HIGH–TEMPERATURE FUEL CELLS, NOT PRECIOUS METALS AS CATALYSTS

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ABSTRACT

Results of the electro — oxidation of the gas mixture ($CO+CO_2+H_2$) in high — temperature are in this paper. Electrodes of these elements did not contain precious metals. EMS and the current density values obtained were respectively equal to IV and 20-30 mA/cm^2.

Keywords: electrochemical generator, fuel electrode, electro-oxidation, borides

1.0 Introduction

The issues of direct conversion of chemical energy of a fuel into electric power make a present-day problem with much importance [1].

An ordinary galvanic cell contains some volumes of active components which by their nature limits for the lifetime of such a cell. In a fuel cell (FC), the active components (i.e. fuel and oxidiser) are supplied continuously hence the lifetime of a cell is not defined by the stock of active components contained in a FC. That feature makes an essential advantage of FCs. For that reason it is not by chance that high-temperature fuel cells have been suggested as stand-by sources of power for spase ships [2].

It is known from thermodynamics [3] that the maximum work done can be defined as

$$A_{max}= -\Delta G \tag{1}$$

Where a change of the isobaric ΔG results from a chemical reaction occurring in an electrochemical system. The value of A_{max} can be presented as:

$$A_{max}=q\cdot E\cdot \tag{2}$$

were E - electromotive force (EMF) and $q = z\cdot F$ - volume of electricity conducted through that system (F- Faraday's constant). Then:

$$E= -\frac{\Delta G}{zF} \tag{3)}$$

According to the second principle of thermodynamics:

$$\Delta G = \Delta H - T\Delta S \tag{4}$$

and hence:

$$E = -\frac{\Delta H}{zF} + \frac{T\Delta S}{zF} \tag{5}$$

When molar enthalpy (ΔH) and entropy (ΔS) are known for the course of a reaction, electromotive forse (EMF) can be calculated for a fuel cell.

The efficiency factor for a FC can be calculated from the equation:

$$\eta = \frac{\Delta G}{\Delta H} = 1 - T \cdot \left(\frac{\Delta S}{\Delta H}\right) \qquad (6)$$

That can approach 100 % when the reaction does not result in any change of the number of moles of a gas, e.g.

$$C + O_2 = CO_2 \qquad (\Delta S = 0) \qquad (7)$$

Utilisation of low-temperature fuel cells faces a number of difficulties. Limitations appear at low temperatures (for aqueous electrolytes) which are imposed by the rules of kinetics. Moreover, the system suffers from considerable polarization losses which result from the formation of hydrogen peroxide at the oxygen-gas electrode [4]. Whenever considerable power is required from a cell, noble metals are frequently needed to be utilised.

2.0 BORIDES OF VARIABLE VALENCE METALS AS THE CATALYTIC AGENT OF FUEL ELECTRODE

Borides of variable valence metals were employed in the investigated cell as catalysts for the fuel electrode. These were produced directly at the metal-ceramic electrode by impregnating the electrode with a salt of applicable metal (Ni, Co, Fe) and its subsequent reduction with the alkaline solution of sodium borohydride (NaBH4)

$$Ni^{2+} + BH_4^{-} + 2OH^{-} - \overset{-}{e} \rightarrow NiB + 2H_2O + H_2 \qquad (8)$$

Lithium-nickel oxide made the oxygen-gas electrode which was obtained by impregnating the electrode with lithium acetate and its subsequent decomposition at 873 K over 6 hours.

$$xLiO_2 + (1 - x)NiO \rightarrow Li_xNi_{1-x}O + \frac{1}{2}xO_2 \qquad (9)$$

The metal-ceramic electrodes were produced by pressing powdered nickel (particle size for nickel powder – $130 \cdot 10^{-6}$ m) in a special mould, at the pressure of $P = 4{,}9 \cdot 10^{-6}$ N/m^2.

An eutectic mixture was used as the electrolyte. Its composition was: anhydrous Na_2CO_3 – 32 %; Li_2CO_3 – 32 %; TiO_2 – 8 %; calcium glass – 8 %; MgO – 20 %.

The pre-treatment of the electrolyte system covered the following procedure: magnesium oxide, titanium oxide, carbonates of alkaline metals and calcium glass were thoroughly mixed in a ball mill and baked at the temperature of 1173 K in order to provide complete intermixing and to remove any adsorbed water. The baked material was again subjected to comminution and to repeated baking. Generation of that paste-like electrolyte prevents penetration of molten carbonates into electrodes [5]. We have defined the following specification for the applicable electrolyte: melting point of 775 ± 5 K and density of $(2.15 \pm 0.05) \cdot 10^{-3}$ kg/m^3. We studied electrolytic oxidation of the ($CO + CO_2 + H_2$) gas mixtures with various percentages as well as the ($CO + CO_2$) mixtures. The gas mixture adopted for electrolytic oxidation represented a model for the fuel mixture obtained from catalytic steam reforming which processes hydrocarbon fuels:

$$C_xH_y + xH_2O \xrightarrow{Nicatalyst} xCO + (y/2 + x)\ H_2 \qquad (10)$$

That exothermic process yields a gas mixture with its enthalpy higher than that for the initial materials. The fuel mixture can also be produced in a different way, e.g.:

$$C_xH_y + \frac{x}{2}\ O_2 \xrightarrow{T=1423K} xCO + \frac{y}{2}H_2$$

The last reaction needs no catalyst [6].

The first series of experiments was based on the following gas mixture as the oxidising agent: CO_2 – 67 % and O_2 – 33 %, while another series of tests utilised just atmospheric air. The necessity to employ an admixture of CO_2 results from the chemical reactions which take place at the electrodes:

1. Cathode: $CO_2 + \frac{1}{2}\ O_2 + 2e \rightarrow CO_3^{2-}$
2. Anode: $CO + CO_3^{2-} \rightarrow 2CO_2 + 2e$

$$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e$$

The test stand for the study on electro-oxidation of gas mixtures comprised an electro-chemical generator, gas meters with the fuel and oxidising mixtures, respectively, and rheometers. The gas lines served as electric contacts at the same time. The electro-chemical generator was placed in a special electric oven wherein the temperature profile was controlled by a thermocouple. Gas was introduced only after the oven had been heated up to 473 K. The gas composition was controlled by means of a gas analyser while the gas velocity was adjusted on the basis of rheometer readings. As the rate of electro-oxidation of the fuel in the cell is dependent on the flow rate of the gas mixture, all the measurements have to be referred to the gas flow rate. Our measurements were taken at v = 5 ml/s.

The polarisation curves were plotted in accordance with the generally applicable method [7].

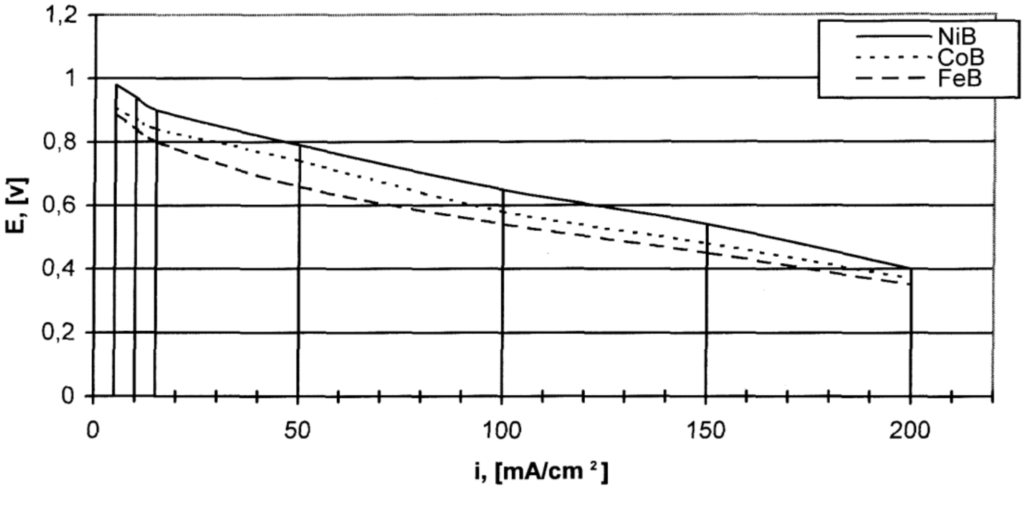

Figure 1. Rate of electro-oxidation of the gas mixture (20% CO – 50% H2 – 30% CO2) on the fuel electrode at temperature of 973 C

Typical polarisation curves for various catalysts at the temperature of 973 K were presented in Figure 1 and the relationship between the rate of electro-oxidation and temperature for the NiB catalyst was provided in Figures 2. The electromotive force calculated on the basis of the equilibrium composition of the fuel gas equals to:

$$E = E_0 + 0.992 \cdot 10^{-4}\, T \log \frac{P_{H_2} \cdot P_{O_2}^{1/2} \cdot P_{CO_2}^{k}}{P_{H_2O} \cdot P_{CO_2}^{A}} \qquad (12)$$

where $P^K{}_{CO_2}$ and $P^A{}_{CO_2}$ stand for CO_2 partial pressures at the cathode and anode, respectively.

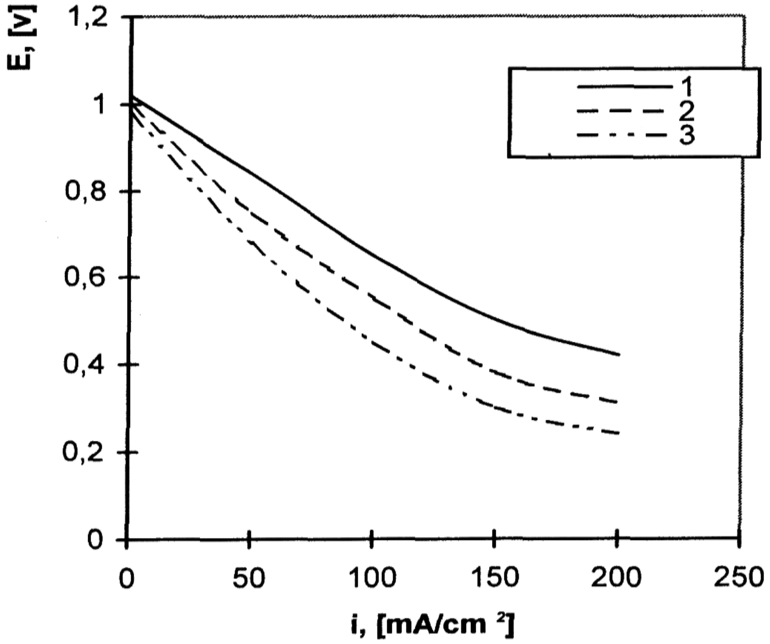

Figure 2. Rate of electro-oxidation of the (20 % CO – 50 % H2 – 30 % CO2) gas mixture on the NiB fuel electrode at various temperatures. 1 - 1073 K ; 2 - 973 K ; 3 - 873 K.

As can be seen in Figure 2, the rate of electro-oxidation of the gas mixture increases to follow the increasing temperature. That dependence was observed for all the borides studied.

The percentage of the fuel mixture actually affects EMF of the cell. However, the potential was lower for any mixture than for pure hydrogen, what was the case for all the borides, and the lower the hydrogen content in a mixture, the lower the potential was. When the ($CO + CO_2$) mixture with the concentration of CO = 70 % and higher was subjected to electro-oxidation, soot deposits could be observed on the electrode made of iron boride. That can be accounted for by shifting the chemical equilibrium of the reaction $2\,CO \rightarrow 2\,C + O_2$ to the right-hand side. All the studied cells yielded the current density of the order of 10-20 mA/cm^2 with the electromotive force of 0.80-1.08 V.

3.0 CONCLUSION

The general possibility to substitute FCs inplatinum by borides of variable valence metals, which are more readily available, was proved in this paper. That substitution material of the catalyst does not result in any noticeable change in the performance parameters of the fuel cell.

The use of a paste-like electrolyte made it possible in all the test runs to avoid any damage of the cell due to short circuit. No noticeable change was observed in the performance of the cell when air was employed instead of the (O_2 + CO_2) mixture. The cell was operated for 1000 hours with the fuel and (O_2 + CO_2) oxidising agent charged to it, and no considerable changes were observed in the specification of the cell. All the examined FCs yielded the current density of the order of 10-20 mA/cm^2 with the electromotive force of 0.80-1.08V.

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