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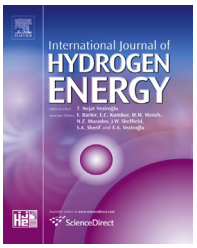

Short Communication

Electrochemical investigation of stainless steel corrosion in a proton exchange membrane electrolyzer cell☆

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ABSTRACT

The lack of a fundamental understanding of the corrosion mechanisms in the electrochemical environments of proton exchange membrane (PEM) electrolyzer and/or fuel cells (ECs/FCs) has seriously hindered the improvement of performance and efficiency of PEM ECs/FCs. In this study, a stainless steel mesh was purposely used as an anode gas diffusion layer that was intentionally operated with high positive potentials under harsh oxidative environments in a PEMEC to study the corrosion mechanism of metal migration. A significant amount of iron and nickel cations were determined to transport through the anode catalyst layer, the PEM and the cathode catalyst layer during the PEMEC operation. The formation/deposition of iron oxide and nickel oxide on the carbon paper gas diffusion layer at the cathode side is first revealed by both scanning electron microscope and X-ray diffraction. The results indicate the corrosion elements of iron and nickel are transported from anode to cathode through the catalyst-coated membrane, and deposited on carbon fibers as oxides. This phenomenon could also open a new corrosion-based processing approach to potentially fabricate multifunctional oxide structures on carbon fiber devices. This study has demonstrated a new accelerated test method for investigating the corrosion and durability of metallic materials as well.

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Introduction

Hydrogen, as a high energy and environment friendly fuel, has the potential to be a promising energy source in the near to intermediate future. An electrolyzer cell taking advantage of a proton exchange membrane (PEM) has attracted more attention for renewable energy storage and pure hydrogen/oxygen production due to their higher energy efficiency/density, faster charging/discharging, and a more compact design [1–4]. The proton exchange membrane electrolyzer cell (PEMEC) splits water into separate streams of hydrogen and oxygen by using electrical power. The integrations of water electrolysis and energy from sustainable resources, including solar, wind and biomass, are very attractive because of its high efficiency, renewable, and pure hydrogen production [5–10]. Once hydrogen is produced and stored, it can later provide a constant supply of electricity with a PEM fuel cell (PEMFC), which is a reverse device of the PEMEC. This regenerative system will allow renewable and hybrid energy systems to effectively provide reliable and multi-scale energy [11–14]. Compared to traditional technologies, both PEMECs and PEMFCs take advantage of proton exchange membranes as electrolytes that permit the transfer of protons with high efficiency. Their performance is highly dependent on properties of the membrane electrode assembly (MEA), including conductivity of the membrane, activation energy of the catalyst layers, and the conductivity and permeability of liquid/gas diffusion layers (LGDLs) [15–21]. PEMFC performance can also be affected by species concentration variations across and within the cells which can reflect changes in reactants and products distribution and transport, localized and possibly dynamic active-site blocking, and membrane degradation [22,23].

Metallic LGDLs and bipolar plates have attracted attentions in both PEMECs and PEMFCs due to their high conductivity, rapid production, and low cost [24–28]. By taking advantage of novel designs and micro fabrications, a thin-film metallic LGDL with well-controllable pore morphologies and surface properties demonstrated excellent multi-functionalities and water managements [24,29]. However, its durability has been challenged due to the aggressive electrochemical environment. In addition, while carbon paper is widely used as the LGDL in fuel cells, it is unsuitable in the anode side of PEMECs because it is easily corroded at the high positive potentials and extreme oxidative environments. 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. Current bipolar plate practically employs the use of more expensive metals such as titanium, and typically with precious metal coatings such as Pt, which significantly increase the cost [10]. It has been reported that metallic cations, especially iron cations, may contaminate the MEA and degrade the performance in PEMFCs [28,30–33]. 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.

In this study, a stainless steel mesh was purposely employed as the anode LGDL to develop an understanding of the metal ion migration and deactivation mechanism and identify alternative materials suitable for use in PEMEC. Scanning electron microscope (SEM) characterizations of both anode and cathode LGDLs before and after testing were performed to compare the extent of metal migration in the materials. X-ray diffraction (XRD) has been demonstrated to be an effective method that readily provides quantitative information about the phase-composition of solid material [34,35]. The LGDLs have also been analyzed by XRD for the identification of the form of the migrating metals. Migration of iron across the MEA resulting in the formation of iron oxide on the carbon paper gas diffusion layer at cathode side is observed, which to our knowledge is the first or among the first reports of this phenomenon for PEMECs.

Experimental details

In the PEMEC used in the present study, 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 and chromium. 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 LGDL is Toray 090 carbon paper treated with 5% PTFE. The anode LGDL is a type 316 stainless steel mesh (nominal composition of 316 is 16–18.5% Cr, 10–14% Ni, 2–3% Mo, <2% Mn, <1% Si, all in weight%). The catalyst-coated membrane (CCM) is Nafion 115 film with Ru/Ir oxides and Pt employed as anode and cathode catalysts with loadings of 3 mg/cm^2, respectively. Eight evenly distributed bolts assembled the cell to a torque of 40 lb-in. Teflon piping and fittings were used throughout the system. While the cathode tubing 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 [21]. The electrolyzer with an active area of 5 cm^2 was operated for 15 h with an average operation voltage of 2.8 V at a current density of 1 A/cm^2 at room temperature. Before and after the water electrolyzer testing, the leak and crossover tests were performed with air. This evaluation produced identical results in the fresh and aged CCMs and no pinhole formation was found.

The morphological characteristics of the LGDLs were observed with a field emission SEM JEOL JSM-6320F with an accelerating voltage of 0.5–30 kV, a magnification of 500× ~650,000× and a 5-axis specimen mount. The EDS detector is an EDAX Octane plus Silicon Drift Detector that works in tandem with EDAX's TEAM EDS software analysis system. The system allows for high resolution mapping and highly accurate point analysis at fast speeds. SEM images were captured, processed, and analyzed by TEAM software.

The characterization of structure and identification of the phase were carried out by XRD with a Philips X'Pert materials research diffractometer (45 kV, 40 mA), controlled by PANalytical's XRD software, in Bragg Brentano reflection geometry with Cu Kα radiation ($\lambda = 1.5418$ Å) and a 2θ scan from 20° to 100° (at 0.01° per 5 s). The diffraction patterns are analyzed by software MDI Jade9.

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