



## Study on the processes of start-up and shutdown in proton exchange membrane fuel cells

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### ABSTRACT

Several different start-up and shutdown processes of a fuel cell were investigated in this paper by measuring cathode, anode and membrane potentials respectively versus reference hydrogen electrode (RHE). The membrane potential was measured by using thin copper wire sandwiched between two membranes. During the formation of hydrogen/air boundary at the anode caused by unprotected start-up and shutdown, the in-plane potential difference between membrane inlet and outlet was measured to be as high as 0.8 V, and the interfacial potential difference between cathode and membrane outlet increased to about 1.6 V, which in turn would cause carbon corrosion. Appropriate start-up and shutdown processes were suggested to avoid the formation of hydrogen/air boundary.

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### 1. Introduction

Proton exchange membrane (PEM) fuel cell is believed to be one of the most promising alternatives to internal combustion engine for automotive power, because of its advantages such as low operation temperature, fast start-up time, and favorable power-to-weight ratio, etc. Although PEM fuel cell has achieved significant progresses in recent years, short lifetime is still one of the primary problems that should be overcome to enable its wide use [1].

It has been reported that the hydrogen/air boundary at the anode could cause extremely fast degradation to the cathode and consequently decrease the lifetime of fuel cells [2–5]. A hydrogen/air boundary would form at the anode when a fuel cell shuts down if the anode outlet is not closed allowing air to diffuse into the anode. A hydrogen/air boundary would also form when this fuel cell starts up, because hydrogen will be filled into the anode full of air. Reiser et al. [6] have modeled the influence of hydrogen/air boundary at the anode with a mathematical approach. They indicated that when the anode was partially exposed to hydrogen and partially exposed to oxygen, the potential of the electrolyte exposed to oxygen would drop from 0 to  $-0.59$  V, which raised the cathode interfacial potential difference to 1.44 V. At this high interfacial potential difference, the cathode carbon could be corroded easily [7], accelerating plat-

inum dissolution, and the thickness and ECA of the cathode could be decreased significantly [8]. Qi and co-workers [9] have found that the formation of hydrogen/air boundary at the anode caused dramatic catalyst active surface area loss and the fuel cell performance loss. By using a dual cell configuration, they detected a portion of corrosion current and showed that the cathode potential was as high as two times of the open circuit voltage. Kim et al. [10] have studied the effects of outlet open/close and application of dummy load during shutdown process on the degradation of a fuel cell by the measurement of polarization curve and impedance. When outlets were open in the shutdown process, the degradation of cell performance was very severe, charge transfer resistance increased dramatically, and ohmic resistance also increased. The application of dummy load during shutdown could largely reduce the degradation of fuel cell performance, and the increase of charge transfer resistance was relatively small.

The hydrogen/air boundary at the anode has attracted so much attention, but until now no expert has directly studied this process by measuring membrane potential, as the membrane potential is relatively difficult to be detected. In this paper, a method of measuring membrane potential was proposed, and the processes of hydrogen/air boundary formation during start-up and shutdown were investigated and illustrated in detail by measuring the changes of cathode, anode and membrane potentials respectively versus reference hydrogen electrode (RHE) with time. Different start-up and shutdown processes were comparatively investigated, and appropriate start-up and shutdown processes were proposed.

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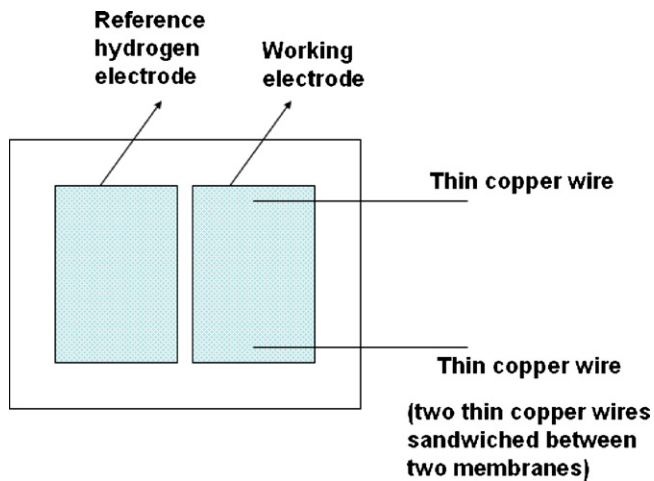


Fig. 1. Schematics of test MEA with reference hydrogen electrode and thin copper wires sandwiched between two membranes.

## 2. Experimental

### 2.1. Fuel cell setup

A PEMFC with a reference hydrogen electrode (RHE) was fabricated. The reference hydrogen electrode shared the same membrane with the working electrode, with a distance of about 2 mm. Constant flowrate hydrogen was fed into the reference hydrogen electrode. Two Nafion® 212 membranes with two thin copper wires sandwiched between them were hot pressed together with anode (Pt:  $0.4 \text{ mg cm}^{-2}$ , Toray paper as gas diffusion layer) and cathode (Pt:  $0.4 \text{ mg cm}^{-2}$ , Toray paper as gas diffusion layer) at  $140^\circ\text{C}$  for 1 min. The diameters of thin copper wires were about  $80 \mu\text{m}$ , and one was near the anode inlet, the other was near the anode outlet (Fig. 1). The insulating paint of the copper wire was removed for about 1 mm at the end of being sandwiched between two membranes.

The active areas of the working electrode and the reference hydrogen electrode were all  $5 \text{ cm}^2$ . The fuel cell was operated at ambient temperature and pressure, and kept at open circuit conditions in all tests. Hydrogen and air were humidified at ambient temperature, and fed into the anode and the cathode respectively at constant flowrates. The detailed schematic of the fuel cell setup is shown in Fig. 2.

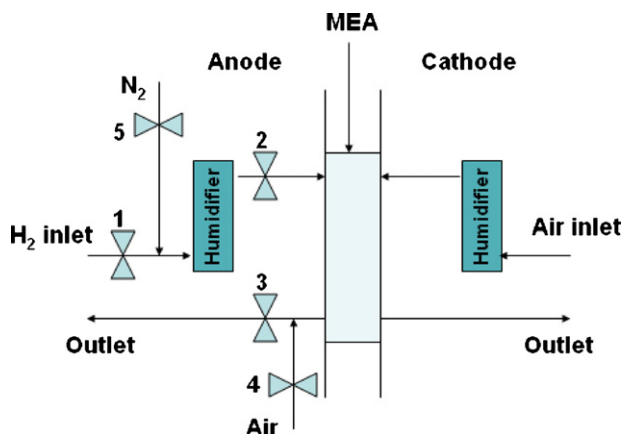


Fig. 2. Schematics of fuel cell setup.

Table 1  
Details of two start-up processes.

Process 1	Hydrogen was directly fed into the anode filled with air.	Valve 1, 2, 3 open, valve 4, 5 closed
Process 2	(2.a) Anode was first purged with nitrogen, (2.b) then Hydrogen was introduced.	Valve 5, 2, 3 open, valve 1, 4 closed Valve 1, 2, 3 open, valve 4, 5 closed

### 2.2. Start-up and shutdown processes

Several start-up and shutdown processes were carried out including unprotected start-up and shutdown, purging with nitrogen at anode and application of dummy load. The fuel cell anode was filled with air when it was started up. Two start-up processes were investigated, as seen in Table 1.

When the fuel cell shut down, there was residual hydrogen at the anode. Three shutdown processes were studied, as seen in Table 2.

### 2.3. Potential measurement

The potentials of cathode, anode, and membrane inlet and outlet versus reference hydrogen electrode were measured and recorded by data acquisition software programmed by Labview. As the thin copper wires were sandwiched between two membranes, and there was interfacial potential difference between copper and membrane, so the measured membrane potential must be corrected. When hydrogen was fed into the anode, the membrane potential should be around 0 V, but due to the interfacial potential difference between copper and membrane, the measured membrane potential was about 0.25 V. Therefore, the interfacial potential difference between copper and membrane could be taken as about 0.25 V, and for this reason, 0.25 V was subtracted from the measured membrane potential as a correction.

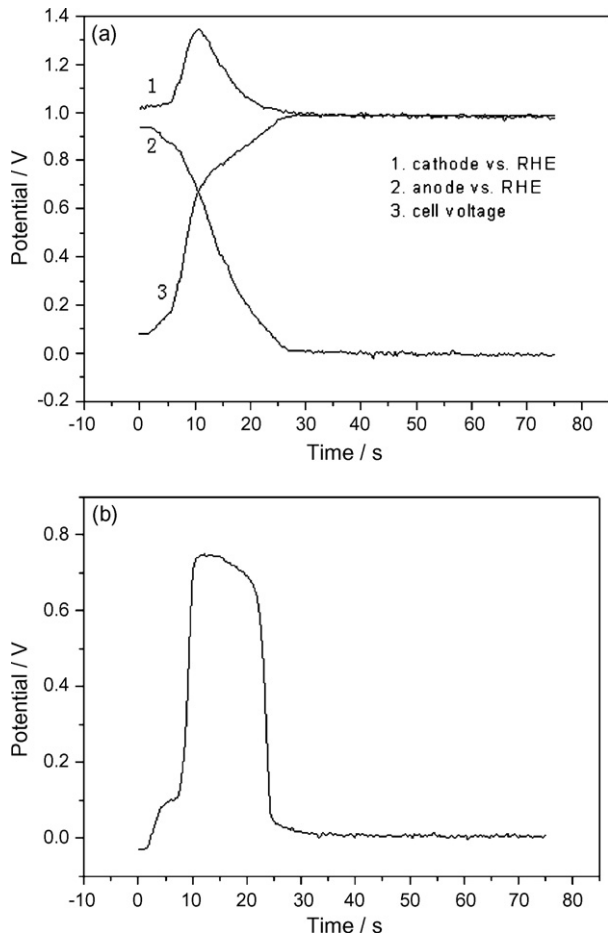
## 3. Results and discussion

### 3.1. Start-up process

Before start-up, fuel cell cathode and anode were both filled with air, so the cathode and anode potentials were around 1 V. For unprotected start-up, when hydrogen was introduced from anode inlet (process 1), hydrogen/air boundary formed. Membrane inlet was exposed to hydrogen, while membrane outlet was still exposed to air. The introduced hydrogen flowrate was  $2 \text{ ml min}^{-1}$ . Fig. 3(a) shows the changes of cathode, anode potentials and cell voltage during the formation of hydrogen/air boundary, and Fig. 3(b) depicts the corresponding potential difference between membrane inlet and outlet. It can be seen that cathode potential increases transiently from about 1 to 1.34 V, and the potential difference between membrane inlet and outlet reaches almost 0.8 V in this process. The potential changes of membrane inlet and outlet are shown detailedly in Fig. 4. Along with the introduction of hydrogen, the anode potential decreases gradually from about 1 to 0 V. As electrode is a very good electron conductor, the potential of membrane

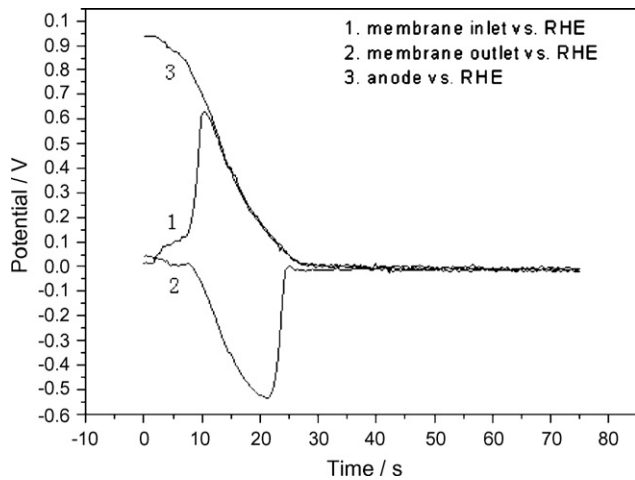
Table 2  
Details of three shutdown processes.

Process 3	Air diffused into the anode filled with hydrogen.	Valve 4 open, valve 1, 2, 3, 5 closed
Process 4	(4.a) Anode was first purged with nitrogen, (4.b) then air diffused in.	Valve 5, 2, 3 open, valve 1, 4 closed Valve 4 open, valve 1, 2, 3, 5 closed
Process 5	Dummy load was applied to consume all the residual hydrogen, then air diffused in.	Valve 1, 2, 3, 4, 5 closed

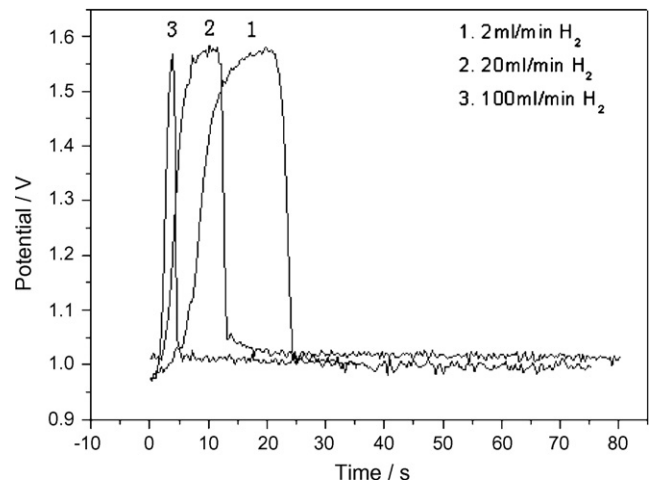


**Fig. 3.** (a) Changes of cathode, anode potentials and cell voltage when hydrogen was directly fed into the anode filled with air (process 1), (b) the corresponding potential difference between membrane inlet and outlet.

inlet increases quickly to near the anode potential, making the interfacial potential difference between anode and membrane inlet to be about 0 V, i.e., the equilibrium potential of hydrogen. While the potential of membrane outlet decreases, maintaining the interfacial potential difference between anode and membrane outlet to be near the equilibrium potential of air. In this experiment, the potential difference between membrane inlet and outlet reaches nearly



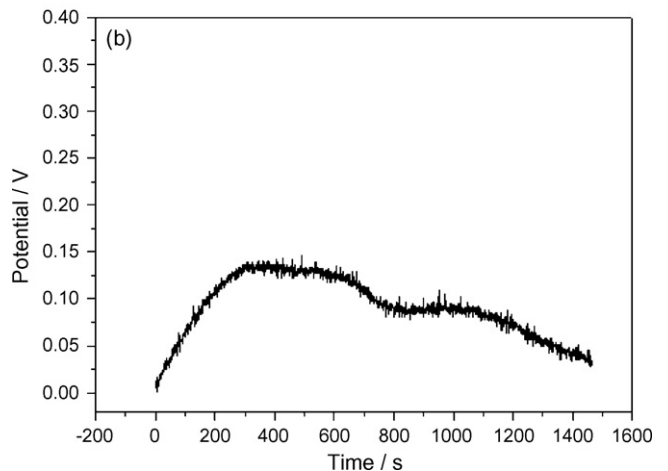
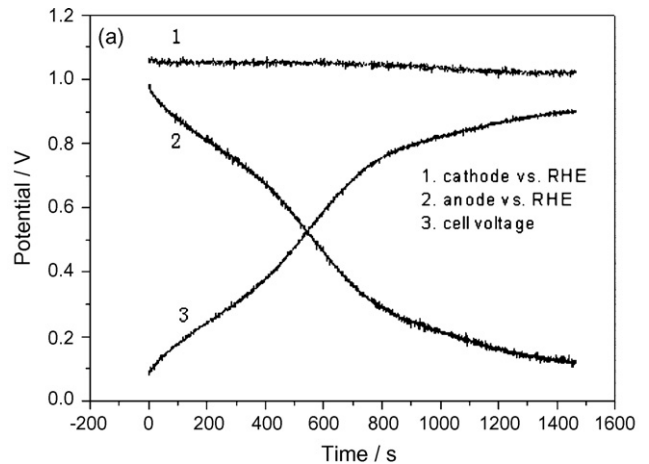
**Fig. 4.** Changes of membrane inlet, membrane outlet and anode potentials when hydrogen was introduced from anode inlet (process 1).



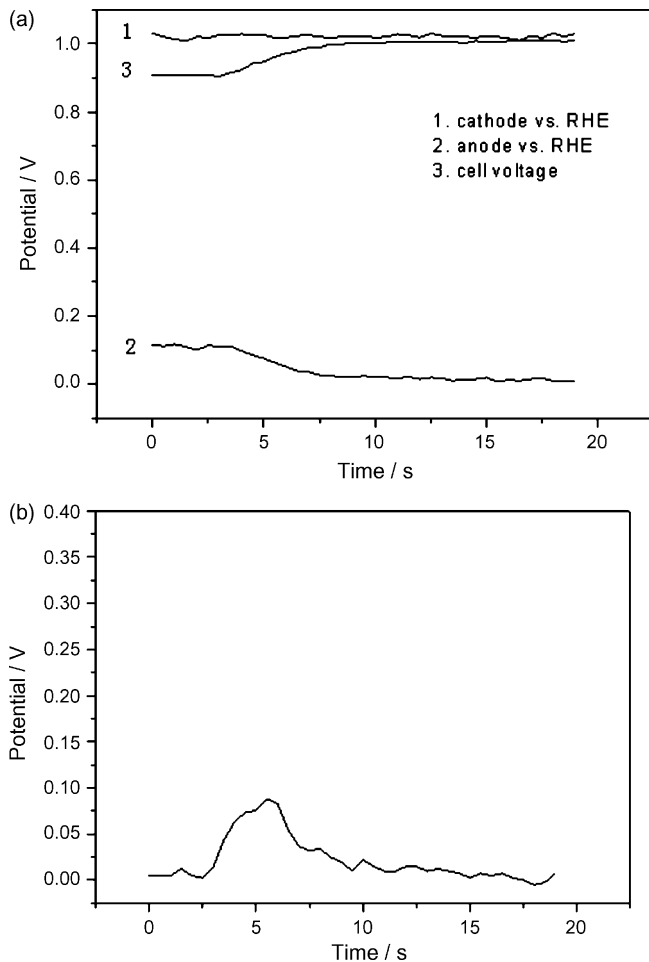
**Fig. 5.** Changes of interfacial potential differences between cathode and membrane outlet at different hydrogen flowrates (process 1).

0.8 V. Such a large potential difference between membrane inlet and outlet could exist, because the membrane is very thin, and the in-plane resistance of membrane is very high.

Since the potential of membrane outlet decreases and cathode potential increases, the interfacial potential difference between cathode and membrane outlet would increase significantly. As seen in Fig. 5, this interfacial potential difference arrives at almost 1.6 V,



**Fig. 6.** (a) Changes of cathode, anode potentials and cell voltage when air was replaced by nitrogen at anode (process 2.a), (b) the corresponding potential difference between membrane inlet and outlet.



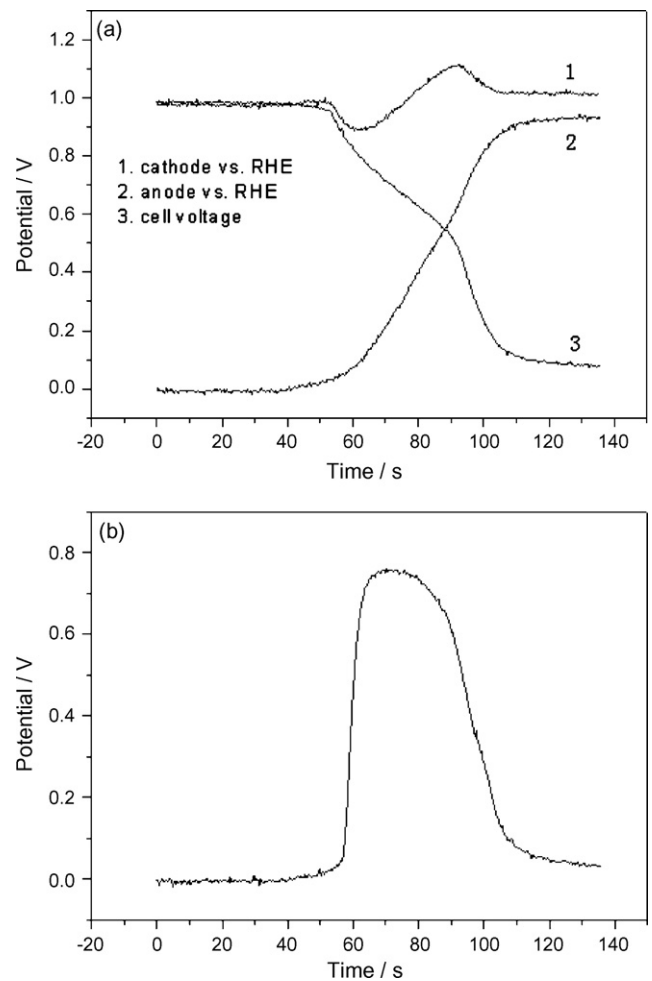
**Fig. 7.** (a) Changes of cathode, anode potentials and cell voltage when hydrogen was introduced into anode filled with nitrogen (process 2.b), (b) the corresponding potential difference between membrane inlet and outlet.

which could corrode the carbon in catalyst layer, accelerate platinum dissolution and make great damage to fuel cells.

If the flowrate of introduced hydrogen is increased, the lasting time of hydrogen/air boundary at the anode would be shortened. Fig. 5 also shows the changes of interfacial potential differences between cathode and membrane outlet at different hydrogen flowrates. It could be seen that the higher the hydrogen flowrate is, the shorter the high interfacial potential difference lasts. Hence, if the hydrogen/air boundary could not be avoided in practice, hydrogen should better be introduced as fast as possible to diminish its damage to electrodes.

Another start-up process (process 2 shown in Table 1) was also investigated, trying to avoid the formation of hydrogen/air boundary at the anode. As seen in Fig. 6(a), when air is replaced by nitrogen at the anode (process 2.a), the anode potential decreases quite slowly. During this process, the potential difference between membrane inlet and outlet only fluctuates a little, as depicted in Fig. 6(b). This fluctuation might be attributed to the charging of electrical double layer, as no faradic process is involved in this process.

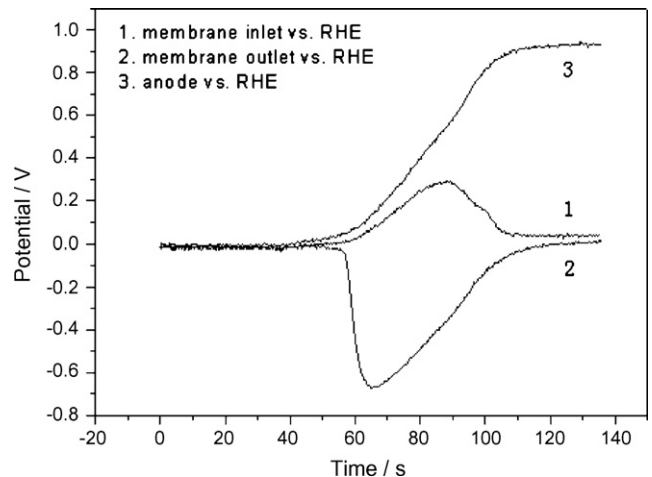
After nitrogen had replaced the air at the anode, hydrogen was introduced (process 2.b). As shown in Fig. 7(a), the cathode potential almost has no change during this process, while the anode potential decreases slightly. The potential difference between membrane inlet and outlet also fluctuates quite little (Fig. 7(b)). Therefore, it could be known that purging with nitrogen during start-up is very effective to avoid the formation of hydrogen/air boundary and reduce damage to fuel cells.



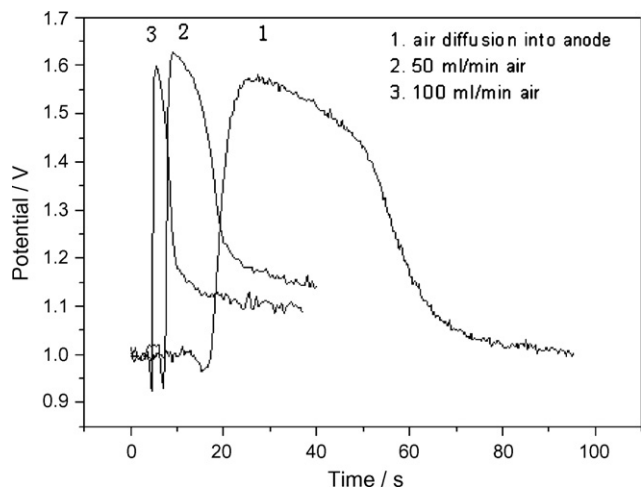
**Fig. 8.** (a) Changes of cathode, anode potentials and cell voltage when air diffused in from anode outlet (process 3), (b) the corresponding potential difference between membrane inlet and outlet.

### 3.2. Shutdown process

After fuel cell shut down, there would be residual hydrogen at the anode. If anode outlet was not closed, air would diffuse into the anode from anode outlet, forming hydrogen/air boundary (process 3). This process was quite similar with the start-up

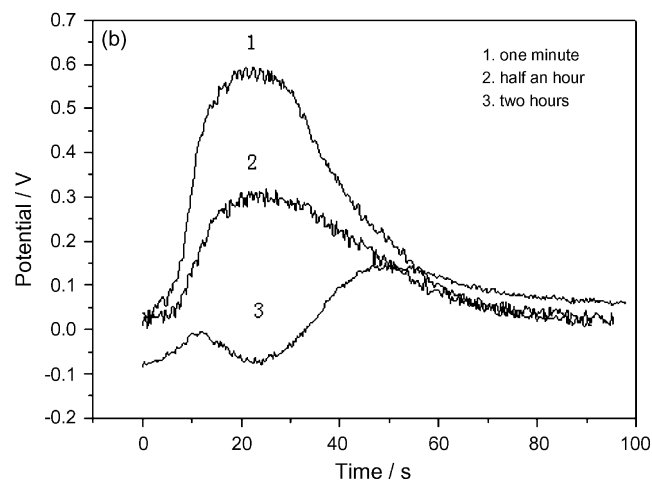
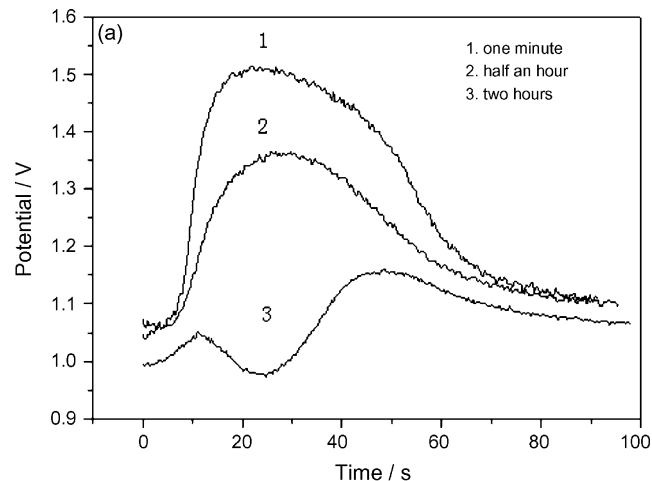


**Fig. 9.** Changes of membrane inlet, membrane outlet and anode potentials when air diffused in from anode outlet (process 3).

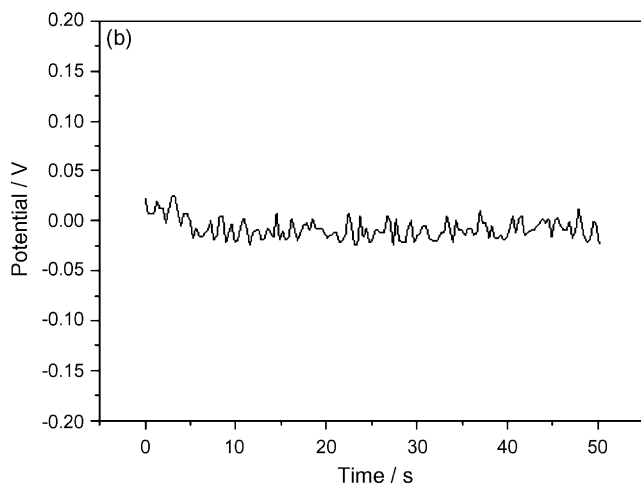
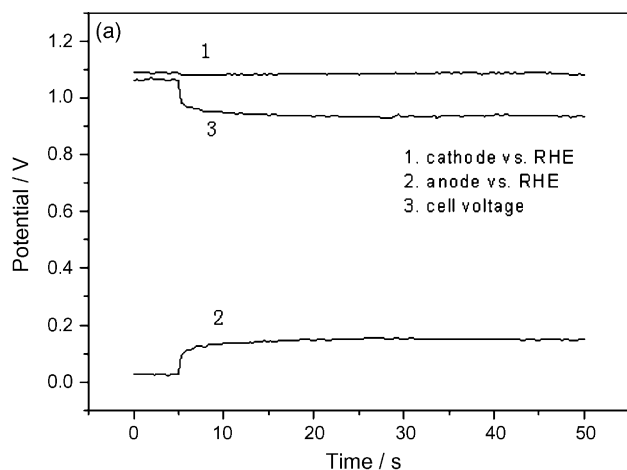


**Fig. 10.** Changes of interfacial potential differences between cathode and membrane outlet at different air flowrates (process 3).

process which hydrogen was directly introduced into the anode filled with air (process 1). Membrane inlet was exposed to hydrogen, and membrane outlet was exposed to air. Fig. 8(a) shows the changes of cathode, anode potentials and cell voltage during process 3, and Fig. 8(b) depicts the corresponding potential difference between membrane inlet and outlet. It can be seen that the experi-



**Fig. 12.** (a) Changes of the interfacial potential differences between cathode and membrane outlet during air diffusing into the anode, when the purging time of nitrogen is different (process 4.b), (b) the corresponding potential difference between membrane inlet and outlet.

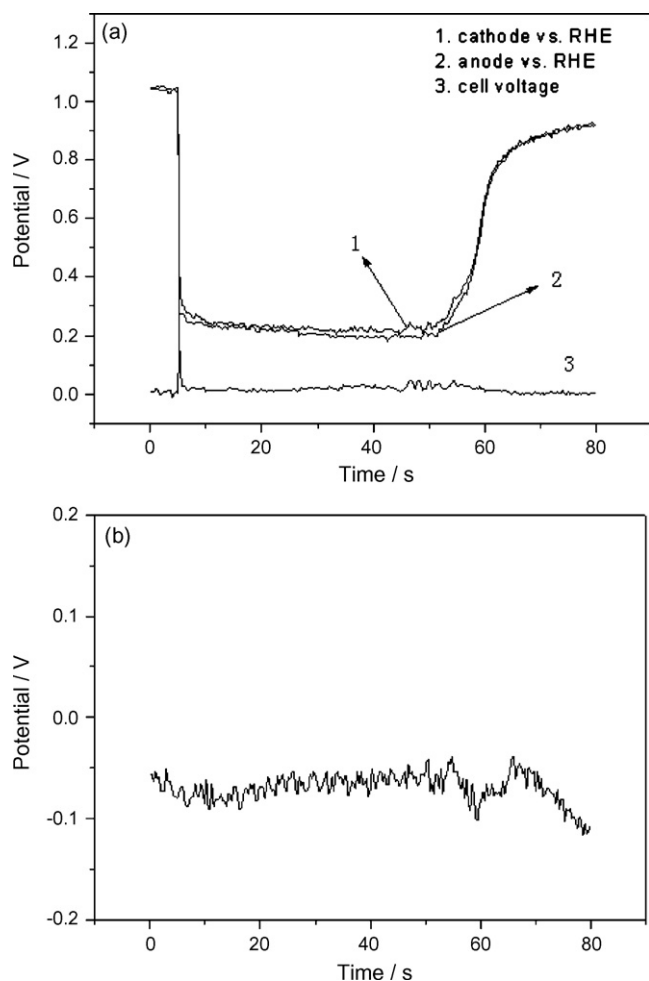


**Fig. 11.** (a) Changes of cathode, anode potentials and cell voltage when anode was purged with nitrogen (process 4.a), (b) the corresponding potential difference between membrane inlet and outlet.

mental results are very similar with those of process 1. When air is introduced from anode outlet, the cathode potential experiences a fluctuation, and the potential difference between membrane inlet and outlet reaches about 0.8 V. As shown in Fig. 9, the potential of membrane inlet increases, and the potential of membrane outlet decreases. The decrease of membrane outlet potential and the increase of cathode potential also cause the interfacial potential difference between cathode and membrane outlet to increase dramatically to be almost 1.6 V, as seen in Fig. 10. Fig. 10 also shows the influence of air flowrate, when air is fed into the anode faster, the lasting time of temporary high interfacial potential difference between cathode and membrane outlet would be shorter. Air diffusion into the anode during shutdown process is shown to be the most harmful.

For process 4, when the anode filled with hydrogen is purged with nitrogen (process 4.a), the anode potential increases slightly and then keeps stable, as shown in Fig. 11(a). The potential difference between membrane inlet and outlet shows no obvious change during this process (Fig. 11(b)).

After anode being purged with nitrogen, air diffused into the anode (process 4.b). Fig. 12(a) shows the changes of the interfacial potential differences between cathode and membrane outlet during air diffusing into the anode, when the purging time of nitrogen is different. Fig. 12(b) depicts the corresponding potential differences between membrane inlet and outlet. It can be seen that the purging time of nitrogen influences the experimental results of process



**Fig. 13.** (a) Changes of cathode, anode potentials and cell voltage during the application of dummy load (process 5), (b) the corresponding potential difference between membrane inlet and outlet.

4.b greatly. When the purging time of nitrogen is 1 min, the interfacial potential difference between cathode and membrane outlet could arrive at about 1.5 V, and the potential difference between membrane inlet and outlet could reach almost 0.6 V. When the purging time of nitrogen increases, the interfacial potential difference between cathode and membrane outlet decreases, so does the potential difference between membrane inlet and outlet. The above results illustrate that the desorption of hydrogen on electrode is relatively difficult. If the purging time of nitrogen is not enough, the hydrogen adsorbed on electrode will not be totally removed. When air diffuses into anode, hydrogen/air boundary will still form. It could be known that purging with nitrogen during shutdown process may not be effective all the time. Enough purging time of nitrogen should be taken to remove all the hydrogen and avoid the formation of hydrogen/air boundary.

When dummy load was applied during shutdown process (process 5), all the valves were closed. Fig. 13(a) shows the changes of cathode, anode potentials and cell voltage during this process. It can

be seen that cell voltage drops immediately to about 0 V after the application of dummy load. The equal value of anode and cathode potentials decreases slowly from about 0.4 to 0.2 V, and keeps stable at 0.2 V for almost 1 min. During this period, hydrogen at the anode is being consumed, which makes the anode gas pressure become lower and lower. Hence the air crossover from cathode to anode would increase due to the increased pressure difference between them. When nearly all the hydrogen is consumed, both anode and cathode are filled with air, so the anode and cathode potentials reach about 0.9 V. As a result, after the application of dummy load, air diffusion into anode would cause no damage to fuel cell. During this process, the potential difference between membrane inlet and outlet only fluctuates a little, as presented in Fig. 13(b). Hence, application of dummy load is a quite effective shutdown process.

#### 4. Conclusions

Several different start-up and shutdown processes were studied in this paper. For unprotected start-up and shutdown, hydrogen/air boundary would form at the anode. During the formation of hydrogen/air boundary, the in-plane potential difference between membrane inlet and outlet was measured to be as high as 0.8 V, and the interfacial potential difference between cathode and membrane outlet could reach about 1.6 V, causing carbon corrosion. The flowrate of hydrogen or air would influence the lasting time of hydrogen/air boundary. If the hydrogen/air boundary could not be avoided in practice, hydrogen or air should be fed in as fast as possible to minish its damage to electrode. Purging with nitrogen during shutdown process would sometimes be harmful to fuel cell, as the desorption of hydrogen on electrode was relatively difficult. It was found that both purging with nitrogen during start-up and application of dummy load during shutdown were very effective to avoid the formation of hydrogen/air boundary and reduce the damage to fuel cells.

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