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Short Communication

Study on corrosion migrations within catalyst-coated membranes of proton exchange membrane electrolyzer cells

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ABSTRACT

The corrosion of low-cost, easily manufactured metallic components inside the electrochemical environment of proton exchange membrane electrolyzer cells (PEMECs) has a significant effect on their performance and durability. In this study, 316 stainless steel (SS) mesh was used as a model liquid/gas diffusion layer material to investigate the migration of corrosion products in the catalyst-coated membrane of a PEMEC. Iron and nickel cation particles were found distributed throughout the anode catalyst layer, proton exchange membrane, and cathode catalyst layer, as revealed by scanning transmission electron microscopy and energy dispersive X-ray spectroscopy. The results indicate the corrosion products of 316 SS are transported from anode to cathode through the nanochannels of the Nafion membrane, resulting in impeded proton transport and overall PEMEC performance loss.

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Introduction

The hydrogen economy is a proposed system of energy storage and delivery which was originally introduced by Dr. J. B. S.

Haldane in 1923 [1]. Hydrogen production is a large and growing industry due to its advantages of having a high-energy-density and being environmentally-friendly, and there are still yet many promising applications and uses in the near future [2–7]. The increasing interest in sustainable

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energy systems has driven the development of polymer electrolyte membrane electrolyzer cells (PEMECs) over the past several decades as a hydrogen production method [8–10]. For renewable energy storage and pure hydrogen/oxygen production, PEMECs have several advantages, such as higher energy efficiency/density, faster charging/discharging, and a more compact design [11–13]. The PEMEC decomposes water into separate streams of hydrogen and oxygen by using electrical power. When the energy supply is higher than demand, the excess energy can be stored by producing hydrogen; with the stored hydrogen available for future energy production via, for example a polymer electrolyte membrane fuel cell (PEMFC). This regenerative PEMEC/PEMFC system approach will potentially allow renewable and hybrid energy systems to effectively provide reliable and multi-scale energy by eliminating the intermittence of renewable energy sources [14–16].

Both PEMECs and PEMFCs take advantage of proton exchange membranes (PEM) as electrolytes, which permit the transfer of protons with high efficiency compared to traditional technologies [12,17–20]. Their performance is highly dependent on the properties of the membrane electrode assembly (MEA), and it can be affected by the concentration of various species (proton, water, oxygen, hydrogen, etc.) across and within the cells which can affect the distribution and transport of reactants and products, block active-sites, and lead to overall membrane degradation [21–29].

Liquid/gas diffusion layers (LGDLs) have a central role in the evolution of PEMEC technology. Traditional materials for manufacturing LGDLs are carbon fiber, metals or coated polymers. Metallic LGDLs and bipolar plates have attracted attention in both PEMECs and PEMFCs due to their high bulk electrical conductivity, amenability to rapid manufacturing, and low cost [20,30–41]. However, durability issues remain due to the aggressive electrochemical environment. While carbon paper is widely used as the LGDL in PEMFCs, it is unsuitable in the anode side of PEMECs because it is easily corroded at the high positive potentials and extreme oxidative environments [42]. Metallic LGDLs with higher corrosion resistance are one potential solution. Metal corrosion and ion poisoning on MEAs are critical issues especially for low-cost metals such as stainless steel (SS). It has been reported that metallic cations, especially iron cations, may contaminate the MEA and degrade the performance in PEMFCs. However, to our knowledge, there are few (if any) reports on the electrode corrosion and transport mechanisms/effects in a MEA, especially with metallic LGDLs.

The most popular membrane used in PEMECs and PEMFCs is made of Nafion. Nafion is a sulfonated tetrafluoroethylene-based fluoropolymer-copolymer, which was discovered in the late 1960s by Walther Grot of DuPont [43]. Nafion's unique ionic properties are a result of incorporating perfluorovinyl ether groups terminated with sulfonate groups onto a tetrafluoroethylene (Teflon) backbone [44,45]. Nafion has received a considerable amount of attention as a proton conductor for PEMFCs and PEMECs because of its excellent thermal and mechanical stability.

In our previous work, a 316 SS mesh was intentionally utilized as a model metal anode LGDL to investigate the metal corrosion and transport inside PEMECs during their operations [46]. In this study, further investigations were conducted

to gain insight into the behavior of metal cation migration in PEMECs and understand corrosion mechanisms affecting PEMEC performance. The uncoated 316 SS is not a viable candidate for PEMEC LGDLs or bipolar plates due to inadequate corrosion resistance; however, its rapid degradation can be leveraged to study corrosion product migration under PEMEC operating conditions in a reasonable period. Scanning electron microscope (SEM) characterization of both anode and cathode LGDLs before and after testing was performed in our previous study to compare the extent of metal cation migration [46]. In this research, scanning transmission electron microscopy (STEM) and energy-dispersive X-ray spectroscopy (EDS) were used to characterize the incorporation of metal cations introduced into the catalyst-coated membrane (CCM) from SS LGDL corrosion. It was found that migration Fe cation across the CCM resulted in Fe cation accumulation inside the PEM, which severely blocked the transportation of proton from anode to cathode.

Experimental

The CCM investigated in this work came from our previous work of electrochemical investigation of SS corrosion in a PEMEC. The CCM has been operated in the PEMEC for 15 h. All details about the devices, set up, and operation conditions can be found in our previous work [46]. This work builds upon our initial study of the impacts of the corrosion of 316 SS LGDLs on the PEMEC performance, which observed significant Fe cation transport through the membrane, but did not pursue advanced characterization of the membrane. In this study, STEM and EDS are used to characterize the tested CCM to reveal the behavior and mechanism of the Fe cation transfer inside the CCM.

STEM – EDS characterization

A field emission JEOL JSM-6320F SEM with an accelerating voltage of 0.5–30 KV was used for observing the morphological characteristic of the LGDLs before and after testing in a regular PEMEC. A 200 KV JEOL 2200FS FEG – TEM/STEM fitted with a spherical aberration corrector was also used for high-resolution imaging of the IrRuOx and Pt nanoparticle catalyst. It was equipped with a Bruker solid state detector (SDD). Cross-sectional CCM specimens were prepared by diamond knife ultramicrotomy with a target thickness of 50–100 nm.

Results and discussion

The experimental results from our previous work demonstrated that there was severe corrosion at the anode 316 SS LGDL (Fig. 1(a) and (b)), and some of those corrosion products were transported through the CCM, and deposited on the cathode carbon-paper LGDL (Fig. 1(d) and (e)). The SEM images comparing of fresh and operated 316 SS LGDLs at the anode side revealed extensive corrosion of the SS mesh after only 15 h of room temperature operation at a current density of 1.0 A/cm² in the PEMEC. Some of corrosion products transported through the CCM and deposited on the surface

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