

SPECIAL ISSUE ON GREEN HYDROGEN AND FUEL CELL SYSTEMS

A novel H₂S/H₂O₂ fuel cell operating at the temperature of 298 K

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SUMMARY

In this study, the oxidation mechanism of hydrogen sulfide (H₂S) is investigated, and a fuel cell operating with acidic peroxide as oxidant and basic hydrogen sulfide as fuel is constructed. A stable solid state H₂S/H₂O₂ fuel cell has been developed at the temperature of 298 K. A nickel anode catalyst has been examined using Nafion-117 as a proton-conducting membrane. In an operating with the acidic hydrogen peroxide (H₂O₂) as oxidant, the cell potential was increased to a value of 0.85 V at 298 K. The main conclusion of this study is the management to increase the cell potential to 850 mV at 25 °C, whereas this value can only be achieved in the H₂S/O₂ fuel cell at 850–1000 °C. Moreover, there exists no prior work on the H₂S/H₂O₂ fuel cell research. Copyright © 2012 John Wiley & Sons, Ltd.

KEY WORDS

hydrogen sulfide; fuel cell; electro-oxidation

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1. INTRODUCTION

Using fossil fuels as the primary energy source has led to a serious energy crisis and environmental pollution on a global scale. Correspondingly, million tons of greenhouse gases are emitted every year because of the combustion of fossil fuels. Hydrogen has been identified as a potential alternative fuel as well as an energy carrier for the future energy supply. Hydrogen is clean, and in practice, it can be produced from several sources such as fossil fuels, natural gas streams, plants, microalgae, and seawater. Seawater is the most abundant water source and an ideal medium for hydrogen production by electrolysis. Moreover, another important source for hydrogen is hydrogen sulfide that is abundantly found in Black Sea, Cariaco Basin, or Framvaren Fjord deep waters. As can be seen in Equation (2), electrolysis of the solution that contains H₂S has been considered to be an alternative strategy because of more favorable thermodynamics compared with water electrolysis.



Sulfide is known to occur in anoxic environments where the rate of oxygen removal is close to its rate of supply. For

decades, chemoclines in stratified water columns such as the Black Sea have attracted scientists from different fields to study sulfide oxidation. All over the world, some seas such as Black Sea are unique because 90% of their seawater is anaerobic. This anaerobic seawater contains hydrogen sulfide, produced by sulfur-reducing bacteria. The interface between anaerobic and aerobic water lies at the depths of about 140 m along the axis of the Black Sea and about 250 m along the sides. The total sulfide of the Black sea is about 4.6×10^3 Tg located between 500 and 2000 m [1]. As it is known from literature, by assuming 100% conversion, total hydrogen contents of the sea are estimated to be around 270 million tons on the basis of the total 4587 million tons of hydrogen sulfide potential. From this amount of hydrogen, 8.97 GWh of electricity energy can be generated theoretically. If it is assumed that almost 10 million families live in the sea coast, and their annual electricity consumption can be estimated as 36 billion kWh; this hydrogen potential can be consumed approximately throughout 250 years [2]. Therefore, hydrogen sulfide may serve as a future energy system.

H₂S is one of the major chemical electron donors. The electric power can be produced from hydrogen sulfide by the anodic oxidation. In the operation of fuel cell, hydrogen sulfide is employed as the fuel itself. From such a process, the electric current is obtainable together with valuable

products such as sulfur, sulfide, and polysulfide [3]. A further advantage is that the source of hydrogen sulfide used may be a low cost and abundant material. A galvanic cell having the anode/membrane/cathode in contact with an electrolyte, which contains the hydrogen sulfide, could be a source of electric power.

In an H₂S fuel cell, the anode reaction depends upon the type of electrolyte used [4]. The electrolyte may be either an acid such as H₂SO₄ or HCl or a base. With the use of a basic electrolyte, a wider selection of sulfur products may be obtained, and the anode is not subjected to severe activation polarization that is encountered while using an acid electrolyte. Therefore, as a practical matter, a basic electrolyte should be used as the anolide. The seawater is accordingly a suitable electrolyte for fuel cell application because of the high pH values and its ionic nature. Hydrogen sulfide is ionized in the basic electrolyte to form disulfide ions according to the following reaction:



The disulfide ions are oxidized to free sulfur as follows:

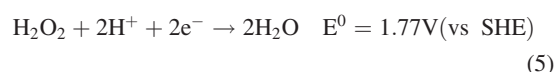


The formation of free sulfur is not required because of the poisoning effect of the sulfur on the electrode surface. The alternative pathway is the conversion of the disulfide to the polysulfides in the alkaline solution (pH = 14). Polysulfides can be dissolved in the solution and can be removed easily from the system. Therefore, the direct oxidation of H₂S in the fuel cells is a more desirable approach compared with the hydrogen production. In the current technology, H₂S usually removed from the natural gases by Claus process oxidizing to steam and sulfur, not to utilize H₂S as an energy source. Although the Claus process is exothermic and generates thermal energy that cannot be utilized and no economic value, the electro-oxidation of H₂S is considered to be an attractive process. A fuel cell using hydrogen sulfide as the fuel can generate electrical energy, leaving behind only sulfur and water.

The feasibility of H₂S fuel cells was revealed in 1987. Fuel cell studies with feeding of the H₂S coming from natural gas streams were carried out with high temperatures (450–1000 °C) in solid oxide fuel cells. The electrolytes and the catalysis influenced fuel cell performance. Currently, O²⁻ conducting yttria-stabilized zirconia electrolytes were used in fuel cells at above 800 °C. By using a proton-conducting electrolyte (Li₂SO₄), the operating temperature can be decreased below 700 °C [5]. Composite metal sulfides (MS_x), wherein *M* is a metal such as Mo, Co, Ni, Fe, Cu, Cr, and Mn, were investigated as an anode material in the high temperature H₂S fuel cells. It was reported by Zhong *et al.* that MoS₂ and the composite materials based on MoS₂ exhibited good catalytic activity on the H₂S fuel cells [6]. For example, whereas the power density of 10 mW/cm² was achieved with the anode catalyst of MoS₂

at 750 °C, the cell power reached 200 mW/cm² by using the MoS₂ + NiS + Ag + YSZ (combining mixed metal sulfides with the conducting material of yttria-stabilized zirconia) at the cell temperature of 850 °C [7]. In one of the studies carried out at 120 °C, the power density of 31 mW/cm² was found with the anode catalyst of NiS₂ and the gas feed of the H₂S [8]. Note that all performance values were taken at the elevated or high temperatures.

This study aims to construct a fuel cell with the acidic peroxide as oxidant and the basic hydrogen sulfide as fuel. At room temperature, a novel H₂S/H₂O₂ fuel cell has been developed. According to the following reaction, the usage of hydrogen peroxide, instead of oxygen as an oxidant, can yield higher cell potential values related to the theoretical cell potential.



2. EXPERIMENTAL DETAILS

2.1. Electrochemical measurements

The classical three-electrode system was used for performing the electrochemical tests. The electrochemical analyses were carried out with Pt disk (Bass) and Ni electrodes (99.99%) having surface area 0.40 cm². Pt wire and SCE were used as the counter and reference electrodes, respectively. A 1 M NaOH solution was the electrolyte solution in which Na₂S with a different concentration was added as a fuel. The electrochemical measurements were recorded by the CH Instruments 660C. A 0.1 M Na₂S stock solution was prepared by dissolving a quantity of Na₂S.9H₂O (from Aldrich) in 1 M NaOH electrolyte solution. Under the present electrolyte conditions, HS⁻ ions are expected to be predominant. Before the experiments, freshly prepared 1 M H₂O₂ was used as an oxidant.

2.2. Fuel cell studies

Pt/C powders (10% from Alpha Aesar) of 15 mg cm⁻² were used at the cathode. Pt/C powders (10% from Alpha Aesar) and Ni powders (Alpha Aesar) of 15 mg cm⁻² were used as the anodes. The catalyst inks were prepared by mixing the metal powders with Nafion solution (Alpha Aesar) and isopropyl alcohol (Alpha Aesar) and were dispersed in the ultrasonic bath. The catalyst inks were brushed onto the carbon papers (Fuel Cell Store) and dried at 60 °C. The electrodes were hot pressed to the Nafion-117 membrane at a pressure of 1200 psi and a temperature of 150 °C. The MEA was prepared and placed the body of the cell.

The single passive cell used in this study was made of the plexy glass material [9]. The cell consisted of two plates without any specific flow field for liquid diffusion; current collectors made from stainless steel plates and the reservoirs of 6 ml for liquid fuel/oxidant were constructed. The geometric area of the electrodes was 4 cm². The fuel

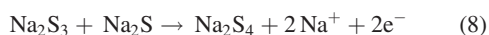
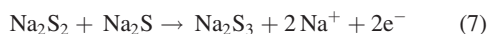
and oxidant were contacted and reacted directly with the catalysis surfaces.

The impedance spectroscopy was examined with the reference electrode replaced to the anode chamber near to the catalyst surface for the determination of the surface characteristics. The cell impedance was performed in the frequency range between 100 kHz and 10 mHz by using the Gamry Instrument as an electrochemical impedance analyzer. An alternative current (AC) signal of 10 mV was applied potentiostatically at an open circuit condition. The results were displayed as Nyquist plots. Equivalent circuits were simulated at Gamry Instrument and Z-Sim.

3. RESULTS AND DISCUSSION

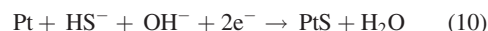
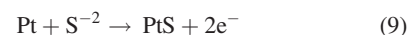
3.1. Electrochemical studies

One problem with the fuel cell performing with gas phase H₂S is that, when free sulfur is formed as an anodic product, the fine sulfur can enter the pores of the porous anode surface and inactivate it causing an increase in the anode polarization and hence an increase in the resistance across the anode-electrolytic interface thereby reducing the electrical output [10]. In the basic electrolyte, unless the anolyte is saturated, the free sulfur will tend to dissolve therein to form polysulfide. The removing and recovering of the polysulfide from the system by the chemical methods are the biggest advantages of the use of the fuel within a basic electrolyte. In the experiments carried out at the laboratories, the preferred electrolyte was an aqueous NaOH solution having a molar concentration of 1 M maintained at a pH of about 14. The polysulfides formed in the basic solution as the following reactions [10]:



The mechanisms for the electrochemical oxidation of sulfide are complicated because sulfur has different oxidation states such as -2, 0, +4, and +6. Upon anodic oxidation, they give elemental sulfur, polysulfide, or sulfur oxyanions depending on the potential, pH, and temperature of the electrolyte. In this study, the concentration of electrolyte used is 0.1 M Na₂S + 1 M NaOH solution where the pH of the electrolyte indicates that HS⁻ ions are the predominant species [11].

Electrochemical oxidation of the hydrogen sulfide was examined upon Pt electrode (Figure 1). It is known that the formation of platinum oxide occurs at potentials higher than 0.55 V versus SCE in a 0.05 M NaOH solution [12]. In Figure 1, the adsorption of sulfide on a Pt surface is much stronger than that of hydroxide, and sulfur adsorption on the Pt surface occurs at the potential of 0.8 V. The reactions occurring on the Pt surface are as follows:



The peak at 0.8 V increases with the increasing of H₂S concentration. This peak is attributed to be the oxidation of sulfur in a Pt-O-S oxide, and this oxide is formed at 0.8 V. It is hypothesized that this Pt-O reacts with the Pt-S to form the Pt-O-S [13]. This Pt-O-S product is difficult to reduce in the back scan, and thus, the reduction peak of the Pt oxides is not observed in the return scan as seen in Figure 1.

In Figure 2, the multicycle cyclic voltammetry (CV) graphs in the NaOH + Na₂S solution can be seen at 0.4 mmol Na₂S addition. A decrease in the peak current with the number of the cycle was observed and then stabilized. The current drop also indicated that there was a built-up sulfur deposition on the surface. When strongly bonded sulfur is formed, Pt sites are deactivated.

Similarly, the anodic oxidation of nickel electrode in alkaline solution in the potential ranges related to the Ni/Ni(OH)₂ and Ni(OH)₂/NiOOH redox reactions was studied under potentiodynamic conditions. In alkaline solutions,

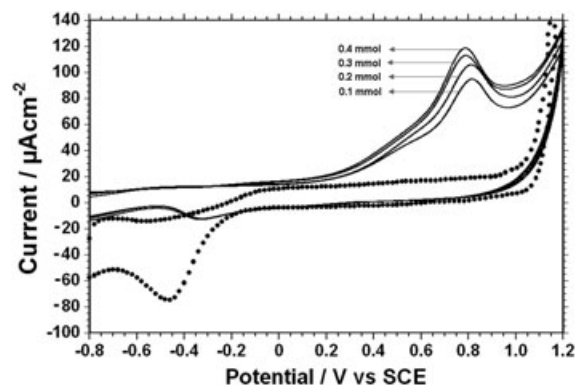


Figure 1. The CV graphs with Pt electrode in (—●—) NaOH, (—) for different Na₂S added into the NaOH solution at scan rate of 50 mV/s (25 °C).

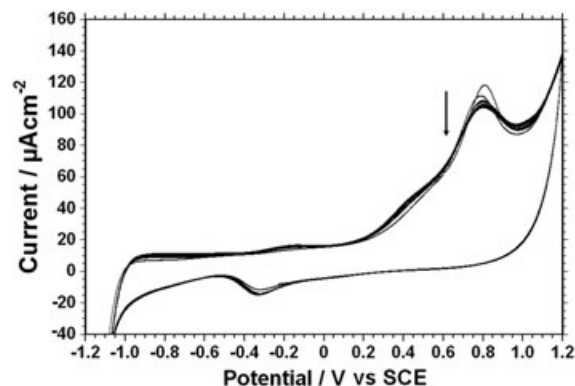


Figure 2. The multicycle of the Pt electrode in the NaOH + H₂S solution at scan rate of 50 mV/s.

dissolution of the metal occurred, followed by the formation of a Ni(OH)₂ adsorbed film according to the Equation (11):



The CV graph of the Ni electrode in 1.0 M NaOH solution was given in Figure 3. As it can be seen from Figure 3, an oxidation peak at +0.42 V (vs SCE) can be attributed to the continuation process of the nickel dissolution and nickel oxide formation.

In Figure 3, the cyclic voltammograms of nickel electrode in 1.0 M NaOH with the addition of Na₂S were given. The anodic peak at 0.42 V shifted to 0.5 V with the increasing of [HS⁻]. The peak currents also showed an apparent increase based on the concentration. Moreover, a decrease in the peak current with the number of the cycle was not observed. This was concluded that oxidation of HS⁻ ions occurred on the Ni(OH)₂ film formed at the nickel electrode in an alkaline solution. This could be ascribed to the oxidation of the newly formed Ni(OH)₂ layer to NiO(OH). The reduction of NiO(OH) back to Ni(OH)₂ was observed at 0.33 V [14].

Consequently, nickel showed an oscillation mechanism in the NaOH + Na₂S solution rather than the Pt anode electrode, and the oxidation of sulfide ions was significantly enhanced at a nickel electrode. Furthermore in the electrochemical cells, hydrogen sulfide could react electrochemically with nickel-based anode according to the following reaction and nickel sulfides formed by the oxidation of sulfide ions dissolved in the electrolyte:



3.2. Fuel cell studies

A fuel cell using H₂S as fuel and H₂O₂ as an oxidant has been shown to produce sulfur and to generate electricity. The following envisioned configuration has been experimentally proven:

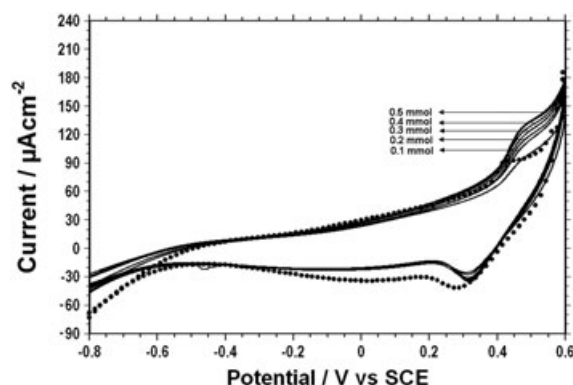
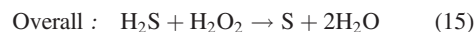
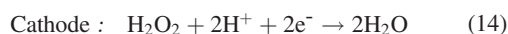
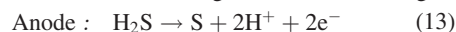


Figure 3. The CV graphs of Ni electrode in (—●—) NaOH, (---) Na₂S added into the NaOH solution with different concentrations at scan rate 50 mV/s (25 °C).



The reaction mechanisms are given as the following:



H₂S reacts on the anode-producing elemental sulfur, protons, and electrons. On the cathode side, peroxide reacts with protons and electrons producing H₂O.

3.2.1. The studies of the cell performances

Pt is one of the known anode catalysis for the oxidation of H₂S at highly elevated temperatures (850–1000 °C). The cell performance strongly depends on the temperature due to the low activation of H₂S at low temperatures. The potentials generated with H₂S are lower than those of H₂. Slavov *et al.* reached the maximum cell potential of 300 mV in the H₂S(g)/O₂(g) fuel cell at the temperature of 22 °C [15].

Comparatively, we have managed to increase the cell potential to 850 mV at room temperature, whereas this value can only be achieved previously in the H₂S/O₂ fuel cell at 850–1000 °C.

In our fuel cell system, the fuel (H₂S within 1 M NaOH) and the oxidant (hydrogen peroxide in an acid electrolyte, H₂SO₄) in liquid forms were fed to the fuel cell. The usage of hydrogen peroxide instead of oxygen as an oxidant can yield higher cell potential values. Hydrogen peroxide is an attractive choice for fuel cell applications and is comparatively safe, stable as 35% solution in water, is not toxic, and produces water from its oxidation. It is observed that, despite the low reactivity, H₂S_(basic, liq)/H₂O_{2(acidic, liq)} fuel cell offers higher power outputs than the H₂S/O₂ fuel cell operating at higher temperatures (850–1000 °C). Moreover, the liquid substances increase the cell potential by decreasing the overpotentials caused by the activation (η_{act}) and concentration (η_{conc}) [16]. The increased cell potential at room temperature is the most important advantage of our fuel cell.

The cell potentials of our fuel cells constructed with Pt anode and Ni cathode were given in Figures 4 and 5, respectively. As expected, both cells show the high open circuit potential values of 855 mV for Pt and 880 mV for Ni anodes at room temperature.

In Figure 4, the effect of Na₂S addition on the cell performance clearly shows that the cell potential of the fuel cell with Pt anode reached 850 mV from 837 mV (after adding Na₂S) and continued to increase.

3.2.2. Polarization curves

Figures 6 and 7 show the I-V and I-P curves of the passive fuel cell constructed with Pt/C and Ni anodes, respectively. Power densities were found to be about 1 mW cm⁻² for both cells. There were just 6 ml fuel and 6 ml oxidant on the containers. It is expected that

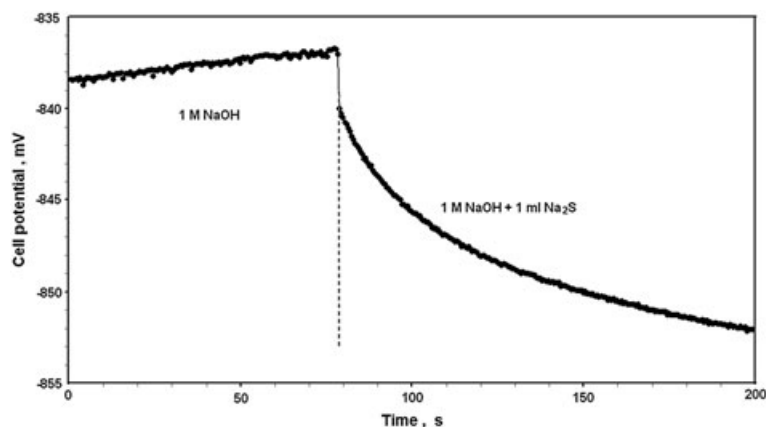


Figure 4. Increasing of the cell potential with the addition of the 1 ml 0.1 M Na₂S into 1 M NaOH solution (the fuel cell constructed with Pt/C anode/cathode is operating with 2 M H₂O₂ acidic solution as catholyte).

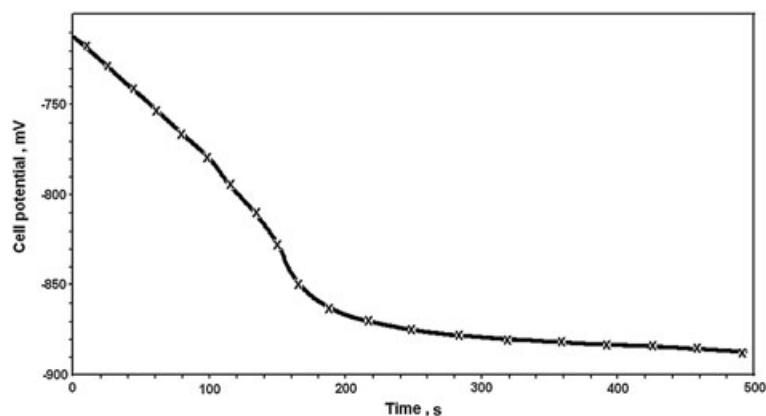


Figure 5. The OCP graph of the fuel cell constructed with Ni anode (17 mg Ni cm⁻²), Pt/C cathode operating with 0.1 M Na₂S + 1 M NaOH solution as anolyte and 2 M H₂O₂ acidic solution as the catholyte.

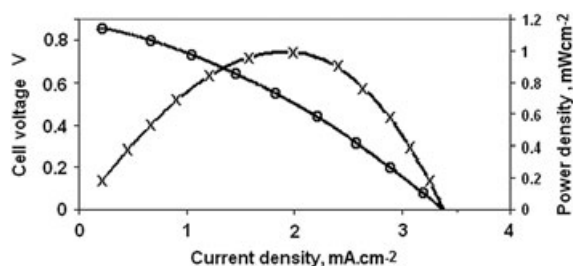


Figure 6. The polarization curves of the fuel cell constructed with Pt/C anode operating with 0.1 M Na₂S + 1 M NaOH, 2 M H₂O₂ acidic solution as oxidant at room temperature.

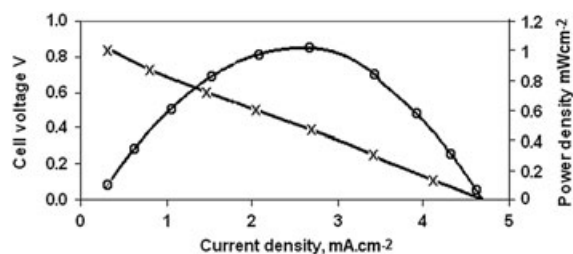


Figure 7. The polarization curves of the fuel cell constructed with Ni anode and Pt/C cathode operating with 0.1 M Na₂S + 1 M NaOH as the fuel, 2 M H₂O₂ acidic solution as the oxidant at room temperature.

if the flow cell is used, the new catalyst is developed, and the fuel cell is operated at mild temperature (<90 °C); the power output will increase to higher values

than that of the passive cell performed in this study. Moreover, an alternative fabrication method could provide the higher power output. For example, direct

application of the catalyst layer onto the Nafion membrane results in more robust catalyst layer; it is called 'thin-film catalyst layer'. High performance was found with a very low catalyst loading in a very thin catalyst layer [17,18].

It is seen from the polarization curves that the maximum current generating in Nickel fuel cell is higher than that of the Pt fuel cell. The current density depends on the reactant concentration at the catalyst surface; the higher the current density, the lower the surface concentration. The surface concentration reaches zero when the rate of consumption exceeds the diffusion rate. Current density at which this happens is called the limiting current density. A fuel cell cannot produce more than the limiting current because there are no reactants at the catalyst surface.

For the stability test, a constant current density of 1 mA cm^{-2} was maintained for 45 min (Figure 8). The

constant current discharging tests showed that Nickel anode fuel cell is more stable than the Pt cell.

3.2.3. The impedance study of the electrode surfaces

The main advantage of electrochemical impedance spectroscopy (EIS) is the possibility to resolve the individual contributions that affected the overall fuel cell performance. Such a separation provides useful information for both fuel cells (FCs) design and the optimal operating conditions. In this study, it is focused on how the electrode surface acted after and before the load current.

The impedance spectroscopy was examined with the reference electrode replaced to the anode chamber near to the catalyst surface for the determination of the surface characteristics. The Nyquist diagrams for Pt and Ni anodes taken upon the surface before (fresh) and after the load

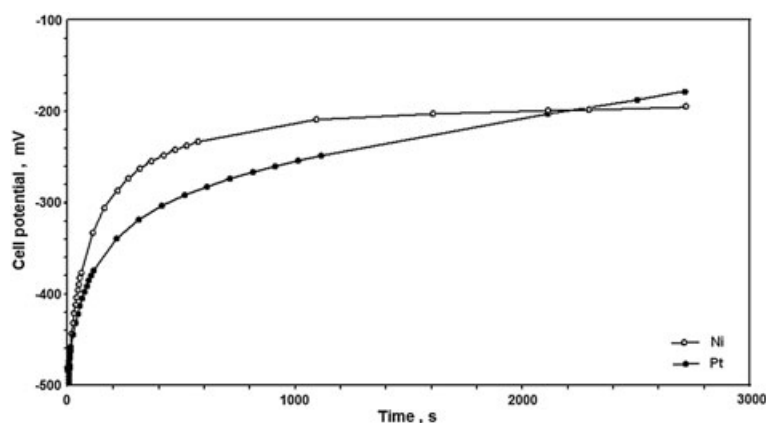


Figure 8. The voltage–time curve of the Pt and Ni fuel cells loaded with the current of 1 mA (operating with Na₂S + NaOH solution as the anolyte and acidic H₂O₂ solution as the catholyte, constructed with Pt/C cathode catalysis).

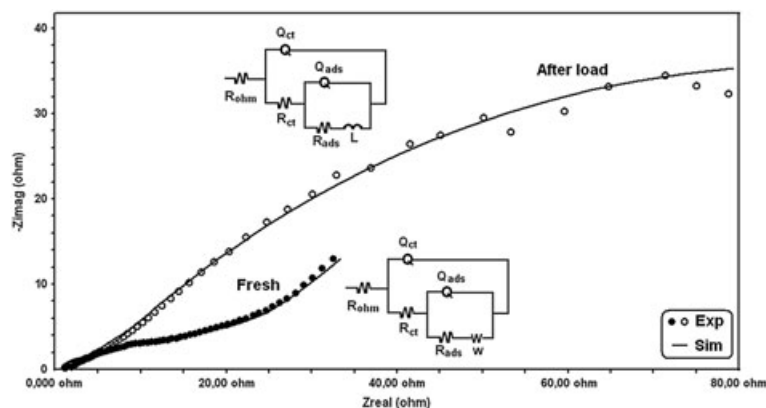


Figure 9. The Nyquist diagrams, simulation curves, and equivalent circuits for the Pt anode surface of fuel cell operating with 1 M NaOH + 0.1 M Na₂S as anolyte, acidic 2 M H₂O₂ solution as the catholyte; (●—) for the fresh electrode surface, (○—) after the load of current.

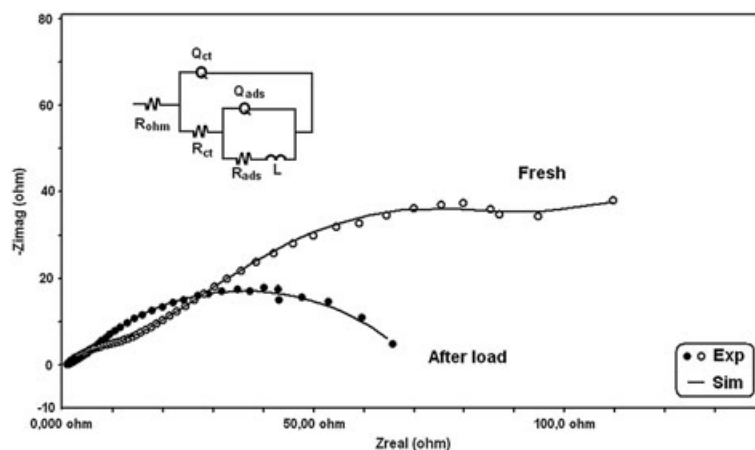


Figure 10. The Nyquist diagrams and equivalent circuit of the Ni anode of the fuel cell operating with 1 M NaOH + 0.1 M Na₂S as anolyte, acidic 2 M H₂O₂ solution as the catholyte; (—○—) the fresh surface and (—●—) after the load of current.

of 4 mA are given in Figures 9 and 10, respectively. The impedance parameters of the anode surfaces are given in Table I.

The EIS results seen in Figure 9 showed that as expected for Pt electrode, sulfur adsorbed strongly and irreversibly on the Pt surface. The experimental results were simulated by the Gamry EIS software. The equivalent circuit is also shown in Figure 9. The impedance parameters of the Pt surface calculated by simulation are listed in Table I. The resistance of the adsorbed layer caused by the poisoning of the sulfur increased to 169.2 Ω from 10.32 Ω . Although the Warburg impedance due to the diffusion mechanism was observed on the fresh electrode, it disappeared after the current load, whereas the inductive effect at low frequencies rose. The electrode deactivation found from equivalent circuit analysis was confirmed with the multi CV graphs given in Figure 2.

The Nyquist diagrams for Nickel anode surface of the fuel cell are shown in Figure 10. The impedance parameters of Nickel anode surface are tabulated in the following text. From Table II, the charge transfer resistance for the Nickel anode interestingly decreased to 3.9 Ω from 12.52 Ω after the current load. Electrochemical reactions

Table II. The impedance parameters of Nickel anode surface.

	Fresh	After load
R_{ohm} , ohm	0.703	1
R_{ct} , ohm	12.52	3.945
Q_{ct} , Sxs^{a1}	2.5e-3	4.265e-3
a_1	0.560	0.540
R_{ads} , ohm	240.2	65.31
Q_{ads} , Sxs^{a2}	20.59e-3	6.069e-3
a_2	0.441	0.636
L , henry	868.7	86.65

occur when the anodic potential reaches the electrode potentials for nickel sulfides formation: the standard electrode potential for the reaction forming NiS and Ni₃S₂ are, respectively, -0.756 V and -0.829 V [19]. At open circuit voltage conditions, the anodic potential is more negative than cell potential of -0.85 necessary for either NiS or Ni₃S₂ formation. However under the current load conditions, the anodic potential increases as a consequence of anodic overpotential effects and reaches the necessary values for electrochemical nickel sulfide formation, dissolved in the electrolyte. The H₂S present in the feed is oxidized into sulfide that further reacts with the metal oxide to form metal sulfides such as CuS₂, Cr₂S₃, WS₂, NiS₂, FeS, and MoS_x, used as the anode catalyst in H₂S/O₂ fuel cells [8]. The fact that the charge transfer resistance of Ni electrode falls after the current load is due to the formation of the Nickel sulfur layer reacting with fuel as a catalyst observed from equivalent circuit.

However, it must be highlighted that although our fuel cell with Nickel anode showed an active behavior during the short-term studies, different results could be obtained in long-term studies because of the poisoning of the electrode surface. It is advised that further studies should be carried out.

Table I. The impedance parameters of Pt anode surface.

	Fresh	After load
R_{ohm} , ohm	1.410	0.82
R_{ct} , ohm	17.03	5.71
Q_{ct} , Sxs^{a1}	9.15e-3	7.55e-3
a_1	0.392	0.445
R_{ads} , ohm	10.32	169.2
Q_{ads} , Sxs^{a2}	47.68e-3	21.74e-3
a_2	0.585	0.528
L , henry	—	2.011
Warburg, $Sxs^{1/2}$	187.9e-3	—

4. CONCLUSION

The main conclusion of this study is the management to increase the cell potential to 850 mV at 25 °C, whereas this value can only be achieved in the H₂S/O₂ fuel cell at 850–1000 °C.

The principle conclusions can be summarized as follows.

1. The hydrogen sulfide undergoes an oxidation reaction in the alkaline fuel cell (H₂S/H₂O₂ fuel cell) leading to opening up the possibility of using less expensive Nickel catalyst where nickel sulfide is formed; hence, it makes the our fuel cell a potentially low cost technology compared with fuel cell technology.
2. The other benefit is that with H₂S utilized as the alkaline liquid H₂S/H₂O₂ fuel cell, sulfide ions are oxidized at the anode releasing electrons: $S^{-2} \rightarrow S^0 + 2e^-$. The sulfur produced reacts with the other sulfide ions to form disulfide and polysulfide ions in basic electrolytes such as Black sea water. Thereby, they dissolve in the electrolyte instead of covering the electrode surface.

ACKNOWLEDGEMENTS

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REFERENCES

1. Neretin LN, Volkov II, Böttcher ME, Grinenko VA. A sulfur budget for the Balck Sea anoxic zone. *Deep-Sea Research I* 2001; **48**:2569–2593.
2. Midilli A, Ay M, Kale A, Nejat Veziroglu T. A parametric investigation of hydrogen energy potential based on H₂S in Black Sea deep waters. *Int. J. Hydrogen Energy* 2007; **32**:117–124.
3. Ferdelman G, Jørgensen BB, Teske A, Thamdrup B. Influence of water column dynamics on sulfide oxidation and other major biogeochemical processes in the chemocline of Mariager Fjord (Denmark). *Marine Chemistry* 2001; **74**:29–51.
4. Bolmer PW. Electrochemical oxidation of hydrogen sulfide. 1966; US-3, 249, 522.
5. Zhong L, Luo J, Kar C. Investigation of cathode catalysts for intermediate-temperature H₂S-AiR fuel cells. *Chinese Journal of Chemical Engineering* 2007; **15**:305–308.
6. Zhong L, Liu M, Wei GL, Luo JL, Chuang K. Influence of metal sulfides as anode catalyst on performance of H₂S SOFC. *Chinese Journal of Chemical Engineering* 2003; **11**(3):245–248.
7. Chuang KT, Lou J, Wei G, Sanger AR. Electrode catalyst for H₂S fuel cells, 2006; US 7,014,941 B2.
8. Donini J, Chuang KT, Slavov SV, Sanger AR, Stanic V. Electrochemical oxidation of hydrogen sulfide, 2001; US 6,241,871.
9. Sanlı AE, Aytac A. Response to Disselkamp: direct peroxide/peroxide fuel cell as a novel type of fuel cell. *Int. J. of Hydrogen Energy* 2011; **36**:869–875.
10. Venkatesan S, Pinsky N, Sapru K. Hydrogen sulfide decomposition cell and catalytic materials therefore, 1985; USP 4,544,461.
11. Chen A, Miller B. Potential oscillations during the electrocatalytic oxidation of sulfide on a microstructured TVTa²O⁵-IrO² electrode. *The Journal of Physical Chemistry. B* 2004; **108**:2245–2251.
12. Miller B, Chen A. Oscillatory instabilities during the electrochemical oxidation of sulfide on a Pt electrode. *J. Electroanal. Chemistry* 2006; **588**:314–323.
13. Mohtadi R, Lee W-K, Van Zee JW. The effect of temperature on the adsorption rate of hydrogen sulfide on Pt anodes in a PEMFC. *Applied Catalysis B: Environmental* 2005; **56**:37–42.
14. Giovanelli D, Lawrence NS, Jiang L, Jones TGJ, Compton RG. Electrochemical determination of sulphide at nickel electrodes in alkaline media: a new electrochemical sensor. *Sensors and Actuators B: Chemical* 2003; **88**:320–328.
15. Slavov SV, Chuang KT, Sanger AR, Donini JC, Kot J, Petrovic S. A proton-conducting solid sate H₂S-O₂ fuel cell. 1. Anode catalyst, and operation at atmospheric pressure and 20–90 °C. *Int. J. Hydrogen Energy* 1998; **23**:1203–1212.
16. Bussayajarn N, Harrinton DA, Therdthianwong S, Therdthianwong A, Djilali N. The cathodic polarization prediction of H₂/H₂O₂ fuel cells by using EIS spectra, 2004; 30th Congress on Science & Technology of Thailand, Vol:30.
17. Wilson MS, Gottesfeld S. High performance catalyzed membranes of ultra-low Pt loadings for polymer electrolyte fuel cells. *Journal of the Electrochemical Society* 1992; **139**:L28–L30.
18. Wilson MS, Gottesfeld S. Thin-film catalyst layers for polymer electrolyte fuel cell electrodes. *J. Applied Electrochem.* 1992; **22**:1–7.
19. Zaza F, Paoletti C, LoPresti R, Simonetti E, Pasquali M. Studies on sulfur poisoning and development of advanced anodic materials for waste-to-energy fuel cells applications. *Journal of Power Sources* 2010; **195**:4043–4050.