X-Ray Diffraction Studies on Material Corrosions in Renewable Energy Storage Electrolyzers

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Abstract. As a core component of the proton exchange water electrolyzer system, membrane electrode assemblies degrade due to the corrosion of the material. This creates a loss of interfacial contact necessary for the electron transports and electrochemical reactions, thus decreasing the performance. X-ray diffraction has been demonstrated to be an effective method that readily provides quantitative information about the phase-composition of solid materials. In this study, a group of materials have been selected and tested in the standard conditions for investigating the corrosion mechanisms with X-ray diffraction. The material lattice parameter and the crystal size were examined by X-ray diffraction spectrum.

1. Introduction
With the development of global energy shortage and climate change associated with the use of fossil fuels, it is extremely urgent to replace fossil fuels by a renewable energy source. Hydrogen, as a high energy and environment friendly fuel, is expected to be one of the most potential energy carriers in the near future. Water electrolysis, the most fundamental way, can split water into hydrogen and oxygen by using electric power. The integration of sustainable energy and water electrolysis is very attractive because of its high efficiency and pure production [1, 2].

In the nature of high efficiency, renewable, environment friendly and zero-close emissions, renewable energy storage will play an important role in our future energy economy. Compared to traditional technologies, polymer electrolyte membrane water electrolyzers have several main advantages, including higher energy efficiency/density, faster charging/discharging, and a more compact design. Water electrolysis can be conducted by the proton exchange membrane water electrolyzer (PEMWE) with Ru/Ir and Pt employed as anode and cathode catalysts respectively [3] PEMWEs use proton exchange membranes as the electrolyte that permits the protons to transfer from anode to cathode. Currently, the performance of PEMWE is not sufficient and highly depends on properties of membrane electrode assembly (MEA). To improve the performance and durability of PEMWEs, the catalyst-coated membrane (CCM) of the PEMWE has been studied and developed [4, 5]. For the time being, there is no research that has been done towards the corrosions in the gas diffusion layer (GDL) and MEA which affects the performance of PEMWE.

Carbon paper is widely used as the GDL in fuel cells, which can’t be run in the anode side of PEMWEs because it is easily corroded at high positive potentials during water electrolysis operation [6]. In this study, stainless steel mesh will be used as the anode side GDL.
The object of this study is to validate X-ray diffraction (XRD), which can be a tool to quantify the corrosions, choose alternative materials suitable for using in PEMWE and develop a high performance PEMWE.

2. Experimental detail
In the PEMWE as shown in figure 1, both end plates are made of aluminum. The anode current distributor with a parallel flow field is fabricated from a titanium plate, while the cathode current distributor is fabricated from copper and coated with nickel. The cathode flow field is also a parallel flow field that is fabricated from graphite. Both anode and cathode gaskets are made from PVC sheets. The cathode GDL is Toray 090 carbon paper treated with 5% PTFE. The anode GDL is stainless steel 316L mesh. The CCM is Nafion 115 film with Ru/Ir and Pt employed as anode and cathode catalysts loading of 3 mg/cm² respectively. Eight evenly distributed bolts assembled the cell to torque of 40 lb/in. The Teflon pipes and fittings were used throughout the system. While the cathode piping was merely intended to safely exhaust hydrogen gas, a diaphragm liquid pump from KNF Neuberger was used to circulate water at a constant volumetric flow rate of 40 ml/min through the anode. The electrolyzer with an active area of 5 cm² was operated for 15 hours at room temperature. Before and after the water electrolyzer testing, the leak and crossover tests were performed with air. The airtightness quality of the used CCM was still the same as the fresh one. No pinholes were found on the used CCM.

XRD is a tool used for identifying the atomic and molecular structure of a crystal, in which the crystalline atoms cause a beam of incident X-rays to diffract into many specific directions. The characterization of structure and identification of the phase were carried out by XRD with a Philips X’Pert materials research diffractometer (45kV, 40mA), controlled by PANalytical’s XRD software, in Bragg Brentano reflection geometry with Cu Kα radiation (λ=1.5418 Å) and a 2θ scan from 20° to 100° (at 0.01° per 5 second). The diffraction patterns are analyzed by software MDI Jade9. The test system mainly consists of Panalytical Philips X’Pert MRD system as show in Figure 2.

The applications of XRD, which related to this study, are as follows. The first one is to identify the composition of material. The sample for anode GDL is stainless steel mesh, which is made of stainless...
steel 316. XRD pattern can identify the major element in this sample which are the same as described in the reference [7]. The second one is to determine crystal structural properties. The grain size can be calculated with the Scherrer Equation.

$$\tau = \frac{K\lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

Here, \(\tau\) is the mean size of the ordered domains, which equal to the grain size, \(K\) is a dimensionless shape factor, has a typical value of about 0.94, \(\lambda\) is the X-ray wavelength, \(\beta\) is the line broadening at half the maximum intensity and \(\theta\) is the Bragg angle.

3. Results and discussion

As mentioned above, the gran size of major crystal in each layer can be calculated by Scherrer equation. In the XRD scanning, all necessary data for the major crystals for the calculations of grain sizes have been collected. The data are shown below in Figure 3, Figure 4 and Figure 5, respectively.

Based on the above data, the grain size of major crystal in fresh sample can be calculated as shown in Table 1.

| Major Crystal             | Grain Size |
|---------------------------|------------|
| Graphite in Carbon Paper  | 34.12nm    |
| Iron in Stainless Steel Mesh | 29.81nm  |
| Pt in Cathode side of Membrane | 11.32nm  |

The major crystals at anode side GDL fresh stainless steel mesh is Fe, Cr and Ni. After testing in the PEMWE, the major crystal in carbon paper GDL on cathode side is graphite-2H.
The occurrence of corrosion at the anode side GDL is due to the iron exposed in a high oxidation and high potential environment; however, the mechanism of corrosion in the cathode GDL is unclear. Since the environment in cathode side is not the same as anode side. It can be assumed that the iron oxide diffused from the anode to the cathode and attached onto the surface of the carbon paper GDL. Based on the assumption, the XRD was used to further examine the material.

After testing all of the materials in the MEA, the XRD patterns have been compared respectively for anode GDL, catalyst coated membrane and cathode GDL. As shown in Figure 6, there is some iron oxide that exists in the used carbon paper compared to fresh one. The corrosion occurred in the anode GDL, this is due to in the extremely harsh environment, the iron changes to iron oxide. In this water electrolysis process, the anode side GDL stainless steel mesh is exposed in the flow to DI water. The iron oxide is easily detached from the substrate. This phenomenon also verified the assumption that the iron oxide not only washed away by water flow but also diffused from the anode side to the cathode side through the membrane.

4. Summary
XRD technology has been demonstrated to quantify the major phases of materials before and after testing, to characterize the effect of oxidation on GDLs, to verify the diffusion of iron oxide through the membrane, has also successfully tracked corrosion pathways from the anode side to the cathode side through the membrane. To find more applications of XRD on PEMWE research, more works will be conducted in the future.

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