

Short communication

# Hydrogen sulfide poisoning and recovery of PEMFC Pt-anodes

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## Abstract

A simple and effective method for reactivation of H<sub>2</sub>S poisoned Pt-anodes is described and the feasibility of the method was examined by single cell tests and 1 kW stack tests. The performance of the H<sub>2</sub>S poisoned Pt-anode can be basically recovered by applying a high voltage pulse (1.5 V for 20 s) followed by a low voltage pulse (0.2 V for 20 s) in a single cell. During the 10 poisoning–recovery cycles, the ohmic resistance and electrochemical surface area did not change significantly. The 1 kW stack tests show that the stack performance decayed severely and the maximum power decreased to 0.366 kW (32% of the original value) after exposure to 18 ppm H<sub>2</sub>S/H<sub>2</sub> for 2 h at 600 mA cm<sup>-2</sup>. The stack performance can be significantly recovered by applying a high voltage pulse (1.5 V for 2 min) followed by a low voltage pulse (0.2 V for 2 min) to each cell. The maximum power recovered to 1.095 kW (97.5% of the original value).

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**Keywords:** PEMFC; H<sub>2</sub>S poisoning; Recovery

## 1. Introduction

Proton exchange membrane fuel cell (PEMFC) is generally considered as a clean, efficient and silent technology that can produce electricity. PEMFC most likely will use reformed fuel as the primary source for the anode feed which always contains carbon dioxide, nitrogen, carbon monoxide, and trace amount of ammonia, hydrogen cyanide and hydrogen sulfide [1]. Some impurities are dramatically detrimental to the PEMFC performance.

Early research of H<sub>2</sub>S poisoning on Pt was performed in aqueous solution [2–4]. Loučka [2] studied the kinetics of H<sub>2</sub>S adsorption and oxidation on Pt electrodes in aqueous solution and found that H<sub>2</sub>S became dehydrogenated completely on adsorption and the hydrogen thus formed was oxidized at positive electrode potentials. Recently, in situ research of the effect of H<sub>2</sub>S on the performance of PEMFC [5–7] and phosphoric acid fuel cell [8] has been performed. Uribe et al. [5] found that the poisoning of H<sub>2</sub>S was cumulative and irreversible by using neat hydrogen and partial recovery could be attained by a cyclic

voltammetry scan between 0 and 1.4 V versus DHE (dynamic hydrogen electrode). In Ref. [9], we reported that the severity of the effect of H<sub>2</sub>S varied depending on the H<sub>2</sub>S concentration, current density, and the cell temperature. The adsorption of H<sub>2</sub>S on the anode is dissociative and this dissociation can produce adsorbed sulfur. The dissociation potential of H<sub>2</sub>S was studied by potential steps, and the values of the dissociation potentials are about 0.4 V at 90 °C, 0.5 V at 60 °C and 0.6 V at 30 °C. The adsorbed sulfur can be oxidized subsequently at about 0.9, 1 and 1.1 V, respectively [9].

To date, most of the efforts in dealing with impurities in reformates have been centered on the issue of CO tolerance. A few approaches have been advanced to cope with CO poisoning, such as replacing anode Pt catalyst by Pt–M alloys [10], injecting a small amount of air along with the fuel stream at the anode inlet [11], and using reconfigured anodes [12,13]. However, fewer approaches have been advanced to improve PEMFC tolerance to H<sub>2</sub>S. Mohtadi et al. [6] found that Ru does not provide additional benefits or tolerance against H<sub>2</sub>S poisoning. Furthermore, in comparison to the effect of CO, the poisoning of H<sub>2</sub>S is cumulative and irreversible. In this paper, we describe a simple and effective method for reactivation of H<sub>2</sub>S poisoned Pt-anodes and the feasibility of the method was examined by single cell tests and 1 kW stack tests.

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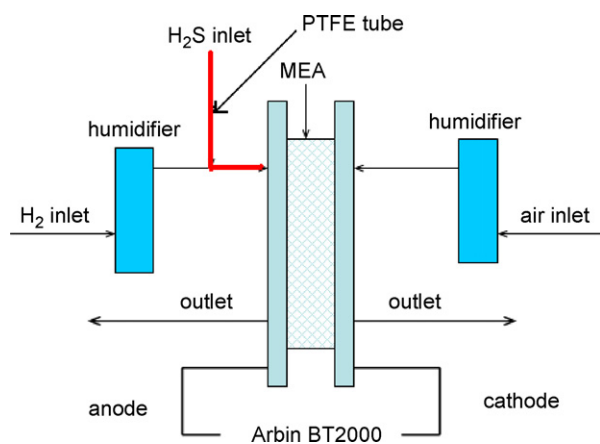


Fig. 1. System for assessing the effect of H<sub>2</sub>S.

## 2. Experimental

### 2.1. Single cell tests

Nafion<sup>®</sup> 212 membrane, anode (Pt: 0.3 mg cm<sup>-2</sup>, Pt/C from Johnson-Matthey) and cathode (Pt: 0.5 mg cm<sup>-2</sup>, Pt/C from Johnson-Matthey) were hot pressed at 140 °C for 1 min to obtain MEA, the active area of MEA was 5 cm<sup>2</sup>. The polarization curves were performed with fuel and air flows of 50 and 600 sccm (standard cubic centimeters per minute = standard milliliter per minute), respectively, and operating pressures  $P_{\text{fuel}}$  and  $P_{\text{air}}$  were all 0.1 MPa. The operating temperature of the single cell was kept at 60 °C. As shown in Fig. 1, H<sub>2</sub>S was mixed with pure nitrogen downstream of the humidifier to avoid H<sub>2</sub>S dissolution in water and adsorption in the humidifier.

After H<sub>2</sub>S poisoning, cell operation was interrupted and pure nitrogen and hydrogen were fed to the anode and cathode, respectively. The positive terminal of an external power supply (BT2000, Arbin instruments) was connected to the anode and the negative terminal was connected to the cathode. Based on our previous potential step measurements, the adsorbed sulfur can be oxidized at 1.0 V when the cell operating temperature is kept at 60 °C [9]. In order to oxidize the chemisorbed particles efficiently and swiftly, a high voltage (1.5 V) pulse was applied across the electrodes for 20 s followed by a low voltage (0.2 V) pulse for 20 s. Then neat hydrogen and air were reintroduced and the performance of the cell was recovered.

Electrochemical impedance spectroscopy (EIS) was performed to measure ohmic resistance by using PARSTAT 2273 (EG&G instruments) with the frequency range from 10 Hz to 10 kHz. Cycle voltammetry (CV) measurements were performed by using PARSTAT 2273 (EG&G instruments) while flowing N<sub>2</sub> on the anode (used as the working electrode) and neat H<sub>2</sub> on the cathode (used as counter and reference electrode). The applied potential range was between 0.05 and 1.3 V versus DHE and the scanning rate was 50 mV s<sup>-1</sup>.

### 2.2. One kiloWatt stack tests

A 10-cell stack was assembled using composite metal bipolar plates and MEAs which were fabricated by the technology

mentioned above. The active area of each cell was 270 cm<sup>2</sup>. The composite metal bipolar plates used stainless plates as the supporting plates and flexible graphite plates as the flow field plates. The performance of the stack was evaluated by measuring the *I*–*V* characteristics using FCATS-H36000 (Hydrogenics, Canada). The stack operating temperature was 60 °C and all reactant gases were kept at ambient pressure. Stoichiometries of hydrogen and air were 1.5 and 2.5, respectively. Similar to single cell tests, H<sub>2</sub>S was mixed with pure hydrogen downstream of the humidifier. Pure nitrogen and hydrogen were fed to the anode and cathode, respectively during the recovery of the H<sub>2</sub>S-poisoned stack. A high voltage (1.5 V for 2 min) pulse followed by a low voltage (0.2 V for 2 min) pulse was applied to each cell of the stack one by one. Then neat hydrogen and air were reintroduced and the performance of the stack was recovered.

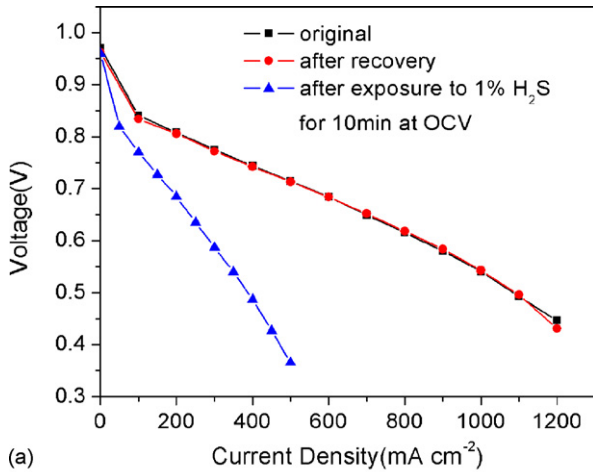
## 3. Results and discussion

### 3.1. H<sub>2</sub>S poisoning and recovery of the Pt-anode in a single cell

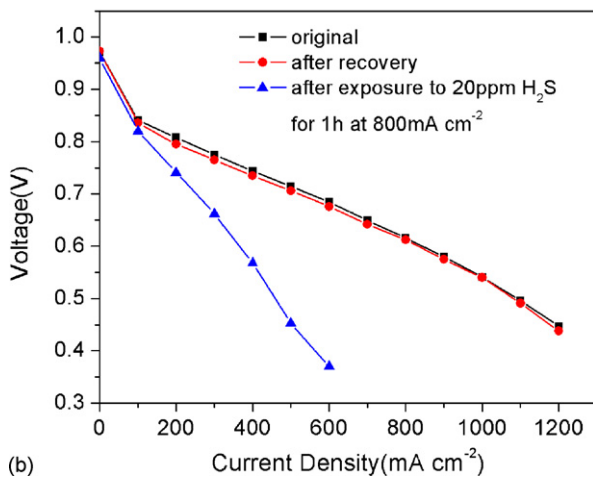
Fig. 2 shows the polarization curves after H<sub>2</sub>S poisoning and recovery of the anode in a single cell. Same to the previous experience, trace of H<sub>2</sub>S can degrade the cell performance dramatically. When the cell was operated at 500 mA cm<sup>-2</sup>, the cell voltages fell to 0.37 V (decreased by 48%) after the anode exposure to 1% H<sub>2</sub>S for 10 min at OCV (open circuit voltage, as shown in Fig. 2(a)) and 0.45 V (decreased by 38%) after exposure to 20 ppm H<sub>2</sub>S for 1 h at 800 mA cm<sup>-2</sup> (as shown in Fig. 2(b)). After H<sub>2</sub>S poisoning, a high voltage pulse (1.5 V, 20 s) was applied to oxidize the chemisorbed species (such as H<sub>2</sub>S, adsorbed sulfur) on the Pt catalyst. At the same time, partial Pt catalyst was oxidized inevitably. Therefore, a low voltage pulse (0.2 V, 20 s) was applied subsequently to reduce the Pt oxide. From Fig. 2, the cell performance can be basically recovered after H<sub>2</sub>S poisoning.

Fig. 3 shows the cyclic voltammograms obtained after the single cell was poisoned with 30 ppm H<sub>2</sub>S/H<sub>2</sub> for 1 h at 600 mA cm<sup>-2</sup>. Because of H<sub>2</sub>S adsorption, there is almost no current peak of hydrogen desorption in the first cycle. When the potential is scanned further toward the anodic direction, the dissociation of H<sub>2</sub>S begins to occur at about 0.5 V [9]. A layer of adsorbed elemental sulfur starts to form on Pt and the oxidation peak at about 1.2 V attributes to oxidation of adsorbed sulfur and partial uncovered platinum. The layer of adsorbed sulfur can prevent the oxidation of the platinum, so the reduction peak in the cathode part is smaller in the first cycle. Fig. 4 shows the cyclic voltammograms obtained after a poisoning–recovery cycle. Compared with the curves in Fig. 3, the current of H-desorption is much bigger in the first cycle, which can explain the performance recovery of the poisoned cell. From Fig. 4, there is an oxidation peak at about 1.2 V in the first cycle which may be likely due to the oxidation of remaining sulfur that was still adsorbed on the Pt surface even after the recovery.

Fig. 5 shows cell performance during 10 poisoning–recovery cycles. The cell was operated at 600 mA cm<sup>-2</sup> for 20 min before H<sub>2</sub>S was mixed. From comparing curves in Fig. 5, 30 ppm H<sub>2</sub>S



(a)



(b)

Fig. 2. Performance of the single cell after  $\text{H}_2\text{S}$  poisoning and recovery: (a) after exposure to 1%  $\text{H}_2\text{S}$  for 10 min at OCV; (b) after exposure to 20 ppm  $\text{H}_2\text{S}$  for 1 h at  $800\text{ mA cm}^{-2}$ . Recovery conditions: 1.5 V for 20 s and 0.2 V for 20 s subsequently.  $T_{\text{cell}} = 60^\circ\text{C}$ ; operating pressure: 0.1 MPa; humidification temperatures of the anode and cathode: 25 and  $60^\circ\text{C}$ .

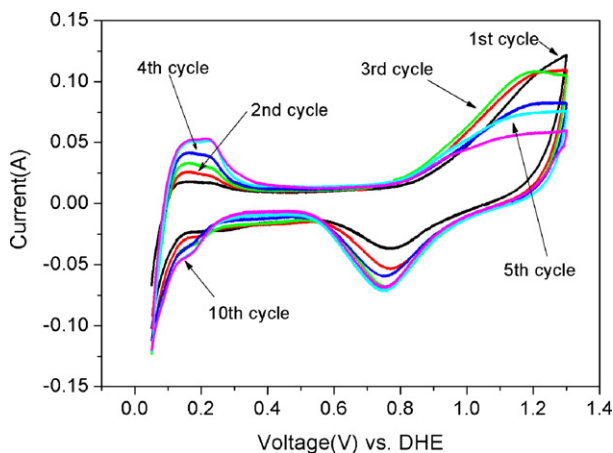


Fig. 3. Cyclic voltammograms obtained after the single cell was poisoned with 30 ppm  $\text{H}_2\text{S}/\text{H}_2$  for 1 h at  $600\text{ mA cm}^{-2}$ .  $T_{\text{cell}} = 60^\circ\text{C}$ ; scan rate:  $50\text{ mV s}^{-1}$ .

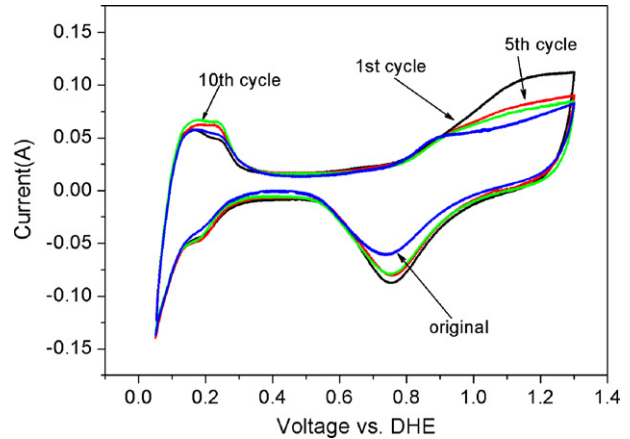


Fig. 4. Cyclic voltammograms obtained after a poisoning–recovery cycle. The cell was poisoned with 30 ppm  $\text{H}_2\text{S}/\text{H}_2$  for 1 h at  $600\text{ mA cm}^{-2}$  and recovered by applying 1.5 V for 20 s and 0.2 V for 20 s subsequently.  $T_{\text{cell}} = 60^\circ\text{C}$ ; scan rate:  $50\text{ mV s}^{-1}$ .

in fuel can degrade the cell performance swiftly and the performance can be recovered during every cycle. It seems that the cell tolerance to  $\text{H}_2\text{S}$  becomes weaker and weaker with the increase of the cycle number. The cell voltage fell to 0.42 V (64% of the original value) in the first cycle and to 0.22 V (34% of the original value) in the last cycle. Fig. 6 shows the polarization curves after the 1st, 5th and 10th poisoning–recovery cycle. The cell performance was severely degraded by 30 ppm  $\text{H}_2\text{S}$  and was basically recovered by the method described above during the 1st, 5th, 10th poisoning–recovery cycle.

Fig. 7 shows the change of ohmic resistance during the 10 poisoning–recovery cycles. From Fig. 7, the ohmic resistance of the single cell does not have a close relationship with the cycle number. The maximum value and the minimum value were  $21.71\text{ m}\Omega$  (cycle number=0, original) and  $17.52\text{ m}\Omega$  (cycle number=7). The cyclic voltammograms obtained after the 5th, 10th poisoning–recovery cycle are shown in Fig. 8. The electrochemical surface area (ECSA) of the catalyst relates to the charge area under H-desorption peak in the CV curve [14]. The ECSA can be calculated by the following equation [14] and

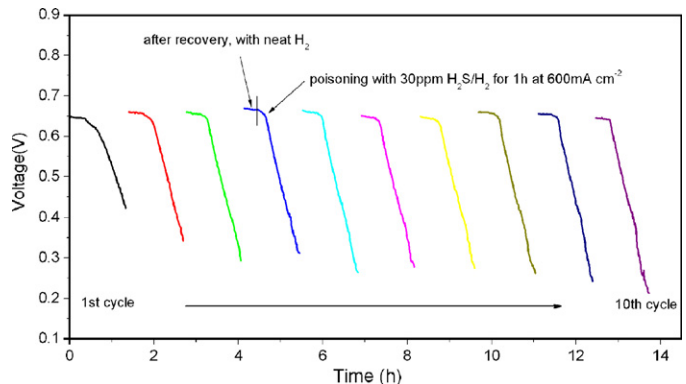


Fig. 5. Performance during 10 poisoning–recovery cycles of a single cell. The cell was poisoned with 30 ppm  $\text{H}_2\text{S}/\text{H}_2$  for 1 h at  $600\text{ mA cm}^{-2}$  and recovered by applying 1.5 V for 20 s and 0.2 V for 20 s subsequently.  $T_{\text{cell}} = 60^\circ\text{C}$ ; operating pressure: 0.1 MPa; humidification temperatures of the anode and cathode: 25 and  $60^\circ\text{C}$ .

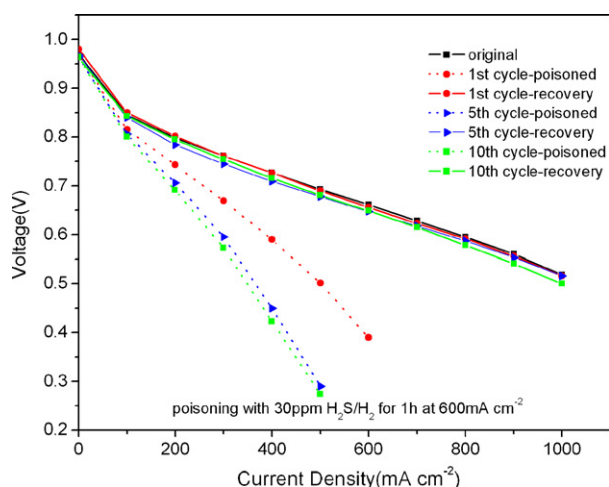


Fig. 6. Cell performance after the 1st, 5th, 10th poisoning–recovery cycle. The cell was poisoned with 30 ppm H<sub>2</sub>S/H<sub>2</sub> for 1 h at 600 mA cm<sup>-2</sup> and recovered by applying 1.5 V for 20 s and 0.2 V for 20 s subsequently. T<sub>cell</sub> = 60° C; operating pressure: 0.1 MPa; humidification temperatures of the anode and cathode: 25 and 60° C.

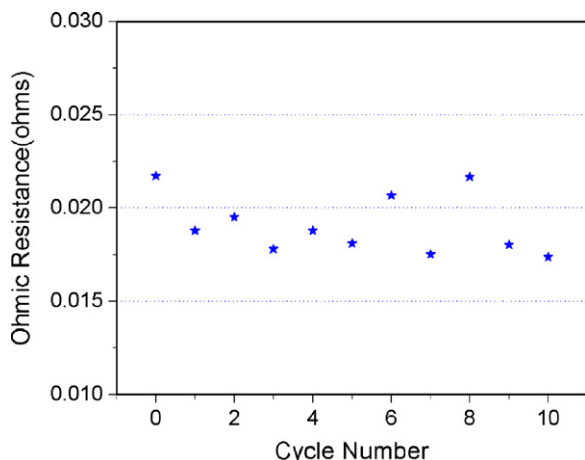


Fig. 7. Ohmic resistance of the single cell during 10 poisoning–recovery cycles. The cell was poisoned with 30 ppm H<sub>2</sub>S/H<sub>2</sub> for 1 h at 600 mA cm<sup>-2</sup> and recovered by applying 1.5 V for 20 s and 0.2 V for 20 s subsequently (T<sub>cell</sub> = 60° C).

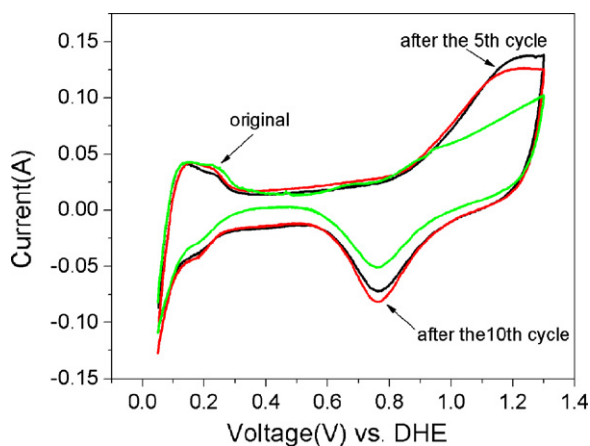


Fig. 8. Cyclic voltammograms obtained after the 5th, 10th poisoning–recovery cycle. The cell was poisoned with 30 ppm H<sub>2</sub>S/H<sub>2</sub> for 1 h at 600 mA cm<sup>-2</sup> and recovered by applying 1.5 V for 20 s and 0.2 V for 20 s subsequently. T<sub>cell</sub> = 60° C; scan rate: 50 mV s<sup>-1</sup>.

there is typically a 10% uncertainty in the CV measurements [15]:

$$ECSA \text{ (m}^2 \text{ g}^{-1}\text{)} = \frac{\text{Charge area } (\mu\text{C cm}^{-2})}{[10 \times 210 (\mu\text{C cm}^{-2}) \times \text{Catalyst loading (mg cm}^{-2}\text{)}]} \quad (1)$$

Values of the ECSA are 40.2 (original), 34.7 (after the 5th cycle) and 35.4 (after the 10th cycle). Measurements of high voltage stability of Pt/C catalyst were performed by Debe et al. [16]. They found the ECSA and performance of the catalyst decayed significantly after 30 min at 1.5 V because of carbon corrosion. In our work, the high voltage (1.5 V) pulse was applied just for 20 s during the recovery course and the electrode was recovered without significant loss of ECSA and performance. After the 5th and 10th poisoning–recovery cycle, the oxidation peaks at about 1.2 V (as shown in Fig. 8) may be also due to the oxidation of a small quantity of sulfur particles that were still adsorbed on the Pt surface even after the recovery. These remaining sulfur particles resulted in the about 10% loss of ECSA after the 5th and 10th poisoning–recovery cycle.

### 3.2. H<sub>2</sub>S poisoning and recovery of Pt-anodes in a 1 kW stack

The initial performance of the 10-cell stack is shown in Fig. 9. Before the measurements of polarization curves, the stack was activated for 24 h. The maximum power was 1.123 kW at the mean voltage of 0.52 V and the current density of 800 mA cm<sup>-2</sup>. After exposure to 18 ppm H<sub>2</sub>S/H<sub>2</sub> for 2 h at 600 mA cm<sup>-2</sup>, the stack performance decayed severely and the maximum power decreased to 0.366 kW (32% of the original value) as shown in Fig. 9. A high voltage (1.5 V for 2 min) pulse followed by a low voltage (0.2 V for 2 min) pulse was applied to each cell of the stack one by one and the stack performance was significantly

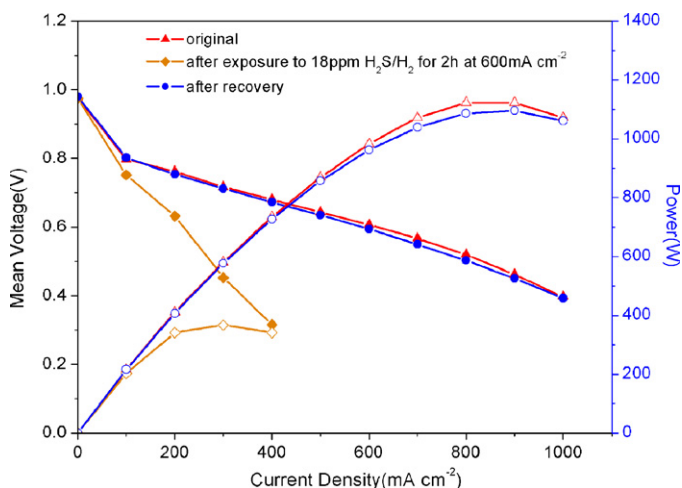


Fig. 9. Initial performance of the 10-cell stack and the performance after H<sub>2</sub>S poisoning and recovery. The stack was poisoned with 18 ppm H<sub>2</sub>S/H<sub>2</sub> for 2 h at 600 mA cm<sup>-2</sup> and recovered by applying 1.5 V for 2 min and 0.2 V for 2 min subsequently. T<sub>stack</sub> = 60° C; operating pressure: ambient pressure; RH<sub>fuel</sub> = 20%; RH<sub>air</sub> = 60%.

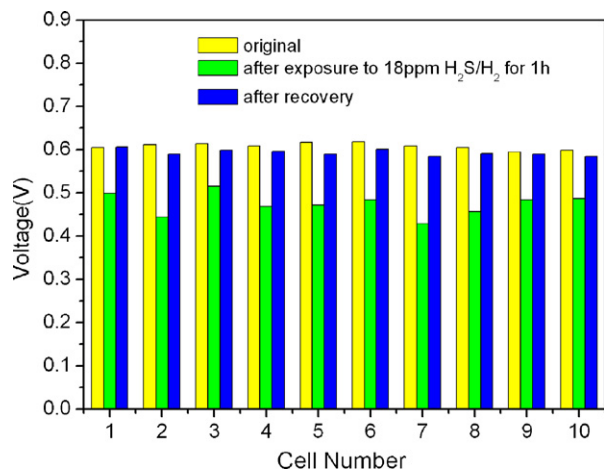


Fig. 10. Voltage distribution in the 10-cell stack at  $600 \text{ mA cm}^{-2}$  after H<sub>2</sub>S poisoning and recovery. The stack was poisoned with 18 ppm H<sub>2</sub>S/H<sub>2</sub> for 1 h at  $600 \text{ mA cm}^{-2}$  and recovered by applying 1.5 V for 2 min and 0.2 V for 2 min subsequently.  $T_{\text{stack}} = 60^\circ \text{C}$ ; operating pressure: ambient pressure;  $\text{RH}_{\text{fuel}} = 20\%$ ;  $\text{RH}_{\text{air}} = 60\%$ .

recovered. The maximum power increased to 1.095 kW (97.5% of the original value) at the current density of  $900 \text{ mA cm}^{-2}$ .

Fig. 10 shows the voltage distribution of the stack at  $600 \text{ mA cm}^{-2}$  after H<sub>2</sub>S poisoning and recovery. Before the anodes exposure to 18 ppm H<sub>2</sub>S, the voltage distribution in the stack was fairly uniform and the difference between the maximum and the minimum voltage values was less than 30 mV. The rate of H<sub>2</sub>S poisoning and the voltage loss are different obviously among the single cells in the stack. The voltages of the 3rd and 7th cell dropped to 0.515 V and 0.429 V after exposure to 18 ppm H<sub>2</sub>S for 1 h. From Fig. 10, the performance of some cells in the stack was totally recovered and other cells performance was recovered partially. For example, the voltage of the 4th cell at  $600 \text{ mA cm}^{-2}$  increased to 0.585 V (96% of the original value) after recovery.

#### 4. Conclusions

A simple and effective method for reactivation of H<sub>2</sub>S poisoned Pt-anodes is described. After H<sub>2</sub>S poisoning, a high voltage pulse (1.5 V) was applied to oxidize the chemisorbed species on the Pt catalyst and a low voltage pulse (0.2 V) was applied subsequently to reduce the Pt oxide. The performance

of the H<sub>2</sub>S poisoned Pt-anode in a single cell can be basically recovered. The about 10% loss of the electrochemical surface area during the 10 poisoning–recovery cycles may be due to the remaining sulfur particles which were still adsorbed on the Pt surface even after the recovery. The 1 kW stack tests show the stack performance can be significantly recovered by applying a high voltage pulse (1.5 V for 2 min) followed by a low voltage pulse (0.2 V for 2 min) to each cell and the maximum power recovered to 97.5% of the original value.

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