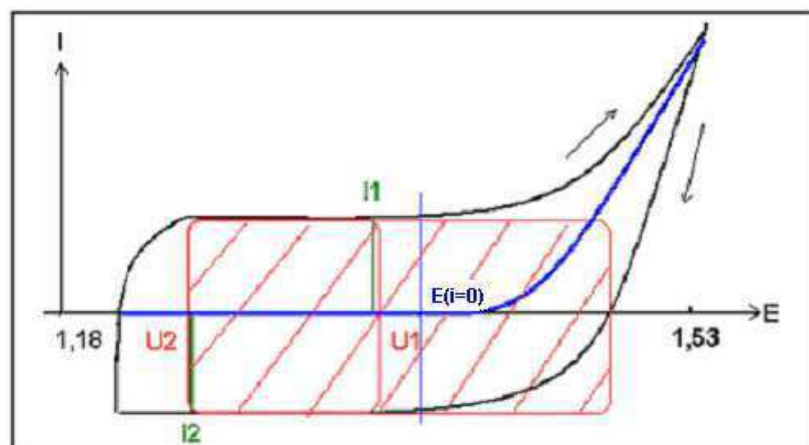


Figure 13 : Faradaic and capacitive currents measured during voltammetry

The black curve represents the response usually obtained for scanning between 1.18 and 1.53 V vs. RHE. For potentials lower than 1.35 V vs. RHE, the electro oxidation reaction of water is not initiated and only the capacitive contribution is I_c present. To determine the onset potential of reaction ($E (I = 0)$), characteristic of catalyst studied, it is necessary to overcome the capacitive part of the current.

The crosshatched in red is subtracted to the black curve to obtain the blue curve corresponding at a first approximation to the faradaic current. It is then possible to determine the value of $E (I = 0)$ or directly by plotting $\log |j|$ vs. E (Tafel curves).

To subtract the capacitive effect, a fixed range of potential (U_1, U_2), is used to determine the current values I_1 and I_2 corresponding respectively capacitive currents of the positive and negative sweep of the voltammogram. It is necessary to determine I_1 and I_2 as these two values are not always equal. I_1 is sometimes more important than I_2 , it may be due, for



example, to a difference between adsorption and desorption of water from the catalyst.

The specific capacity of the sample can then be calculated as follows:

$$C_s = \frac{Q}{\Delta U} = \frac{I_1 + I_2}{V_b} \quad (1.5)$$

I_1 and I_2 are expressed in A.

V_b is the scanning speed $V.s^{-1}$.

C_s is expressed in F.

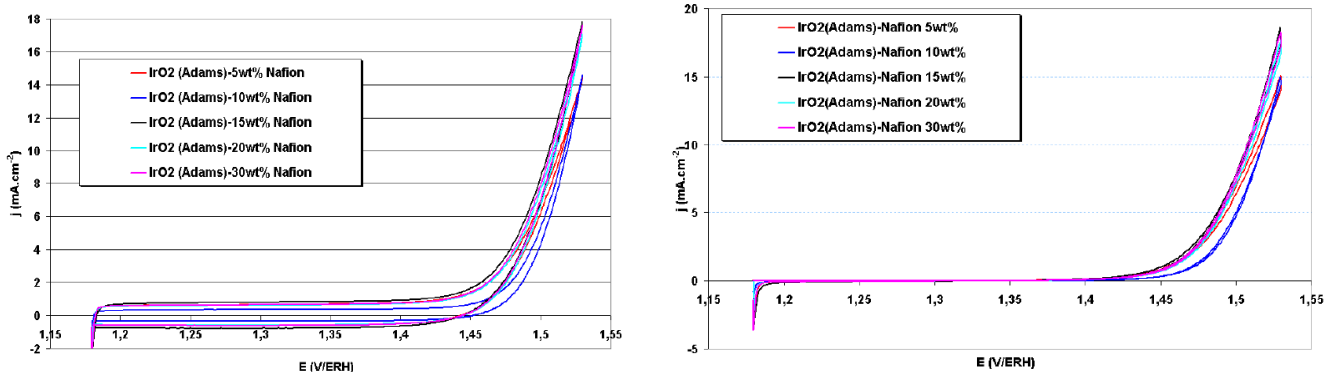


Figure 14 : CV curves before (left) and after (right) correction of capacitive effect

It is however still very difficult to determine accurately the potential $E_{(i=0)}$. Then we use "arbitrary" values that allow a consistent and more relevant interpretation:

- **E at 0.1mA.cm^{-2}** ; this value provides a comparison of potential more reliably the potential to which the reaction begins. The potential values are taken at the scan to negative potentials.

- **j at 1.5 V vs. RHE**; Comparison of current densities for low voltage. The current density values are also read from the scan to the potential negative.

Table 10 : Example of values determined on catalyst

	C_s (F)	R_{Ω} (Ω)	E (V vs RHE) at 0.1mA.cm^{-2}	j (mA.cm^{-2}) at 1.5V vs. RHE
Catalyst 1	0.18	6.7	1.414	12.2
Catalyst 2	0.17	6.9	1.431	12.4
Catalyst x

IV.4 Impedance spectroscopy measurements

The frequency range typically used for impedance spectroscopy characterization of PEM electrolysis MEAs is generally comprised between a few tens of kHz and several hundred MHz.

Depending on the equipment used, it is possible apply a current or a voltage signal. The amplitudes of the signals can be highly variable, but mainly for measurements of impedance spectroscopy to observe the following conditions:

- Linear response over a solicitation (user refines $U = f(j)$)
- Stationary (not changing the system over time)

It is essential to define accurately the frequency range, the type of solicitation electrical (current or voltage) and the amplitude of the signal.

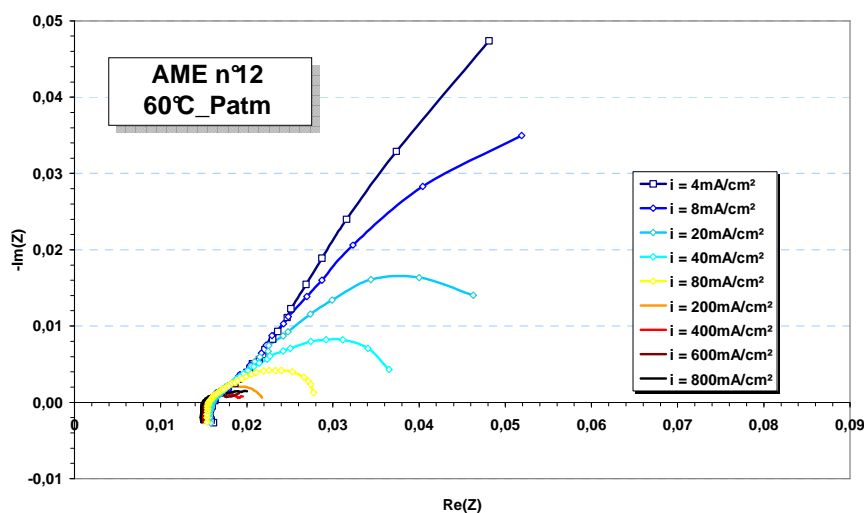


Figure 16 : impedance spectroscopy measurements on a PEM-WE MEA at various current densities

A special attention should be paid to the electrical connections of the device with the system under study. It will obviously minimize the potential sources of capacitive and inductive phenomena (connexions, crocodile clips, length of electrical wires, etc ...).

Measurements of electrochemical impedance spectroscopy are generally also performed on rotating ring disc electrode and half cell to evaluate the ohmic resistance of the system and the charge transfer resistance. The frequency range of study is 200 kHz - 100 mHz and the amplitude peak to peak of 10 mV. It is interesting to make these measurements different points of the polarization curve.



IV.5 Stability criteria (half cell and single cell tests)

The stability conditions at an operating point should verify the following criteria:

- 1 - Stability of pressure ($\Delta P < 10\%$ pressure) over a period of 2 minutes
- 2 - Stability of gas flow rates ($\Delta Q < 1\%$ rate) over a period of 2 minutes
- 3 - Stability of the amount of hydrogen in oxygen and oxygen levels in hydrogen ($\Delta \tau < 0.1\%$)
- 4 - Stability of temperature ($\Delta T < 2^\circ\text{C}$) over a period of 2 minutes
- 5 - Voltage stability ($\Delta U < 5\text{mV}$) over a period of 2 minutes

- Procedure:

- After applying a stabilized current density, observation of pressure, flow and temperature variation versus time (2min).
- If the parameters are stable ($\Delta P < 10\%$, $\Delta Q < 1\%$, $\Delta \tau < 0.1\%$, $\Delta T < 2^\circ\text{C}$), the voltage is considered stable when the voltage variation is less than $\pm 5\text{mV}/\text{cellule}$ on the period of 2 minutes.
- In case of oscillations, measure the oscillation frequency and the average value of at least 3 periods. Voltage is considered stable when changing the voltage is below where $5\text{mV}/\text{cell}$ on the period of 2 minutes.



IV.6 Polarisation curve (single cell tests)

This procedure must be followed to record a polarization curve.

1- The cell must operate at fixed conditions (current, pressure, temperature, etc...) for at least 30 minutes and verify the following criteria:

- Stability of pressure, gas flow, purity, temperature during the last 2 minutes
- Stability of cell tension $< \pm 5$ mV over 2 minutes

2- Polarization curve begins after stabilization of current density at 1 A/cm^2 .

3- The current is then increased to 2 A/cm^2 by steps of 0.2 A/cm^2 , 2 minutes long.

- The current increase will be restricted if the cell voltage reaches 2.5 V. Then, the maximum current density j_{max} will be defined.

4- Current is then stabilized at the maximum current density (j_{max}) for 2 minutes, verifying stability criteria next reduced by steps of 0.2 A/cm^2 still verifying stability criteria.

- It is important to note τ_{H_2} and τ_{O_2} . When reaching the highest value of safety (1%), decreasing current steps are interrupted. The current density then correspond to the minimum current of system operation in these conditions: j_{min}

5- If possible, a step at 0.1 A/cm^2 stabilized will be realized.

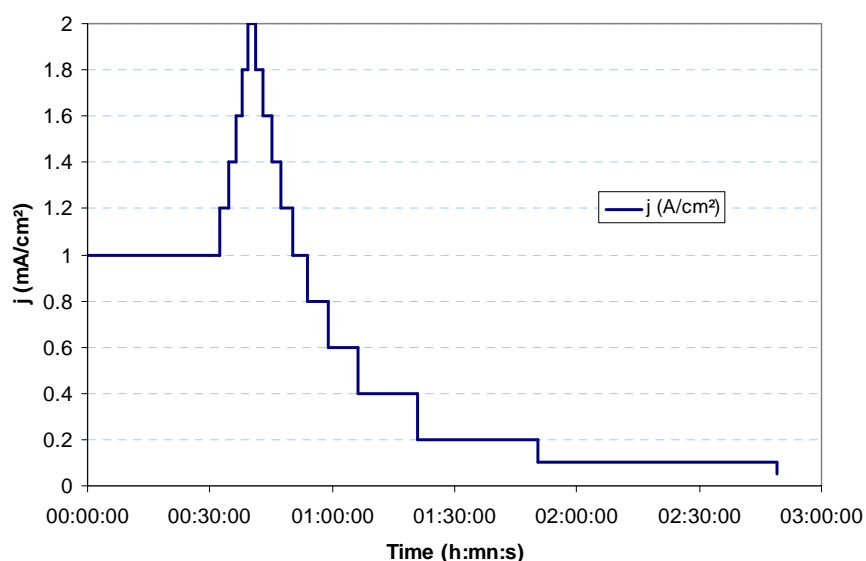


Figure 17 : example of proposed protocol for polarization curve recording

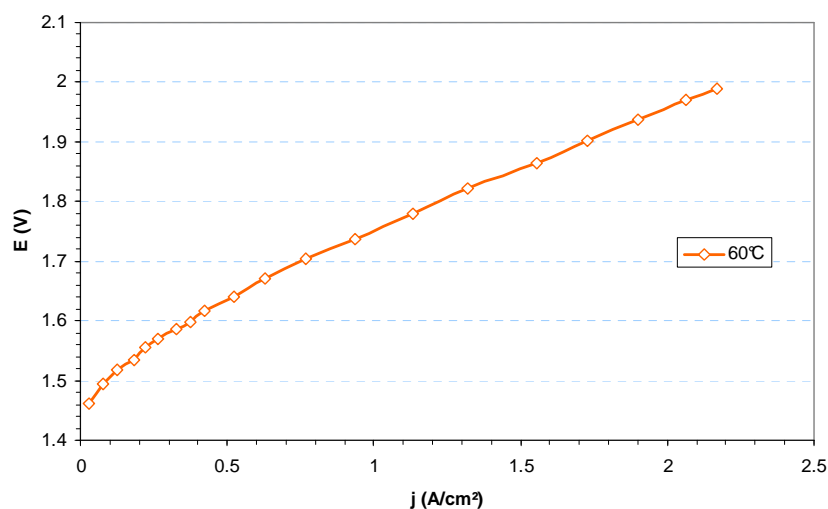


Figure 18 : example of polarization curve

Table 11 : Example of table showing the main performance results

	E (V) at 1A/cm ²	R _Ω (mΩ.cm ²)	j _{max} (A.cm ⁻²)	j _{min} (A.cm ⁻²)	τ _{H2} (%) at 1A.cm ⁻²	τ _{O2} (%) at 1A.cm ⁻²
MEA 1 (60°C, P _{atm})	1.73	0.175	-	0.1	0.8	0.5
MEA 2 (T°C, P)	1.82	0.205	1.75	0.1	0.6	0.4
MEA X (T°C, P)	



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