METAL-HYDRID CATALYST FOR ALKALINE FUEL CELL

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ABSTRACT

Electrode material was prepared by mixing carrying substrate (different types of carbon) and metal-hydrid catalyst dust. Physical properties of them were measured and compared with the best possible values obtained in ideal case. Reviewing the results material suitability for alkaline fuel cell electrode were pinpointed. Preparing method, electrode cell montage and measuring methods were investigated. H₂-O₂ system was used.

1. INTRODUCTION

Main point of this research was to find out suitability of electrode substances with metalhydrid catalyst as electrode material for alkaline fuel cells.

In present platium is used as a catalyst in almost all commerical applications. As production cost will be one of the main challenges for the commercialization of fuel cells, an important research and development goal is to increase efficiency of the fuel cell by producing efficient fuel cell electrodes beside lowering the cost of the cell stack components [1-3]. Today the most important cost contribution comes from the platinum content, so it is essential to the optimum platinum content to overcome the restrictions coming from the cost.

Generally, porous gas diffusion electrodes are used for both anode and cathode in fuel cell systems. They do not only serve as a reaction zone for energy conversion, but also provide pores for gas transport and act as a barrier to the electrolyte. Therefore, gas diffusion electrodes must have a large number of active sites by a thin and porous structure with a high surface area.

For preparation of an electrode material different types carbon substrate were used (exfoliated graphite, nanosorb, chezacarb A, chezacarb B). Into this mixture metal-hydrid catalyst was added. Mixture was layed on rotation disc elektrode (RDE). For measuring was used half-cell system with standard calomel electrode (SCE). Measuring was performed for positive and negative electrode (using O_2 (g) from air, pure H_2 (g)). By using cyclic voltammetry method cyclicvoltamograms were acquired. Analyzing these graphs were obtained halfwave potentials and limiting currents for each sample. Measured values were compared with an ideal conditions.

2. EXPERIMENTAL

In the first step detailed description of preparation of the electrode material will be showed. Second step describes measuring method. Finally the results will be discussed.

Standard electrode potencial E_0 at 25 °C measured against standard hydrogen electrode (SHE) is 0,401 V for reduction of O_2 (1)

$$O_2 + {}^{\prime}H_2O + {}^{\prime}e^- \rightarrow DH^-, \qquad (1)$$

and -0,828 V for oxidation of $H_2(2)$

$$2\mathrm{H}_{2} + 4\mathrm{OH}^{-} \rightarrow 4\mathrm{H}_{2}\mathrm{O} + 4e^{-}, \qquad (2)$$

Overall maximum generated cell voltage by this reaction is 1,229 V [4,5]. In a half-cell and by using SCE (+0,244V against SHE) ideal potentials have to be recomputed:

For oxidation of H_2 it means -0.828V - 0.244V = -1.072 V (vs. SCE).

For reduction of O₂ it means 0,401V - 0,244V = 0,157 V. Because of air oxygen was used for measurement (O₂ in air is 23,2 % wt) is needed to recount influence of this change of concentration by Nernst equation (3).

$$E = E_0 - \frac{0,0592}{4} \log \frac{[O_2]}{0,232[O_2]}$$
(3)

Ideal potential for reduction of O₂ is + 0,144 V (vs. SCE).

2.1. PREPARATION OF AN ELECTRODE MATERIAL WITH METAL-HYDRID CATALYST

Base of an electrode substances were different types of carbon substrates. Four types of carbon were used: Exfoliated graphite, Nanosorb, Chezacarb A, Chezacarb B. Each of carbon substrate has its own properties.

Into carbon substrate was added metal-hydrid catalyst dust in certain weight ratio (wt. 33%, wt. 0%) all together in beaker with distillated water. This mixture was heated (80 °C) and stirred (magnetic stirrer) together for 30 minutes. Mixture was filterated through filtering paper. This squash was mixed with wt. 4% teflon to get better consistency. After that substance was layed on RDE in 1 mm thickness and putted to heater for 30 minutes with temperature around 80 °C. Rest of water has been vaporized and electrode was prepared for measurement.

2.2. MEASURING METHOD

For measuring was used three electrode half-cell system connected to a potenciostat μ -AUTOLAB PGSTAT10. Cyclic voltammetry method was used. As a electrolyte was used 2M KOH. As reference electrode was used SCE (Standard calomel electrode). Measuring cell is demonstrated on figure 1.

First measuring on a negative electrode was performed and solution was bubbled by H_2 (g). Voltage range was from -0,4 V to -1 V and back (1 cycle) through a scan rate 1 mV/s.

After that was applied measuring with gageus nitrogen N_2 to eliminate possible sideway reactions, which are not put together with oxidation of H_2 . Nitrogen is neutral gas for this case and also clean all residual previous gas. Identical voltage range as for hydrogen was used.



Figure 1: Scheme of measuring compartment (1. RDE (working electrode), 2. SCE (reference electrode), 3. Platinum (auxiliary electrode), 4. inflow gas tube)

Measuring system for positive electrode was bubbled by air. Voltage range was from 0,15 V to -0.6 V and back (1 cycle) through a scan rate 1 mV/s. Again after measurement of the positive electrode same measuring with $N_2(g)$ was applied, but with voltage range corresponding to oxygen voltage range. N_2 curve was substracted from H_2 curve or O_2 graph. Observed parametrs were half-wave potential $E_{0.5}$ and a limiting current i_{lim} .

The best measured results for negative electrode shows figure 2, for positive electrode figure 3.



Figure 2: Cyclic voltammogram of nanosorb substrate with 33% wt. of an catalyst. Scan rate was 1 mV/s. Middle dash-and-dot line shows the point of reading halfwave potential $E_{0.5}$ and limiting current i_{lim} on a forwards wave.



Figure 3: Cyclic oltammogram of nanosorb substrate with 33% wt. of a catalyst. Scan rate was 1mV/s. Middle dash-and-dot line shows the point of reading halfwave potencial $E_{0.5}$ and limiting current i_{lim} on a backwards wave.

2.3. RESULTS

In this thesis were measured properties of electrode substances (carbon substrate and metal-hydrid catalyst).

The substrate, which provided highest voltage for positive electrode is Nanosorb with wt. 33 % of a catalyst, see Tab 1. This type of electrode can afford -0.18 V (vs. SCE). Loss from ideal state is 0,324 V (26%). Limiting currents were almost the same for all substances. After adding metal-hydrid catalyst to substance, limiting current increased by 20% with exfoliated graphite and chezacarb A, and by 65% with nanosorb and chezacarb B, but practically had not any effect to potential changes.

Substrate	positive electrode O ₂		
	E _{0.5} [V]	i _{lim} [A]	alpha *n
Nanosorb	-0.18	1.7E-04	0.85
Chezacarb B	-0.19	1.9E-04	0.62
Chezacarb A	-0.19	1.4E-04	0.60
Exfoliated graphite	-0.21	1.9E-04	0.97

Tab 1: Comparison table of samples with different substrate in accordance to $E_{0.5}$ for positive electrode (33 % wt. of a catalyst, potentials measured vs. SCE).

Results of negative electrode substances are discutable. Best value of potential, -0.970 V, provided substance Nanosorb with wt. 33 % of catalyst. Loss from ideal state is 0,1 V (9%). But its limiting current was very low, 1.5E-5 A. Best value of limiting current had Chezacarb B, 5.2E-4 A, with value of potential -0.70 V. Majority measured values could not be read, catalytic reactions not progressed in these substrates.

Substrate	negative electrode H ₂		
	E _{0.5} [V]	i _{lim} [A]	alpha *n
Nanosorb	-0.970	1.50E-05	2.31
Chezacarb B	-0.70	5.2E-04	0.70
Chezacarb A	-	-	-
Exfoliated graphite	-	-	-

Tab 2: Comparision of samples with different substrate in accordance to $E_{0.5}$ (33 % wt. of a catalyst, potentials measured vs. SCE).

3. CONCLUSION

According to all results of measurement was not found suitable substance for negative electrode of the fuel cell. Although some results provided substance with nanosorb substrate, half-wave potential could be read only from one branch of voltammogram, so result is not so trustable. Its consider if measuring method is suitable in this case.

The substance nanosorb with wt. 33 % of catalyst provided value $E_{0.5}$ = -0,18V for positive electrode. This value means loss 0.32 V. Effectivity of the fuel cell using this electrode will be decreased by 26 %.

Catalytic material based on metal-hydrid composition was found as non effective for using in fuel cell systems.

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REFERENCES

- Shibli, S., Noel, M.: Development and evaluation of platinum-ruthenium bimetal catalyst based carbon electrodes for hydrogen-oxygen fuel cells in NaOH Media. J Power Sources 1993; 45:139±52.
- [2] Bevers, D., Wagner, N., von Brake, M.: Innovative production procedure for low cost PEFC electrodes and electrode membrane structures. In: Hydrogen Energy Progress XI, Proceedings of the 11th World Energy Conferences, 1996, 2. p. 1767-76.
- [3] Yasuda K, Amine K, Mizuhata M, Keisuke O, Takenaka H. Material research on polymer electrolyte fuel cell. In: Hydrogen Energy Progress XI, Proceedings of the 11th World Energy Conferences, 1996. 2. p. 1933-39.
- [4] Berger, C.: Handbook of fuel cell, Prentice-hall, Inc., Englewood Cliffs, New Jersey, USA, 1968, p. 20-21
- [5] Antropov, L.: Teoretical electrochemistry, Mir Publishers, Moscow, CCCP, 1972, p.33