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Review

A review of accelerated conditioning for a polymer electrolyte membrane fuel cell

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ABSTRACT

A newly fabricated polymer electrolyte membrane (PEM) fuel cell usually needs a so-called break-in/conditioning/incubation period to activate it and reach its best performance. Typically, during this activation period the cell performance increases gradually, and then reaches a plateau without further increase. Depending on the membrane electrode assemblies, this process can take hours and even days to complete, which consumes a considerable amount of hydrogen fuel, leading to a higher operating cost. To provide for accelerated conditioning techniques that can complete the process in a short time period, this paper reviews established conditioning protocols and reported methods to condition PEM single cells and stacks, in an attempt to summarize available information on PEM fuel cell conditioning and the underlying mechanisms. Various techniques are arranged into two categories: on-line conditioning and off-line conditioning. For each technique, the experimental procedure and outcomes are outlined. Finally, weaknesses of the currently used conditioning techniques are indicated and further research efforts are proposed.

Contents

1. Introduction

A newly fabricated polymer electrolyte membrane (PEM) fuel cell usually needs a so-called break-in/conditioning/incubation period to be activated and reach its best performance [1]. This break-in period is necessary to test and condition the membrane electrode assemblies (MEAs) and other assembled components for operation and to ensure the stack is performing according to specifications before assembling the entire fuel cell system. Typically, during this break-in period the cell performance increases gradually, and then reaches a plateau without further increase, e.g., the power density is monitored until the current density at a given

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voltage stops increasing. At this point, the break-in procedure is thought to be complete and the cell is broken in and ready to operate under normal use conditions. Depending on the MEAs, this process can take hours and even days to complete, if no special measures are taken. With today's cell/stack technology, a break-in period of 24 h is not uncommon. This not only consumes a considerable amount of hydrogen fuel, but also takes up significant time, resulting in a high cost for operating the fuel cell. Thus, MEA conditioning and testing techniques are required to significantly reduce the break-in period [2]. Ideally, not only would one like to have the highest possible power density after the break-in procedure, but one would also like to minimize the time to reach this point [3]. The US Department of Energy (DOE) has proposed research projects in an attempt to either condition the MEA before stack assembly and thereby significantly reduce the process duration, or develop novel design concepts that eliminate the need for conditioning steps [4].

To our knowledge, no in-depth investigations have been made into the causes for this conditioning process. This can be attributed to both the lack of diagnostic tools available to analyze the results and the lack of experimental designs to explore the underlying mechanisms. To shorten the time for electrode activation and maximize fuel cell performance, several methods have been examined [5]. The specific conditioning or break-in procedure used among practitioners varies, ranging from performing a number of polarization curves on the newly assembled cell/stack, or applying an external load to the cell and holding the voltage or current constant for a fixed time period, to steaming or boiling the electrode for a short time. The US Fuel Cell Council (USFCC) has established cell break-in protocols to standardize the process [6]. However, no standard measurement has been established to determine the effectiveness of a break-in or conditioning procedure. The following methods were recommended by Murthy et al. [3] by monitoring a fuel cell's output current density at 0.6 V and recording it as a function of time during the application of a given break-in procedure. After break-in completion (18 h), the power density at 0.6 V is extracted from the polarization curve. This power density can then be used as a means of comparison between cells that have been conditioned with various procedures. Additionally, to measure the break-in time, two values are calculated from the recorded current density at 0.6 V versus time. The first is the time required to reach 75% of the current density achieved at 18 h. The second is the time required to reach 90% of the current density achieved at 18 h. Apparently, better break-in or conditioning procedures will give shorter times.

Understanding the fundamentals of the conditioning process helps to establish manufacturing procedures that permit accelerated break-in of the cell stack [7]. Possible theories have been put forward to explain conditioning phenomena:

(i) The activation of the fuel cell has advantageous effects on the catalyst, e.g., removal of impurities introduced during the process of manufacturing the MEA and the fuel cell stack, activation of a catalyst that does not participate in the reaction, and creation of a transfer passage for reactants to the catalyst [8].
(ii) The membranes of a newly assembled fuel cell stack typically need an incubation phase, a period of stack operation to "break-in" the membranes. One theory is that the membranes may include catalyst residue that hinders their performance. Another theory is that the membranes are initially dry, hindering the stack performance until the membranes hydrate during the incubation period [9].
(iii) To improve PEM fuel cell performance, electrode structures have evolved from polytetrafluoroethylene (PTFE)-bonded electrodes [10] to Nafion-impregnated PTFE-bonded electrodes [11] and Nafion-bonded electrodes [12]. The introduction of Nafion electrolyte into the catalyst layers (CLs) extends the electrode reaction zone, improves catalyst layer ionic conductivity, and thus increases catalyst utilization. However, the initial performance of a new MEA with Nafion-bonded electrodes usually improves with time, as the electrolyte contained in the electrodes needs hydration to ensure the passage of hydrogen ions.

From these theories, it is clear that one of the most important requirements for successful activation of the fuel cell stack is to control the water content at a certain level.

To provide for accelerated conditioning techniques that can complete the process in a short time period, as well as present an understanding of the mechanisms behind the break-in methods, this paper reviews various methods to condition PEM fuel cells/stacks, including on-line and off-line conditioning techniques.

2. On-line conditioning

2.1. Traditional break-in

2.1.1. Current control

Investigations have indicated that forced activation at varied currents can activate the MEA [13]. Some examples that apply current control to condition the cell are listed in Table 1.

A constant current density of 1 A cm^{-2} has been applied by Xie et al. [14] to activate a cell, using the following procedures. The

Table 1
Comparison of conditioning protocols under current control.

Test cell conditions	Additional approach	Available protocols	Authors	Reference
25 cm^2 cell, 80 °C, Nafion NRE-211 membrane, 0.40 mg Pt cm^{-2} for both electrodes	Short circuit for a few minutes	1 A cm^{-2} drawn from the cell for 6 h	Xie et al.	[14]
65 °C, Nafion 111 membrane and Pt/C electrodes with Pt loadings of 0.3 and 0.5 mg Pt cm^{-2} on the anode and cathode	Open-circuit operation for 2 h	A 25 h MEA conditioning procedure by controlling the current density and holding for 5 h at 50, 200, 500, 800, and 1000 mA cm^{-2}, respectively	Bi	[15]
50 °C	–	First step: 100, 200, 300, and 400 mA cm^{-2} for 10 min, respectively, followed by 500 mA cm^{-2} for 30 min and a rest period for 15–20 min. Second step: holding the current at 500 mA cm^{-2} for 10 min, then at 800 mA cm^{-2} for 40 min, followed by a rest period for 15–20 min. Third step: repeat the second step 4–6 times	Shan et al.	[16]
DMFC, 25 °C, Nafion® 117, Pt/C for the cathode and PtRu/C for the anode	–	Constant current of 100 mA cm^{-2} for up to 50 h	Kim et al.	[17]