The Effects of Additional Treatment of Activated Coal on the Increase of Special Characteristics of Gas Diffused Cathods of Aluminum-air Electrochemical Generator

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Abstract: The possibility of a significant increase in the specific characteristics due to the treatment of carbon materials with ammonia is shown in the work. In the course of the work, techniques were developed for processing a carbon material with aqueous ammonia and pure ammonia, a procedure for the synthesis of an iron-cobalt-nitrogen-containing catalyst. It has been established that the additional processing of carbon materials with ammonia improves the characteristics of the experimental samples due to the deposition of nitrogen-containing functional groups on the surface: for activated carbon from coal raw materials brand UAF treated at 900 ° C, a current density of 0.041 mA / cm^2 is achieved at a polarization of -0.3 V. It is shown that the application of iron- cobalt-nitrogen-containing pyrocatalyst synthesized on a activated carbon brand UAF well catalyzes the oxygen reduction reaction.

1 INTRODUCTION

Currently, much attention is paid to solving the problems of creating environmentally friendly autonomous current sources with high energy intensity for use in various portable electronic devices, in transport and in electric power industry, which is caused by environmental pollution by using hydrocarbon fuels, whose share in large cities is over 90% (Zhuk et al., 2012).

Metal-air energy sources based on aluminum are promising because they have a high theoretical and feasible specific energy intensity (250-400 Wh / kg), low cost, they are environmentally friendly and fire-proof. Currently, the specific power of air-aluminum elements is limited by the specific power of the air electrode (gas diffusion cathode). When discharging air-aluminum elements with an alkaline electrolyte at a working temperature of 60 ° C, the current density at the aluminum anode can reach 1000 mA / cm^2, while the current density at the gas diffusion air cathode is several times lower (150-300 mA / cm^2).
The most critical and complex component of an Al-air element is a gas diffusion cathode, which is responsible for the reduction of air oxygen, and determines the specific power and working life of the current source.

The reduction of oxygen can be carried out in two parallel ways (Bidault et al., 2009; Cheng and Chen, 2012):

a) by a four-electron reaction to a hydroxide ion:

$O_2 + 2H_2O + 4e- = 4OH^-$

$E^0O_2 / OH- = + 0.401$ V,

b) by a two-electron reaction to hydrogen peroxide:

$O_2 + H_2O + 2e- = HO_2^- + OH^-$

$E^0 = -0.076$ V

The resulting hydrogen peroxide, depending on the properties of the catalyst, is then either reduced to OH^- or decomposed into oxygen and water.

In order to intensify the process of oxygen reduction, it is carried out in a porous, hydrophobized electrode. The efficiency of such an electrode is determined both by the activity of the catalyst used and the porous structure formed during the hydrophobization process, which should have an optimal ratio of hydrophobic and hydrophilic pores (Chervin et al., 2012).

In addition to the catalytically active layer, the GDC, as a rule, contains a hydrophobic layer, the task of which is to prevent the electrolyte from getting wet on the back side of the cathode and to

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ensure diffusion of air to the active layer.

In this paper, various methods of increasing the electrochemical activity of activated carbons used as catalysts for the reduction of oxygen on gas diffusion cathodes are investigated. One of such methods is the additional treatment of activated carbon with activated carbon from coal raw materials brand UAF (UAF) with ammonia in order to saturate the carbon surface with nitrogen-containing functional groups. Another method is the synthesis of a nitrogen-containing catalyst based on ethylenediamine and salts of transition metal (Co, Fe) treated with ammonia, followed by pyrolysis of the resulting product. Figure 1 presents a hypothetical scheme of an iron-cobalt-nitrogen-containing pyrocatalyst.

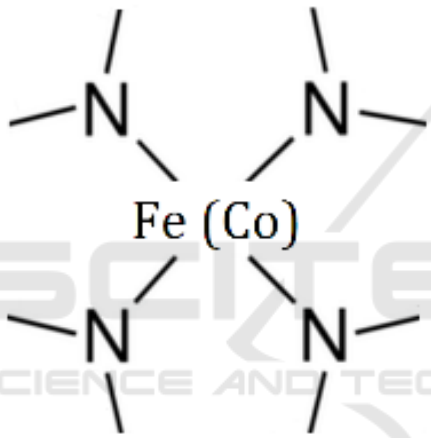

Figure 1: Estimated scheme of iron-cobalt-nitrogen-containing pyrocatalyst.

2 EXPERIMENTAL TECHNIQUE

A three-layer gas diffusion cathode consists of a nickel grid, a barrier layer based on acetylene black and an active layer based on: 1- UAF coal, 2- UAF coal with additional treatment in ammonia at 350 °C for 3 hours, 3- UAF coal with additional treatment in an atmosphere of ammonia at 350 ºC for 3 hours with the addition of the catalyst 15% TMPPCo/ Vulcan XC72.

The catalyst was synthesized by pyrolysis of TMPPCo (tetra- (p-methoxyphenyl) -porphyrin cobalt), adsorbed on Vulcan XC72, at 800 °C in argon atmosphere for 1 hour. The active layer was obtained by calendering a mixture of catalyst/ fluoroplastic (9: 1 by weight), pressing with a nickel mesh and a barrier layer, having in its composition 35% fluoroplastic.

The test of the cathode was carried out in a three-electrode cell. A silver chloride (Ag | AgCl) electrode was used as a reference electrode, and 8 M NaOH as an electrolyte. Air purified from CO_2 was supplied to the cathode. Polarization measurements were performed by the potentiodynamic method, the potential sweep rate was 1 mV / s. The potential transient was measured by the galvanostatic method at a current density of 200 mA / cm^2. The values of the potentials are given in the scale of the normal hydrogen electrode with regard to pH and temperature. The test of the laboratory layout of the Al-air element was carried out in a special cell (Figure 2).

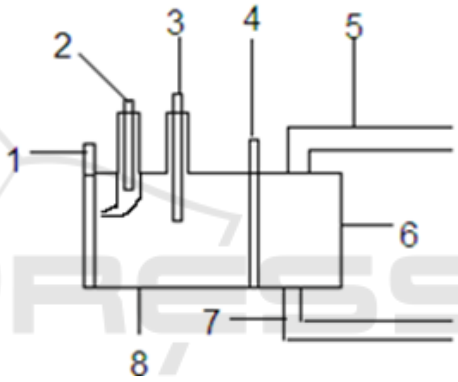

Figure 2: Electrochemical cell diagram: 1-working electrode, 2-reference electrode, 3-thermometer, 4-auxiliary electrode, 5-warm water supply tube, 6-heater, 7-warm water drain tube, 8-capacitance with electrolyte.

The anode material was Al-In alloy (A99+0.45% In), which is more stable in alkaline electrolyte than Al. The composition Na_2SnO_3 sodium stannate (0.1 M) was introduced with the electrolyte to reduce chemical corrosion of the alloy. Heated to 60º C, the electrolyte was continuously circulated through the working space of the cell, whose width was 3 mm. The geometric surface of the electrodes was 8 cm^2.

3 RESULTS AND DISCUSSION

At the first stage, the dependence of polarization curves for raw coal UAF and coal UAF treated with water vapor and ammonia without catalyst and with a supported catalyst was investigated (Table 1).

Table 1: Data of open-circuit potential and current density at different polarization for UAF coal, UAF coal additionally treated in the atmosphere of ammonia and coal UAF with additional treatment in the atmosphere of ammonia with the addition of a catalyst 15% TMPPCo/ Vulcan XC72.

Active layer material	Open-circuit potential, V	Current density at 0.3 V (A /cm^2)	Current density at 0.4 V (A /cm^2)
activated carbon UAF	-0,159	0,025	0,078
UAF treated with aqueous ammonia at 350 ° C for 3 hours (UAF in NH_3 + H_2O 350 ° C for 3 hours)	-0,131	0,048	0,074
UAF is treated with aqueous ammonia at 350 ° C for 3 hours + pyrolysis of the catalyst at 800 ° C (UAF in NH_3 + H_2O 350 ° C for 3 hours, at a 800 ° C for 1 hour)	-0,111	0,076	0,108

Additional treatment with ammonia and pyrolysis of the catalyst has a positive effect on the characteristics of the open-circuit potential. For UAF, the current-free potential is -0.159 V, and for UAF it is treated with aqueous ammonia at 350 ° C for 3 hours and the iron-cobalt-nitrogen-containing catalyst pyrolyzed on it at 800 ° C is -0.111 V.

With the additional treatment of carbon material with UAF with ammonia at 350 ° C for 3 hours, the values of current density increase by 0.023 A / cm^2, as compared to untreated UAF.

The addition of a synthesized catalyst with pyrolysis at 800 ° C to the treated coal in an ammonia atmosphere also has a positive effect on the current density values.

Figure 3 shows the polarization curves of air cathodes.

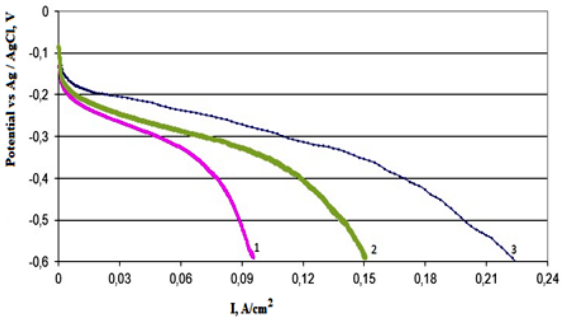

Figure 3: Polarization curves of air cathodes from: 1- UAF coal, 2- UAF coal with additional treatment in ammonia at 350 ° C for 3 hours, 3- UAF coal with additional treatment in an atmosphere of ammonia at 350 ºC for 3 hours with the addition of the catalyst 15% TMPPCo / Vulcan XC72.

Synthesis of catalytically active materials produced specifically for electrocatalysis oxygen reaction is carried out in two principally different methods. First, the most commonly used method is based on modifying the carbon or other carrier precursors of various types, including metals and nitrogen, followed by pyrolysis or without it. The literature describes many techniques of this method from simple precursors coadsorption before the synthesis in pairs (Wood et al., 2008) or plasma (Olson et al., 2013). However, regardless of the synthesis procedure for the first method of catalytically inert carrier is retained, but with doped surface having a pronounced catalytic activity. The second method is a meaningful synthesis of substantially new catalytically active material uglepodobnogo (Charreteur et al., 2008; Wu et al., 2011) modified by the atoms (N, Co, Fe, etc.) Which may be included in the alleged active centers. After introduction of the particulate carbon in (Charreteur et al., 2008) or ion exchange (Lefevre and Dodelet, 2012) is carried material necessary precursor pyrolysis and deep activation system in ammonia atmosphere to a weight loss of 60 ÷ 80%. This method allows the synthesis of the catalyst system with a high volume concentration of active centers, which we got as a result of our research work.

4 CONCLUSIONS

1. In the course of the work, methods of processing carbon material in an ammonia atmosphere, a method of synthesis of a pyrocatalyst, were developed.

2. Experimental samples of air gas diffusion cathodes were made from the obtained carbon

materials, and galvanostatic and galvano-dynamic characteristics of experimental samples of cathodes were investigated.

3. The analysis and comparison of the results obtained for various groups of carbon materials studied was carried out in order to determine the best characteristics for gas diffusion cathodes.

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