



A three-step activation method for proton exchange membrane fuel cells

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ABSTRACT

Here we introduce an improved activation process using a three-step method in conjunction with a cooling-after-a-stop technique for proton exchange membranes. Detail information and rationale for each step is presented along with intermediate results. By carefully optimizing the operation temperature of each step of the activation procedure, the performance of a newly fabricated fuel cell can be increased and the variability decreased. In addition, we show that the cooling-after-a-stop technique can stabilize and improve fuel cell performance. The improved three-step method results in a maximal current density of 1008 mA cm^{-2} , an increase of 14.5%, compared to the 880 mA cm^{-2} achieved by the one-step method.

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1. Introduction

The proton exchange membrane fuel cell (PEMFC) is a promising power source for electric vehicles, portable electronic devices and residential use due to its fast start-up, high efficiency and stable performance [1]. The key component that determines the performance of a PEMFC is its membrane electrode assembly (MEA). Typically, the MEA consists of five layers: a proton exchange membrane, an anode catalyst layer, a cathode catalyst layer, and two gas diffusion layers. The construction process used to fabricate a MEA greatly influences its final effectiveness. One very effective procedure to enhance performance is to activate the MEA.

Activation not only humidifies the proton exchange membrane, but also creates transport channels for electrons, protons, gases and water. Activation also optimizes the electrode structure [2] and improves the activity and utilization of the catalyst by opening “dead” regions in this layer [3]. As a result, activation greatly increases the performance of a newly fabricated PEMFC to its maximal value and guarantees its reproducibility.

Currently, published research on activation is sparse and few reports analyzing the mechanisms underlying this phenomenon exist. In a pioneering study, Qi and Kaufman [4] enhanced performance by steaming/boiling the electrode. The resultant enhancement was thought to mainly derive from the hydration of the Nafion in the catalyst layer. In addition, Qi and Kaufman

also tried (1) elevating the cell, and humidification temperatures and increasing the cell pressure [3,5], (2) hydrogen evolution at the cathode [6], (3) CO adsorption on Pt followed by CO_2 desorption from the Pt [7]. The best performance was achieved when the electrode was activated using a combination of elevated cell temperature, humidification temperature and cell pressure [8]. Zhu and Chen [2] carried out additional activation studies by comparing with the application of a constant current profile with a stepped current profile as depicted in Fig. 1. They showed that the activation with a stepped current profile not only reduced the time required, but also improved the final performance.

Unfortunately, the aforementioned studies failed to explore activation conditions outside of the constant parameters used in their studies. For example, their activation temperatures and pressures were kept constant and they did not test any time-varying conditions. For this reason, we call their process ‘one-step activation’. Moreover, they also neglected to comment on the reproducibility of their methodologies and neither intermediate results nor any detailed information on their activation procedure was given.

Here we introduce a novel ‘three-step activation’ procedure in conjunction with a stepped current profile. By varying the activation temperature in a time dependent way, the performance of a fuel cell can be greatly improved. We present each step in detail along with intermediate results. The new three-step activation procedure improves the maximal current density of the PEMFC to 1008 mA cm^{-2} , a 14% improvement compared to the current density of 880 mA cm^{-2} resulting from the traditional one-step activation.

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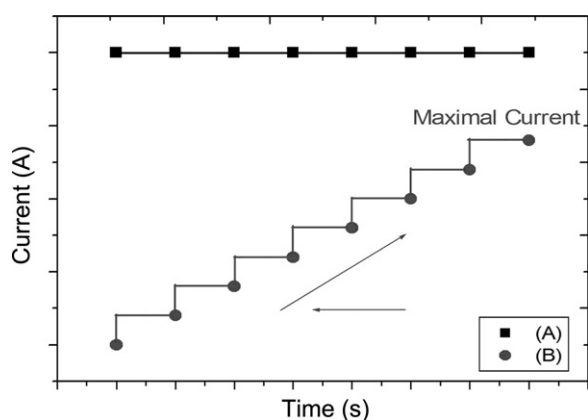


Fig. 1. Two current profiles for activation of PEMFC.

2. Experimental procedures

2.1. MEA fabrication

We used the catalyst coated membrane (CCM) method [9] to coat the catalyst layers. The anode catalyst ink was prepared by directly mixing Pt-Ru/C catalyst (40%Pt/20%Ru/XC72R, Johnson Matthey, Hispec10000) with Nafion Solution (DuPont). The Nafion content within the anode catalyst ink was 35%. Cathode catalyst ink was composed of Pt/C (Johnson Matthey 4100) and Nafion Solution (25%). The catalyst ink was sonicated for 30 min with isopropyl alcohol as the solvent, and brushed onto a pretreated Nafion-212 Membrane (anode Pt loading: 1.5 mg cm^{-2} , cathode Pt loading: 0.4 mg cm^{-2}) with an active area of 335 cm^2 . As the Nafion membrane has a tendency to swell after the pretreatment process, two precautions must be undertaken to ensure satisfactory results. First, the periphery of the active area on a membrane must be stable enough to prevent wrinkling, and second the temperature must be elevated to evaporate water and solvent from the membrane and catalyst, respectively. Here, Pt-Ru/C was used as the anode catalyst because the MEA was tested using reformed gas after it had been activated using pure hydrogen.

Carbon paper (Toray TGP-H-060) was soaked in 30% PTFE aqueous solution. After air-drying, the carbon paper was sintered at 360°C for 25 min. A homogeneous suspension of 30% PTFE and Vulcan XC-72 carbon powder was then coated onto the carbon paper with an active area of 335 cm^2 to form a micro-porous layer. Subsequently, the whole gas diffusion layer (GDL) was sintered again at 360°C for 25 min.

Two small CCMs were cut from the 335 cm^2 CCM, and four small GDLs were cut from the 335 cm^2 GDL. Finally, two MEAs each with an active area of 6.25 cm^2 were formed by hot pressing (155°C , 10 Bar and 210 s) the small GDLs onto small CCMs. As the two MEA derived from the same initial sample, we considered them to be fully identical. One MEA was activated using the three-step method and the other was activated using the one-step method.

2.2. Three-step activation method

We improve on the conventional one-step activation process by carefully controlling the cell temperature and humidity. This leads to three distinct activation steps.

- (1) Step 1: the cell is activated with the cell temperature set to 70°C and the humidification temperatures set to 60°C on both sides;
- (2) Step 2: the cell is activated with the cell temperature set to 60°C and the humidification temperatures set to 70°C on both sides;

- (3) Step 3: the cell is activated with the cell temperature set to 70°C and the humidification temperatures set to 60°C on both sides.

During the activation process, the pipe temperatures for both the anode and cathode sides were set to 90°C to prevent water vapor leaving the humidification bottles from condensing. The cell was air-cooled to room temperature after a certain round. (The cells were not purged during each cool down period.) This is the cooling-after-a-stop technique. A detailed outline of Step 1 is given in Fig. 2. Step 2 and Step 3 are similar to Step 1 except for differences in cell and humidification temperatures.

The activation of a single cell was carried out on a FC5100 fuel cell testing system (CHINO Co. Ltd., Japan.) Pure hydrogen and air were used as anode/cathode reactants. No back pressure was used during the entire experiment.

3. Results and discussion

3.1. Notes on the following figures

- (1) Each figure records all or a portion of the data from a test round. A test round consists of several test I - V loops. The numbers (i.e., 1, 2, 3...) in each figure represent I - V curves from successive test loops, i.e., small numbers represent earlier loops while large numbers represent later loops. The Maximal Current means the maximal current set on the load bank in each test round as shown in profile Fig. 1(B).
- (2) The limiting voltage of the fuel cell testing system is 0.2 V , i.e., if the voltage is lower than 0.2 V , the system will stop testing.
- (3) The relative humidity at the gas entrance is calculated to be 63.92% when the cell and humidification temperatures are set to 70°C and 60°C , respectively (Step 1 and Step 3). The relative humidity at the gas entrance is more than 100%, i.e., an over-saturated environment in which the liquid water may exit (Step 2).

3.2. Step 1: activation with cell temperature at 70°C and the humidification temperatures at 60°C

The purpose of Step 1 is (1) to disclose as much as possible the three phase points in the catalyst layers of the newly fabricated MEA without being disturbed by the gas transport limitation resulting from the accumulation of liquid water inside the fuel cell, i.e., the cell temperature was set higher than the humidification temperatures to form unsaturated reactant gases entering the fuel cell; and then (2) try to increase the maximal current for Step 2.

The results from Step 1 are depicted in Fig. 3. From Fig. 3(1) to (5), the maximal current was increased from 2.5 A (i.e., 400 mA cm^{-2}) to 5.5 A (i.e., 880 mA cm^{-2}) continuously, i.e., no cooling-after-a-stop technique was used between these five rounds. As shown in these figures, the cell performance gradually increased after successive test loops and test rounds. This phenomenon may be attributed to the gradual humidification of the proton exchange membrane and formation of the three-phase points in the catalyst layers. The transport channels for electron, proton, gas and water may have formed gradually as well [2]. We tried to use a maximal current of 6 A (i.e., 960 mA cm^{-2}) but failed. This means that the voltage was lower than the limiting voltage, i.e., 0.2 V .

After the above test rounds, we allowed the fuel cell to cool to room temperature (cooling-after-a-stop). This reduced the variability of the I - V curves considerably (Fig. 3(6)). Thus the cooling-after-a-stop technique was effective at stabilizing and improving cell performance. Condensed liquid water in the fuel cell could be fully absorbed by the Nafion phase in the catalyst

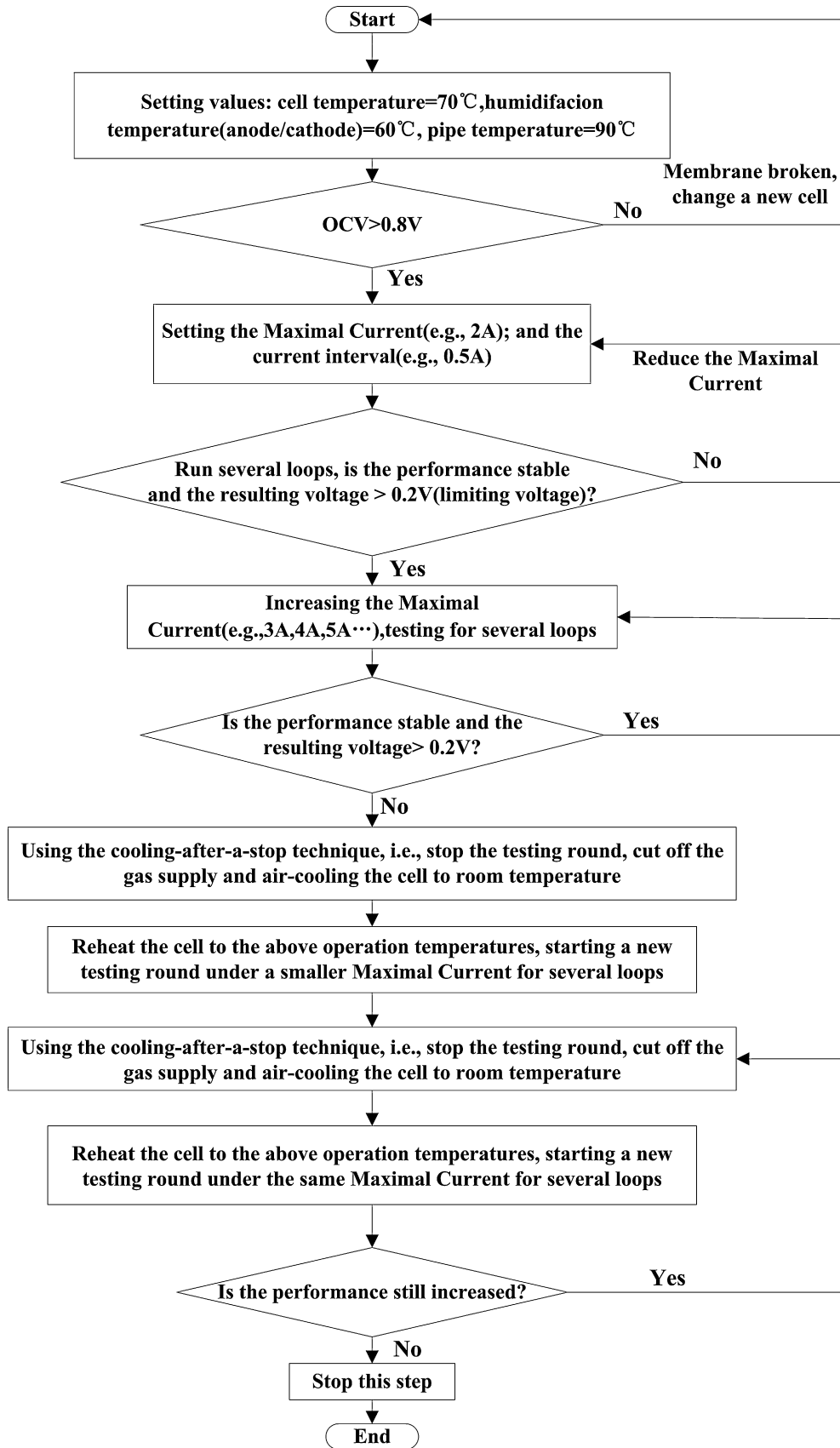


Fig. 2. Flow chart of Step 1.

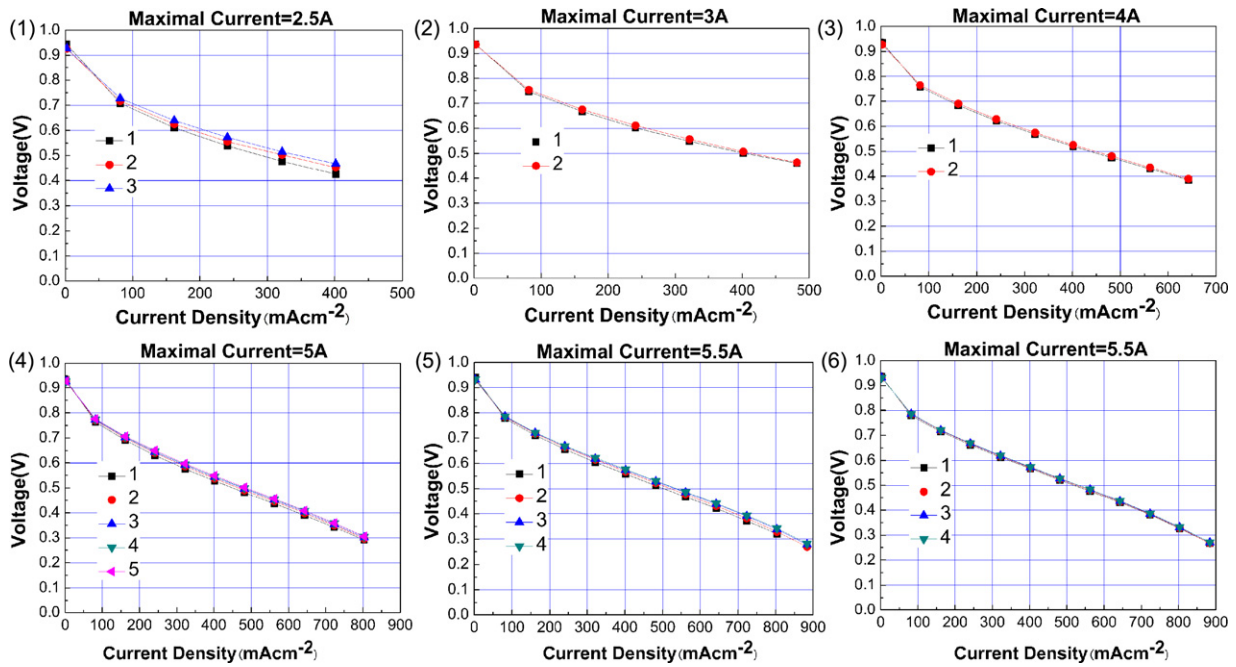


Fig. 3. Activation *I*-*V* curves from Step 1 (1–6).

layers and the Nafion membrane. As a result, both the activation overpotential and the Ohmic overpotential were reduced.

3.3. Step 2: activation with the cell temperature at 60 °C and the humidification temperatures at 70 °C

The purpose of Step 2 is to increase the water content in the Nafion phase of the catalyst layers and the Nafion membrane using

an over-saturated environment in order to further decrease the activation overpotential and Ohmic overpotential for Step 3. To achieve this, a high humidity greater than 100% was used.

The results shown in Fig. 4(1) and (2) were tested continuously without using the cooling-after-a-stop technique while increasing the maximal current from 1.5 A (i.e., 240 mA cm⁻²) to 2.5 A (i.e., 400 mA cm⁻²). While there was a marked increase in performance, there also existed significant variability as shown in

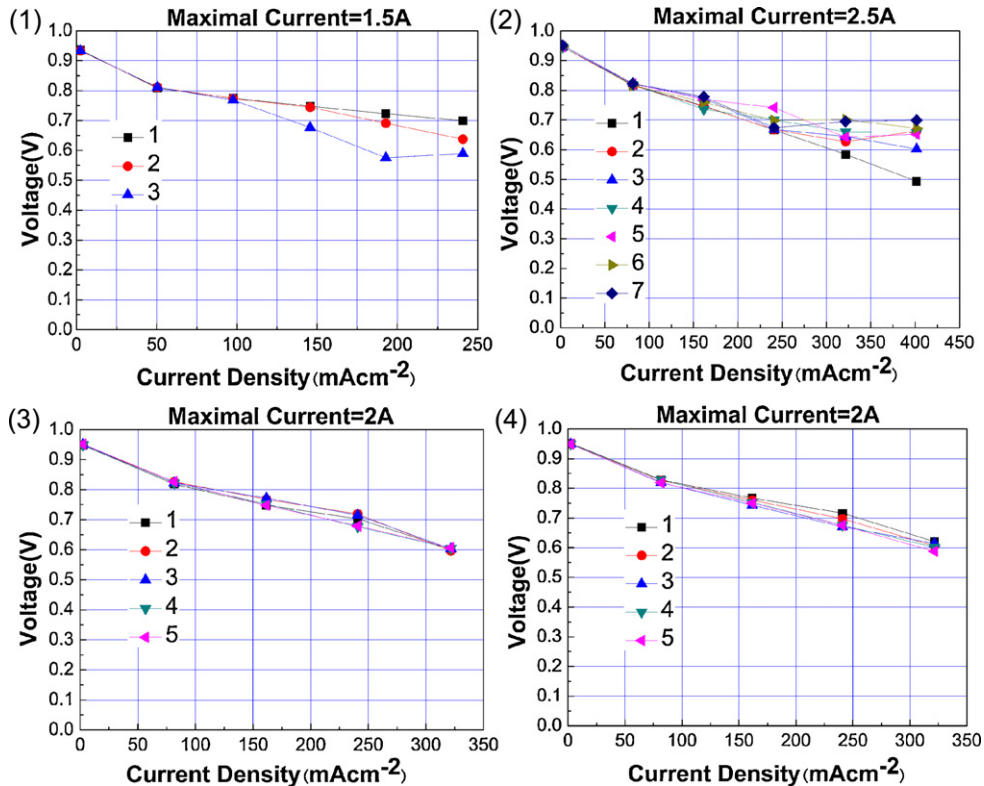


Fig. 4. Activation *I*-*V* curves from Step 2 (1–4).

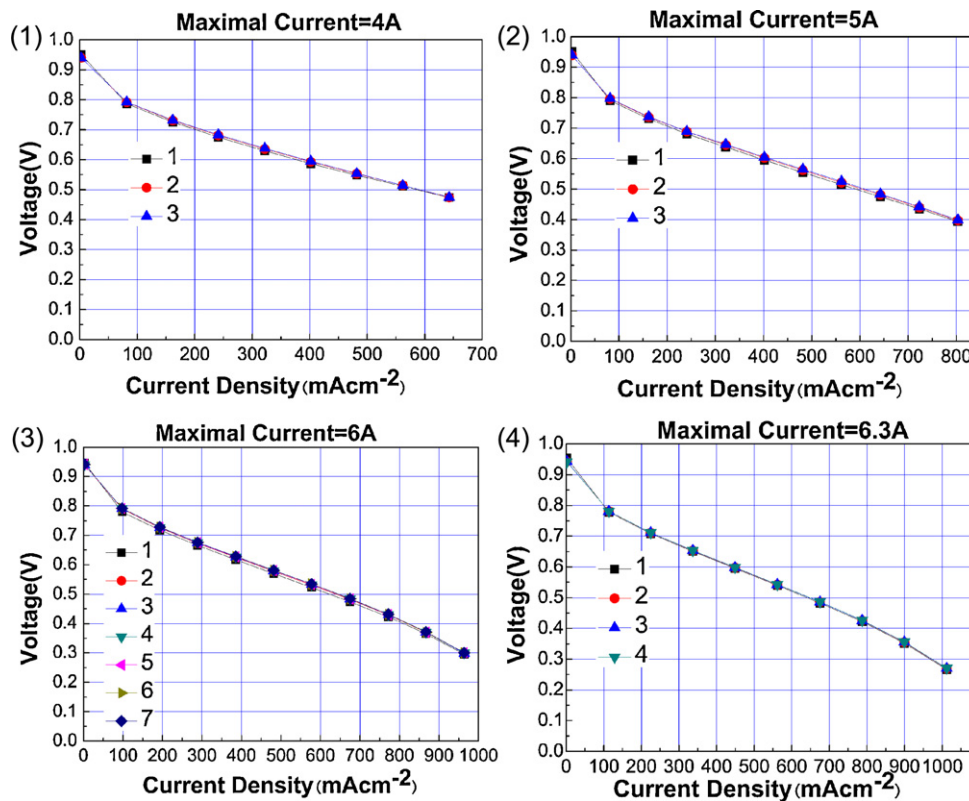


Fig. 5. Activation I - V curves from Step 3 (1–4).

Fig. 4(2). Although the voltage at the maximal current level shown in Fig. 4(2) was much higher than 0.2 V, the over-saturated environment and the increasing water production limits further increase in current.

For the same reasons stated before, the maximal current was reduced to 2.0 A (i.e., 400 mA cm^{-2}). (The entire procedure is outlined in Fig. 2.) Fig. 4(3) and (4) shows the I - V curves after cooling the cell. Comparing Fig. 4(3) and (4) with Fig. 4(1) and (2), it is obvious that both the performance and stability improved after cooling. Further comparisons between Figs. 4(4) and 3(6) show that performance had dramatically increased for currents lower than 240 mA cm^{-2} . For example, the voltage was 0.7718 V at 160 mA cm^{-2} in Loop 3 of Fig. 4(4) while the voltage was only 0.7201 V at the same current density in Loop 3 of Fig. 3(6). This suggests that the hydration of the Nafion phase in the catalyst layers and the transport channels for proton, electron, gas and water had been significantly enhanced. Moreover, the open circuit potential was 0.9500 V at 160 mA cm^{-2} in Loop 3 of Fig. 4(4) while the voltage was only 0.9316 V at the same current density in Loop 3 of Fig. 3(6). Thus the over-saturated environment helps to hydrate the membrane and as a result decreases the number of pores in the membrane.

3.4. Step 3: activation with cell temperature (70°C) and humidification temperature (60°C)

The purpose of Step 3 is to increase the performance, i.e., the maximal current, to a maximal value. After Step 2, the water content in the Nafion phase of the catalyst layers and the Nafion membrane had reached its highest level. Thus Step 3 repeats the same operating conditions as Step 1, i.e., activate using a relatively low entrance humidity (63.92%), in order to avoid flooding.

The results shown in Fig. 5(1)–(3) were tested continuously without using the cooling-after-a-stop technique while increasing the maximal current from 4 A (i.e., 640 mA cm^{-2}) to 6 A (i.e., 960 mA cm^{-2}). As shown in these three figures, all of the testing loops and rounds were stable, and the performance increased but not evidently before 4 A (i.e., 640 mA cm^{-2}), which indicated that three-phase points and transport channels for proton, electron, gas and water in the catalyst layers were disclosed and formed thoroughly. In order to further increase the maximal current, we used the cooling-after-a-stop technique. This resulted in an increase of the maximal current to 6.3 A (1008 mA cm^{-2}) as shown in Fig. 5(4). Moreover, the I - V curves exhibited dramatically smaller variability.

3.5. Comparison with one-step activation method

In order to make a direct comparison between the conventional one-step method and our three-step method, an identical twin cell mentioned above was activated using the one-step method. For this one-step activation, we used the stepped current profile shown in Fig. 1 along with the cooling-after-a-stop technique while keeping the cell temperature at 70°C and the humidification temperatures at 70°C for both sides.

Comparisons between these two activation methods are shown in Fig. 6. (The data for the three-step method was extracted from Loop 4 from Fig. 5(4).) The performance of the PEMFC activated by the three-step method is overwhelmingly higher than that activated by the one-step method. The maximal current density of the three-step method reached 1008 mA cm^{-2} , an increase of 14.5% compared with the maximal current density of 880 mA cm^{-2} of the one-step method.

The improved three-step method in conjunction with the cooling-after-a-stop technique was also tested [10] using a Pt/C

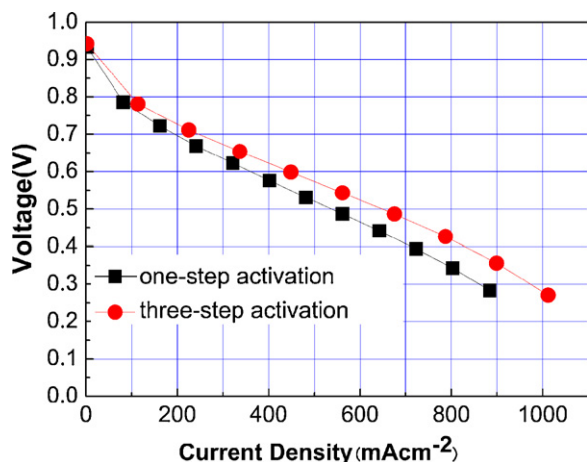


Fig. 6. Comparison of two activation methods (6.25 cm²).

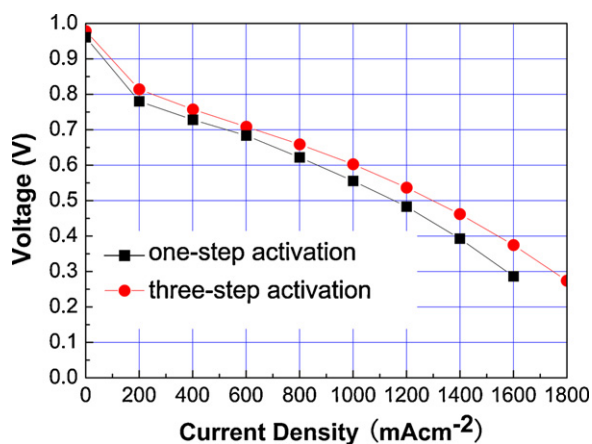


Fig. 7. Comparison of two activation methods (25 cm²).

as the anode catalyst. The active area of the fabricated fuel cell was 25 cm². The other fabrication procedures were identical to the ones mentioned above. Three-step activating this MEA also increased its performance as shown in Fig. 7.

4. Conclusions

A three-step activation method combined with a cooling-after-a-stop technique for PEMFC was introduced. Detailed information of each step was presented along with intermediate results. By varying the operation temperatures of each step, the performance of a newly fabricated fuel cell could be increased dramatically. Air-cooling the fuel cell in each step, (cooling-after-a-stop), stabilized and improved fuel cell performance because the condensed liquid water in the fuel cell could be fully absorbed by the Nafion phase in the catalyst layers and in Nafion membrane. As a result, both the activation overpotential and Ohmic overpotential could be reduced. The three-step method resulted in a final maximal current density of 1008 mA cm⁻², a 14.5% improvement compared to the maximal current density of 880 mA cm⁻² achieved by the one-step method.

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