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Challenges and Possibilities of EIS on PEMEC

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Abstract

Electrochemical impedance spectroscopy (EIS) has been proven a very strong electrochemical characterization tool in electrochemical research in general and in the areas of fuel cell and battery research in particular. However, this is not the case for polymer electrolyte membrane electrolysis cells (PEMEC), for which relatively few reports on the application of systematic EIS studies are available. Asking experienced researchers in the field about why, the answer has often been that these cells reveals too much electrical noise to obtain EIS with acceptable quality due to O₂ and H₂ bubble formation.

Our view of the ideal structure of a PEMEC is that there ought not to be any effect of gas bubbles on the EIS as the current paths should not be disturbed by bubbles. However, we also see noise in our spectra, but the level of noise varies very much from one cell type to another. We have studied noise on three types of PEMEC and two type of alkaline electrolysis cell (AEC) for comparison. A characteristic feature of the studied PEMEC is that there is no or very little noise seen in the EIS in the frequency range above ca. 500 Hz and again not much noise below 5 Hz.

Our hypothesis is that this phenomenon is related to bubbles that are adhering to active sites of the electrocatalyst. When the catalyst layer is subjected to alternating current (AC) during the EIS then, in the PEMEC case, the O₂ pressure and volume of the bubbles growing on the catalyst layer will oscillate with the frequency of the AC. The volume change will naturally change with the frequency. The longer the wave period (the lower the frequency) is, the bigger is the change in the amount of O₂ production during an AC period. In other words, a vibration of the O₂ bubble size and internal pressure must be induced by the AC current. Thus, we imagine that at some low frequency, the bubbles adhering to the catalytic layer get more unstable and detach with an uneven rate from the catalyst surface. This causes the noise observed.

Presumably, the structure and the properties of the interface of the catalyst to the liquid aqueous phase as well as the operation parameter will affect the frequency range and the size of noise in the EIS.

1. Introduction

The research within the area of water electrolysis has increased a lot during recent years, in particular research on PEMEC and AEC, both types of which are commercially available for demonstration purposes but still are too expensive in order to compete with hydrogen production from fossil fuels. Therefore, there is still a need for improving the electrolysis cells and stacks, and for this we need to improve our methods for characterizing the electrolysis cells in order give proper feedback to the cell developers.

EIS is a strong and popular electrochemical characterization technique in electrochemical research in general and in the areas of fuel cell and battery research in particular. However, EIS has not been a preferred technique for investigation of PEMEC, and relatively few reports on the application of systematic EIS studies are available. Some experienced researchers in the field have the opinion that PEMECs exhibit too much electrical noise to get EIS spectra with acceptable quality due to O₂ and H₂ bubble formation. This opinion seems in contradiction to the fact that the electrocatalyst is in close contact to electrolyte membrane, i.e. it should not be possible for any gas bubbles to block temporarily any part of the ionic conduction path.

Therefore, we decided to look into this problem, and experiments on both a conventional PEMEC and an AEC with a polybenzimidazole (PBI) membrane have been performed. No interference with gas bubbles were expected in these types of cells. Surprisingly, noise in the impedance spectra was observed, and we present a preliminary hypothesis on the mechanism of this noise as an interaction with gas bubbles.

2. Experimental

Three variations of PEMECs produced by EWII Fuel Cells A/S (EWII) were investigated using EIS. All three cell types were of the same design. The cells have an active electrode area of 2.9 cm² and contain a Nafion 117 membrane. The anode catalyst is 0.3 mg cm⁻² IrO_{2±x}, or Ir_{0.8}Ru_{0.2}O_{2±x}, with a contact layer of iridium metal. Titanium felt is used as current collector, and the anode flow plate is made of titanium. The cathode catalyst is 0.5 mg cm⁻² platinum, carbon felt is used as current collector, and the cathode flow plate is made of carbon. Figure 1 shows a sketch of the cell design with indications of the materials used. Further details will soon become available elsewhere (1). The three types are: 1) a cell from an early stage production at EWII, here called “early” cell with an IR metal contact layer of 1.7 mg Ir cm⁻², 2) a cell in which 20 % of the IrO₂ was substituted by RuO₂, called IrRuOx with an IR metal contact layer of 2.5 mg Ir cm⁻², and 3) the more mature EWII PEMEC, here called the EWII benchmark cell with an IR metal contact layer of 2.7 mg Ir cm⁻². This is the cell that EWII uses as the benchmark in the process of the further cell development.

All EIS measurements on PEMEC cells reported here were carried out at 61 °C.

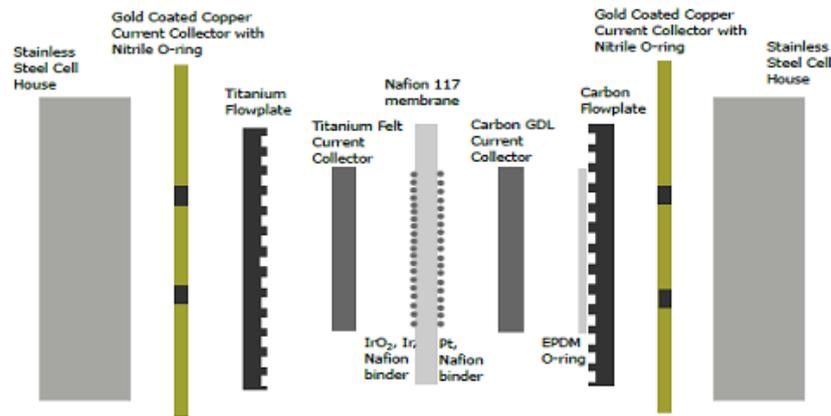


Figure 1. Sketch of an expanded view of the PEMEC cell design of EWII cells.

Figure 2 shows sketches of the two types of AECs that were tested: 1) a perforated nickel plate with a Raney-NiMo coating as cathode, a 40 μm *m*-PBI membrane, and a perforated Ni plate as anode (R-NiMo|PBI|Ni), see Figure 2 A, and 2) a pressed Ni foam as cathode, a 40 μm *m*-PBI membrane and a perforated nickel plate as anode (Ni-foam|PBI|Ni), see Figure 2 B. The flow plates used have a pin-type pattern and active electrode area was 5 x 5 cm^2 . PTFE was used as gasket material.

The AECs were operated in a partially separated mode in which 24 wt% KOH (aq.) was circulated in independent electrolyte circuits. Flow rates were controlled by diaphragm pumps and depending on electrodes it was 5 ml/min (Ni foam) or 50 ml/min (perforated plate). To ensure good temperature stability at 80 °C, the electrolyte was flowed through a pre-heating cell prior to the electrolyzer cell. Heating was done by pairs of heating elements in the end-plates of both the pre-heating and the electrolyzer cell. More details will become available later in 2017 (2).

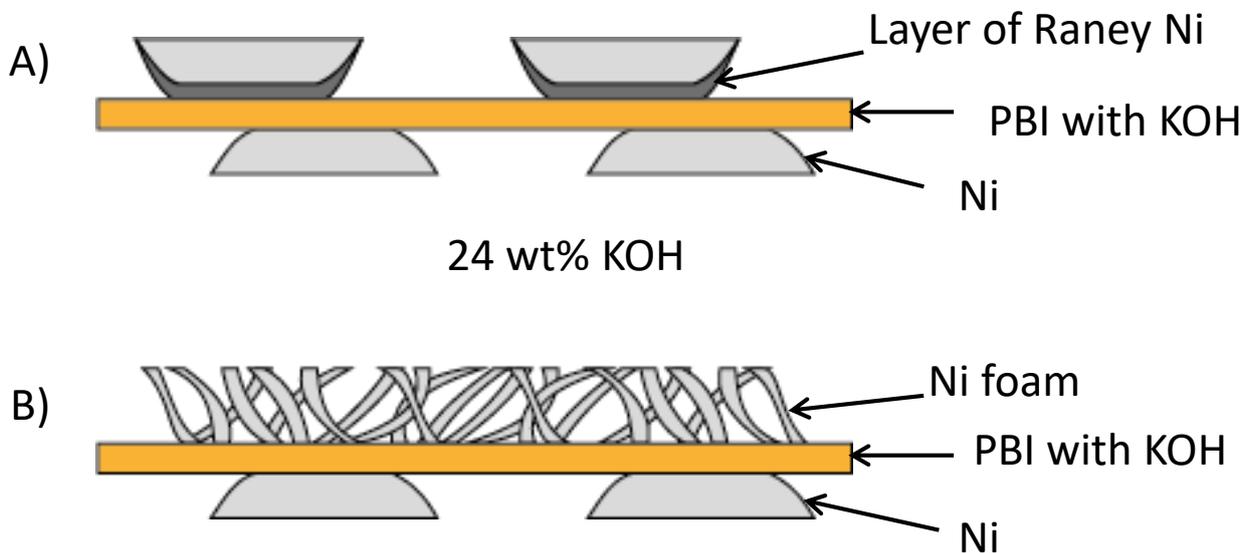


Figure 2. Sketches of the two types of tested AECs.

3. Results

Figure 3 shows EIS Bode plots the “early” EWII PEMEC with the real part (left) and the imaginary part (right), respectively. The y-axes have linear scales, and this is the case for

all the Bode plots that are shown here. A very significant noise is observed in the frequency range from 5 – 400 Hz in both plots, even though the relative noise is significantly more pronounced in the plot of the imaginary part. A kind of outlier is noticed at 50 Hz in the plot of the real part. This may be due to the 50 Hz irradiation from the electrical grid.

Figure 4 presents the Bode plots of the IrRuOx cell. Here it is noticed that there is no observed noise in the real part, but there is a significant noise in the imaginary part in two frequency intervals from 0.01 - 1 Hz, and from 50 – 400 Hz.

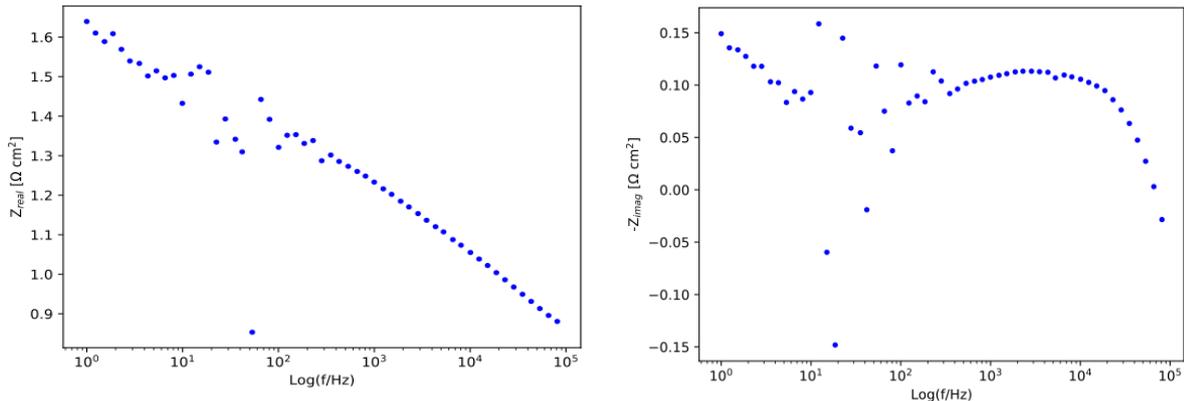


Figure 3. Real part (left) and Imaginary part (right) of the impedance of an EWII “early” PEMEC as a function of log(frequency) at 1 A cm⁻² during initiation at 61 °C. An “outlier” is observed at 50 Hz in the left Figure.

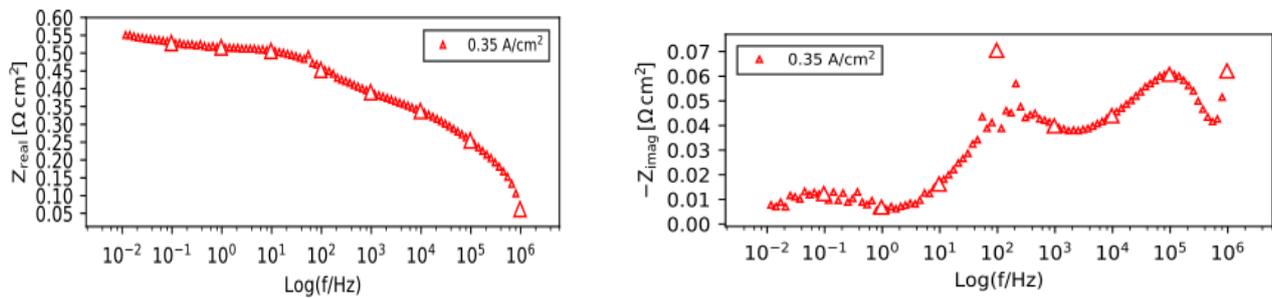


Figure 4. Real part (left) and Imaginary part (right) of the impedance of an EWII IrRuOx PEMEC as a function of log(frequency) at 61 °C and 0.35 A cm⁻².

Figure 5 illustrates that a case with almost no significant noise in the EIS spectrum of the benchmark cell at 0.35 A cm⁻². The one point above the curve in the plot of the imaginary part happens to be at 50 Hz, and may thus be caused by the grid.

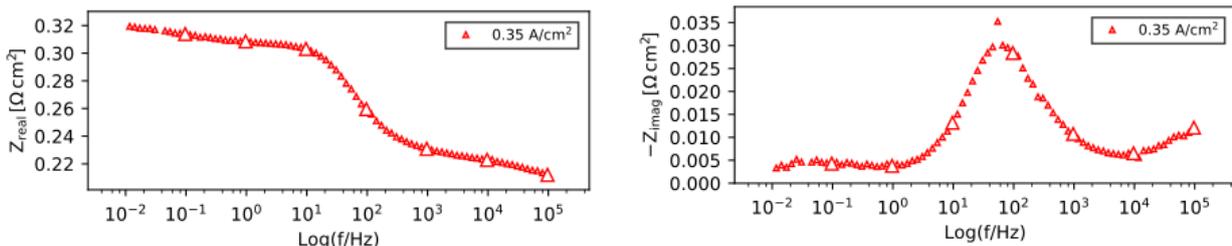


Figure 5. Real part (left) and Imaginary part (right) of the impedance of an EWII benchmark-cell as a function of log(frequency) at 61°C and 0.35 A cm⁻².

Figure 6 presents the EIS of same cell at 1 A cm⁻². Little noise is seen apart from the 50 Hz points, and the small noise in the imaginary part seems to be more or less even over the whole range of measured frequencies.

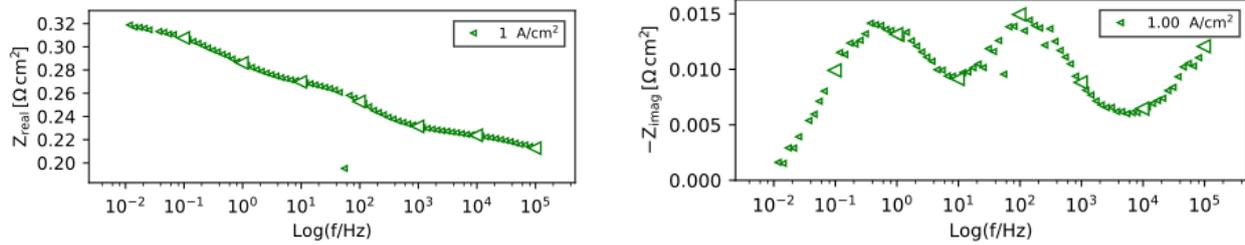


Figure 6. Real part (left) and Imaginary part (right) of the impedance of an EWII benchmark-cell as a function of log(frequency) at 61 °C and 1.00 A cm⁻².

Figure 7 and 8 show the analogue plots for the two alkaline projects. Also for these cells some noise in the EIS is observed, and here it is only observed at frequencies below 10 Hz.

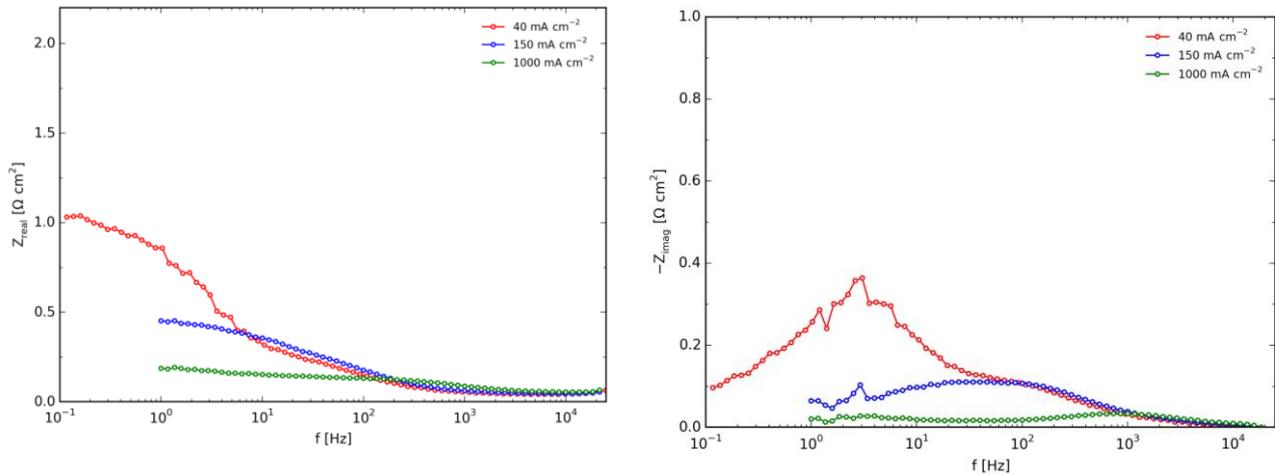


Figure 7. Real part (left) and Imaginary part (right) of the impedance of a Raney Ni AEC as a function of log(frequency) at 80 °C and 0.04, 0.15 and 1.00 A cm⁻².

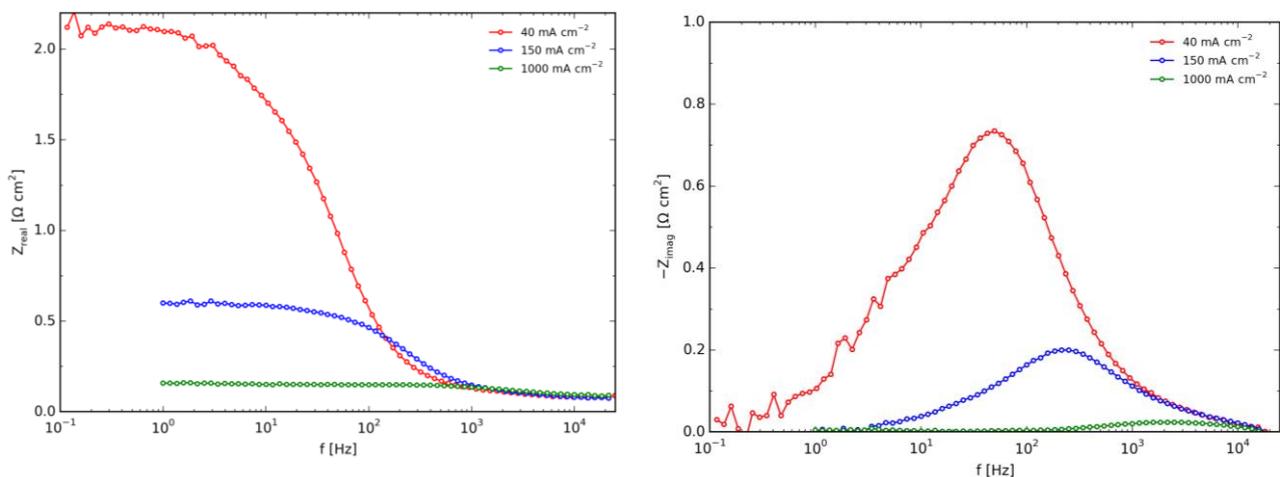


Figure 8. Real part (left) and Imaginary part (right) of the impedance of a Ni foam AEC as a function of log(frequency) at 80°C and 0.04, 0.15 and 1.00 A cm⁻².

4. Discussion

An inspection of the Figures 1 and 2 reveals that the electrocatalysts in both cases are in close contact with the solid electrolyte membrane. This means that the bubbles have no chances to disturb the ionic current path through the electrolyte, and therefore, we would not expect any noise from bubbles due to temporally blocking of current paths. Anyway, we see in several cases significant noise in the EIS, and apart from 50 Hz there is no indication that the noise originates from the impedance analyzer instruments or from electrical noise from outside. Furthermore, it seems that the noise pattern is a kind of fingerprint of the cell type. Thus, this points towards a phenomenon related to stochastic events in the O₂ and/or H₂ evolution processes, which in turn indicate a phenomenon related to bubble formation and release.

Our hypothesis is that this phenomenon is related to bubbles that are adhering to active sites of the electrocatalyst. When the catalyst layer is subjected to alternating current (AC) during the EIS then, in the PEMEC case, the O₂ pressure and volume of the bubbles growing on the catalyst layer will oscillate with the frequency of the AC. The volume change will naturally change with the frequency. The longer the wave period (the lower the frequency) is, the bigger is the change in the amount of O₂ production during an AC period. In other words, a vibration of the O₂ bubble size and internal pressure must be induced by the AC current. Thus, we imagine that at some low frequency, the bubbles adhering to the catalytic layer get more unstable and detach with an uneven rate from the catalyst surface. This causes the noise observed.

We think that it is bubbles at the O₂ electrode as the changes in the PEMEC types was only changes in the O₂ electrode. The change between “early” and “benchmark” cells are only related to the manufacturing details as they are nominally equal. The “new” electrode was the IrO₂ electrocatalyst in the EWII manufacturing process, because the Pt on carbon in the H₂ electrode is the same as EWII used in the manufacturing of the PEM fuel cells. In the AEC case, it seems to be the H₂ bubbles that are into play as there the change in the noise pattern is related to the changes in H₂ electrode (cathode).

We presume that the bubble noise contains important information about the structure and properties of the electrode, in particular about the interface between the electrocatalyst and the liquid aqueous phase, but e.g. also about properties like porosity of the catalyst layer. Further studies are planned to investigate these possibilities of obtaining knowledge about electrolysis cell electrodes using EIS.

5. Conclusions

A number of different PEMEC and AEC-PBI cells were investigated by EIS with respect to their noise pattern. In spite of the fact that no noise from bubbles due to temporally blocking of the electrolyte conductivity is to be expected, we hypothesize: (1) that the observed noise patterns are related to bubbles that are adhering to active sites of the electrocatalyst, and (2) that the vibration in pressure and volume of the bubbles caused by the small AC current makes the bubbles more unstable, and make them detach with an uneven rate from the catalyst surface, and this is the cause of the noise.



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