The use of pyro-polymeric catalysts and a new cylindrical cell design in oxygen-aluminum generators

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Abstract. The increase in energy consumption, the economic crisis, the development of certain areas of engineering and energy, as well as the related deterioration of the environmental situation, require the development of new electrochemical current sources with high specific characteristics. In the field of creating air-hydrogen fuel cells, the problems of safety and mobile storage of hydrogen have not been completely solved, stagnation in the development of lithium-ion, lithium-air and lithium-sulfur batteries has been outlined. All this requires searching for new technological solutions, ways to increase the energy and resource characteristics of electrochemical current sources (ECS), reducing their cost [1-2]. The use of metals (aluminum, zinc, magnesium) as an energy carrier is due to their high energy intensity (in combination with the lack of transport, storage and on-board storage problems) of the relatively low cost of metals, their availability, storage safety and the absence of harmful emissions when used. As in the chemical and electrochemical use of metals, safe products (oxides, hydroxides) are formed, which are reduced to metals within the framework of traditional production technologies. Thus, a closed cycle of energy use is organized. The task of this paper is to evaluate the possibility of reducing the cost and increasing the specific power of ECS using oxygen depolarization. The goal is achieved by using non-platinum catalysts and optimizing the design of the current source.

1. Introduction

The task of this paper is to evaluate the possibility of reducing the cost and increasing the specific power of ECS using oxygen depolarization. The goal is achieved by using non-platinum catalysts and optimizing the design of the current source.

One of the most promising electrochemical systems is oxygen (air) -aluminum (AA) [1], which has a high specific energy intensity (in the future up to 800 W-h / kg), which is noticeably higher than for the most common lithium-ion battery batteries (80-150 W • h / kg). The high efficiency of obtaining electric energy air-aluminum systems allows the heat to be released to be fully used, for example, for heating (conditioning) the passenger compartment of an electric vehicle [2-3]. The disadvantages of such systems include low specific power and a high price of platinum oxygen reduction catalysts.

The most probable total current-forming process in an air-aluminum element in an alkaline medium is described by the following equation:

\[
4\text{Al} + 3\text{O}_2 + 6\text{H}_2\text{O} + 4\text{NaOH} \rightarrow 4\text{Na}[\text{Al(OH)}_4]^{-}
\]
Electrochemical oxidation (anodic dissolution) of aluminum in an alkaline medium, according to the literature [1-5], proceeds with the formation of the complex hydroxoion Al(OH)₄⁻ and is described by equation

$$\text{Al} + 4\text{OH}^- \rightarrow \text{Al(OH)}_4^- + 3e^- \quad (2)$$

The cathodic reduction of oxygen on a positive electrode in an alkaline medium is described by the following electrochemical reaction with a standard reaction potential:

$$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \quad (3)$$

The reduction of oxygen can be accelerated by applying electrodes with a highly developed surface, for example porous electrodes [6], whose active layer consists usually of a catalyst, a hydrophobizer (fluoroplastic), and a conductive component. As a catalyst in cathodes, platinum is used [7].

Alkaline electrolyte, along with platinum metals, can be used more readily available catalysts - skeleton nickel, activated carbon and soot, modified by various promoters. Pyro-polymers, cobalt porphyrins deposited on dispersed carbon carriers and subjected to pyrolysis, are considered as effective catalysts for gas-diffusion oxygen (air) electrodes for an alkaline electrolyte [8, 9].

In this work, the synthesized catalysts were tested in the composition of the active layer of the gas-diffusion cathode of a semi-element with a liquid alkaline electrolyte. The hydrophobized gas-diffusion electrode consisted of three parts: a shut-off hydrophobized layer, an active layer and a nickel substrate (current collector). Such an electrode structure makes it possible to realize a stably developed three-phase catalyst-electrolyte-oxygen boundary, which is necessary for the oxygen reduction reaction [8]. As a cathode catalyst, a pyro-polymer of cobalt tetra (pmethoxyphenyl) porphyrin (PP TMPPS) was used. The main carbon carrier was acetylene carbon black AD-100 and for comparison – activated carbon UAF.

2. Materials and methods

The laboratory technology for manufacturing cathodes was as follows. A nickel mesh substrate (electrode area 5 cm²) with a pre-welded current collector was placed in a mold and a hydrophobic layer of hydrophobized carbon black (HPCB) with 35 wt% fluoroplastic F-4D was applied thereto. The hydro-clay layer placed in the mold was pressed at low pressure and an active layer was applied over it. Previously, the active layer components, HPCB and catalyst were mixed in a certain ratio. The electrode was then pressed at a pressure of 280 kg / cm² and held for 3 minutes. Similarly, electrodes based on other carbon materials.

The volt-ampere characteristics of air cathodes with a working surface of 2 cm² were obtained with the help of the «PR-50-1» potentiostat and the «PR-8» programmer. The measurements were carried out in the potentiostatic regime from the stationary potential in the cathode direction with a step of 25 mV to a polarization of 300 mV with an exposure at each given potential of 3 min.

3. Results and discussion

In figure 1 presents comparative polarization curves for the recovery of air oxygen for cathodes with various catalysts synthesized on carbon UAF: 10% PP TMFPSO, 15% PP TMFPSSO and carbon black AD-100: 20% PP TMPPSO. Here, too, is a curve for an electrode with a UAF carbon without a promoter in the active layer.
Figure 1. Figure with short caption (caption centred). Comparative volt-ampere curves of cathode gas diffusion electrodes in an air atmosphere with various catalysts based on carbon of UAF and carbon black AD-100, measured at 60 °C in 5M NaOH: 1–UAF; 2–UAF + 15% PP of the TMPPSo; 3–UAF + 10% PP of the TMPPSo; 4–UAF + 20% PP of TMPPSo.

As can be seen from figure 1, the positive effect of catalytic additions begins to appear already at the initial section of the curves. At a potential of 850 mV, the currents obtained at the cathode with the TMPPSo / AD-100 PP are approximately 20 mA/cm² higher than the currents obtained at the carbon electrode and at 10 mA/cm² higher than on the TMPPSo-promoted angle. The overall dimensions of the currents for large polarizations differ even more: at a potential of 730 mV for the same types of cathodes, the differences are 90 and 50 mA/cm², respectively. On the basis of the data, all the catalysts for the activity in the oxygen reaction can be arranged in the following order: 20% PP TMPPSO / AD-100 > 10% PP TMPPSo / UAF > 15% PP TMPPSo / UAF. The maximum current on the most active catalyst with a 20% FS of TMPPS with a potential of 730 mV is -155 mA/cm².

The optimized gas-diffusion cathode with the catalyst TMPPSo / AD-100 reaches a current density of 300 mA/cm² at E = 0.73 V and a temperature of 60 °C.

The cathode with PP catalyst TMPPSo / AD-100 was tested in an air-aluminum electrochemical current source.

Widely known AA generators use flat electrodes in their design when the anode and cathode of the same area are opposite each other [10-13], or the anode is located between two electrically connected cathodes [14-17]. At the same time, the equality of the cathode and the anode over the area of the working surface should be attributed to the shortcomings that do not allow the efficient use of aluminum having better energy yield characteristics than air cathodes. In the elements of a flat construction, the stock of consumable electrolyte is limited by the value of the interelectrode gap and to ensure complete solubility of aluminum in the electrolyte volume it is necessary to introduce additional capacity and an electrolyte circulation system into the generator design. In this case, the organization of a uniform (without stagnant zones) circulation of electrolyte presents a complex technical problem. The circulation speed of the electrolyte is determined not by the speed of consumption of the components, but by the rate of heat removal from the interelectrode gap. The main share in the weight of such, certainly, compact elements is occupied by their case (more than 30% by
weight) [18], which provides rigidity of the design and sealing of cathodes along the perimeter. Sealing cathodes along the perimeter, taking into account the physical and chemical properties of the alkaline electrolyte, is also a complex technological task, so reducing the length of the sealed zone increases reliability, simplifies and reduces the cost of production of elements.

In order to reduce the weight of the element and eliminate the above deficiencies, we proposed a cylindrical design of air-aluminum elements [18], in which the casing of the air-aluminum element performed the cylindrical shape of the cathode. In this case, the length of the cathode sealing seam decreased by a factor of 3. Such a design of the elements made it possible in principle to solve a number of engineering problems in a new way, connected with the organization of heat removal and adjusting the concentration and volume of the electrolyte in the discharge process.

The object of the study is an air-aluminum element, shown in figure 2. The body of the element is an air gas diffusion cathode of cylindrical shape, blown from the outside by air. A cylindrical aluminum anode is placed inside the gas diffusion cathode. The space inside the anode and the interelectrode gap are filled with electrolyte.

Figure 2. Diagram of a cylindrical air-aluminum current source.
1- Nickel mesh and hydro-blocking layer, 2 - air cathode, 3 - thermocouple, 4 - cathode current lead, 5 - aluminum anode, 6 - anode current lead, 7 - thermocouple leads, 8 - correction electrolyte supply capillary, 9 - upper cathode plug, 10 - overflow windows, 11 - thermo insulating layer, 12 - discharge air flow, 13 - lower gap, 14 - lower cathode cap, 15 - radiator, 16 - fan, 17 - heat pipe.

The air cathode (2) in the upper and lower part is closed by cathode plugs (9, 14), forming a closed volume. End seams on the border with plugs are sealed with a sealant. The lower plug 14 is provided
with protrusions for mounting the cylindrical anode 2 with the formation of a gap 12 between its end and the bottom of the bottom plug 13. An electrolyte is enclosed in the cathode and cap-capped area and an aluminum anode 5 is coaxially inserted. In the upper part of the anode, its windows are provided with windows 10 for overflowing Electrolyte from the interelectrode gap to the inner cavity of the anode. The inner surface of the anode is provided with a heat-insulating layer 11.

In the inner cavity of the anode, a heat pipe 17 is provided, provided with a radiator 15 outside. The radiator warms the air pumped by the fan (16), which was directed to the outside of the cathode, thereby increasing its activity. Fan 16 switches on when the set temperature is reached.

The installation scheme for recording the discharge characteristics of a cylindrical air-aluminum current source is shown in figure 3. The discharge of the element was carried out at a constant load of Rn (49.5 mΩ) + Rш (2.5 mΩ). Recorded discharge parameters of a cylindrical air-aluminum element (shunt 30A; 75mV; 2.5 mΩ) and temperature (thermocouple) were controlled by an 8-channel analog input module, signals from which were transmitted via an interface converter for registration to a computer. The time was counted by a computer.

![Diagram](image)

**Figure 3.** Scheme of installation for registering discharge characteristics.

In the process of discharging an air-aluminum current source, the electrolyte is expended on the formation of sodium aluminates and evaporation. This leads to a gradual decrease in the electrolyte level in the element and a decrease in the concentration of NaOH [19]. When the electrolyte level falls below the edge of the overflow windows, its circulation between the volume inside the anode and the interelectrode gap stops. In order to maintain a constant level and concentration of NaOH in the electrolyte, a corrective electrolyte was supplied during the tests. For an air-aluminum element of 30W power, the correct concentration of the correcting electrolyte (15M NaOH) was set and its feed rate (0.12 ml / min).

The discharge curve of a cylindrical air-aluminum element with simultaneous recording of the potentials of the Al anode and the air electrode (with the TPMPPso / AD-100 PP catalyst) is shown in figure 4. The element was activated by pouring 112 ml of electrolyte (8M NaOH + 0.015 M Na2SnO3 · 3H2O). In the discharge process, another 20 ml of 15M NaOH was added as a correction. According to calculations, 22 g of aluminum is dissolved in 132 ml of electrolyte, which corresponds to an electrolyte capacity of 66 A·h.

After activation, the element was held for 8 minutes without load to stabilize the voltage and potential of the electrodes. The voltage of the open circuit of the element at a temperature of 25 °C
was 1.88V. Concerning the Ag / AgCl reference electrode, the anode potential was -1.75V, the cathode 0.13V. When the load was switched on, the anode potential shifted to the cathode side to -0.93V and was set at -1.25 ÷ -1.3V. After 12 minutes after the load was switched on, after the power of the element was reached 30 W and the temperature of the electrolyte was 53 °C, a fan was switched on. At the same time, the temperature increase slowed down, and by the end of the discharge it reached a value of 69 °C.

![Graph showing discharge parameters](image)

**Figure 4.** Parameters of the discharge of a cylindrical air-aluminum current source.

The average power of the element was 23 W. All in the process of discharge are realized: capacity - 64 А·ч; electricity - 76 Wh. The discharge was terminated due to a sharp drop in the cell's power due to a shift in the anode potential to the cathode side. The reason for the passivation of the anode was the development of the installed electrolyte capacity, which is determined by the limiting concentration of alumimates in the electrolyte.

Taking into account the total weight of the element 440 g (including the weight of the cathode, anode, electrolyte and heat sink system), the specific power was 52 W / kg. The average specific power of a dry cell without electrolyte is 72 W / kg, and the maximum - 116 W / kg. The specific energy content of the element, taking into account the total weight, is 173 W · h / kg and 285 W · h / kg of element without electrolyte.

4. Conclusion

1. The electrocatalytic activity of the oxygen depolarization catalyst - pyrolypolymer tetra (pmethoxyphenyl) porphyrin cobalt under model conditions and as part of a gas diffusion electrode.
2. The characteristics of gas-diffusion cathodes based on various carbon materials and promoters.
3. The optimized gas-diffusion cathode with the TPMPPso / AD-100 PP catalyst achieves a current density of 300 mA / cm2 at E = 0.73V and a temperature of 60 °C.
4. The design of a cylindrical air-aluminum current source with a specific power of 116 W / kg and a specific energy capacity of 285 W · h / kg.

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