

Short communication

The influence of hydrogen sulfide on proton exchange membrane fuel cell anodes

WeiYu Shi^{a,b}, Baolian Yi^a, Ming Hou^{a,*}, Fenning Jing^a, Hongmei Yu^a, Pingwen Ming^a

^a Fuel Cell R & D Center, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, PR China

^b Graduate School of the Chinese Academy of Sciences, Beijing 100039, PR China

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Abstract

The effect of hydrogen sulfide on proton exchange membrane fuel cell (PEMFC) anodes was studied by cyclic voltammetry (CV), potential steps and electrochemical impedance spectroscopy (EIS). The severity of the effect of H₂S varies depending on the H₂S concentration, current density and the cell temperature. The anode humidification does not impact the poisoning rate much when the anode is exposed to H₂S. The adsorption of H₂S on the anode is dissociative and this dissociation can produce adsorbed sulfur. The dissociation potential of H₂S was studied by potential steps, and the values of the dissociation potential are about 0.4 V at 90 °C, 0.5 V at 60 °C and 0.6 V at 30 °C, respectively. The adsorbed sulfur can be oxidized at a higher potential. During CV scans, two oxidation peaks for the adsorbed sulfur at 1.07 and 1.2 V were observed at 90 °C, however a single oxidation peak could be observed at 1.2 V at 60 °C and at 1.27 V at 30 °C. Application of EIS to a H₂S|H₂ half-cell shows that the charge transfer resistance increases when the anode is exposed to H₂S because of H₂S adsorption.

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1. Introduction

The proton exchange membrane fuel cell (PEMFC) is generally considered as a clean, efficient and silent powering technology. The PEMFC most likely will use reformed fuel which always contains carbon dioxide, nitrogen, carbon monoxide and trace amounts of ammonia, hydrogen cyanide and hydrogen sulfide [1]. Extensive research has been done on the issue of CO poisoning, but there is much less in the literature on H₂S and NH₃ poisoning although these impurities are dramatically detrimental to the PEMFC performance.

Early research of H₂S poisoning on Pt was performed in aqueous media [2–4]. Loučka [2] studied the kinetics of H₂S adsorption and oxidation on Pt electrodes and found that H₂S became dehydrogenated completely on adsorption and the hydrogen thus formed was oxidized at positive electrode potentials. Najdeker and Bishop [3] studied the oxidation of H₂S in 0.1 M sulfuric acid on Pt electrodes by cyclic voltammetry and potentiostatic

testing. They ascribed the anodic wave at 0.625 V to the formation of platinum sulfide and the anodic wave at 1.42 V in hydrogen sulfide solution to oxidation of H₂S to sulfur. Using potentiodynamic oxidation at certain temperature, Contractor and Lal [4] demonstrated the presence of two forms of chemisorbed sulfur at 80 °C. These two forms of chemisorbed sulfur were distinguished by the number of platinum sites occupied per sulfur atom. They attributed the oxidation peak at 0.97 V to the oxidation of linear-bonded sulfur and the oxidation peak at 1.1 V to the oxidation of bridge-bonded sulfur.

Recently, in situ research of the effect of H₂S on the performance of PEMFC [5–7] and phosphoric acid fuel cell [8] has been performed. Uribe and Zawodzinski [5] found that the poisoning of H₂S 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. Mohtadi et al. [6] studied H₂S poisoning of membrane electrode assemblies (MEAs) in PEMFC consisting of Pt and PtRu alloy electrodes; they found partial recovery of the MEA after 3.8 h of exposure to H₂S could be gained with neat hydrogen. Two oxidation peaks were observed during the CV scan on the Pt anode giving evidence of the presence of two forms of chemisorbed sulfur.

* Corresponding author. Tel.: +86 411 84379051; fax: +86 411 84379185.

E-mail address: houming@dicp.ac.cn (M. Hou).

According to their work, the presence of Ru did not appear to provide higher H₂S tolerance. Furthermore, they studied the effect of temperature on the adsorption rate of H₂S on Pt anodes in situ by cyclic voltammetry, and found the sulfur adsorbed more strongly at lower cell operating temperature and the rate of Pt–S formation at 50 °C was 69% lower than that at 90 °C [7].

Based on previous experience, a trace of H₂S can degrade cell performance, so the first objective of this study was to generally assess the performance of PEMFC in the presence of H₂S in different cell operating conditions, including at different H₂S concentrations, at different cell operating temperatures and operating current densities. The fuel humidification effect was considered too. Although there is general agreement that a layer of sulfur in some form covers the Pt electrodes and affects the electrochemical process, the dehydrogenating potential of H₂S and the oxidation potential of sulfur on a solid polymer electrolyte (SPE)–Pt electrode are not well-defined. The second objective was to investigate the behavior of H₂S on the anode by cyclic voltammetry, potential stepping and electrochemical impedance spectroscopy (EIS).

2. Experimental

Nafion® 212 membrane, anode (Pt: 0.3 mg cm⁻², Pt/C from Johnson-Matthey) and cathode (Pt: 0.5 mg cm⁻², Pt/C from Johnson-Matthey) were hot pressed at 10 MPa, 140 °C for 1 min to obtain MEA, the active area of MEA was 5 cm². The polarization curves were performed with fuel and air flows of 50 and 600 sccm (standard milliliter per minute), respectively, and operating pressures P_{fuel} and P_{air} were all 0.1 MPa. As shown in Fig. 1, high purity hydrogen containing H₂S was mixed with pure hydrogen downstream of the humidifier to avoid H₂S dislocation in water and adsorption in the humidifier.

CV measurements were performed by using a PARSTAT 2273 (EG&G instruments) while flowing N₂ on the anode (used as the working electrode) and neat H₂ on the cathode (used as counter and reference electrode). The applied potential range was between 0.05 and 1.4 V versus DHE and the scanning rate was 20 mV s⁻¹. Potential steps were performed with the 1% H₂S + N₂|H₂ half-cell by using BT2000 (Arbin instruments).

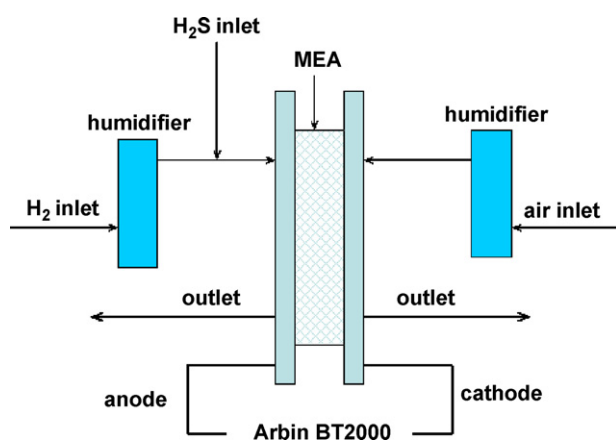


Fig. 1. System for assessing the effect of H₂S.

During potential steps, H₂S was flowing on the anode (used as working electrode) and H₂ was flowing on the cathode (used as counter and reference electrode). A N₂|H₂ half-cell was also measured to get the base line. The cell temperatures were kept at 30, 60 and 90 °C, correspondingly the humidification temperatures of cathode (H₂) were kept at 35, 65 and 95 °C to insure a well-humidified MEA. The flow rate of 1% H₂S + N₂ was 20 sccm, and the potential steps were applied from 0.1 to 1.2 V with the step length of 0.1 V. During the whole experiment, the time–current densities were recorded.

The electrochemical impedance spectroscopy of a fuel cell in operation can provide information about the cathode and the anode impedance [9]. In most studies, neat hydrogen oxidizes so fast that its impedance is negligible and the impedance spectrum of the full cell eventually equals the cathode impedance. But when the anode is poisoned, its impedance cannot be negligible [10]. In this study, EIS measurements were performed in a H₂S + H₂|H₂ half-cell by using PARSTAT 2273 (EG&G instruments) while flowing H₂ on the cathode (used as counter and reference electrode) and 50 ppm H₂S + H₂ on the anode (used as working electrode). The impedance spectra were recorded by sweeping frequencies over the range of 30 mHz to 10 kHz with 10 points recorded per decade. During the EIS measurements, the cell temperature was kept at 60 °C and the humidification temperatures of the anode and cathode stream were both 70 °C to ensure a well-humidified MEA.

3. Results and discussion

3.1. Effect of H₂S

The effect of 5 ppm H₂S in fuel on the PEMFC performance is shown in Fig. 2. The cell was operated galvanostatically at 500 mA cm⁻² till the performance became stable, and then H₂S was added to the fuel gas. The performance of the cell decreased dramatically and the potential fell to 0.2 V in about 7 h. Fig. 2 also shows that the cell performance cannot be recovered when neat H₂ is introduced and partial recovery can be attained by the CV scan between 0.05 and 1.4 V versus DHE. This result

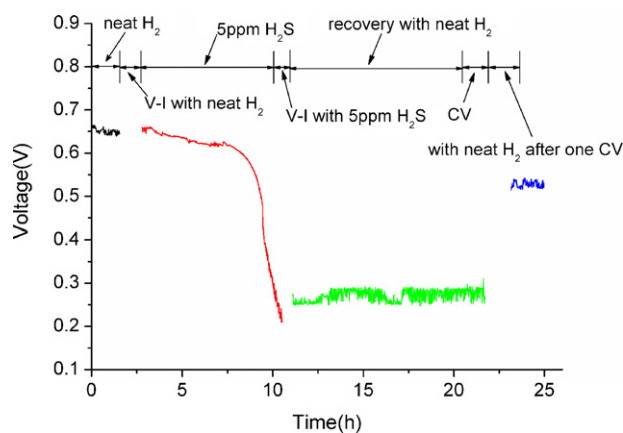


Fig. 2. Effect of 5 ppm H₂S in fuel on the PEMFC performance. $T_{\text{cell}} = 70$ °C, humidification temperatures of the anode and cathode: room temperature and 70 °C.

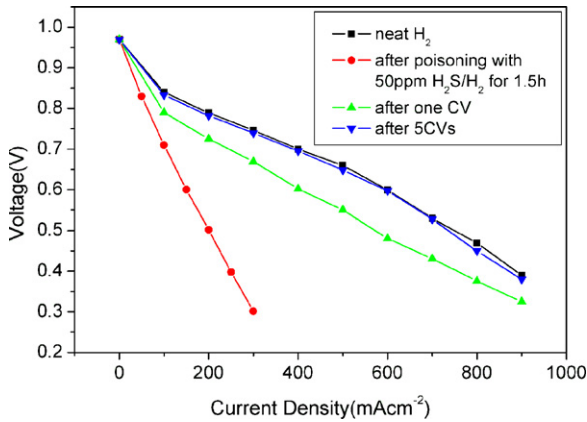


Fig. 3. The cell performance recovery by CV scans after poisoning with 50 ppm H₂S/H₂ for 1.5 h. $T_{\text{cell}} = 70^\circ\text{C}$, humidification temperatures of the anode and cathode: room temperature and 70°C .

agrees with that of Uribe and Zawodzinski [5]. The polarization curves in Fig. 3 show that the cell performance is significantly recovered after one CV scan and total recovery can be attained after five CV scans.

Fig. 4 shows that the cell voltage, measured at a fixed current density of 500 mA cm^{-2} , as a function of time during exposure to the gases with different H₂S concentrations. From comparing curves in Fig. 4, it is clear that the rate of H₂S poisoning is a strong function of the H₂S concentration. With the higher H₂S concentration, the higher poisoning rate is observed. During exposure to 5, 10, 20 and 50 ppm H₂S/H₂, it took 7.2, 2.9, 2 and 1.5 h for the cell voltage falling to 0.3 V. Fig. 5 shows the effect of the current density on the cell performance during the anode exposure to 20 ppm H₂S/H₂. Being similar to the effect of the H₂S concentration, the poisoning rate has a close relationship with the current density. After exposure to 20 ppm H₂S/H₂ for 1 h, the performance decreased by 2% at 200 mA cm^{-2} as compared to 17% decrease at 500 mA cm^{-2} and 35% decrease at 800 mA cm^{-2} .

Fig. 6 shows the effect of cell temperature on the cell performance during the anode exposure to H₂S/H₂. The extent of

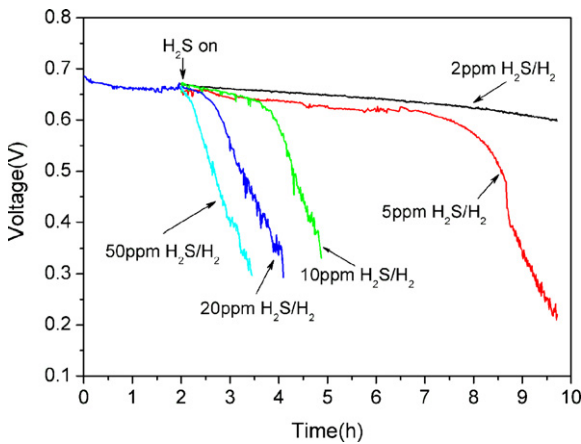


Fig. 4. Effect of H₂S concentration on the cell performance at 500 mA cm^{-2} . $T_{\text{cell}} = 70^\circ\text{C}$, humidification temperatures of the anode and cathode: room temperature and 70°C .

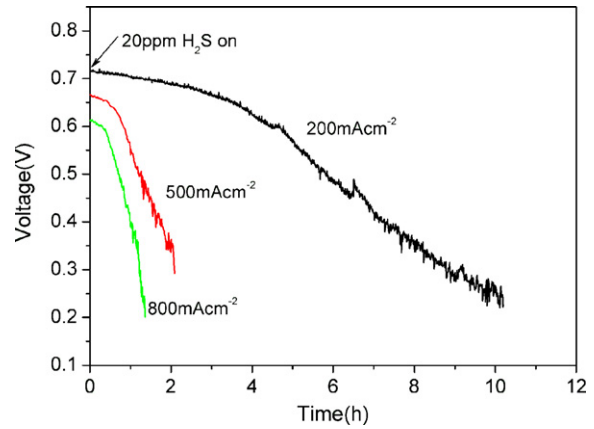


Fig. 5. Effect of current density on the performance deterioration during exposure to 20 ppm H₂S/H₂. $T_{\text{cell}} = 70^\circ\text{C}$, humidification temperatures of the anode and cathode: room temperature and 70°C .

H₂S poisoning decreased with increasing temperature and the cell operated at 90°C showed the greatest tolerance to H₂S. The cell performance decreased by 45% (35°C), 32% (60°C) and 25% (90°C) after exposure to 10 ppm H₂S/H₂ for 3 h as shown in Fig. 6(a). When the cell operating temperature was fixed at 35°C , the performance decreased obviously as soon as H₂S was injected, but when the cell operating temperature was fixed at 90°C , the obvious decrease was observed after the

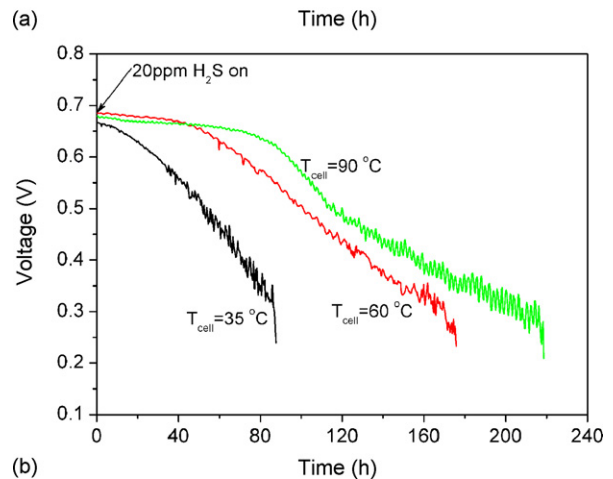
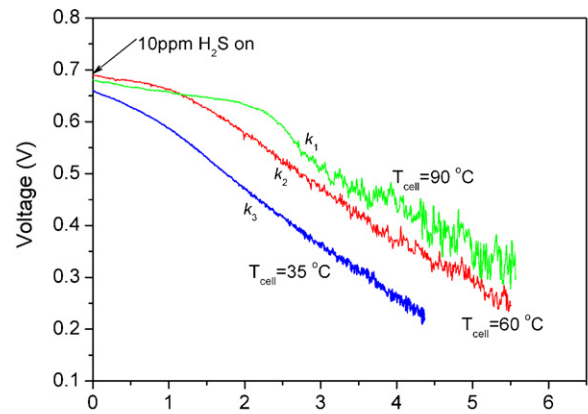


Fig. 6. Effect of temperature on the cell performance during exposure to 10 ppm H₂S/H₂ (a) and 20 ppm H₂S/H₂ (b) at 500 mA cm^{-2} .

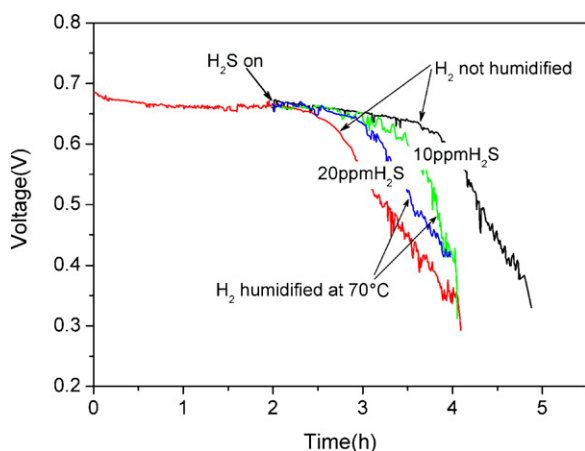


Fig. 7. Effect of H_2 humidification on the cell performance during exposure to 10 ppm $\text{H}_2\text{S}/\text{H}_2$ and 20 ppm $\text{H}_2\text{S}/\text{H}_2$ at 500 mA cm^{-2} . $T_{\text{cell}} = 70^\circ\text{C}$, the humidification temperature of the cathode: 70°C .

anode exposure to 10 ppm $\text{H}_2\text{S}/\text{H}_2$ for 2 h. However, the electrode was severely poisoned eventually at 35, 60 and 90°C . It should be noted that the decline slopes of the $V-t$ curves (k_1 , k_2 , k_3) are similar even at different temperatures. Mohtadi et al. [7] assumed that the adsorption of H_2S on Pt is dissociative and this dissociation occurs instantly and produces a Pt-S species. They studied the rate of Pt-S formation at different temperatures and found this rate at 50°C was 69% lower than that at 90°C , which seems to contradict our results.

The effect of the anode humidification on the cell performance during exposure to $\text{H}_2\text{S}/\text{H}_2$ is shown in Fig. 7. From Fig. 7, the anode humidification did not affect the cell performance while neat H_2 was fed in at the anode. Similarly, when the anode was exposed to $\text{H}_2\text{S}/\text{H}_2$, the anode humidification whether or not did not affect the cell performance too much, and there is not an obvious relationship between the anode humidification and the cell performance.

3.2. CV and potential steps

There is general agreement that H_2S adsorption on Pt is dissociative and elemental sulfur and hydrogen is thus produced at certain potentials. Mathieu and Primet [11] studied the chemisorption of H_2S on Pt and found H_2S adsorbed dissociatively and the dissociation led to adsorbed sulfur and gaseous hydrogen. Because the gaseous hydrogen can be oxidized at positive potentials, potential steps were applied to determine the H_2S dehydrogenation potential within a 1% $\text{H}_2\text{S} + \text{N}_2/\text{H}_2$ half-cell. Fig. 8(c) shows the anodic current transients with time with a H_2/N_2 cell. Because hydrogen (flowing on the cathode) permeated through the membrane and accumulated at the anode, there were two current peaks of hydrogen oxidation when the potentials were stepped to 0.1 and 0.2 V. With the consumption of permeated hydrogen, there was not obvious current peak until the potential was stepped to 0.9 V. At 0.9 V or the higher potential, the current peaks related to the oxidation of Pt. From Fig. 8(b), when the cell temperature was kept at 90°C , an obvious oxidation current peak could be observed as soon as the

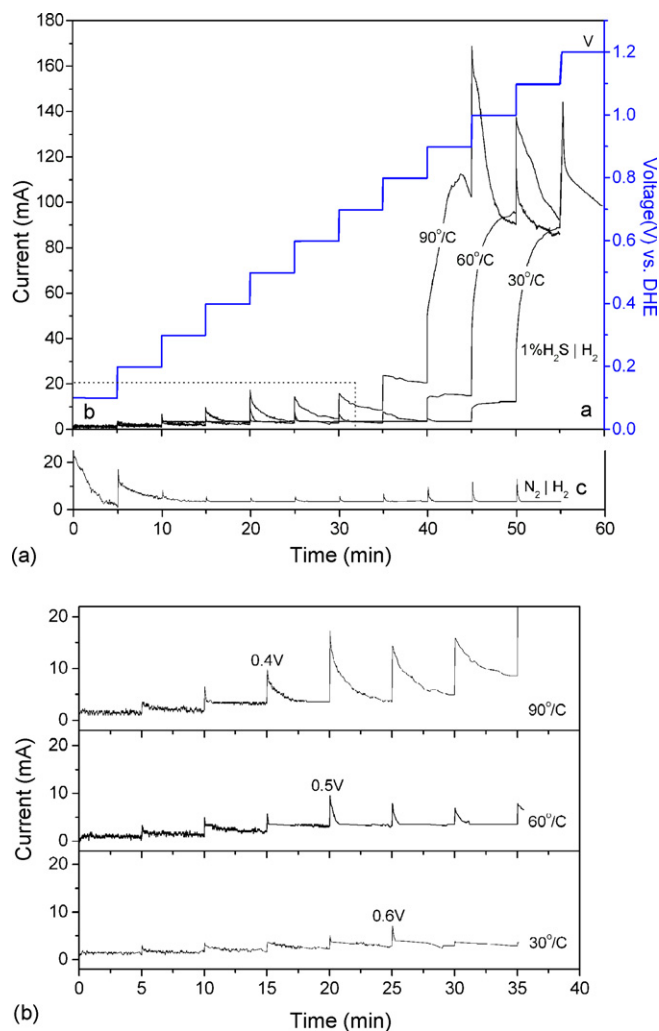


Fig. 8. (a) The anodic current transients with 1% $\text{H}_2\text{S} + \text{N}_2/\text{H}_2$ cell by applying potential steps, (b) enlarged partial anodic current transients for comparison of hydrogen oxidation peaks and (c) the anodic current transients with N_2/H_2 cell to attain the base line.

potential was stepped to 0.4 V. We suggest that H_2S is dehydrogenated at this potential according to Reaction (1) and the hydrogen thus formed is oxidized. Furthermore, the dissociation potential of H_2S increases with decreasing temperature. The values of the dissociation potential at different temperature are about 0.4 V at 90°C , 0.5 V at 60°C and about 0.6 V at 30°C .

When the potential is stepped to the dissociation potential, a layer of adsorbed elemental sulfur starts to form on Pt. This sulfur layer can inhibit the adsorption and dissociation of H_2S on Pt, so the current peaks become smaller slightly even at higher potential. When the potential is stepped further toward the anodic direction, the adsorbed sulfur begins to be oxidized to SO_3 or SO_4^{2-} at certain potential according to the following Reactions (2) and (3) proposed by Loučka [2] in the aqueous phase. At this potential, not only the adsorption and dissociation of H_2S but also the oxidation of sulfur can occur, so the chronoamperometric current reaches a steady state value. From Fig. 8(a), the appearance of the constant current was observed at 0.8 V at 90°C , at 0.9 V at 60°C and at 1.0 V at 30°C , and the values of the constant current increased dramatically when

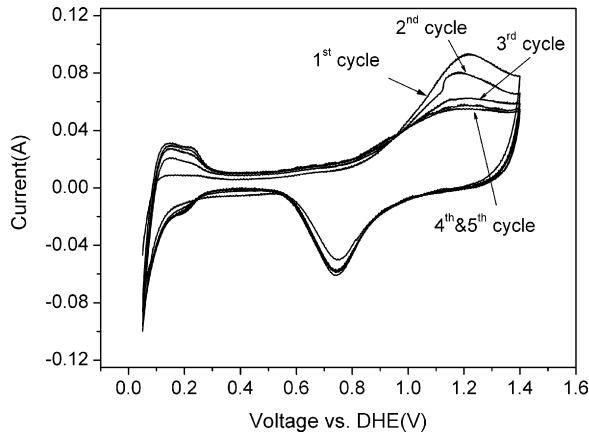
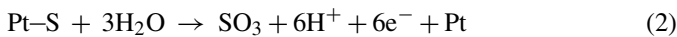


Fig. 9. Cyclic voltammograms obtained after anode exposure to 500 ppm $\text{H}_2\text{S}/\text{N}_2$ for 30 min. $T_{\text{cell}} = 60^\circ\text{C}$, scan rate: 20 mV s^{-1} .

the potential was stepped to 0.9, 1.0 and 1.1 V, respectively. At this high potential, the oxidation of Pt occurred simultaneously. With more and more Pt sites being oxidized, the adsorption and dissociation of H_2S were prevented, and the current decreased evidently at 1.0 V at 90°C , at 1.1 V at 60°C and at 1.2 V at 30°C . After potential steps, neat H_2 and air were introduced to the anode and the cathode, and polarization curves were measured. According to polarization curves, the cell performance deteriorated severely, which confirmed the formation of platinum oxide. From Fig. 8(a), we can also realize that the oxidation potential of the adsorbed sulfur shifts negatively with increasing temperature.



Because of H_2S adsorption, there is no current peak of oxidation of adsorbed hydrogen in the first cycle as shown in Fig. 9.

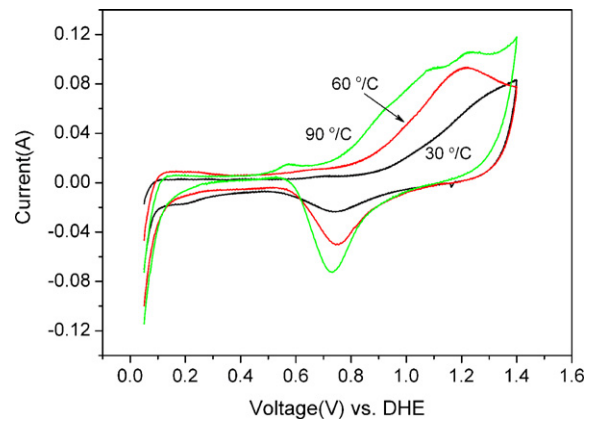


Fig. 10. Cyclic voltammograms obtained after anode exposure to 500 ppm $\text{H}_2\text{S}/\text{N}_2$ for 30 min at 30, 60 and 90°C . Scan rate: 20 mV s^{-1} .

When the potential is scanned further toward the anodic direction, the dissociation of H_2S begins to occur at about 0.5 V and a layer of adsorbed elemental sulfur starts to form on Pt. The single oxidation peak at 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. In Fig. 9, it can be seen that more than three CV scans are required for complete oxidation of the sulfur. Fig. 10 shows the CV (first cycle) performed at 30, 60 and 90°C . There were two oxidation peaks at 1.07 and 1.2 V when the cell temperature was fixed at 90°C . According to Contractor and Lal [4], these two peaks corresponded to two forms of chemisorbed sulfur which were distinguished by the number of platinum sites occupied per sulfur atom. At 60 and 30°C , a single oxidation peak was observed at 1.2 and 1.27 V, respectively.

3.3. EIS measurements

Fig. 11 shows the Nyquist plots after the anode exposure to 50 ppm H_2S for different durations at open circuit potential

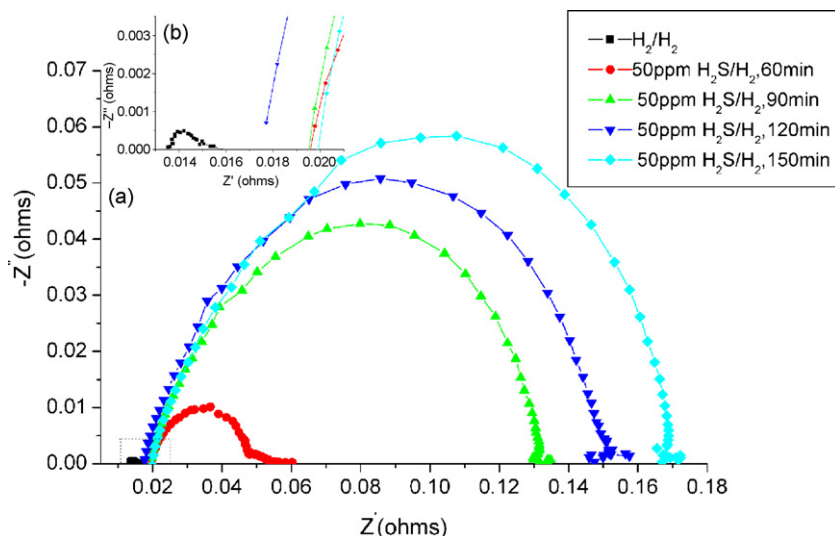


Fig. 11. (a) Anode Nyquist plots after the anode exposure to 50 ppm H_2S for 60, 90, 120 and 150 min with $\text{H}_2\text{S} + \text{H}_2/\text{H}_2$ half-cell; (b) enlarged partial of Nyquist plots at low frequencies. $T_{\text{cell}} = 60^\circ\text{C}$, humidification temperatures of the anode and cathode both 70°C .

(OCP). The high frequency interception on the real impedance axis of the Nyquist plot represents the total ohmic resistance of the cell, which contains the ohmic resistance of the cell components such as the membrane, catalyst layer, backing layer, end plate, as well as the contact resistance between each of them [12]. Among these, the membrane resistance is dominant and is strongly dependent on the hydration state of the membrane [13]. During the measurements, the MEA was well-humidified, the ohmic resistance of the cell increased little (about $6\text{ m}\Omega$) after the anode exposure to H_2S for 150 min as shown in Fig. 11(b). The complex impedance plot for the unpoisoned cell ($\text{H}_2|\text{H}_2$) consists of two depressed arcs. According to Ciureanu et al. [14], these two arcs may be assigned to the chemisorptive dissociation of hydrogen molecules ($\text{H}_2 = 2\text{H}_{\text{ads}}$) and the reversible charge-transfer process involving the adsorbed hydrogen atoms ($\text{H}_{\text{ads}} = \text{H}^+ + \text{e}$). As soon as H_2S was fed to the anode, H_2S began to cover the active Pt sites and the adsorption and dissociation of hydrogen were inhibited. Thus, the charge transfer resistance increased. The impedance spectra in Fig. 11(a) show a strong exposure time dependence. With increasing H_2S exposure time, the real as well as the imaginary part of the impedance increased and the two arcs were no longer resolvable. And the increasing impedance is responsible for the power loss of fuel cells fed with a H_2S -containing fuel gas. The value of the charge transfer resistance increased from 3 to $170\text{ m}\Omega$.

4. Conclusions

The effect of H_2S on the PEMFC anodes in different cell operating conditions was studied. The poisoning of H_2S is irreversible and total recovery can be attained by five CV scans between 0.05 and 1.4 V versus DHE. The rate of H_2S poisoning is a strong function of the H_2S concentration and current density. With a higher H_2S concentration and current density, a higher poisoning rate was observed. Moreover, the poisoning rate decreased when the cell temperature was increased. When the anode was exposed to $\text{H}_2\text{S}/\text{H}_2$, the anode humidification did not affect the poisoning rate. Potential steps were set up to

determine the H_2S dehydrogenating potential on the (SPE)-Pt electrode, and the values for this dehydrogenating potential were about 0.4 V at 90°C , 0.5 V at 60°C and 0.6 V at 30°C . There are two oxidation peaks for adsorbed sulfur at 1.07 and 1.2 V at 90°C , and a single oxidation peak is observed at 1.2 V at 60°C and at 1.27 V at 30°C . Results of EIS measurements with 50 ppm $\text{H}_2\text{S}/\text{H}_2$ half-cell showed that the value of the charge transfer resistance increased with anode exposure to H_2S , and the increasing impedance is responsible for the power loss of fuel cells fed with a H_2S -containing fuel gas.

Acknowledgements

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