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Experimental metal hydride-air fuel cell

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Commercially available metal hydride alloys of the AB_5-type and air gas-diffusion electrodes were used as anode and cathode materials for the experimental fuel cell where $NaBH_4$ is used as hydrogen supply.

Air gas-diffusion electrodes with identical gas-supplying layer, and catalytic layer from pyrolysed CoTMPP were prepared, characterized, and selected as suitable for cathode material.

Experimental low-temperature borohydride fuel cell was constructed and optimized. The exploitation of the developed cell is safe, since the fuel is dissolved in the electrolyte and there is no need to work with compressed or condensed hydrogen.

The proposed fuel cell structure comprises an experimental plastic two-electrode electrochemical cell. The obtained operational characteristics indicated for its possible application as a real fuel cell.

Key-words: metal hydride alloys, air gas-diffusion electrodes, borohydride fuel cell

INTRODUCTION

The fuel cell represents an electrochemical energy transformer. It directly transforms chemical energy into thermal and electric. There are different types of fuel cells, each one having an optimal application. They are classified mainly by the type of used electrolyte or in terms of their working temperature.

Methanol and sodium borohydride ($NaBH_4$) are important fuel candidates for portable and mobile applications at an ambient temperature. Since the late 1990s, $NaBH_4$ is presented as a promising hydrogen storage material and an attractive fuel to use in the so-called Direct Borohydride Fuel Cell (DBFCs) [1–3]. The resent rapid progress in the development of DBFCs is reviewed in [4]. However, the discussion of DBFC was brief. This is not surprising since there is little literature published before the year of 2000.

A direct borohydride fuel cell uses the $NaBH_4$ solution as fuel, and electricity is produced via the following reaction:

$$NaBH_4 + 2O_2 \rightarrow NaBO_2 + 2H_2O \qquad E^0 = 1{,}64 \text{ V}$$

The DBFC can be compared, thermodynamically and energetically, to the direct methanol fuel cell (DMFC) and to the polymer electrolyte membrane fuel cell (PEMFC). The comparison is favourable to the DBFC technology [5]. The DBFC theoretical open circuit voltage of 1.64 V is higher than those of the DMFC (1.21 V) and the PEMFC (1.23 V).

In principle, the DBFC can only work in an alkaline environment because BH_4^- is unstable in neutral or acidic medium. The electrocatalysts for both, the anode and the cathode in the DBFC with alkaline fuel, are not necessarily limited to noble metals [6]. Low cost catalysts can be expected to result in a good performance. The research of catalysts for the DBFC anode has been well documented [7, 8]. Non-platinum cathode catalysts such as MnO_2 [9], Co-porphyrins [10], perovskite oxides [11], etc. have been studied extensively. Ma and co-workers [12] demonstrated DBFC in which iron phtalocyanine is used as a cathodic catalyst, and hydrogen storage alloy can be used as an anodic catalyst.

In this work we present an experimental metal hydride air fuel cell which uses complex alkaline hydrides as a fuel. This fuel cell will demonstrate the possibility to use conventional metal hydride alloys as anodes, on one hand, and air gas diffusion electrodes as cathodes, on the other hand.

EXPERIMENTAL

The proposed fuel cell structure comprises an experimental plastic two-electrode electrochemical cell. The anode and the cathode are placed in an electrolyte space, filled in with electrolyte. In most experiments 6 or 7 M KOH, containing 1M $NaBH_4$, was used as working electrolyte.

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Three types of commercial AB_5 metal hydride alloys, AKL-86, AKL-1002, and AKL-1519 (Triebacher, Germany) were investigated as a potential anode material in the DBFC. The initial alloys were pre-treated in a $NaBH_4$ solution (12–24 h), filtered, mixed with PTFE (polytetrafluorethylene) paste, and coated upon Ni foam.

The air gas-diffusion electrodes with gas layers are prepared from a special hydrophobic material, carbon black P 1042 and PTFE by a special technology. Four types of catalysts are used for the catalytic layer: VS 50-CoTMPP 700, pyrolyzed CoTMPP, AC CoNi, and NORIT NK. The catalytic layers of all electrodes are made from 20 mg/cm^2 of catalyst. For the initial experiments, the air electrodes are mounted on the experimental electrochemical cell filled in with 7M KOH electrolyte. The cell is equipped with Zn reference electrode and counter electrode of stainless steel. The characteristics of the electrodes are measured when operating on air or on pure oxygen.

Round shared anode and cathode with geometric area of 7.5 cm^2 and effective working area of about 5 cm^2 were prepared. The electrodes were sintered at 280º C under pressure of 200 kg/cm^2 in the course of 2 min. The electric current collector (Ni-plated Fe grid) was pressed on each electrode.

The electrochemical measurements with the described fuel cell were performed using computerized potentiostat – galvanostat, GAMRY module, and various digital multimeters.

RESULTS AND DISCUSSION

The polarization curves of the air gas-diffusion electrodes, operating on air and pure oxygen in alkaline electrolyte, are presented in Figure 1 (a. and b.). The air electrodes are prepared with identical gas-supplying layers. Four types of catalysts are used for the catalytic layer. It is well known that the performance of the air electrode is influenced not only by the activity of the catalyst, but also by all transport processes, taking place in its porous structure. Transport hindrances in the electrode are function not only of its overall structure, but also of the porous structure and the surface properties of the catalyst. Methods for diagnostic the activity and the transport properties of the air gas-diffusion electrode are proposed. It is theoretically and experimentally shown that the value $\Delta E = E_{oxygen} - E_{air}$ can be used as a measure for the transport hindrances in the air electrode [13, 14].

The activities of the catalysts are compared based on the experimental Tafel plots (Fig.2). It is seen that the most active catalysts are the VS 50-CoTMPP 700 and the pyrolyzed CoTMPP.

The effect of the cell structure upon the electrochemical behaviour was studied in detail. The long-term experience in the development,

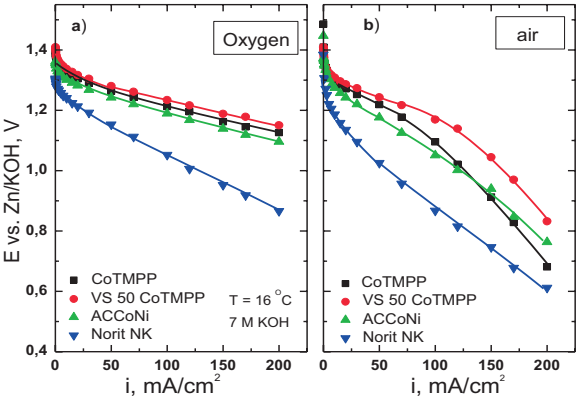

Fig. 1. Polarization curves of air electrodes with catalysts NORIT NK, VS 50-CoTMPP 700, pyrolyzed CoTMPP and AC CoNi, operating with pure oxygen (a) and with air (b).

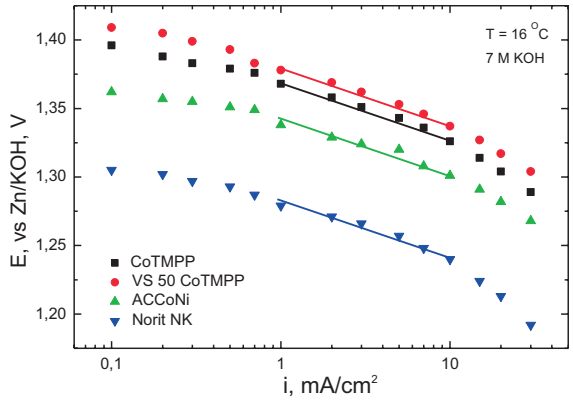

Fig. 2. Tafel plots of the air electrodes with the investigated catalysts.

Fig. 3. Photograph of the described electrochemical cell.

testing, and construction of various types of power sources [15] will serve as a base for the successful construction of the experimental borohydride fuel cell, presented in this work (Fig. 3).

The current voltage and the corresponding power characteristics of the cell are given in Fig. 4. The power values are over 140 mV for the cell equipped with an AKL-86 anode.

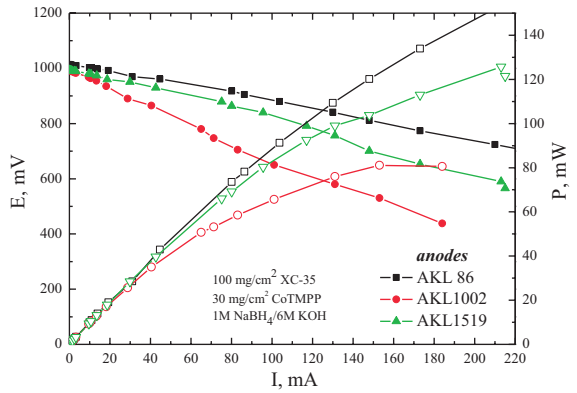

Fig. 4. Polarization and power characteristics of a borohydride fuel cell

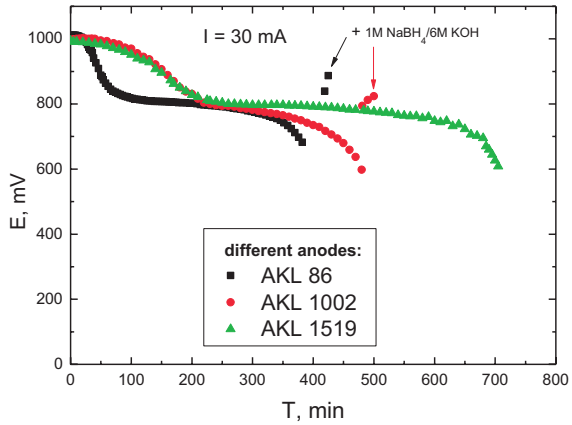

Fig. 5. Discharge curves of the experimental fuel cell.

Borohydride participation in the electrode reaction is clearly evident when we compare the discharge curves, obtained in the alkaline electrolytes which contain sodium borohydride (Fig.5). The immersion of different type of electrodes in sodium borohydride solution leads probably to a hydrogen absorption or hydride formation like the electrochemical charging does. This also explains the appearance of the second plateau on the curves as a result of the electro-oxidation of hydrogen, absorbed in the electrode.

For the application in practice, however, more detailed experiments and data analysis for optimization of the operation conditions such as the borohydride concentration, temperature, etc., should be performed with electrodes of AKL-86, AKL-1002, and AKL-1519 alloys.

CONCLUSIONS

An experimental metal hydride-air fuel cell was constructed, tested, and optimized. AB_5 – type metal hydride alloys and air gas-diffusion electrodes were used as electrode materials. The current-voltage, power, and discharge characteristics of the described system render the characteristics suitable for use in low-temperature borohydride fuel cells.

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ЕКСПЕРИМЕНТАЛЕН ГОРИВЕН ЕЛЕМЕНТ МЕТАЛЕН ХИДРИД-ВЪЗДУХ

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(Резюме)

Метал хидридни сплави тип AB_5 и въздушни газодифузионни електроди са съответно анодни и катодни материали в експериментален горивен елемент. $NaBH_4$ е използван за доставяне на водород.

Изготвени, охарактеризирани и селектирани са подходящи за катодни материали въздушни газодифузионни електроди. Те са с идентичен газов слой и каталитичен слой от пиролизиран CoTMPP.

Конструиран и оптимизиран е експериментален нискотемпературен борхидриден горивен елемент. Получените работни характеристики показват възможности за бъдещо приложение като реален горивен елемент.