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# **Stable Reference Electrode in Polymer Electrolyte Membrane Electrolyser for Three-Electrode Measurements**

## Olli Sorsa, Jussi Nieminen, Pertti Kauranen, and Tanja Kallio

Department of Chemistry and Materials Science, Aalto University, 00076 Aalto, Finland

In this study, various methods to study individual electrodes in polymer electrolyte membrane cells are reviewed and a novel reference electrode design is developed for a laboratory scale single cell polymer electrolyte membrane water electrolyser. The design uses an internal pseudo-reference electrode which is proven to enable galvanostatic electrochemical impedance spectroscopy studies. The setup is used to study the state-of-the-art electrode materials with high loadings in a start-stop cycling durability test. The cycled catalyst layers are characterized ex-situ with SEM, TEM and XRD. As a result, on the anode the mass transport resistance increases, the macro porosity increases and a structural change from amorphous  $IrO_x$  toward crystalline  $IrO_2$  is detected. On the cathode the platinum particle size increases and an intensifying corrosion phenomenon is detected. In overall, this degradation has still low effect on the full cell performance during the studied 1750 hours. However, there is a clear indication that if the start-stop cycling is further continued, the cell will experience a dramatic performance loss much sooner than when operating it in a constant current mode.

For sustainable life, we must learn how to harvest and store renewable energy. During the last decade, huge amounts of research has been put into technologies for harvesting renewable energy<sup>1–3</sup> and the cost of renewable energy is expected to decrease further.<sup>4,5</sup> Since most of the renewable energy sources are intermittent, after reaching a low enough cost for renewable energy, we have to be able to store it. Most of the current storage technologies (e.g. hydro storage, batteries and compressed air) provide power as the output, but we can also use the power to produce high value chemical compounds.<sup>6</sup>

As the most facile molecules to electrosynthesize, hydrogen gas is seen as one of the best options as a product. It has a high energy density and its chemically bound energy can be converted back to electrical energy with a relatively high efficiency. Another option is to use hydrogen for CO<sub>2</sub> reduction in a separate process and to produce hydrocarbons for fuels or for the chemical industry.<sup>7,8</sup> One requirement for hydrogen production devices utilizing intermittent renewable energy is that they should endure short start-up and shut-down cycles as the device might be turned on and off multiple times during the day. Polymer electrolyte membrane (PEM) cells have relatively short startup periods and they can be used to produce hydrogen. This device is called polymer electrolyte membrane water electrolyser and is hereafter referred as PEMEL. For the PEMEL, as for many other similar devices, it is a challenge to find inexpensive, active and durable materials. Electrocatalysts are the extreme case as non-other than platinum group metals has been widely used to catalyse the electrochemical reactions in PEMELs.9

PEMEL is a device that works with a two-electrode configuration. This does not allow accurate methods to study the materials used for the electrodes because in the two-electrode configuration, both electrodes contribute the performance. However, a three-electrode configuration would allow the study of an individual electrode. For PEM fuel cells (PEMFCs), such configurations have been assembled and tested since the 1960s.<sup>10,11</sup> For the PEM water electrolyser, however, such designs are scarce and only few studies have been published.<sup>12–15</sup>

Herein we design a three-electrode configuration for the PEMEL and show that it can be used for electrochemical impedance spectroscopy (EIS). We use start-stop cycles to test how the stateof-the-art materials behave in a single cell PEMEL over time. The start-stop cycling durability is important due to intermittency of the renewable power sources.

#### **PEM Cell Configurations**

*Two-electrode configurations for PEM fuel cells.*—By default, fuel cell is a two electrode system. The basic operation mode is that hydrogen is fed to the anode and oxygen or air to the cathode. In

practice, this creates an open circuit voltage (OCV) of roughly 1 V which can be polarised toward 0 V to draw current. Usually, the peak power is reached at 0.7 V.<sup>16</sup> For the study of an individual electrode, there are a few alternative means.

*Rate-determining electrode.*—The anode polarises much less than the cathode in a PEMFC. This means that by increasing the loading of the anode and/or decreasing the loading of the cathode, the performance of the cell is mainly determined by the cathode. It is more difficult to establish a rate-determining anode, because the kinetics of the cathode is slower. However, this can be achieved by diluting the hydrogen with an inert gas, such as nitrogen.<sup>17</sup>

Symmetrical gas flows.—One option to study individual electrodes in a fuel cell is to use symmetrical gas flow and measure EIS at OCV. For this case, the electrodes have to be also identical. By using  $H_2/H_2$  gas flow, the result is the impedance of two anodes and by using  $O_2/O_2$  gas flow, the result is the impedance of two cathodes.<sup>18</sup> Unfortunately, here the cell can only be studied at OCV and not at the real operating conditions.

*Cyclic voltammetry.*—Another method to study an individual electrode is the cyclic voltammetry (CV). If the cell is operated at  $H_2/N_2$  or  $N_2/H_2$ , the  $H_2$  electrode can be used as the counter and the reference electrode, similar to the reversible hydrogen electrode (RHE).<sup>16,19</sup> This means that by serving the  $N_2$  electrode as a working electrode we can record a CV similar to a three-electrode cell with acidic electrolyte. The operation mode is called the *driven-cell mode*. The CV shows us the redox reactions and the specific adsoptions/desorptions of the studied catalyst. If a platinum catalyst is used, the electrochemically active surface area can be calculated either using the hydrogen underpotential adsorption/desorption method or the CO oxidation method. However, there is some uncertainty involved with this method<sup>20</sup> and the CV does not provide much information about the catalytic activity of the studied material in itself.

*Three-electrode configurations for PEM fuel cells.*—Because the two-electrode configuration methods do not always meet the requirements of the studies, several different reference electrode designs have been developed. A more detailed analysis of different reference electrodes in PEMFCs has been reviewed by Hinds.<sup>11</sup> In general, there are two types of reference electrodes used in PEM cells: the external type and the internal type. For the internal type, the reference electrode is connected directly to the PEM whereas for the external type, the electrode is connected using for example a liquid electrolyte bridge.<sup>21</sup>

*External type reference electrode.*—For the external type, one can use any conventional reference electrode in any acidic solution. This

is useful, because the potential of the reference electrode is known. However, the connection should be constructed cautiously so that the liquid would not interfere with the cell or dry so that a concentration gradients would appear. Additionally, the Donnan-potential has to be taken into account due to the liquid/membrane connection. A few examples of the constructions can be found in Refs. 22–24.

Internal type reference electrode: pseudo reference.—The simplest method for an internal type of reference electrode is to place a pseudo reference electrode on the PEM and connect it with a thin wire. Common materials for this are carbon, platinum black and Pt/C. The reference electrode can be placed either between two separate membranes<sup>25</sup> or next to either the cathode or the anode.<sup>26</sup> The advantage of the pseudo reference electrode is the simple construction but because its potential is not known, other internal designs have been developed. Another method is to flow hydrogen on a platinum reference electrode to construct a pseudo-reversible hydrogen electrode (p-RHE).<sup>27-30</sup> The p-RHE requires a flow field to be construct to the cell hardware for the hydrogen flow. However, in a hydrogen PEMFC the hydrogen feed of the anode can be used for the reference electrode as well, using a common flow field.<sup>31</sup> Eccarius et al. and Gerteisen<sup>32,33</sup> have shown another method to prepare pseudo-reversible reference electrodes by separating a small electrode island on the cathode and anode sides of the MEA with laser ablation. This method can be used to correct the misalignment of the catalyst layers avoiding edge effects and to separate the reference electrode with an exact distance from the working electrode with high precision. In this method, the reference electrodes use the same flow fields with the anode and cathode meaning that the potential of a reference electrode is equal to the equilibrium potential of the reaction of the feed gas.

Internal type reference electrode: dynamic hydrogen electrode.-Another common reference electrode in PEMFCs is the dynamic hydrogen electrode (DHE) which was introduced for the first time by Giner in the 1960s.<sup>10</sup> The idea is to make a small water electrolyser MEA next to the fuel cell MEA and use it as a reference electrode. An external power source is used to split water with a low constant current and the gas products are flown out of the cell. When using this type of a reference electrode, the water electrolysis induced membrane drying must be prevented. However, in the case of direct methanol fuel cell, it is not an issue because the anode feed is liquid.34-37 In comparison to p-RHE, DHE is less sensitive to poisoning by contaminants, such as CO, because the hydrogen is being produced on the surface of the electrode, and by reversing the direction of the current such contaminant species are oxidised and desorbed.<sup>21</sup> This means that the DHE maintains the same potential better than the p-RHE. The DHE is generally considered as the most useful reference electrode for the PEMFC and in the literature there are many different designs how to implement it.34-41

In each of the internal type reference electrode, the positioning of the electrode is critical, because the potential field caused by the operating anode and cathode can influence the potential of the reference electrode if it is placed too close to the working electrode.<sup>40,42,43</sup> On the other hand, the ohmic resistance between the reference electrode and the working electrode increases as the distance increases.

*Two-electrode configurations for PEM water electrolysers.*— Similar to the PEMFC, the PEMEL is also a two-electrode system. The basic operation mode is that water is fed to both electrodes (or at least the anode). The oxygen evolution reaction (OER) takes place on the anode and the hydrogen evolution reaction (HER) takes place on the cathode after an onset voltage of roughly 1.4 V is reached. The cell is operated with a current of 0.6-2.0 A cm<sup>-2</sup> at a voltage of 1.8–2.2 V.<sup>9</sup> For the study of individual electrodes, there are a few alternative means. However, the conditions of the electrodes are more difficult to modify, as the standard operation does not include feeding any gases that could be easily substituted. *Rate-determining electrode.*—In contrary to the PEMFC, the anode causes majority of the kinetic losses in PEM water electrolyser. Consequently, the anode can be considered as the rate-determining electrode if the catalyst loadings are relatively even. Therefore, when studying the anode it is often assumed that the cathode electrode will not polarise.<sup>44,45</sup> For the study of the cathode, Bernt et al.<sup>46</sup> have estimated the kinetic overpotential for the HER by linearization of the Butler-Volmer equation and calculating the effective proton transport resistance according to Ref. 16. This method requires to determine the exchange current density of HER on the cathode catalyst and the electrochemically active surface area.

*Cyclic voltammetry.*—If special arrangements are done to the electrolyser setup, it is possible to measure cyclic voltammetry similar to the PEMFC. Instead of water, the counter electrode needs to be fed by hydrogen in order to guarantee that it will not polarize, and if platinum is used the electrode functions as an RHE. If water flow is used on the working electrode, it should be deoxidized. For example, Elsøe et al.<sup>47</sup> have recorded the CV of an IrO<sub>x</sub> anode in nitrogen saturated water versus a Pt/C in a humidified hydrogen flow. They showed that the typical redox behavior of IrO<sub>x</sub> can be measured in an electrolyser cell. The technique can be further used to calculate the total voltammetric charge<sup>44</sup> which is directly proportional to the total surface area.<sup>48</sup> However, the surface area obtained by this method is not valid for the potentials of the OER. On the other hand, EIS can be used to estimate the surface area of the electrode at the desired potential.<sup>49</sup>

*Electrochemical impedance spectroscopy.*—With electrochemical impedance spectroscopy it is possible to identify how the overall losses of the system are distributed. The ohmic losses are easy to identify as the high frequency resistance. The rest of the losses are due to charge transfer of the reactions and mass transport.<sup>45</sup> This method is often used to calculate the *IR*-free cell voltage or a quantity called overvoltage  $\eta$  which is the sum of the anodic and cathodic overpotentials.

$$\eta = E_{\text{cell}} - E^0(p, T) - IR_{\text{ohmic}} = \eta_{\text{anodic}} + \eta_{\text{cathodic}}$$

Here  $E_{cell}$  is the total cell voltage,  $E^0$  is the equilibrium cell voltage (which depends on the pressure p and temperature T), I is the current and  $R_{ohmic}$  is the ohmic resistance. Overvoltage represents with higher accuracy the efficiency of the catalyst layers, but cannot be used to separate the anode and cathode losses from each other. Generally, in EIS an electrochemical reaction is described with a resistor R and a capacitor C in a parallel connection. If the time constants  $(\tau = R \cdot C)$  of the anode and cathode differ by at least one decade, it is possible to separate the anodic and cathodic losses.<sup>50</sup> This is more often possible for the PEMEL than for the PEMFC because in the latter the MEA is often symmetric as for the PEMEL different catalysts are used for the anode and cathode. Even if two separate semi circles can be distinguished, it is important to bear in mind that a single circuit component can always comprise of multiple similar components. Thus, one can never be certain if a semicircle is caused by only one RC-circuit. However, if a three-electrode setup is used, the anode and cathode responses can be separated with certainty.

*Three-electrode configurations for PEM water electrolysers.*— The few studies that have been done so far for PEMELs use an external reference electrode,<sup>12,14</sup> DHE<sup>13</sup> or an external platinum pseudo reference electrode.<sup>15</sup> None of these studies show the use of EIS in the study of individual electrodes. For some reason, the internal pseudoreference electrode that is often used in PEMFC is not that common for PEMEL. Nevertheless, in this study we have designed one and proven that it can be used for the EIS which requires high stability from the reference electrode.

As already mentioned earlier, the positioning of the reference electrode in the solid electrolyte is very important. The essential parameters here are the thickness of the polymer electrolyte ( $\delta$ ) and the distance of the reference electrode from the edge of the working

electrode (L). Adler et al.<sup>51,52</sup> showed that with a perfect alignment, the measured potential is the same on both sides of the MEA if  $L/\delta > 3$ . However, a small misalignment of the anode and cathode will unbalance the potential field severely.<sup>42</sup> Consequently, if the reference electrode is far enough from the working electrode, the measured potential is equal to the potential at  $0.5\delta$  in the middle of the MEA. However, too high distance will increase the IR-loss. One method to overcome these issues is to use two reference electrodes: one for the anode and one for the cathode.<sup>43</sup> The dimensions of the three-electrode setup are shown in supplementary information (Fig. S1) and the ratio  $L/\delta = 2 \text{ mm} / 0.254 \text{ mm} \approx 8$ . However, due to the symmetrical design, we only acquire one value from the anode and the cathode. Also, the effect of misalignment of the electrodes is minimized by the circular shape of the reference electrode. The work of Adler et al.<sup>51,52</sup> was done for a high temperature oxygen generator and the work of He et al.42 and Liu et al.<sup>43</sup> for the PEMFC. Such simulations have not been done for the PEMEL.

#### Experimental

**Chemicals.**—The used membrane was Nafion 115 (DuPont) bought from Ion Power. The catalysts, 40 wt -% Pt/C (HiSPEC 4000),  $IrO_x \cdot 2H_2O$  (Premion) and platinum black (HiSPEC 1000) were purchased from Alfa Aesar. All the solvents were reagent grade purity and ultrapure ion-exchanged Milli-Q water (Millipore) was used for all water purposes. For MEA preparation, 5 wt -% Nafion dispersion in lower aliphatic alcohols and water (Aldrich) was used as a binder, and the platinum wire (100  $\mu$ m, 99.999% purity) working as the reference electrode contact was purchased from Alfa Aesar.

*MEA preparation.*—MEA preparation was constructed by sandwiching two separate Nafion 115 membranes which had a 24 mm diameter disc electrode on one side and a ring electrode (32 mm outer diameter and 28 mm inner diameter) on the other side. Schematics and photographs of the MEA are presented in Fig. 1. Membranes were pretreated by boiling them first in 5 wt -% H<sub>2</sub>O<sub>2</sub>, then in 0.5 M H<sub>2</sub>SO<sub>4</sub> and finally three times in H<sub>2</sub>O. The rings and the cathode were coated with 40 wt -% Pt/C and the anode with IrO<sub>x</sub>·2H<sub>2</sub>O. The inks were prepared by dispersing the catalyst in a mixture of water and i-PrOH using a magnetic stirrer and an ultrasonicator. The loadings were 0.5 mg cm<sup>-2</sup> Pt for cathode, 2 mg cm<sup>-2</sup> IrO<sub>x</sub> for anode and 0.1 mg cm<sup>-2</sup> Pt for the rings. Ionomer content was 30 wt -% for all the electrodes.

The disc electrodes were prepared first and the membranes were heat pressed with 5 t at 130°C for 2 min before preparing the ring electrode. Before spraying the ring electrode, the ring side of the membrane was sprayed with 180  $\mu$ l 5 wt -% Nafion ionomer (Aldrich) diluted with 640  $\mu$ l i-PrOH to improve the proton contact between the membranes. After spraying the ring, the membranes were sandwiched with a 100  $\mu$ m thick platinum wire between the membranes, allowing a contact for the ring reference electrode. The tip of the platinum wire was treated as platinum black by reducing it with 100 mA cm<sup>-2</sup> for 60 s in aqueous 100 mM H<sub>2</sub>PtCl<sub>6</sub> (Aldrich). The membranes were heat pressed on top of each other with 5 t at 130°C for 2 min.

**PEM electrolyser setup.**—The electrolyser setup consists of a circular cell that has an anode and a cathode compartment separated by the MEA.  $H_2O$  is circulated through both compartments at 50 ml min<sup>-1</sup>. The compartments consist of a titanium piston, a titanium mesh and a platinum coated titanium sinter. The MEA is placed between the sinters and the cell is closed by four screws that are tightened to 3 Nm. A pressure of 10 bar is being applied on the titanium pistons by technical grade N<sub>2</sub>. This ensures a proper electric contact between the cell parts. The circulated H<sub>2</sub>O is heated by heat exchangers and purified by ion exchangers (Amberlite IRN-150, Alfa Aesar) before entering the cell. The temperature of the cell is measured from the outlet of the H<sub>2</sub>O circulation and is set to 50°C when characterising the cell and to 60°C when cycling. Measurements were conducted using AUTOLAB PGSTAT302N potentiostat with a Booster20A and Nova 2.1 software.



Figure 1. Construction of the three-electrode setup. The anode and cathode are painted on separate membranes and then sandwiched together with a reference electrode ring in between. A platinum wire is used as a contact for the reference electrode.

PEM electrolyser experiments.—After assembying the cell, it was left to stabilize for at least 1 hour. The cell was then set to a galvanostatic cycling in which the cell was set at 1 A cm<sup>-2</sup> for 60 s and off for 300 s (see Fig. 2a). Galvanostatic impedance at 500, 200, 100 and 50 mA cm<sup>-2</sup> with 10% amplitude from 10 kHz to 10 mHz was measured once a week using three electrode configuration utilizing first the anode as the WE and the cathode as the CE and then vice versa. The impedance data of MEA3 was fitted to the model circuits shown in Fig. 3 using the Matlab impedance fitting script Zfit (v. 1.2) by Jean-Luc Dellis.<sup>53</sup> The impedance of the full cell was measured using the same parameters after the three-electrode impedance measurements. The polarization of the cell was tested at the beginning of the cycling by first applying the highest current (1 A cm<sup>-2</sup>) for 30 minutes and then measuring each current step for 10 minutes. This was done first in two electrode setup and then in three electrode setup utilizing first the anode as the WE and the cathode as the CE and then vice versa.

**MEA characterization.**—Scanning electron microscopy (SEM) imaging was carried out using a Tescan Mira3 microscope and the transmission electron microscopy (TEM) imaging was carried out using a JEOL JEM-2800 microscope. Cross-sectional SEM samples were prepared by breaking the membrane in liquid nitrogen resulting in a smooth cross-sectional surface with the thickness of the membrane and the catalyst layer (CL) remaining unaffected by the cut. TEM samples were prepared by dispersing some of the CL in i-PrOH and applying two drops of the dispersion on a holey carbon film 400 mesh Cu TEM grid (Agar Scientific). X-ray diffraction (XRD) was performed using a PANalytical X'PertPro diffractometer equipped with a Cu K<sub>a1</sub> X-ray source. The samples were placed on a stainless steel disc which was pressed level with a spring. The Scherrer's equation<sup>54</sup> was used to determine the average crystal size *d*.

$$d = \frac{K\lambda}{\beta_{2\theta} \cos\theta}$$



Figure 2. The start-stop cycling procedure and the response of the voltage in (a), the voltage at 1 A cm<sup>-2</sup> during the cycling for the three studied MEAs in (b), the response of the full cell, anode vs. reference and cathode vs. reference when 1 A cm<sup>-2</sup> is applied in (c) and the polarization of the electrodes in (d).

The shape factor K is considered to be 0.9 due to spherical particle shape.  $\lambda$  is the wave length of the X-ray source (0.15406 nm),  $\beta_{2\theta}$  is the full width at half maximum of the reflection and  $\theta$  is the incident angle of the reflection.

#### Results

Electrolyser cell experiments .- Three separate MEAs were investigated in this study. Two of them were constructed as three-electrode MEAs as described in the Experimental section and one was constructed as a regular two-electrode MEA from a single membrane as a reference sample for the ex-situ characterization. As mentioned in the experimental section, the MEAs were cycled using a start-stop procedure. The procedure and the typical response of the cell is shown in Fig. 2a. The 1 min/5 min times were chosen because the time is just enough to stabilize the cell in order to simulate a complete startup/shut-down cycle. The cell voltage during the cycling is shown in Fig. 2b. The voltages are slightly increasing during the studied period, but major cell performance degradation is not observed. The discontinuity in the signal is caused by the three-electrode EIS measurements which take roughly 10 h and are measured in a constant current mode. The reference MEA1 has much lower cell voltage because it is constructed of a single membrane which has roughly half the ohmic resistance of the three-electrode MEAs.

The stabilisation of the potentials is shown in Fig. 2c when 1 A cm<sup>-2</sup> is applied to the cell. Full cell stabilises after one minute and is very stable, as expected. The anode and cathode stabilize in less than ten minutes and stays stable allowing the measuring of EIS in the range of 50–1000 mA cm<sup>-2</sup>. The polarization of the cell is shown in Fig. 2d and demonstrates that the difference of the individual poten-

tials follows consistently the voltage of the full cell. The onset of the cathode should be close to 0 V vs. SHE which means that the potential of the reference electrode is roughly -200 mV vs. SHE. Additionally, the EIS of the full cell is compared to the point by point sum of the anode and cathode in the supplementary information (Figs. S2 and S3). Since the spectra are similar to each other, it can be confirmed that the reference electrode is valid for individual electrode investigations.

EIS was used to study if degradation of the cell components can be detected during the cycling. The EIS of the anode and cathode of the MEA3 at the beginning of the cycling are shown in Fig. 3. The interpretation of the EIS data is found in the Discussion. The values of the fitted key parameters are shown in Figs. 4 and 5 for anode and cathode, respectively.

*Ex-situ characterization.*—*Scanning electron microscopy.*—SEM images were taken in order to study if the morphology of the catalyst layers has been affected by the start-stop cycling. In Fig. 7 we can see that no clear structural changes are observed. The thickness of the catalyst layer increases, from 9 to 13  $\mu$ m for the anode and from 5 to 10  $\mu$ m for the cathode. The anode<sup>44,46</sup> and cathode<sup>16,46</sup> initial thicknesses are in good agreement with the literature. After taking into account the fact that the MEAs were hand-painted using an airbrush, we can say that the increase is not that substantial.

*Transmission electron microscopy.*—TEM images were taken in order to study if the catalyst particles are affected by the start-stop cycling. In Fig. 8 we can see that the platinum particles grow during the cycling whereas the iridium oxide particles remain unaffected. For the cathode, a particle size analysis was conducted to more than 200 particles per MEA and the size distribution is seen in the insets. The



Figure 3. Equivalent circuits of the anode and the cathode and example fits of the measured EIS to these circuits. The data is marked with circles ( $\circ$ ) and the fits with crosses (X). The data presented here is the first set of the fitted EIS.

mean particle size grew from 4.3 to 5.8 nm after 550 h and to 7.0 nm after 1750 h of cycling.

*X-Ray diffraction.*—The XRD patterns of the catalyst layers are shown in Fig. 9. The XRD patterns of the stainless steel sample holder and a Nafion 115 membrane are shown, because they are located under the catalyst layer in the measurement setup and therefore their patterns are also seen in the actual samples. The stainless steel holder shows several iron reflections within the measured window and all of them can be seen in the actual samples, but with a lower intensity. The Nafion 115 membrane shows a wide reflection at a low angle, approximately 16° and another at 39°. The first one is also seen in the actual samples, but it is far less intense. Additionally, a weak reflection at roughly 26° is seen in the cathode which is caused by graphite in the support material.

#### Discussion

**Interpretation of the anode EIS.**—The anode impedance is interpreted as a resistor and two *RC*-circuits as shown in Fig. 3. The equivalent circuit is the same as in Ref. 55 and similarly interpreted. The values of the fitted key parameters are shown in Fig. 4.  $R_{el}$  is caused by the ohmic resistances of the system which are the membrane, catalyst layer (CL), porous transport layer (PTL), end plate and connections of the potentiostat. The majority of the ohmic resistance is caused by the membrane, but if the PTL is oxidised it can also increase the ohmic resistance substantially. Our setup is not optimal for studying  $R_{el}$  because the MEA is made of two sandwiched membranes. Thus, we do not pay much attention to its value or changes in it during the cycling.

The high frequency semi-circle is caused by mass transport (fluids and ions) in and out of the pores where the reaction happens. The

low frequency semi-circle is caused by the OER. We see two separate semi-circles because there are two phenomena happening at different time constants. The mass transport is limited in only a secluded area of the CL which has less electrochemically active surface area than where the reaction happens. Consequently, they have different values of capacitance and therefore also different time constants. The mass transport is significant in this case because the loading of the anode is high (2 mg cm<sup>-2</sup>).  $C_1$  does not have a clear trend versus current which means that the mass transport limitation takes place roughly at the same locations independent of the magnitude of the reaction. However, the mass transport resistance,  $R_{mtx}$ , clearly increases with the current which simply means that higher mass transport generates higher resistance. C2 decreases with the current which can be explained by the fact that with higher reaction rate more active sites are blocked by the evolving gas bubbles.<sup>49,55</sup>  $R_{ct}$  decreases with increasing current because with higher current the overpotential for the reaction is higher and thus the anodic charge transfer resistance lower.

It is important to note that after 1000 hours  $C_1$  starts to decrease and  $R_{mtx}$  starts to increase. Also,  $C_2$  increases slightly during the whole cycling. This implies that something is happening to the pores. If the bubble formation starts to happen closer to the micro pores where the reaction is taking place it would decrease the electrochemically active surface area of the pores where the limiting mass transport is happening and increase the mass transport resistance. This would require the growth of macro pores inside the CL to the size where a bubble starts to form. On the other hand, if the limiting mass transport is caused by proton transfer in the CL, an increased porosity can cause the ionomer chains to lose contact and thus increase the mass transport resistance. It is generally known that with high iridium loading the performance of the anode CL should not decrease by applying constant current,<sup>56</sup> but with start-stop cycling it happens already after 1000 hours.



Figure 4. The development of the impedance parameters during the 1750 hours of cycling on the anode of MEA3. Top left is the first capacitance, top right is the second capacitance, bottom left is the mass transport resistance and bottom right is the charge transfer resistance.

**Interpretation of the cathode EIS.**—The cathode impedance is interpreted as a coil, a resistor, an *RC*-circuit and an *RL*-circuit as shown in Fig. 3. The values of the fitted key parameters are shown in Fig. 5. The first coil is due to the wires and is only influencing the cathode impedance because the time constant of the first element of the anode is higher.  $R_{el}$  is caused by the ohmic resistances similar to the anode. The *RC*-circuit is caused by the HER. In Fig. 5 we see that *C* is almost independent of the current and fairly stable over time.  $R_{ct}$  is also quite stable over time, but, in contrary to the anode, increases with increasing current. However, the magnitude of this dependency is much smaller and a possible explanation is that the charge transfer *RC*-circuit and the mass transport *RC*-circuit are overlapped and thus the current dependency partially neglected.

The interpretation of the *RL*-circuit requires more attention. It is known that a corroding component can result in an inductive loop at low frequencies.<sup>57</sup> The question is that which component on the cathode would corrode at cathodic conditions. The start-stop cycling used in this study results in a situation where the remaining hydrogen on the cathode CL is repeatedly chemically oxidised by oxygen diffusing through the MEA. During this process, the formation of hydrogen peroxide is possible. Hydrogen peroxide, on the other hand is known to break the Nafion membrane and release fluoride ions.<sup>58</sup> By repeating this process it is possible that such species are generated in the CL and therefore increase the magnitude of the inductive loop. In Fig. 5 we can clearly see that the corrosion resistance increases by current and by cycling time. Generated hydrogen peroxide and fluoride ions can also cause another component in the cell (platinum, titanium or carbon) to corrode. It is important to note that the corrosion of the

Nafion membrane cannot be seen in the EIS because the membrane does not conduct electricity.

Babic et al.<sup>59</sup> have shown that possible cation contaminants (Ca<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Fe<sup>3+</sup>, Ti<sup>2+</sup>) in a PEMEL will gradually accumulate on the cathode CL due to the electric field and decrease the cell performance. Therefore, another possible explanation for the *RL*-circuit is the corrosion of contaminants on the cathode CL. However,  $R_{ct}$  does not increase during the cycling as would be expected in the case of contamination. Also, the water circulation in the PEMEL system used for this study has ion exchangers right before the cell which means that any foreign ions should be removed from the water. Consequently, we do not attribute the inductive loop to contamination.

Similar low frequency inductive loops have also been recorded for the cathode of a PEMFC.<sup>60</sup> A common understanding has not yet been reached in the scientific community for this phenomenon, but two most common plausible explanations are side reactions with intermediate species and water transport characteristics. One model<sup>61</sup> suggests that hydrogen peroxide can lead to formation of PtO<sub>x</sub> and subsequently dissolution of platinum. In comparison to the PEMEL, the potential is much higher in the PEMFC cathode which means that corrosion of platinum in the PEMEL is less likely to happen during operation.

In order to study if the inductive loop is caused by carbon corrosion we assembled an MEA with platinum black as the cathode and subjected it to the same measurement procedure. The EIS of platinum black cathode is shown in the supplementary information (Fig. S4) and show no inductive loop after 380 h of cycling. This means that the most probable reason for this phenomenon is corrosion of the catalyst support. Based on the Pourbaix diagram<sup>62</sup> carbon should be



Figure 5. The development of the impedance parameters during the 1750 hours of cycling on the cathode. Top left is the capacitance, top right is the corrosion inductance, bottom left is the charge transfer resistance and bottom right is the corrosion resistance.

stable at the pH and potential of the cathode CL, but the influence of hydrogen peroxide (a strong oxidizer) and fluoride ions (strong corrosive) can cause carbon to corrode and form  $CO_2$  and  $H_2CO_3$ . In PEMFCs, carbon corrosion is a well-known degradation mechanism especially during start-stop cycles.<sup>63</sup> Carbon corrosion can cause the Pt nanoparticles to detach from the support and ultimately to collapse the porous structure of the CL.<sup>64</sup>

Interpretation of the full cell EIS .- In theory, the EIS of the full cell impedance should be the sum of the anode and cathode,  $Z_{\text{Full Cell}}(\omega)$  $= Z_{Anode}(\omega) + Z_{Cathode}(\omega)$ . Therefore, we might expect to see four different features in the full cell impedance as we saw two features in both the anode and cathode. However, because the time constant of the  $R_{\text{mtx}}C_1$ -circuit in the anode (~0.8 ms) and the time constant of the  $R_{ct}C$ -circuit in the cathode (~0.1 ms) are close to each other, these features are combined into one RC-circuit where  $R_{1,\text{Full Cell}} = R_{\text{mtx,Anode}}$ +  $R_{ct,Cathode}$  and  $1/C_{1,Full Cell} = 1/C_{1,Anode} + 1/C_{Cathode}$ . Also, because the time constant of the  $R_{ct}C_2$ -circuit in the anode (~10-200 ms) and the time constant of the  $R_{cor}L_{cor}$ -circuit in the cathode (~2-10 ms) are close to each other, these features subtract each other and the one with the higher resistance (in our case the anode) will remain in the total cell circuit. We use the symbol X for this component in Fig. 6 because it can act either as a capacitor or a coil. The resistor, parallel to this component  $R_{2,\text{Full Cell}} = [R_{\text{ct,Anode}} - R_{\text{cor,Cathode}}].$ 

Consequently, we can only separate two features in the full cell impedance, even though it is constructed of at least four different ones. The ohmic resistances are naturally also cumulated. The fitted parameters of the anode and cathode shown in Figs. 4 and 5 have been used to draw an EIS spectrum of the full cell in Fig. 6. The match is good considering that the spectra of the individual electrodes and that of the full cell are obtained in successive measurements. The plot highlights the fact that the majority of losses in the PEMEL are caused



Figure 6. EIS of the modelled and measured full cell EIS and the anode and cathode fits that have been used to derive the full cell model at  $200 \text{ mA cm}^{-2}$ .



Figure 7. Cross-sectional SEM images of the catalyst layers of the three studied MEAs after the cycling.

by the anode. Without the information of the individual electrodes the full cell impedance would be interpreted as two *RC*-circuit. This is basically observed also here but based on the measurements carried out for the individual electrodes we know that these semi-circles are a reconstruction of different features.

*Morphology of the catalyst layers.*—Based on the SEM images in Fig. 7 we found a trend that the cycling causes the catalyst layers to expand. This can be caused by pore size increment which is in agreement with the anode capacitance development shown in Fig. 4. The porosity development of the cathode is more difficult to observe based on the EIS because the reaction is only taking place on the platinum particles which are covering only a minor part of the carbon support.

Siracusano et al.<sup>65</sup> reported that neither of their catalyst layer thicknesses changed considerably during 3500 h of constant current at 1 A cm<sup>-2</sup>. However, they noticed that the membrane thickness decreased by up to 50%. Our setup is not optimal for studying the



Figure 8. TEM images of the cathode and anode catalyst layers of the three studied MEAs after cycling. Size distributions of the platinum particles are shown in insets for the cathodes.



Figure 9. XRD patterns of the three studied MEAs. The diffraction of the stainless steel sample holder is seen through the MEAs and is therefore shown here. The rest of the reflections are related to iridium<sup>71</sup> and iridium dioxide<sup>72</sup> on the anode (left) and to platinum<sup>71</sup> on the cathode (right).

membrane, but we also noticed a decrease in ohmic resistance. Another cause for decrease in ohmic resistance is the increased mechanical contact between the PTL and the CL which has been observed in the beginning of durability tests.<sup>66</sup>

Anode catalyst degradation.—In the XRD spectra of the anodes in Fig. 9 we can see that the metallic iridium reflections remain sharp. However, the iridium oxide reflections are becoming clearer after cycling. This is because the iridium oxide is initially amorphous and during cycling forms small crystals which grow. Iridium oxide has higher activity toward the OER in amorphous  $IrO_x$  state due to increased amount of hydroxyl groups.<sup>67</sup> In this respect, crystallisation of iridium oxide is considered degradation. In the cathode we can see that the platinum reflections become sharper during the cycling. This is caused by platinum particle size increment. The Scherrer's equation<sup>54</sup> is used to find out that the average crystal size increases from 4 nm to 7 nm after 550 h and to 8 nm after 1750 h of cycling. This is in good agreement with the analysis done with the TEM images. The peak positions do not change considerably on either of the electrodes, taking into account the inaccuracy caused by the sample preparation.

**Cathode catalyst degradation.**—Significant platinum particle size growth was detected in the TEM images (Fig. 8) and XRD spectra (Fig. 9) of the cathode catalyst layer. The common platinum particle size growth mechanisms are Ostwald ripening, particle migration, particle agglomeration and particle detachment.<sup>68</sup> Xu et al.<sup>69</sup> showed that platinum particles grow fast in the potential of 0.4 - 0.6 V vs. RHE and even faster when the potential is cycled over that range. This is exactly what happens in the PEMEL cathode during start-stop cycling and therefore is an expected result. Particle size growth affects directly the surface area of the platinum catalyst. However, no changes in the capacitance of the cathode is seen in the impedance implying

that even the reduced platinum surface are does not limit the PEMEL performance.

Similar cathode catalyst degradation has been published by Siracusano et al.<sup>65</sup> and Rakousky et al.<sup>66</sup> In these studies, the platinum particles grew from 10 to 12 nm during 3500 h of constant current at 1 A cm<sup>-2</sup> and from 4 to 8 nm during 1150 h of constant current at 2 A cm<sup>-2</sup>. In these studies, the anode catalyst particle size was unaffected by the durability experiment which is the same result as what we received.

#### Conclusions

An MEA with an integrated reference electrode was designed and the state-of-the-art materials tested in a 1750 hours long start-stop cycling in a laboratory scale single cell PEM water electrolyser. The reference electrode was proven to enable EIS measurements. EIS was used to study the degradation of the anode and cathode separately and supplemented with ex-situ characterization using SEM, TEM and XRD. The following conclusions were deduced.

• Degradation is taking place both on the anode and on the cathode catalyst layer.

• On the anode, an increase in mass transport resistance, an increase in macro porosity and a structural change from amorphous  $IrO_x$  toward crystalline  $IrO_2$  is detected.

• On the cathode, an increase in platinum particle size and an intensifying corrosion phenomenon is detected which is most likely due to carbon corrosion.

• These degradation phenomena still have minor effect on the total cell performance during the measured 1750 hours.

The cell voltage at 1 A  $\text{cm}^{-2}$  was throughout the whole cycling fairly stable (1.9–2.0 V) and did not have a clear trend of increasing or

decreasing. This is most likely due to the high catalyst loading used in this experiment. Decreasing the loadings is the main challenge for the industry and so far techniques to maintain the high cell performance with decreased loading has already been developed. Unfortunately, the degradation methods described here and elsewhere<sup>56,68–70</sup> prevent the use of low loading (total PGM loading < 100  $\mu$ g cm<sup>-2</sup>) industrially. The three-electrode setup demonstrated in the study is designed for the research of individual electrodes and especially their degradation.

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Tanja Kallio https://orcid.org/0000-0001-6671-8582

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