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Recovering hydrogen sulfide from sulfurous waters with PEM fuel cells

S.M. Iordache[a,*], A. Ciocanea[b], A. Balan[a], I. Stamatin[a], S. Budea[b], C. Ceaus[a], A.M.I. Trefilov[a], S. Voinea[a]

[a]*University of Bucharest, Faculty of Physics, 3Nano-SAE Research Center, PO Box MG-38, 077125, Bucharest-Magurele, Romania*
[b]*Politehnica University of Bucharest, Faculty of Power Engineering, 313 Independentei Spl., 060042, Bucharest, Romania*

Abstract

Hydrogen sulfide is an environmental pollutant and abundant in various sulfurous waters such as Black Sea. Hydrogen sulfide is in the same time a potential energetic materials as source for hydrogen production. In this respect, designing an appropriate fuel cell with proton exchange membranes (PEMFC) for hydrogen sulfide recovering from sulfurous water is challenge. This study reports a PEMFC with Pt/Pt-Ru catalysts and membrane with perflurosulfonic ionomer. PEMFC was run at different concentrations of hydrogen sulfide in water (50-150 mg/L). Even though power densities are in the range microwatts the experimental set-up shows a promising perspective for sulfurous water treatment. A short overview on the actual state of the art in hydrogen sulfide recovering and potential applications of the fuel cells is presented in introduction.
Keywords: Fuel cells; hydrogen sulfide; wastewater treatment; sulfur recovering

1. Introduction

Hydrogen sulfide is a well-known environmental pollutant, largely resulted as by-product from petroleum and coal industries [1], also from natural processes due to the microorganisms' activity such as sulfur reducing bacteria. In addition, hydrogen sulfide could be a potential raw material for hydrogen production, a future fuel for energy carrier and sustainable development. Hydrogen sulfide, potentially, has economic value if both sulfur and hydrogen

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* Corresponding author. Tel.: +40 21-457-4838; fax: +40 21-457-4838.
E-mail address: stefan@3nanosae.org

might be recovered. The amount of hydrogen sulfide in the world counted from natural gases and petroleum industries reaches 10 million tons/year which is oxidized in the Claus process to produce sulfur [2]. The largest reserves in hydrogen sulfide is found in Black Sea where the concentrations range from 1.5 to 2.3 mL/L at depths 200-1500 m and 90% of sea water is anaerobic [3,4]. From natural processes only Black Sea (volume ~547·1012 m3 [5]) store around of 4.6 billion tons H2S in anoxic layer with a production potential of 270 million tons hydrogen [6]. Other studies based on increasing the content of hydrogen sulfide in environment as well in the Black Sea water were a subject of discussion for the ecologists for a long time. In addition, the petroleum industry is concerned with hydrogen sulfide to find eco-innovative technologies to reduce impact on the environment respective, to exploit its economic value. Hydrogen sulfide decomposition in hydrogen and sulfur was approached by different techniques still under development [7,8]: catalytic and noncatalytic decomposition (thermochemical processes), electrochemical, photochemical, plasmochemical methods, critical reviewed in [2,3] from point of view, energy consuming, cost-effective, conversion yield. On the other hand hydrogen sulfide could be a potential source for hydrogen production as an alternative to the classical systems: water electrolysis, from natural gas and biogas by steam reforming or by Kvaerner carbon black & hydrogen process [9,10,11] to name few. Unfortunately, there is no method or mature technology to recover both hydrogen and sulfur from hydrogen sulfide. Actual mature technology based on Claus process recover only sulfur, and requires high-energy consumption at nominal working temperature 800-8500C. Another method proposes superadiabatic decomposition with partial oxidation reached simultaneous recovery of hydrogen and sulfur with reasonable yield but still is an energy intensive method [7,12]. Proposals to use renewable energies in the catalytic assisted thermochemical decomposition of hydrogen sulfide reports 15% yield [13]. Further developments are exemplified on hydrogen sulfide recovery from Black Sea using solar thermolysis process for hydrogen and sulfur production [4]. This in combination with stripping technology based on Henry's law for hydrogen sulfide concentration from few ppm up to 10,000 ppm could be a promising perspective [14]. Another direction in research is to develop appropriate set of catalysts and procedures to implement electrocatalytic dissociation or to direct conversion in fuel cells at moderate, even lower temperature if any mechanism can be used. In this respect one step ahead in the electrocatalytic decomposition of H2S in hydrogen and sulfur was reported based on nonelectrochemical modification of catalytic activity (NEMCA) phenomenon observed at Platinum surface deposited on a O2- conducting yttria-stabilized zirconia (Pt-YSZ) under one applied potential [15,16]. The decomposition rate of H2S significantly increased up to a factor of 11 at 6000C. Even though NEMCA is a promised path, a critical review [16] analyses factors that must be overcome for a mature technology. Earlier reports show possibilities for electrolysis of hydrogen sulfide in high concentration of aqueous NaOH solution at 60-800C [17,18]. The electrolysis of hydrogen sulfide in alkaline solutions could be carried with various electrodes (nickel, graphite, titanium, stainless steel) in excess of hydroxyl radicals. That is important feature to drive decomposition of the hydrogen sulfide dissolved in water. By comparison with methanol or ethanol fuel cells, their oxidation reactions are carried in excess of hydroxyls using bi-functional catalysts such as PtRu [19,20]. It is expected as hydrogen sulfide dissolved in water to be oxidized to hydrogen and sulfur in a fuel cells designed as a direct methanol fuel cells (DMFC) [21]. This contribution shows these types of fuel cells with PtRu catalysts can be a good approaches in further development for hydrogen sulfide recovering and conversion in useful products.

2. Materials and methods

2.1. Fuel cell

Fuel cell used in the experimental set-up consists of: membrane electrode assembly (MEA), two current collector plates, the anode compartment for fueling with hydrogen sulfide solution, the cathode compartment for the oxidant access (air), figure 1.

Fig. 1. Experimental set-up. 1) Fuel cell 2) vessel with hydrogen sulfide solution 3) peristaltic pump

The anode compartment is connected to peristaltic pump to supply and recirculate liquid fuel from an external reservoir (2, figure 1). The collector plates are perforated stainless steel plate (1 mm thickness). They are in contact with MEA respective, on the back side with fuel and oxidant.

MEA has active area 5x5 cm and consists of membrane (perfluorosulfonate ionomer, Nafion™ 117) and two carbon papers as fluid diffusion layer (FDL). Each FDL is coated with mesoporous nanocarbon, support for catalyst layer. On the mesoporous supports are deposited appropriate catalyst layers for anode and cathode: 1) anode loading: 3 mg/cm2, catalyst PtRu (1:1 molar ratio); 2) cathode loading 1.3 mg/cm2 Pt/C.

FDL with microporous and catalyst layers are assembled on membrane and hot pressed at 120-1300C and 4 kgf/cm2 for 20 min. The procedures for MEA assembling and catalyst ink preparation are described elsewhere [20].

Catalysts: PtRu- HiSPEC 6000 (Johnson Matthey); Pt/C- (Pt 60 wt.% on high surface area advanced carbon support, Vulcan X72).

Carbon paper: Toray™ carbon paper; 0.28 thick; Teflon™ 20 (+/- 5) wt. % treated.

Hydrogen sulfide solutions of concentrations 50, 100, 150 mg/L are prepared by dissolving H2S gas in water under stirring.

The volume occupied by fluid in the anodic space during circulation V=5x5x0.5 cm3.

2.2. Experimental conditions

For each concentration the peristaltic pump was set at two flows 20 respective 70 mL/min. For each flow rate is recorded open circuit potential and time reach a constant value (table 1). After 1 day in stationary regime with replenishing and keeping constant the hydrogen sulfide concentrations are carried out the polarization curves (figure 2). At cathode the oxygen is supplied from air fan with low ventilation at overpressure of +10KPa over normal conditions (specific for a calm atmosphere over Black Sea).

3. Results and discussions

The polarization curves and power densities are shown in figure 2 for two representative experiments at low concentration and flow rate respective at high concentration, high flow rate. Open circuit potential (OCP) for all concentrations and flow rates keeps in the range 450-575 mV (table 1). OCPs decrease with the flow rate in average

with ~100 mV. The residence time (time for 1 mL fluid remains in the anodic space) estimated from geometrical characteristics of the anodic space is ~37 s at a flow rate 20 mL/min and ~11 s for 70 mL/min. Therefore, the residence time decreases OCP with the residence time.
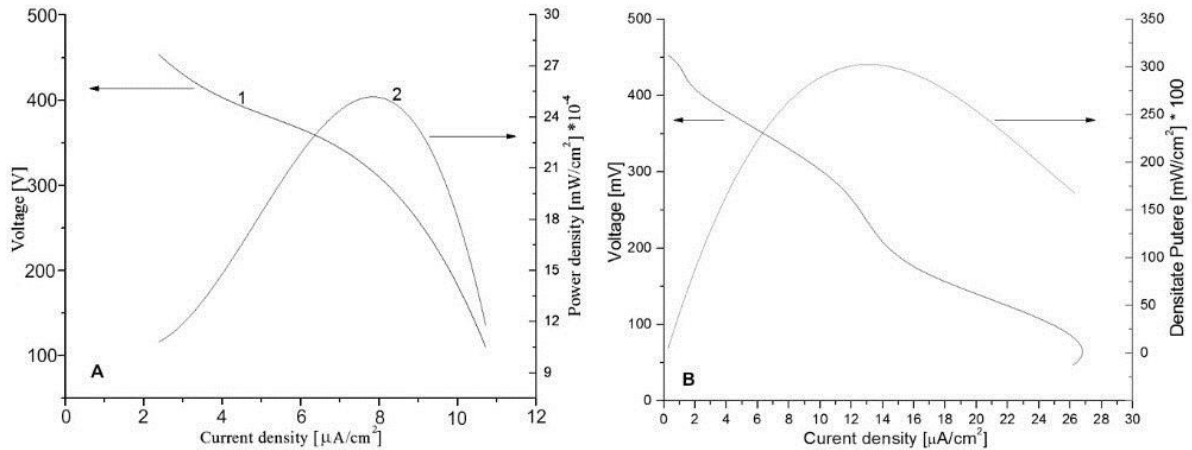

Fig. 2. The polarization curve (1) and power density (2) for hydrogen sulfide concentration 50 mg/mL and flow rate 20 mL/min (A) respective 150 mg/mL and 70 mL/min (B).

The polarization curves are quite different in shapes and dependent of the flow rate. At low flow rate, the polarization curve has a standard shape where the first region of activation polarization (activation loss) decreases up to 400 mV, a short Ohmic loss (middle region) and a large region of concentration polarization (mass transfer loss). The power density curve has a maximum near to the region of concentration polarization. At high flow rate and low concentration, the polarization curve has a fast transition towards mass transfer loss. At medium (100 mg/mL) and high concentration (150 mg/mL) and high flow rate of 70 mL/min still the mass transfer loss is dominant. Power density reaches at maximum values of 300 - 500 μW/cm2 at high flow rate but the cell shows high instability due to the dominant region is mass transfer loss (table 1).

Table 1 Characteristics of the PEMFC

Concentration (H$_2$S, mg/ml)	Flow rate ml/min	OCP (mV)	Time OCP Const. value	Power density (μW/cm^2)	Current density (μA/cm^2)
50	20	550	>3h	25	8.5
	70	300	~ 3h	42	12
100	20	575	30 min	322	23
	70	460	20 min	443	14
150	20	574	20min	518	57
	70	450	15 min	276	15

During conditions of operation in vessel with hydrogen sulfide solution are observed sulfur deposition. After dis-assembling, on the carbon paper (FDL) is deposited sulfur. In figure 3 is shown the sulfur distribution on FDL (image recorded with atomic force microscope NtegraPrima).
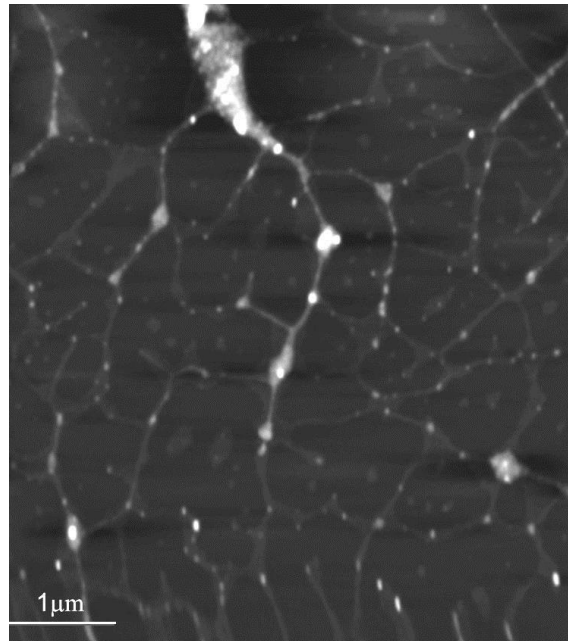
Fig. 3. Sulfur distribution on FDL (carbon paper) for 2 days in operation at 50 mg/L and 20 mL/min flow rate

The sulfur deposition on FDL induces a low durability and stability for this experimental set-up. In the same time, PEMFC with PtRu as anode catalyst could be an appropriate solution in recovering of hydrogen sulfide and conversion in sulfur from sulfurous waters.

4. Conclusion

The fuel cell designed with PtRu catalysts shows promising approaches for hydrogen sulfide recovering at low concentration of water solutions. Improvements need to be performed in sulfur exhausting in removing from deposition on the fluid diffusion layer. In addition, PEMFC with appropriate catalysts and geometries can be applied as a method for recycling wastewaters.

Acknowledgements

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