Studies on Sodium Borohydride Fuel Cells

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Experimental results obtained with a sodium tetraborohydride (SBH) fuel cell equipped with a Nafion 117 membrane are presented in this paper. For both electrodes, anode (Pt-Ru/C) and cathode (Pt/C), the same catalyst loading of 1 mg cm\(^{-2}\) has been used. The increasing of performance has been realized by the optimization of the operating parameters: temperature, SBH concentration, reactants flow and oxidant nature (air or oxygen). In order to increase the contact region between reactant – catalyst layer – membrane, with a favorable effect on fuel cell performance, the Nafion 117 was added in the catalyst layer. Maximum power density of over 74 mW cm\(^{-2}\) has been achieved at 100°C with oxygen as oxidant.

Keywords: fuel cell, sodium borohydride fuel cell, proton exchange membrane, sustainable power supply

Sodium borohydride (SBH) has been developed as a viable alternative to hydrogen or methanol for fuel cells [1,2]. One of the advantages of sodium borohydride fuel cells (SBHFC) is given by the high chemical stability of the fuel in alkaline media, making it easy to store and handle [3]. Another advantage refers to the fact that the reaction products of the anodic reaction do not contain carbon oxides, which eliminates the risk of catalysts poisoning [1,3,4]. Also, it is not to neglect that during functioning carbon dioxide is not eliminated in the atmosphere. Besides, the sodium metaborate resulted during the energy generation is a non-toxic and non-polluting compound [5]. Another interesting aspect is the possibility to regenerate the reactant from the reaction product, realizing a closed transformation cycle [6]. The disadvantage of high cost of sodium borohydride could be reduced, since according to some recent researches [7] it is possible to lower the production costs to 1 USD/kg.

The electrochemical processes taking place at the electrodes during the electrical energy generation are described by the following equations:

- anodic oxidation of borohydride ions:
  \[ \text{BH}_4^- + 8\text{OH}^- \rightarrow \text{BO}_2^- + 6\text{H}_2\text{O} + 8\text{e}^- \qquad E^o = -1.24\text{ V} \]  
- cathodic reduction of oxygen:  
  \[ \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \qquad E^o = +0.40\text{ V} \]

The overall reaction implies the transfer of 8 electrons for each borohydride ion:

\[ \text{BH}_4^- + 2\text{O}_2 \rightarrow \text{BO}_2^- + 2\text{H}_2\text{O} \qquad E^o = 1.64\text{ V} \]

Based on the standard potential values of the electrode processes it may be concluded that the electromotive force of SBHFC (1.64 V) is higher than the electromotive force of hydrogen (1.24 V) or methanol (1.21 V) fuel cells [1,8].

However, the performance of direct sodium borohydride fuel cell is affected by the secondary reactions taking place at the electrodes. It is noteworthy to mention the combustion hydrolysis reaction described by the following reaction:

\[ \text{BH}_4^- + 2\text{H}_2\text{O} \rightarrow \text{BO}_2^- + 4\text{H}_2\]

For this reason, the solution fed in the anodic compartment is alkalinized with sodium hydroxide, since the reaction rate is lower in alkaline media.

The aim of this paper was to study the influence of the operating conditions on the performances of a SBHFC. The functioning parameters of the constructed fuel cell were optimized based on a detailed study on the influence on several factors, such as: temperature, fuel concentration, reactant flow and oxidant nature.

The SBHFC was constructed using a low catalysts loading (Pt-Ru/C) of 1 mg cm\(^{-2}\) for both the anode and cathode. A cation exchange membrane (Nafion 117) was used to reduce the SBH crossover from the anodic to the cathodic compartment, a phenomenon which occurs with anion exchange membranes [9].

Experimental part

Experimental measurements were carried out on a SBHFC with a cross-sectional area of 9 cm\(^2\). Details about the construction of the fuel cell are given elsewhere [10].

In case of the Nafion 117 membrane the electrical current through the membrane is given by the migration of Na\(^+\) cations from the anodic towards the cathodic compartment. Due to the oxidation reaction (1) the hydroxyl concentration in the anodic compartment decreases but it may be compensated by recirculation of the sodium hydroxyl solution resulting at the cathode.

The fuel cell was tested in a self designed set-up containing a potentiostat/galvanostat. Anodic polarization curves were recorded using as reference the internal hydrogen electrode, according to the procedure developed by Ren et al. [11,12]. The anode was polarized galvanostatically in the potential range 0 ¿ ± 700 mV vs. the internal hydrogen electrode. The overall polarization curves were recorded galvanostatically as well. The anolyte was prepared using sodium borohydride (SBH, p.a.) and sodium hydroxide (NaOH p.a.) purchased from Merck.

Results and discussion

The influence of several parameters, such as working temperature, SBH concentration, reactant flow and nature of oxidant (air or oxygen) on the performances of the constructed fuel cell have been studied extensively. Temperature influence...
The influence of temperature on the cell voltage and current density response was evaluated from the anodic and global polarization curves obtained at different working temperatures, using air and oxygen as oxidant.

Measurements were carried out using a 1 mol L\(^{-1}\) SBH solution with a fuel solution flow rate of 2.78 cm\(^3\) min\(^{-1}\) and the oxidant flow rate of 0.4 cm\(^3\) min\(^{-1}\). No exterior pressure was applied to the cathodic compartment.

Figure 1 shows the anodic polarization curves obtained at 60°, 80° and 100°C. It may be concluded that temperature has a substantial effect on the limiting currents of SBH oxidation and it is to be expected that the same influence will affect the overall cell performance.

The increase of the anodic limiting current with the temperature may be explained by intensification of the diffusion processes of fuel towards the active reaction centres and of the reaction products away from the catalytic anodic site.

At the same time, several negative effects are present, affecting the proper functioning of fuel cells. Thus, the temperature increase influences the hydrolysis degree of SBH and correspondingly higher quantities of SBH will crossover the membrane, shifting the cathode potential to more negative values, which in turn lowers the electromotive force of the fuel cell.

Similar results have been obtained in case of oxygen used as oxidant. It should be however mentioned that the power supplied in this case is higher, due to the higher amount of oxygen diffusing at the cathodic catalytic layer.

The power densities and the current densities corresponding to the maximum power density vs. temperature are given in figure 3 for the sodium borohydride – oxygen fuel cell and for the sodium borohydride – air fuel cell.

The results indicate that the global effect of temperature increase on the fuel cell performance is benefic. Thus, the power density increases from 58 mW cm\(^{-2}\) at 60°C to 74 mW cm\(^{-2}\) at 100°C, while the current density corresponding to the maximum power density increases from 102 mA cm\(^{-2}\) to 136 mA cm\(^{-2}\). Comparing the results from figure 2 and 3, it may be observed that, independently on the operating temperature, the use of oxygen allows to achieve superior performances. For example, at 60°C, the effect of using oxygen instead of air as oxidant is the increase of the power density with approximately 20%. This tendency is maintained for all the investigated operating temperatures of the fuel cell.

Figure 2 shows the overall polarization curves obtained at the same operating temperatures (60, 80, 100°C) using air as oxidant, as well as the corresponding calculated power densities.

The data presented in figure 2 indicate an increase of the cell performance with increasing temperature. This behaviour may be explained since the temperature increase leads to the activity increase of both catalytic layers correlated with an intensification of the mass transfer processes, thus to the acceleration of both electrode processes.

Simultaneously, the hydrolysis degree of the solid polymer electrolyte increases, which is equivalent to the lowering of the internal resistance of the membrane-electrode assembly, with benefic effects on the performances of the fuel cell.

Based on the experimental results it may be concluded that the benefic effects of temperature increase are predominant and the undesired effects due to hydrolysis and SBH crossover through the membrane are practically negligible. As a matter of fact, it can be considered that a part of the hydrogen obtained through the SBH hydrolysis is oxidized at the anode, diminishing the fuel losses in secondary processes.
Influence of SBH concentration

Besides temperature, the concentration of the fuel also influences the performances of the fuel cell. To study the influence of this factor, the anodic and overall polarization curves were recorded for different concentrations of the SBH solution (0.125; 0.5; 1; 1.5 and 2 mol L⁻¹ NaBH₄). Both air and oxygen were used as oxidant. All the measurements were performed in the following conditions:
- temperature 80°C;
- oxidant flow 0.4 L min⁻¹;
- fuel flow 2.78 mL min⁻¹;
- no exterior pressure was applied to the cathodic compartment.

Figure 4 gives the anodic and overall polarization curves obtained with SBH solutions of different concentrations, using air as oxidant.

At low SBH concentration, a net limiting current can be observed, due to the limitation of the SBH ions transport, which at low concentrations is done exclusively by diffusion.

At higher SBH concentrations the anodic current density increases up to a certain limit, since at higher current densities the pH of the solution in the reaction zone decreases, favouring the SBH hydrolysis with the formation of hydrogen gas which blocks the access path of the fuel to the reaction site. The limitation of the anodic current density is partly due to the SBH crossover through the membrane. This fact is responsible for the mixed potential at the cathode, shifting the cathode potential to more negative values and reducing the performances of the fuel cell.

The power density generated by the fuel cell increases significantly when the SBH concentration changes from 0.125 M to 0.5 M. A further increase of the concentration leads to the enhancement of the negative influences, which is equivalent to the decrease of the power density produced by the fuel cell. A similar behaviour has been observed in case of using oxygen as oxidant. Figure 6 gives the overall polarization curves and the calculated power densities for different SBH concentrations when using oxygen as oxidant.

Fig. 6. Overall polarization curves and power densities at different SBH concentrations for the NaBH₄/O₂ fuel cell

The results obtained with oxygen as oxidant are comparable to those obtained with air. The performances of the fuel cell increase with the fuel concentration until a maximum is reached at 0.5 mol L⁻¹. Afterwards, any further increase of the concentration leads to the diminishing of the performances.

Analysing the data shown in figures 5 and 6, it can be observed that the maximum power is obtained for a concentration of 0.5 mol L⁻¹ SBH, independently on the nature of the oxidant. Thus, in case of air as oxidant a maximum power output of 92 mW cm⁻² is reached and in case of oxygen as oxidant the maximum power output increases up to 104 mW cm⁻². Also, the peak power current is influenced by the SBH concentration. Increasing the SBH concentration from 0.125 to 0.5 mol L⁻¹ the peak power current shifts from 106 mA cm⁻² to 189 mA cm⁻² (for oxygen as oxidant). In both cases (air and oxygen) a further increase of the SBH concentration has the same effect, shifting the peak power density to lower values.

Influence of the reactants flow

Subsequently, the effect of reactants flow on the performances of the fuel cell has been studied. The anodic and overall polarization diagrams have been recorded for different fuel and oxidant flows.

The influence of the anodic fuel flow has been studied under following conditions:
- SBH concentration 1 mol L⁻¹;
- working temperature 80°C;
- oxidant flow 0.4 L min⁻¹;
- no exterior pressure was applied to the cathodic compartment.

Figure 7 shows the anodic and overall polarization curves obtained for different fuel flows and with oxygen as oxidant.

The data presented in figure 7 indicate a strong effect of the anodic flow on the cell performances. A limiting current can be observed at low anodic flows, due to the limitations of the mass transport in the anodic catalytic layer. The increase of the anodic flow leads to a slight improvement
of the performances, explained by an improved mass transport at the anode level. The overall behaviour of the fuel cell was assessed from the overall polarization curves and the corresponding calculated power densities. Figure 8 shows the power densities obtained for different anodic flows in case of oxygen as oxidant.

It has been found that the power density increases with the anodic flow until a maximum value. A further increase of the anodic flow has a detrimental effect, since the negative influences become more significant and the final effect is a slight decrease of the maximum power outlet of the fuel cell. A similar behaviour was registered for air as oxidant (fig. 9). It should be mentioned that the performances obtained in this case are inferior, since the oxygen concentration is lower.

The variation of the cathodic flow has the same effect on the power densities as on the overall polarization curves. The use of air as oxidant leads to a similar behaviour of the fuel cell.

The performance of the SBHFC has been evaluated during continuous operation. Five different catalyst loadings have been chosen to assure a current output between 300 and 1500 mA. During short term continuous tests the generated current density was monitored each 5 min in the first 6 h, after that each 30 min for the next 5 h, and finally after 10 h. This pattern has been repeated until a total time of continuous functioning of 100 h. A
representative example on the variation of the current density as a function of operating time is given in figure 12. The results of the short term continuous tests indicate that the SBHFC is stable over a fairly long period of time during the energy generation in the external circuit.

Conclusions
The results of the present study have shown that the performances of the SBHFC equipped with a cation exchange membrane (Nafion 117) are strongly influenced by several factors, such as: operating temperature, SBH concentration, nature of the oxidant, fuel and oxidant flow. The use of cation exchange membrane allows increasing the operating temperature, which contributes to the intensification of the electrode processes. However, the performances obtained with the SBHFC equipped with a cation exchange membrane are lower than those obtained with an anion exchange membrane (ADP) [13]. The temperature has a complex influence on the operation of SBHFC. Increasing the temperature leads to the intensification of the electrode processes and to the enhancement of the catalytic activity of catalyst layers with positive effects on the performances. Simultaneously, the hydrolysis degree of SBH increases, as well as the amount of fuel which passes through the membrane, with detrimental effects on the performances of the fuel cell. The optimal fuel concentration in case of SBHFC equipped with anion exchange membrane is about 2 mol L⁻¹, while for the SBHFC equipped with cation exchange membrane the optimal fuel concentration does not exceeds 0.5 mol L⁻¹. Concerning the oxidant, it has been shown, as expected, that using oxygen instead of air significantly improves the performances of the fuel cell.

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