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Short Communication

Mitigation of catalysts degradation upon stopping work of polymer electrolyte membrane fuel cells for longer time

Wojciech Tokarz, Piotr Piela *

Mościcki Industrial Chemistry Research Institute, Rydygiera 8, 01-793 Warsaw, Poland

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ABSTRACT

A method for stopping work of a polymer electrolyte membrane fuel cell (PEMFC) fueled with a gaseous fuel such as hydrogen has been elaborated that allows to instantly fill the anodic compartment of the fuel cell with air. The method utilizes three elements of proceeding: (i) isolation of hydrogen with opening of the PEMFC's anodic compartment to the external atmosphere, (ii) stopping the flow of air through the PEMFC's cathodic compartment, and (iii) electrically loading the PEMFC with a large load. It is shown that only the combination of all these three elements is effective in reducing corrosive catalyst degradation typically occurring when the PEMFC is stopped for a longer period of time.

Introduction

With the energy conversion performance level of polymer electrolyte membrane fuel cells (PEMFCs) no longer constituting an industrial application obstacle for the technology [1,2], the main research focus is now on the imperfect PEMFC durability [3]. Degradation of PEMFCs occurs mainly in the membrane-electrode assemblies (MEAs) and concerns the catalyst layers and the membrane the most [2,4].

Phases of stopping and starting the PEMFC are especially critical. When the work of the PEMFC supplied with hydrogen and air is stopped, the fuel cell voltage will obviously rise. A high voltage of the PEMFC, the work of which has been stopped, is unfavorable because it causes oxidation reactions in the catalytic layer of the cathode that assumes a high electrical potential. These processes lead to cathode catalyst corrosion and, consequently, to an irreversible loss of fuel cell performance. The corrosion processes become particularly severe when the anode is partially in contact with hydrogen and partially with air (so-called hydrogen–air fronts) due to a mechanism [5,6] shown in Fig. 1. The mechanism, which points to the destructive influence of the oxygen evolution potential, has been identified as the primary cause of catalysts

* *Corresponding author*. Tel.: +48 22 568 2908.
E-mail address: piotr.piela@ichp.pl (P. Piela).
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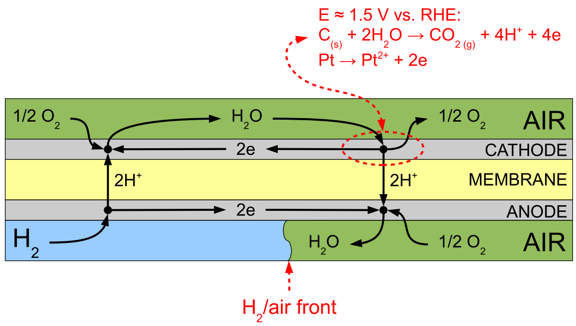

Fig. 1 – PEMFC catalyst corrosion mechanism due to hydrogen–air fronts. Dash-circled area is where local highly corrosive potential develops.

degradation in practical PEMFCs utilizing carbon-supported catalysts at low loadings [7,8]. One strategy is to develop more oxidation-resistant materials [9], however, without preventing uncontrolled H_2–air fronts the risk of quick destruction of a costly PEMFC stack will remain high.

To avoid the corrosion, particularly long residence of the hydrogen–air fronts, it is necessary to lower the voltage of the fuel cell at the time of stopping its work. In general, this can be achieved by making sure that the gas compartments of both electrodes are filled with gases of similar composition. The most advantageous situation for the PEMFC shut down for a longer period of time is to leave the fuel cell with both electrode compartments filled with air. This is because when it is left with hydrogen in at least one of the gas compartments, at a certain moment the corrosive conditions described earlier will appear due to inevitable replacement of the hydrogen with air from the fuel cell surroundings through existing thin diffusion barriers (MEAs, fuel cell walls, valve sealing surfaces, etc.) [10].

A number of procedures for stopping work of a fuel cell fueled with a gaseous fuel are known and have been summarized for example by Yu et al. [11]. The most frequently used methods of corrosion-preventing turning off of a fuel cell rely on purging the anode with an inert gas or air and/or oxidizing the residual gases in the fuel cell by connecting an external shunt resistor to the fuel cell. In a typical industrial method [12] the blower existing in the anode recirculation loop or the cathodic air compressor together with some additional valves are used to quickly blow out hydrogen from the anodic compartment with air. An essential drawback of this method is the questionable safety of bringing together in one piping the active supplies of fuel and oxidant.

From a comparison of different fuel cell stopping procedures provided by Kim et al. [13] it follows that for least fuel cell degradation the most advantageous proceeding relies on simple shutting off of the inlets and outlets of hydrogen and air at the fuel cell at the moment of stopping the drawing of current. Under such conditions, hydrogen crosses the MEA and catalytically burns off the oxygen in the air compartment over the cathode catalyst. Since stoichiometrically more hydrogen than oxygen is (usually) retained in the stack at the beginning, both the anode and cathode become ultimately flooded with hydrogen after the burn-off and assume a low potential. A similar effectiveness of such hydrogen protection of the cathode was found by Oyarce et al. [14], however, as pointed earlier, it is more prudent to fill both sides of the fuel cell with air upon stop for a longer time.

Here, we communicate a recently developed method for instant flooding of the whole PEMFC with air upon stopping its work for a longer period of time without resorting to active air purging of the anode compartment [15]. The method also permitted very significant reduction of the PEMFC performance degradation associated with the stops.

Material and methods

Hardware

A hydrogen-fueled, liquid-cooled PEMFC stack (ZSW, Germany) having 10 cells of 96 cm^2 geometrical working area each and the nominal electrical power of 480 W was tested. The stack had composite bipolar plates and 5-layer commercial MEAs (Solvicore, Germany, H400 type). A stack test bench (Fuel Cell Technologies, Inc., USA) was supplied with hydrogen 5.0 grade, nitrogen 5.2 grade, de-ionized water, and ambient air from an oil-less compressor. Two solenoid valves were additionally provided at the connections of hydrogen to the stack, one at the inlet and one at the outlet (V1 and V2 in Fig. 2). One of the valves was a simple shut-off valve and the other was a three-way valve that allowed shutting off the hydrogen line at the stack and simultaneously opening air access from the stack surroundings to the anodic gas compartment of the stack. The valves were operated concertedly to either allow normal passage of hydrogen through the stack or to isolate the hydrogen lines and open the air access.

Testing procedures

A single start/stop stack durability test evaluating a particular stopping procedure was composed of 7 consecutive parts: (i) safe start-up of the stack and work under nominal conditions for 15 min (conditioning), (ii) polarization curve 1 (assessment of stack condition), (iii) 37 start/stop cycles, (iv) polarization curve 2, (v) safe shut-down of the stack and leaving it filled

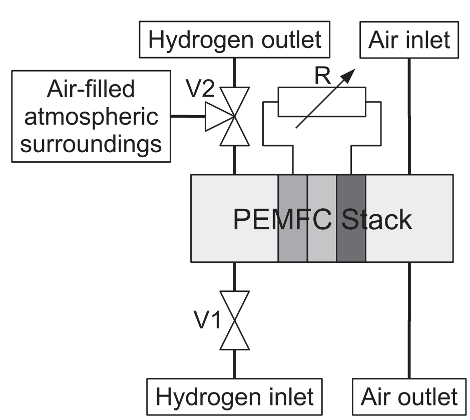

Fig. 2 – Schematic representation of the setup for practicing start/stop cycles involving measures I–III.