INFLUENCE OF DIFFERENT PH MEDIUM IN AFC POSITIVE ELECTRODE PREPARATION

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ABSTRACT

In this paper were obtain electrocatalic substanes based on carbon black carrier with MnO_x catalyst as a AFC positive electrode material. Manganese oxides were reduced on carbon black from KMnO₄. This reduction was performed in medium with different pH factor. The aim was find if different pH factor has influence in reduction KMnO4 on carbon black 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 $(C+MnO_x)$ different molarity of KOH, respectively H_2SO_4 , were used. Mixture was layed on rotation disc elektrode (RDE). For measuring was used half-cell system with mercury mercury oxide electrode (HgHgO). Measuring was performed for positive electrode (using O_2 (g), 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)

$$O_2 + 2H_2O + 2e^- \rightarrow 4OH^-, \qquad (1)$$

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 HgHgO (+0,113V against SHE) ideal potentials have to be recomputed:

For oxidation of H_2 it means -0.828V - 0.113V = -0.941 V (vs. HgHgO).

For reduction of O_2 it means 0,401V - 0,113V = 0,288 V.

Ideal potential for reduction of O₂ is + 0,288 V (vs. HgHgO).

PREPARATION OF AN ELECTRODE MATERIAL WITH METAL-HYDRID CATALYST

Catalytic substance was prepared by reduction KMnO₄ on carbon black (Chezacarb A). 1g of carbon black was stirred up in 300 ml 1M, 0,5M, 0,1M KOH (or H₂SO₄) solution (6 samples). Substance was heat up to boil point. After that 1,46g of KMnO₄ was added. Substance, which arised after 5 mins of boiling, was decanted, filtrated and dried up for 5 hours in 130 °C. After that ink for measuring was prepared. Ink contained 10mg prepared substance, 0,6ml destilled water, 0,3ml izopropylalcohol, 4ul supspense PTFE (60% Sigma-Aldrich). Ink was twice homogenised for 9 mins in ultrasonic bath. 5ul of ink was added to glassy carbon RDE (r=1,5mm). Elctrode was dried up for 15 mins in 130 °C. Electrochemical measurement was realised on RDE by cyclic voltametry method in three elctrode engagement. Measuring cell is demonstrated on figure 1. Counter electrode was used (+0,113 V vs. NHE). 1M KOH electrolyte was used and was bubbled by oxygen and nitrogen.

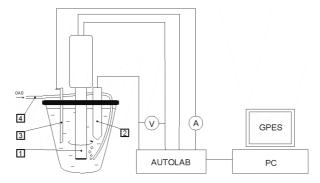


Figure 1: Scheme of measuring compartment (1. RDE (working electrode), 2. HgHgO (reference electrode), 3. Platinum (auxiliary electrode), 4. inflow gas tube)

3. RESULTS

All results are sumarized in Table 1 and oreder by lowest value $E_{0,5}$. On Figure 2 cyclic voltamograms are seen. Each one matches different molarity of acid (resp. basic) solution, in which reduction of KmnO₄ took place.

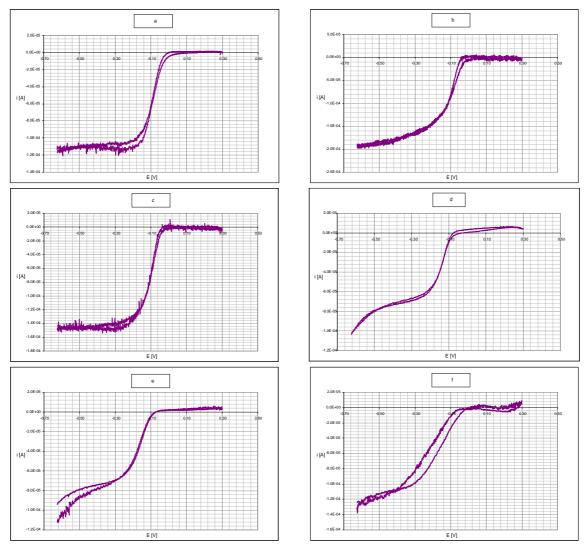


Figure 2: Voltammograms of reduction of O₂(-N₂) (HgHgO ref.electrode), MnO_x catalyst, 1M KOH electrolyte, rotation speed 500 rpm, scan rate 1mV/s. Preparation in a) 1M KOH b) 0,5M KOH c) 0,1M KOH d) 1M H₂SO₄ e) 0,5M H₂SO₄ f) 0,1M H₂SO₄

Material (medium pH	E _{0,5} [V] vs. HgHgO	E _{onset} [V] vs.HgHgO	i _{lim} [A]	αn [-]
C+MnO _x (0,5M KOH)	-0.078	-0.031	1.10E-04	1.10
C+MnO _x :(1M KOH)	-0.085	-0.030	1.10E-04	0.52
C+MnO _x (0,1M KOH)	-0.088	-0.045	9.80E-05	1.40
C+MnO _x (1M H ₂ SO ₄)	-0.132	-0.086	5.49E-05	1.42
C+MnO _x (0,5M H ₂ SO ₄)	-0.155	-0.098	6.29E-05	0.99
C+MnO _x (0,1M H ₂ SO ₄)	-0.181	-0.050	9.16E-05	0.47

Tab 1: Properties of electrode materials sorted by E0,5,O2 reduction, scan rate 1 mV/s

4. CONCLUSION

Measured values $E_{0,5}$ i Eonset are more negative with H_2SO_4 preparation than with KOH. Values ilim are also lower. This point out that reduction KMnO₄ on carbon black doesnt work fine in acid mediums. Acid mediums are not suitable for reduction KMnO₄. KOH results are not obvious. $E_{0,5}$, Eonset and ilim values almost not differ from each other. Only one criterium can be charge transfer coefficient αn , which is highest in 0,1M KOH solution. Further investigation will due through this issue.

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