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Publisher’s version / Version de l'éditeur:
https://doi.org/10.1016/j.jpowsour.2011.06.098
Journal of Power Sources, 196, 22, pp. 9097-9106, 2011-07-26

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Journal of Power Sources 196 (2011) 9097–9106

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Review

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

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ARTICLE INFO

Article history:
Received 27 May 2011
Received in revised form 28 June 2011
Accepted 29 June 2011
Available online 26 July 2011

Keywords:
Conditioning
Pre-conditioning
Activating
Commissioning
Break-in
Incubation

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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doi:10.1016/j.jpowsour.2011.06.098

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]

single cell was connected to the test station and heated to 80 °C without gas being supplied to the cell. After the anode and cathode humidifiers were heated to 80 °C and the gas supply inlet lines were heated to 83 °C, the anode was electrically shorted to the cathode for a few minutes, and hydrogen gas was then supplied to the anode. After removal of the shorting leads, humidified O_2 was introduced to the cathode. When an open circuit voltage (OCV) of ~1.0 V was reached, a DC load was applied to the cell and 1 A cm^{-2} was drawn from the cell for 6 h. The potential stabilized after ~3 h. At the end of the conditioning period, the variation in the steady state potential was <+1 mV.

Following open-circuit operation for 2 h for cell wet-up, a 25-h MEA conditioning procedure by controlling the current density and holding it for 5 h at 50, 200, 500, 800, and 1000 mA cm^{-2} was accomplished by Bi [15] in the process of studying Pt/C dissolution and deposition in Nafion electrolyte. The catalyst-coated membrane (CCM) was Nafion 111 membrane and Pt/C electrodes with Pt loadings of 0.3 and 0.5 mg cm^{-2} on the anode and cathode, respectively. Cell operating conditions were 65 °C with fully humidified anode and cathode gases at atmospheric pressure.

A similar procedure of controlling currents sequentially was patented by Shan et al. [16]. The entire conditioning process consists of three steps. The first step includes 100, 200, 300, and 400 mA cm^{-2} for 10 min each, followed by 500 mA cm^{-2} for 30 min and a rest period of 15–20 min. The second step includes 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 of 15–20 min. Then the second step is repeated 4–6 times.

Applying a constant current to condition a fuel cell was also studied with direct methanol fuel cells (DMFCs). Kim et al. [17] investigated the effect of an MEA conditioning method on the performance of a DMFC (Pt/C for the cathode and PtRu/C for the anode) using an impedance technique. The fuel cell was fed with a methanol solution (2 M, 5 mL min^{-1}) and oxygen (250 sccm) at 90 °C and 1 atm. Temperature (25 or 90 °C) and a constant current of 100 mA cm^{-2} (applied or not) were selected as variables during the conditioning period to study their effects on the DMFC's performance. Cell performance was measured every 6 or 12 h during MEA conditioning. Immediately after cell performance measurement, an impedance measurement was taken. The results showed that the MEA at 25 °C with constant current (100 mA cm^{-2}) applied had the best performance, and the resistance decreased gradually due to hydration of the proton-conducting material during the entire conditioning period.

Other conditioning processes under current control are more or less similar to the above procedures. Techniques related to current control that are used for other purposes might also be introduced to the conditioning process. A high-frequency ripple current has reportedly been used for an aging test [18]. The current ripple is produced by submitting the output fuel cell current to a high-frequency switch. The ripple current effects on the fuel cell are then studied using an experimental ripple current aging test on a 220 cm^2 5-cell stack and compared with a reference aging test. The stack is run in nominal conditions but an ac component is added to the dc load. The ac component is a 5 kHz triangle with an amplitude of ~20% of the dc component, to simulate a boost waveform. The results show that the degradation slopes of the high-frequency ripple current test are much higher than those of the reference test. Although this method is intended for a degradation test, it may well be considered as a conditioning approach.

2.1.2. Potential control

In addition to current control, many different break-in protocols for new materials within the fuel cell industry are related to potential control, with variations in duration, load cycle, and cell conditions.

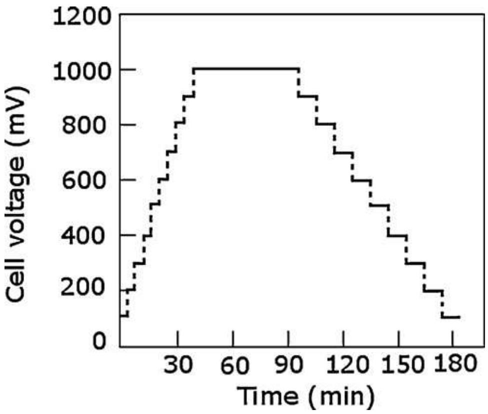

Fig. 1. A sequential voltage profile for cell conditioning under potential control [8].

2.1.2.1. Potential cycling. Potential cycling is one of the most commonly used methods to condition a PEM fuel cell. A typical initial cell operating condition at Gore for Gore CCMs is as follows. The cell is cycled between 0.6 V, 0.3 V, and OCV, with each set point held for 30–90 s, and the cycle is repeated until no further increase in cell performance is observed. Generally, 6–8 h of break-in are required. The operating conditions or initial set point are: Tcell = 70 °C, with 100% RH hydrogen at 1.2× stoichiometric flow at ambient pressure, and 100% RH air at 2.5× stoichiometric flow at ambient pressure. Using Gore/PRIMEA® Series 5510 MEAs with an active area of 100 cm^2 and a catalyst loading of 0.8 mg cm^{-2}, Weng et al. [19] performed cell conditioning based on the Gore protocol. The MEA conditioning was repeated 5–6 times or more until the performance reached a relatively steady state by holding a constant voltage of 0.6 V for 30 min, 0.4 V for 30 min, and then OCV for 1 min. A similar cycling method was also patented by Lee [20]: holding at OCV for 2 min, 0.6 V for 30 min, and then 0.4 V for another 30 min, at 55 °C.

Lim et al. [8] patented a method of applying sequential voltages to activate a fuel cell. The voltage profile is shown in Fig. 1. After supplying hydrogen and air (oxygen) to a fuel electrode and an air electrode, respectively, a predetermined load sequence is applied to the fuel cell under predetermined operating conditions. The active load sequence may be applied in three steps: (1) cell voltage is increased from 100 mV to 900 mV and maintained for 2 min at each increase of 100 mV; (2) cell voltage is increased up to 1000 mV and maintained for 30 min; and (3) cell voltage is decreased from 900 mV to 100 mV and maintained for 5 min at each decrease of 100 mV. The same patent gives another example: the load is sequentially applied in the order of (1) OCV (15 min), (2) 600 mV cell^{-1} (75 min), (3) 850 mV cell^{-1} (20 min), and (4) 600 mV cell^{-1} (30 min), with steps (3) and (4) repeated 3 times.

Murthy et al. [3] from Gore also recommended in their patent a method to apply during the first 24 h of operation, or alternatively after 24 h of operation, to improve the performance of a fuel cell: applying a first external load to produce a first voltage (around 0.6 V) that is less than OCV, for less than about 20 min (or 15 min); removing the external load for less than about 2 min (or 1 min); and applying a second external load (around 0.3 V) to produce a second voltage that is less than OCV, for less than 20 min (or 15 min). This process should be repeated at least twice, possibly three times, at a cell temperature between 60 and 90 °C. An additional step may also include removing the external load for between 5 and 120 s. They have discovered that the use of such a conditioning regime improves power density at 0.6 V and decreases break-in time, giving a 75% break-in time of less than about 2 h and a 90% break-in time of less than about 4 h.

Basically, these methods control the voltage in different steps at various frequencies, allowing the cell, on and off, to work under

Table 2
USFCC cell break-in load sequence [6] (Table courtesy of USFCC).

Test condition	Step time (min)	Cumulative time (h)
Initial start-up	As required to warm up to 80 °C	
Cycling step 1 (perform once)		
0.60 V	60	1.0
Cycling step 2 (perform 9 times)		
0.70 V	20	
0.50 V	20	7.0
Constant current operation		
10 amps	720	19.0

duty and to relax. There are also methods that combine current control and voltage control to activate the cell. For example, Ion Power recommended the following conditioning process:

(1) While the cell is still at room temperature, control the current to 0.15 A cm^{-2}.
(2) After 5 min, change the load to voltage control at 0.2 V without changing the gas flow rates at the outlet, and allow the cell to draw as much current as it can.
(3) Hold this voltage for 5 min.
(4) Continue this load cycling procedure until no further improvements in performance are observed, or a minimum of 6 h.

A combined current control and voltage control break-in procedure has also been described in the USFCC single-cell test protocol, as shown in Table 2 [6]. A similar three-step break-in procedure can be found in [21], with a slight difference in the first cycling step, in which voltage cycling was set at 30 min per setting (0.94–0.6 V at 10 stoich, 10 A) and followed by a 20 A load for 4 h after the three-step break-in. Examples of performance increase during the second and third steps are presented in Figs. 2 and 3 [21].

2.1.2.2. Short circuit. Different from potential cycling, a short circuit method was reported by Xie et al. [14]. This method served as part of the conditioning or pre-conditioning process. After the set temperatures of the cell and lines were achieved, the anode was electrically shorted to the cathode for a few minutes, followed by a conditioning process of current control for 6 h. This short circuit process was described as intended to deplete traces of hydrogen.

Surprisingly, short circuiting has been used as the entire conditioning approach as well. Sun et al. [2] provided a short circuit method to activate the electrode. The method includes three steps:

(a) connect the anode and the cathode to short the cell
(b) supply the stack with cycling cooling water, fuel, and oxidant
(c) adjust the flow rate.

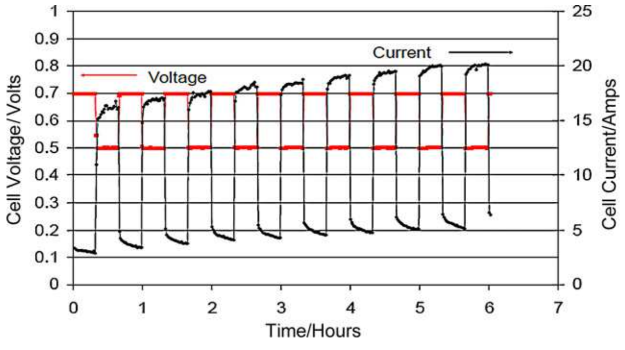

Fig. 2. Voltage and current profiles during step 2 of break-in, with cycling between 0.7 V and 0.5 V for 6 h (20 min each setting). (Cell temperature: 60 °C; back pressure: 3.7 psig; H_2/air: 696/1740sccm (fixed flows).) [21]. (Image courtesy of the author.)

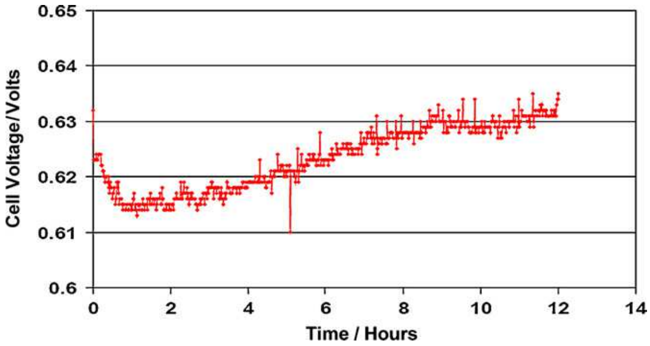

Fig. 3. Voltage profile during step 3 of break-in, with constant current at 10 A for 12 h. (Cell temperature: 60 °C; back pressure: 3.7 psig; H_2/air: 696/1740sccm (fixed flows).) [21]. (Image courtesy of the author.)

When the cell or stack is shorted, the current depends on the flow rate of the reactants, denoted as the maximum value of the current, and the cell voltage is around 0 V. In cases where reverse voltage for any of the cells in the stack exceeds a time limit, say 30 s, adjust the times for the low flow rate and the high flow rate to ensure that the reverse voltage time remains within the reference time for reverse voltage. With a low flow rate of 1 min, a high flow rate of 3 min, and 7 repetitions, this accelerated conditioning process can be completed in 30 min. At the end of this process, supply hydrogen at a minimum rate and stop supplying oxygen. When the cell voltage is below 0.1 V, stop supplying hydrogen. Thus, at the end of the activation, eliminating the oxygen supply helps to disconnect the wire safely and reduce the possibility of carbon corrosion at the cathode side. This method is advantageous because the voltage is about 0 V, which can activate both the membrane and the catalyst layer, and the activation time is significantly reduced to 1/10 of the conventional method time. Thus, hydrogen consumption is greatly reduced, lowering the cost considerably.

2.1.3. Temperature control

Temperature control has also been studied and reported to condition a PEM fuel cell. Usually, temperature control is performed together with current/potential control or pressure control.

Fumio et al. [22] have disclosed a fuel cell system and temperature related method to condition a fuel cell stack to be ready for use. The method includes temperature rise, electric power generation, dry purging, and temperature drop, which are repeatedly executed. The first step of the cycle is to raise the fuel cell to a normal operating temperature, upon which humidified fuel and oxidizer gas are supplied for a given time interval to generate electric power. After stopping the generation of electric power and supplying dry air and fuel to the fuel cell stack, residual moisture is purged from the stack. After purging, the temperature of the stack is lowered to a value below freezing point, causing moisture to condense in a solid polymer membrane to contain the water.

A standard thermal cycle used to break in the MEA was presented by Debe from 3 M [23]. The cell is first warmed up to 75 °C, with the humidification temperature set at 70 °C for both the anode and cathode, and operated with polarization curves or potential holding. Then the cell is cooled down to room temperature with gases off and liquid water injected to both anode and cathode for 45 min. Another example presented was based on temperature control and current cycling. The cell is first warmed up to 75 °C without any humidification on either side and with current cycling at 0 A cm^{-2} for 2 s, 0.1 A cm^{-2} for 10 s, and 0.2 A cm^{-2} for 3 s. After a performance check, more current cycling at 75 °C is performed. Then the cell is cooled down to 55 °C with current cycling at 0 A cm^{-2} for 2 s, 0.1 A cm^{-2} for 10 s, and 0.2 A cm^{-2} for 3 s.

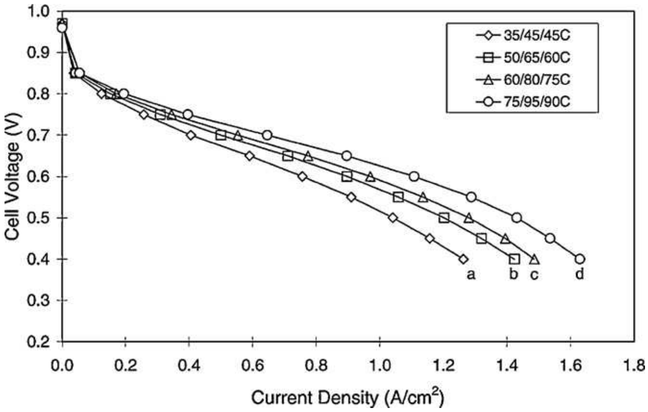

Fig. 4. Performance of an activated cell at different temperatures. Nafion 112 membrane, Pt 1/4 0:12 mg cm^{-2} [24]. A cell temperature of 35 °C, hydrogen inlet temperature of 45 °C, and air inlet temperature of 45 °C is denoted herein as 35/45/45 °C. During activation, the cell voltage was set at 0.40–0.60 V for most of the time to sustain a current density of 1.0–1.5 A cm^{-2}, but periodically the load was adjusted in such a way that the cell voltage was changed from open circuit voltage to as low as 0 V.
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Qi et al. [24–26] provided an effective and fast activation procedure by exposing the fuel cell to elevated temperature combined with elevated pressure. The procedure not only is much shorter than a traditional break-in process but also increases catalyst utilization dramatically, especially for electrodes with low catalyst loadings made using supported catalysts [24]. For instance, after less than 2 h of running the cell under aggressive conditions, e.g., 75/95/90 °C, the fuel cell performance could be boosted dramatically. Here, 75/95/90 °C denotes a cell temperature of 75 °C, a hydrogen humidification temperature of 95 °C, and an air humidification temperature of 90 °C (with a hydrogen back pressure of 20 psig and an air back pressure of 30 psig). Fig. 4 shows the effect of conditioning temperature on cell performance. As can be seen, 75/95/90 °C yields the best performance after activation. The cell achieved 78% activation at 0.70 V and 93% activation at 0.40 V after as little as 5 min. After 30 min, the cell achieved 87% activation at 0.70 V and 97% activation at 0.40 V. After 60 min, the cell achieved 93% activation at 0.70 V and 100% activation at 0.40 V. After 90 min, the cell achieved 100% activation at 0.70 V too.

They found that under elevated temperature, the current density at certain cell voltages could be doubled after this activation procedure, and the activation could be completed extremely quickly, with most of it achieved in the first few minutes. It was proposed that the activation process increases catalyst utilization by opening many “dead” regions in the catalyst layer. Although a proton conductor such as Nafion is mixed into a catalyst layer to make it conduct protons in three dimensions, many of the catalyst sites are not available for reaction for various reasons: (1) the reactants cannot reach the catalyst sites because the latter are blocked, (2) Nafion near these catalyst sites cannot be easily hydrated, or (3) an ionic or electronic continuity is not established with these sites. When a fuel cell is operated at elevated temperature and pressure, many of these “dead” regions are “opened” and then become active [24].

The activation effect also proved to be long-lasting; for example, the activated electrode lasted for about 4 weeks. During this time period, the cell was either operated continuously for a few days or shut down for one or several days, then started the next day, and at one time, the cell was frozen at −17 °C for 3 days. In these 4 weeks, the performance fluctuated slightly but the trend showed very little decrease. It was believed that the fluctuation was due to water management rather than activation loss [24].

Further study [24] shows that under elevated temperature a variety of supported catalysts can all be fully activated within several hours, although different catalysts may need different activation times. Generally speaking, the improvement in performance after activation is greater for catalysts with lower Pt content on a support. The activation procedure is also applicable to electrodes made using unsupported catalysts such as Pt black, but the increase in performance is normally less than for electrodes made using supported catalysts. MEAs consisting of different types of membranes, or the same type of membrane but with different thicknesses, are all able to be activated quickly.

2.2. *Hydrogen evolution/pumping*

H_2 evolution, also known as hydrogen pumping, on electrodes is an effective way to improve PEM fuel cell performance by moving hydrogen from one side of the membrane to the other. For example, to activate the cathode, hydrogen is passed through the anode and an external power source is applied to the fuel cell, with the cathode side having a lower voltage than the anode side. Hydrogen at the anode is oxidized to form protons, which are transported through the membrane to the cathode, where they are reduced to form hydrogen. The reactions for H_2 evolution on the electrodes are as follows:

$$\text{Fuel cell anode: } H_2 = 2H^+ + 2e^-$$

$$\text{Fuel cell cathode: } 2H^+ + 2e^- = H_2$$

$$\text{Overall: } H_2\,(\text{anode}) = H_2\,(\text{cathode})$$

As a result of this change, electrode catalyst utilization is increased and MEA performance is improved [5]. This is achieved by reducing the overpotential of both oxygen reduction and methanol oxidation. The reduction in cathode and anode overpotentials is thought to be due to the change in the porosity and tortuosity of the catalyst layers when H_2 evolves from them, leading to an increase in the number of reactant-catalyst-electrolyte 3-phase sites.

Qi et al. [27] have conducted an activation procedure that involved hydrogen evolution at the electrode. The detailed hydrogen-evolution/hydrogen-pumping procedure was as follows. Air at the cathode side was replaced by nitrogen, while the anode side was fed with pure hydrogen. An external power supply was used to generate a current density of ca. 200 mA cm^{-2} through the cell, with hydrogen being oxidized at the anode, and the protons transporting through the membrane to the cathode, where they were reduced. This procedure was carried out at a cell temperature of 35 °C and lasted for 30 min. After H_2 evolution on the cell cathode, the cell performance was reevaluated with H_2 and air. As shown in Fig. 5, after hydrogen pumping, an increase in cell performance was observed; this was explained by the change in catalyst utilization, which may be identified by the fuel cell performance difference in the low current density region. At low current densities, the performance of fuel cells is mainly controlled by the electrode kinetics, which is directly related to the total number of reactant-catalyst-electrolyte sites.

Apart from hydrogen evolution, a procedure of hydrogen exposure has been patented by Ballard to accelerate fuel cell conditioning [28]. The brief exposure to dry, ambient temperature hydrogen appeared to accelerate the conditioning process, although the cells were still not completely conditioned. One test showed that after dry, unheated hydrogen was piped through the stack anodes and cathodes for 5 min, immediately the average voltage of the cells increased by 20–32 mV. Another test showed that brief exposure to heated and humidified hydrogen (80 °C, 100%

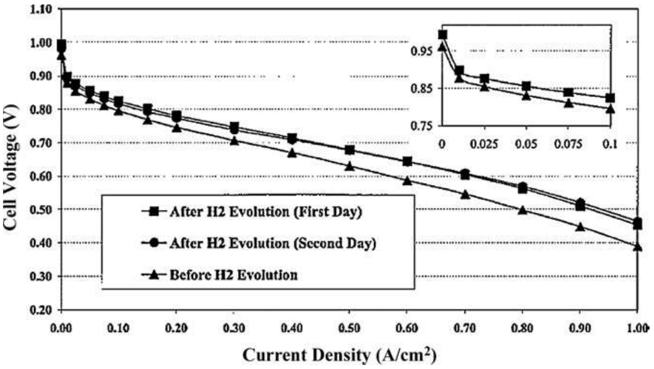

Fig. 5. Performance of a H_2/air fuel cell before and after H_2 evolution on the cathode. Catalyst loading 0.55 mg Pt cm^{-2} for both anode and cathode; temperature 70 °C; ambient pressure; Nafion 1135 membrane [1].
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RH for 5 min) brought the stack almost to the nominal operating voltage (within 95% of normal).

2.3. CO oxidative stripping

It is well known that carbon monoxide (CO) can seriously poison a PEM fuel cell due to its strong adsorption onto catalysts; hence, CO has been considered a nuisance and obstacle to the development of fuel cells. Interestingly, a special activation procedure that involves CO was reported by Qi et al. [29], wherein they found that CO adsorption could be used to activate PEM fuel cells. Fig. 6 compares performance under conventional break-in and CO oxidative stripping conditions. As can be seen, after each CO oxidative stripping process, cell performance increases. The performances indicated by curves 2, 3, and 4 are apparently higher than the curve 1 performance (traditional break-in) in the entire current density region, which means that a CO-adsorption/CO_2-desorption process pushed the fuel cell performance over the limitation of a traditional break-in procedure [29]. This shows that under those experimental conditions, three CO-adsorption/CO_2-desorption cycles were needed to achieve maximum performance, which was about 29% higher than the result obtained by a traditional break-in procedure.

Here, the conventional break-in procedure uses pure hydrogen and air as the reactants. The test was carried out at 35/45/45 °C for more than 4 h. During this period, the fuel cell was set at around 0.4 V for most of the time, and periodically the cell voltage was scanned from open circuit to nearly 0 V. After about 3 h no apparent further increase was observed [29]. The detailed procedure for CO oxidative stripping was as follows. At a cell temperature of 35 °C, initial adsorption of CO onto the catalyst surface was followed by potential sweeping to oxidize CO into CO_2. During the CO adsorption process, a mixed gas containing 0.5% CO (balanced by 99.5% nitrogen) was used at the cathode side, and the cathode voltage was set at 0.50 V. The adsorption was allowed to last for about 30 min to ensure full coverage of CO on the cathode Pt catalyst (a much shorter adsorption time could be enough, especially if a higher CO concentration were used). Then the mixed gas was replaced by nitrogen to flush out of the cathode compartment all the CO molecules that did not adsorb onto the catalyst. The potential sweeping was carried out between 0.5 and 1.0 V at a scan rate of 30 mV s^{-1}. The main purpose of controlling the cathode voltage at 0.5 V or higher during both CO adsorption and potential scanning steps was to avoid hydrogen evolution because that can also activate fuel cells. After CO is oxidized, CO_2 should leave the catalyst surface readily because it adsorbs very weakly onto the catalyst surface.

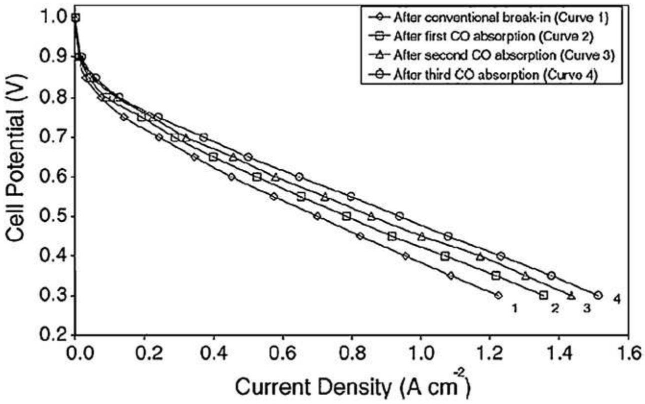

Fig. 6. Comparison of performance under conventional break-in and CO oxidative stripping conditions [29].
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2.4. Air braking

Ballard [30] discovered that performance could be improved by briefly drawing power from the fuel cell in the absence of oxidant. This method can be used not only to activate a fuel cell after initial manufacture, obviating a lengthy activation process, but also to rejuvenate a fuel cell following prolonged storage. During the process, the voltage of the fuel cell remains greater than or equal to zero. Performance improvements may be obtained even when the voltage remains greater than 0.4 V. For example, after a storage period of 141 days, a 47-cell stack was rejuvenated by subjecting it to several conditioning cycles. Each cycle involved shutting off the supply of air while still supplying hydrogen to the anode, and connecting the stack across a resistor until the stack voltage dropped below 2 V. The supply of air was then restored and the stack voltage recovered. Each cycle took about 1 min to complete and the stack was subjected to 5 consecutive conditioning cycles. Significant performance improvement was observed. This method helps to condition the fuel cell because drawing current from a fuel cell in the absence of oxidant yields reducing conditions at the cathode, resulting from the higher concentration of hydrogen and lower concentration of oxidant. Oxidized species can thus be reduced.

An "air break" method was also reported by Eickes et al. [31] to recover the performance of a DMFC cathode. This air break method consisted of a sequence of steps performed in the following order: (i) stopping airflow to the cell, (ii) immediately switching cell operation to constant-current mode using the same current as the current generated by the fuel cell at the time of the switch, (iii) restarting airflow as soon as the cell reaches a preprogrammed low-voltage limit, and (iv) immediately returning to the life test in constant-voltage mode. The results show that the average power output of the cell operated with the air break is significantly higher than that of the cell operated continuously without air pulsing.

2.5. Other on-line conditioning methods

Aside from the above discussed on-line conditioning methods, special techniques like circulating hot water [32] and supplying a reducing agent [33] can also be found in patents. For the former technique, hot water is used as cleaning water communicated to the anode and the cathode via a hot water supplying system. Water is heated to a predetermined temperature to economically carry out a cleaning process of an electrolyte film-electrode structure in a short time, then is returned to a tank to be circularly used. In the latter case, activation is achieved by supplying a reducing agent to at least the cathode. These reducing agents include hydrogen, hydrogen peroxide aqueous solution, hydrazine aqueous solution, and citric acid aqueous solution, which help to obtain high-performance electric battery output.

2.6. Combination of stressors

Any of the above activation methods can significantly increase fuel cell performance. It is also possible to accelerate the conditioning period and thereby improve cell performance by combining these techniques in a specific order. Qi et al. [1] found that combining the accelerated stressors could yield better PEM fuel cell performance than if only a single activation method was used. For example, carrying out either hydrogen evolution or CO stripping after elevated temperature and pressure could further increase the fuel cell performance. If elevated temperature and pressure were introduced after either hydrogen evolution or CO stripping, the fuel cell performance could also be further increased, but the final performance was similar to what was achieved with only elevated temperature and pressure.

3. Off-line conditioning

Traditionally, fuel cell conditioning is operated on-line by connecting the fuel cell into the system and controlling the voltage, current, and operating conditions. Various strategies have also been reported to condition the CCMs or electrodes before they are assembled into the cell/stack.

3.1. Electrochemical conditioning of the MEA

It is generally believed that the membrane hydration level, the number of proton conduction channels, and the catalyst layer porosity continue to increase during the conditioning period. Palanichamy et al. [34] proposed an electrochemical technique for conditioning the MEA – consisting of a CCM fabricated by the decal process and two porous graphite current collectors on each side – by immersion in dilute (0.50 M) H_2SO_4. This is achieved by maintaining the potential between the limits of platinum oxide (PtO) formation and hydrogen evolution to clean the Pt surface, as well as by creating proton conduction pathways and pores in the catalyst layer. During this cleaning process, one side of the MEA attains a positive potential value where electrochemical oxidation of the impurities, PtO formation, and O_2 evolution will occur. Apart from chemical oxidation, the impurities will also be physically disengaged from the electrode surface by the evolved O_2. The other side of the MEA attains a negative potential value, with H_2 evolution being the possible reaction, which will also clean the Pt surface. Then, the polarities of the two sides are switched and the cleaning process is continued until the active surface area of Pt in the MEA reaches a reproducible value.

3.2. Steaming or boiling the electrode

Another off-line method is to treat electrodes or MEAs using hot water or steam before they are assembled into a stack. Qi et al. [35] reported that treatment of electrodes or CCMs by either boiling in water or steaming in a household pressure cooker for as short as 10 min could dramatically increase their performance when tested in PEM fuel cells afterwards. The improved performances are shown in Figs. 7 and 8. The treatment was only applied to the cathodes because they limit/determine the whole MEA performance when pure hydrogen is used as the fuel. When boiled in water, the electrodes floated on its surface, so the catalyzed side was arranged to face the water. When steamed, they either floated in the liquid water phase or were supported by a stand so that only water vapour could be in contact.

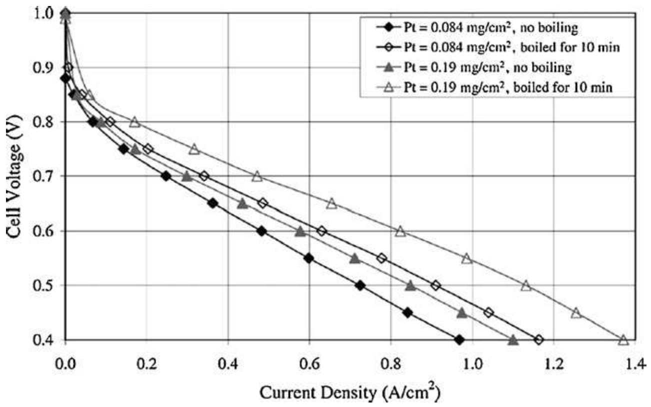

Fig. 7. V–I curves of electrodes that were boiled for 0 and 10 min, respectively. 40% Pt/C [35].
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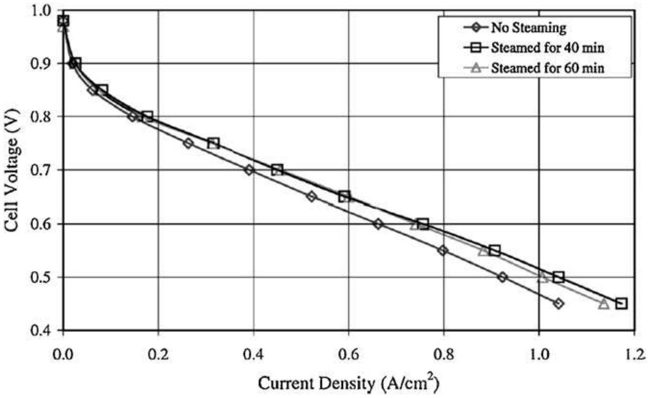

Fig. 8. V–I curves of CCMs that were steamed for 0, 40, and 60 min, respectively. The commercial CCMs have a membrane 25 μm thick and a catalyst loading of 0.3–0.5 mg cm^{-2} on each side [35].
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Since steaming or boiling enhances electrode performance in the whole voltage region, as shown in Figs. 7 and 8, the enhancement is believed to be due to an increase in Pt utilization. Therefore, one explanation proposed by Qi et al. [35] was that the treatment increases the number of active sites or regions in the catalyst layer, leading to enhanced catalyst utilization. As we know, Nafion or another ionic conductor is always added to the CL to ensure its three-dimensional activation, and the electrodes are then dried to remove the solvents. However, Nafion needs to be hydrated to achieve sufficient proton conductivity. When the electrodes are steamed or boiled in water, the Nafion in the MEA can achieve complete hydration, including the Nafion membrane and the Nafion in the CL, leading to enhanced MEA performance. Another explanation they proposed was that steaming or boiling may be able to open some otherwise “dead” regions in the CL. Some regions could be blocked or enclosed in such a way that gaseous reactant cannot gain access, so these regions are effectively “dead”. When treated in hot water or steam, some of these regions are opened, becoming accessible and active [35].

A similar procedure of exposing the MEA to saturated steam at superatmospheric pressure (at least 110 kPa) was patented by 3 M [36] to pre-condition the MEA. The process typically lasts for at least 10 min and more typically at least 25 min, and can reduce the start-up or conditioning time required when the MEAs are first installed in a fuel cell system, improving current density at relatively high voltage.

3.3. Component conditioning

3.3.1. Membrane

As a key component of the MEA, the membrane transports protons in the form of an electrolyte and acts as a barrier between the anode and cathode to prevent gas permeation. The most commonly used membrane is composed of perfluorosulfonic acid (PFSA), such as Nafion membrane. For improved performance, Nafion membrane should be conditioned before use. To analyze and quantify the effect of conditioning techniques on membrane performance, Barrio et al. [37] have carried out various experiments with Nafion 117 cation exchange membranes, for example, at room temperature and higher temperatures. Through measuring the water content (membrane swelling) of the treated membrane, and testing the fuel cell assembled with the treated membrane, including polarization curves, impedance spectroscopy, and lineal and cyclic voltammetries, they found that using acidic conditions and high temperatures (around 80 °C) to condition the membrane obtained a maximum power in a fuel cell up to 6 times that of an untreated commercial supply.

3.3.2. GDL

The GDL is a carbon-based porous substrate between the CL and the flow field that enables gas phase transport, water transport, electronic and thermal conduction, and mechanical support. The most commonly used diffusion media material for the GDL is carbon fiber paper, made by, for example, Toray of Japan, Spectracorp of Massachusetts, and SGL of Germany. During cell operation, the cell is compressed at a certain pressure. As a result of this compression, geometrical distortion of the GDL thickness can occur. One of the consequences can be significant loss of compression pressure in the fuel cell stack, causing an increase in contact resistance and thereby degrading the fuel cell performance, particularly when high power output is needed. Another consequence of compressing the GDL material is an intrusion of the material into the flow channels, which causes maldistribution of reactant gases. To prevent fuel cell compression loss over time, various strategies have been developed. For example, a bladder-type compression device has been used to maintain a constant stack compression force; however, this device is bulky and not useful for automotive applications. Rapaport et al. [38] provided a method for reducing (1) the compression set of the GDL during fuel cell operation and (2) the intrusion of the GDL into the flow-field channels. These outcomes were achieved by precompressing/preconditioning the GDL, via simulating compression before actually assembling the GDL into the fuel cell. This helped to reduce excessive and nonuniform intrusion into the channels, and eliminated the need for future recompression of the fuel cell stack due to loss of compression pressure. Ultimately, higher power output and more stable performance can be thus obtained.

4. A rapid break-in for PBI fuel cells

As discussed previously, the most commonly used membranes are Nafion membranes containing PFSA. Fuel cells fabricated with these membranes usually work below 100 °C. Phosphoric acid doped polybenzimidazole (PBI) membranes were developed for use at an intermediate operating temperature (>160 °C), and offer the same advantages as other intermediate- and high-temperature fuel cell technologies (phosphoric acid, solid oxide, and molten carbonate) in terms of thermal management and tolerance toward impurities. But similar to Nafion fuel cells, PBI fuel cells also need to be conditioned in an initial period of operation, to enable reproducibility and comparability of cell performance.

For low-temperature PEM fuel cells, single-cell testing protocols by USFCC [6] and cell component accelerated stress test protocols by DOE [39] have been developed. Other organizations that work on cell testing and standardization include, for example, the Fuel Cell TEsting and STandardisation thematic NETwork (FCTESTNET) [40] and the Japan Automobile Research Institute (JARI) [41]. Even rapid and reproducible break-in methods have been developed by USFCC [6] as part of standardized test protocols, and are widely studied by researchers, as discussed in this review. These break-in methods are crucial to ensure reproducibility and comparability of experimental results within the field of PEM fuel cell research. Currently, standardized test protocols or recommendations for rapid break-in of PBI fuel cells are rarely found.

Tingelöf et al. [42] provided different types of break-in procedures for state-of-the-art PBI fuel cells. The focus lay on methods that could rapidly and reproducibly ensure stable cell behavior for performance and contamination studies in cells and stacks. The cells were operated at constant current (0.2 A cm^{-2}) and 160 °C between different steps in the experiments and between polarization curves.

- Galvanostatic break-in

  A 100-h constant current break-in at a relatively low current (0.2 A cm^{-2}) is recommended. During galvanostatic break-in, the performance of an MEA increases noticeably.
- Potential cycling

  All standardized single-cell test protocols for low-temperature PEM fuel cells contain some cycling of the cell voltage, either as cycling between different potential levels or as repeated polarization curves. This method was also tried for the PBI fuel cell; however, it seems that potential cycling is in this case not a suitable break-in method.
- High-temperature galvanostatic break-in

  In this experiment, the cell was first operated for 100 h at 160 °C and 0.2 A cm^{-2}. Then the cell temperature was increased to 200 °C while maintaining the current density. Increasing the temperature of a PBI fuel cell for a limited period of time can be used as a break-in procedure to avoid very long galvanostatic cell break-in. We know that operating a PBI fuel cell above the designed temperature will inevitably cause a decrease in performance, due to evaporation of H_3PO_3 and consequent lowering of membrane conductivity; this loss of conductivity will eventually degrade cell performance to an unacceptably low level. However, if a PBI fuel cell is operated above the designed temperature only for a limited period of time, the consequences for the MEA are not very severe [42].

5. Reconditioning/cell maintenance

A reconditioning process may also be needed for a stack after a certain storage period. This reconditioning process should be similar to the conditioning procedure. For example, exposing the cathode to a reductant (e.g., hydrogen) can be used to activate a fuel cell after initial manufacture and provide for normal performance levels without the need for a lengthy initial operating period [28]. Alternatively, this method may also be used to rejuvenate/recondition a fuel cell following prolonged storage. The method is particularly advantageous for manufacturing purposes and commercial applications, where the fuel cell stack spends prolonged periods inactive, yet needs to deliver normal output power in a timely manner.

To avoid reconditioning, several strategies may be deployed to prevent a temporary loss in performance. It is believed that methods that prevent the formation of oxides and/or hydroxides on the cathode catalyst may be useful in forestalling performance loss. Such methods include applying a potential to the fuel cell dur-

Table 3
Comparison of on-line conditioning time using various methods.

Test conditions	Examples	Conditioning time (h)	References
Current control	Constant current of 1 A cm^{-2}	6	Xie et al. [14]
	Step current control	25 (plus 2 h OCV for wet-up)	Bi [15]
	Sequential current control	7–10	Shan et al. [16]
Potential control	Potential cycling	6–8	Weng et al. [19]
	Sequential voltage	3–4	Lim et al. [8]
	Combined current and voltage control	Ion Power: >6 USFCC: 19	USFCC [6]
	Short circuit	0.5	Sun et al. [2]
Elevated temperature	75/95/90 °C	<2	Qi et al. [24]
Hydrogen pumping	External power supply of 200 mA cm^{-2}	0.5	Qi et al. [27]
CO oxidative stripping	0.5% CO	>3 (after a 4-h traditional break-in)	Qi et al. [29]
Air braking	47-cell stack	>5 min	Voss et al. [30]

ing the storage period (e.g., from 0 to 0.6 V/cell), storing the fuel cell at a temperature below ambient (e.g., below about −20 °C), or storing the fuel cell with a blanket of inert gas on the cathode. For example, a 47-cell stack stored at −20 °C showed little to no voltage loss over 7 months of storage and testing, whereas a stack stored at ambient temperature showed stack voltage losses between about 0.1 and 0.33 V $month^{-1}$ over 11 months of storage and testing. A stack stored at 70 °C showed stack voltage losses of about 1.2 V $month^{-1}$ over the first 3 months, then levelled off at a total stack voltage loss of about 4 V over the total 8 months of testing and storage [30].

Not only can reconditioning be avoided by strategic storage of fuel cell stacks, but the normal conditioning process may be eliminated if the cathode catalyst is adequately reduced, then maintained in an inert atmosphere or reduced state until manufacturing is complete. An atmosphere essentially free of oxygen and water is suitably inert to maintain the catalyst in a reduced state. The reducing step can also be accomplished by exposing the cathode catalyst to a fluid comprising a reducing agent (e.g., hydrogen gas) [30].

6. Concluding remarks

A newly fabricated PEM fuel cell usually needs a conditioning or break-in period to maximize its initial performance. This paper reviews various methods to condition PEM single cells and stacks, seeking effective accelerated conditioning techniques that can complete the process in a short time period. These methods include on-line and off-line conditioning techniques, with conditioning periods ranging from a couple of hours to days. The conditioning times for on-line conditioning techniques are compared in Table 3. However, this comparison is relatively limited, as different research groups or companies use their own preferred MEAs. Depending on the type of MEA components, the actual conditioning time may vary.

Compared with fuel cell durability studies, research on fuel cell conditioning is relatively limited. In most cases, procedures are given and results are presented without digging further into the mechanisms. As a result, the reports contain more hypotheses than facts. Most mechanisms proposed are hypothetical because they lack direct experimental support or concrete experimental verification. A systematic investigation of conditioning and its mechanisms is still required. Also, the stressors for conditioning, which are for the most part operating conditions like temperature, relative humidity, potential, and load cycles, strongly affect the microstructures of the MEA, which in turn will strongly affect the long-term behaviour and durability of the cell [43], as MEA nanomaterial degradation is heavily history-dependent. Surprisingly, the effects that the PEM fuel cell conditioning phase has on degradation are still rarely studied in the available literature. In addition, it may be advantageous to prevent the lengthy and costly conditioning process from occurring in the first place by taking appropriate steps during the manufacturing process.

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