Energy Dispersive X-Ray and Electrochemical Impedance Spectroscopies for Performance and Corrosion Analysis of PEMWEs

S M Steen III and F-Y Zhang
Nanodynamics and High Efficiency Lab for Propulsion & Power
Department of Mechanical, Aerospace and Biomedical Engineering
UT Space Institute, University of Tennessee, Knoxville

Email: fzhang9@utk.edu

Abstract. Proton exchange membrane water electrolyzers (PEMWEs) are a promising energy storage technology due to their high efficiency, compact design, and ability to be used in a renewable energy system. Before they are able to make a large commercial impact, there are several hurdles facing the technology today. Two powerful techniques for both in-situ and ex-situ characterizations to improve upon their performance and better understand their corrosion are electrochemical impedance spectroscopy and energy dispersive x-ray spectroscopy, respectively. In this paper, the authors use both methods in order to characterize the anode gas diffusion layer (GDL) in a PEMWE cell and better understand the corrosion that occurs in the oxygen electrode during electrolysis.

1. Introduction
Proton exchange membrane water electrolyzers (PEMWEs) are a promising energy storage technology, highlighted by their high efficiency (theoretical maximum of 94%), compact design, rapid charging/discharging, and ability to be a part of a renewable and regenerative energy storage system [1]. With the onset of climate change, the need for clean energy is greater than ever before, and PEMWEs are a promising source of clean energy storage. A PEMWE is operated by electricity, and uses a catalyst coated membrane (CCM) in order to split water into hydrogen and oxygen [2-3]. These elements may then be stored easily using existing methods, and be used as the fuel and oxidizer for fuel cells, respectively.

Currently, there are several challenges the development of commercial scale PEMWEs are faced with. A vital component of the membrane electrode assembly (MEA), the gas diffusion layer (GDL) is responsible for facilitating the transport of reactants/products, electrons, and heat to and from the catalyst layer with minimal voltage, current, thermal, interfacial, and fluidic losses [4-6]. The GDL is also needed to provide structural integrity to the cell, and needs to be a porous material while still maintaining a good contact area with the catalyst in the membrane. For PEM fuel cells, carbon-based materials (graphite electrode, carbon cloth, and carbon paper) are desired and well suited as the material of choice for the GDL. However, the oxygen electrode (anode) in a PEMWE has a harsh, corrosive environment due to the high overpotential. In this environment, the carbon-based materials described above are ill-suited, as the material will corrode and degrade easily, leading to poor performance in the cell. As such, highly conductive and corrosion-resistant materials are desired for
use as the anode GDL in a PEMWE. To decide which materials may be desirable, a better understanding of the mechanics of the corrosion at the oxygen electrode is needed.

For our research, there are two powerful methods of analysis that may be used to investigate the corrosion that occurs in a PEMWE. They are electrochemical impedance spectroscopy (EIS), and energy dispersive x-ray spectroscopy (EDX). For this study, both of these methods were employed in order to perform in-situ and ex-situ analysis on a PEMWE developed in lab, and from the results of the analysis were able to reach a greater understanding of the mechanisms of corrosion that occur in a PEMWE.

2. Experimental details
For the in-situ investigation performed, a test system that consisted of an electrolyzer test stand, EIS, a flow control and measurement system, and a hydrogen evacuation setup was used. The cell was attached to the control system with a current range up to 100A and a voltage range up to 5V. The hardware was connected and used in tandem with Bio-Logic’s EC-Lab software. This was used to conduct performance and efficiency testing, as well as EIS. For the flow control, a system of plastic tubing was connected to the PEMWE. While the cathode piping was for the safe exhaustion of hydrogen gas that formed during electrolysis, the anode piping used a diaphragm liquid pump from KNF Neuberger to circulate deionized (DI) water at a constant volumetric of 40 ml/min through the anode.

The PEMWE cell was assembled using parts fabricated in lab. Two end plates were fashioned from commercial grade aluminum and used to provide an even compression pressure to the cell. The anode bipolar plate used a titanium plate with a parallel flow field which also served as the current distributor. The cathode bipolar plate used a copper plate as the current distributor, and a graphite plate with a parallel flow field. The cathode GDL was Toray 090 carbon paper treated with 5% PTFE, while the anode GDL was a mesh of 316L stainless steel. The membrane was Nafion 115 with RuIrOx and PtB catalysts with a 3 mg/cm² loading on the anode and cathode, respectively. The active area of the membrane was 5 cm². Gaskets for both GDLs were fashioned from PVC in order to improve the sealing of the cell. Once assembled, eight bolts were used to evenly tighten the cell to 40 lb-in. of torque. The cell was operated at room temperature.

3. Results and discussion
3.1 Electrochemical impedance spectroscopy
For the in-situ testing, galvanostatic EIS (GEIS) is desirable, because it is a macroscopic electrochemical technique that may be used while the cell is performing electrolysis. It is the most useful for studying the electrode-electrolyte interface as well as analyzing corrosion that may occur in a PEMWE. From performing GEIS, the ohmic, activation, and transport resistances in a specific electrolyzer may be determined respectively. In a typical GEIS test a frequency range from 10 kHz – 0.1 Hz is performed, with the current applied to the cell remaining constant. The ohmic resistance typically dominates the losses in performance for the PEMWEs of interest. The activation impedance can be derived from the slope of the arc in the Nyquist Plot in the middle of frequency range, and the transport resistance may be found from the difference between the values of the x-axis intercepts at the low frequency range. Figure 1 below shows an example of data that may normally be obtained from GEIS analysis, plotted in the complex plane.
In the figure, the real and imaginary axis are normalized by multiplying the values measured by the active area of the cell. There is one more step of normalization, where the real axis values are further normalized by subtracting each value by the ohmic resistance. In a Nyquist plot, the ohmic resistance is the value of the leftmost x-axis intercept at high frequency end.

GEIS allows for conclusions regarding the nature of the GDL in the anode of a PEMWE to be reached. As the interfacial contact increases and the thickness of the GDL decreases, the ohmic impedance greatly decreases. From other GEIS analysis performed during testing it is shown that even though some GDLs may have a low porosity (<40%), their favorable interfacial contact leads to a low ohmic resistance and thus a higher performance.

Figure 1 shows that the transport resistance in a PEMWE varies depending on the current density the cell is run at. The transport resistance is denoted as the rightmost x-axis intercept in low frequency range. The reason for the change in transport resistance at different current density is because there is a greater liquid water consumption and the difference in $\text{H}_2/\text{O}_2$ production between each current density.

3.2. Energy dispersive x-ray spectroscopy

After testing of the PEMWE has concluded, the cell may be disassembled and a further investigation of the GDL may occur. This can be done using SEM microscopy in tandem with EDX. The EDX detector used is from EDAX, and uses their TEAM software to perform both image processing and mapping of the sample of interest. EDX allows for viewing the physical characteristics of the materials before and after testing, and an analysis of the elements that make up the sample. Figure 2 shows images of the cathode GDL before and after testing. As seen in Figure 2B, there is a large amount of contamination on the used sample of carbon paper. From EDX analysis, it was found that this contamination was iron oxide. In the PEMWE used for testing, the only possible source of iron oxide was from the anode GDL.
Table 1 below shows the atomic concentration of elements found in both the fresh and used GDL samples. An example of the spectrum found during EDX analysis is shown in Figure 3. As mentioned above and seen in Table 1 below, there is a large amount of iron and oxygen found on the used carbon paper. After testing concluded, testing was performed on the membrane to test for any leakage, but none were found. This leads us to believe that iron contaminants from the anode GDL migrated through the membrane and attached to the cathode GDL. While the mechanism of this reaction is unknown, further research is planned to better understand the phenomenon.

| Test sample | Atomic concentration |
|-------------|----------------------|
|             | Iron  | Carbon | Fluorine | Oxygen | Chromium | Nickel |
| Fresh SS    | 60.27 | 0      | 0        | 12.67  | 15.63     | 11.43  |
| Used SS     | 18.21 | 26.28  | 0        | 47.29  | 5.55      | 2.67   |
| Fresh CP    | 0     | 95.8   | 4.2      | 0      | 0         | 0      |
| Used CP     | 28.45 | 19.25  | .89      | 51.41  | 0         | 0      |

Figure 3. Example of spectrum found during EDX analysis

4. Conclusion
From the testing conducted, impedance spectroscopy allows for the in-situ investigation of the effects of porosity and thickness of the anode GDL on the performance and efficiency of a PEMWE cell. In addition, GEIS has been demonstrated to characterize the interfacial contact between the GDL and the CCM. SEM and EDX spectroscopy, when used together, characterize the effects of oxidation on
GDLs, and provide power tools to verify the diffusion of iron oxide through the membrane. The exact diffusion mechanism will be explored in future research.

**Acknowledgements**
The authors acknowledge support from the U.S. DOE under Award DE-FE0011585. The authors also wish to express gratitude to Douglas Warnberg, Jingke Mo, Dr. Bo Han, Rong Chen, Dr. Lino Costa, and Kate Lansford for their help.

**References**
[1] Ayers K E, Dalton L T, Anderson E B 2012 *Electrochemical Synthesis of Fuels* 41 27
[2] Park S, Lee J-W, Popov B N 2006 *Journal of Power Sources* 163 357
[3] Marshall A, et al. 2007 *Energy* 32 431
[4] Wilde P M, et al. 2004 *Fuel Cells* 4 180
[5] Eom K, et al. 2013 *International Journal of Hydrogen Energy* 38 6249
[6] Prasanna M, et al. 2004 *Journal of Power Sources* 131 147