Electrolyte for Hydronic Chemical Current Source Used as Hydrogen Generator with Aluminum Anode

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ABSTRACT

This paper presents the results of experimental studies of the electrochemical characteristics for various anodic and cathodic materials used in a hydronic chemical current source with an aluminum anode in various electrolytes. And it was shown that it is advisable to add only organic inhibitors into an alkaline electrolyte instead stannate-ion to suppress corrosion of an aluminum anode.

INTRODUCTION

Due to the ecological and energy crises nowadays the priority direction of the world economy is the development of hydrogen energy. Hydrogen is already quite a long time been considered and used as an environmentally friendly fuel. The advantages of hydrogen as an energy carrier are in its almost unlimited reserves within the water resources of the planet, in the highest specific energy (119.0 MJ/kg) among the known fuels and in ecologically clean product (water) in reaction with oxygen. The most energy-efficient power plants among autonomous, that use hydrogen as fuel, are oxygen-hydrogen (O₂/H₂) fuel cells (FC). They are able to achieve the highest efficiency among all known power plants (up to 94%). Oxidizer – oxygen – for O₂/H₂ FC is used from air, when operating in ground conditions. For the fuel – hydrogen – the main difficulty is the problem of its storage and transportation. There are several ways to store hydrogen: gas balloon, cryogenic, and "associated". Gas balloon hydrogen storage...
significantly reduces the specific energy-mass characteristics of the entire power plant (PP) [1]. Cryogenic storage, despite the fact that it is the most efficient from the point of view of the energy-mass characteristics of the PP, is not applicable during long pauses in operation or during a delayed launch, since the cryo-liquid evaporates quite actively. The “associated” storage of hydrogen in the composition of some molecules, for example, in water molecules, makes it possible to obtain it as needed, reduce it by active metals during the reaction of their interaction with water. According to the efficiency of hydrogen generation per mass unit of the working components, when hydrogen is reduced from water, only the “lithium-water” system is more efficient than the “aluminum-water” system.

It is given much attention worldwide to the study and development of autonomous hydrogen generators based on the aluminum-water system due to the high safety of the associated hydrogen storage method [2-5]. However, most often hydrogen is supposed to be obtained by chemical dissolution of aluminum in aqueous solutions. One of the main disadvantages of the method of aluminum’s chemical dissolution in water (aqueous solutions) is that the energy released during dissolution is not useful and is completely converted into heat ($\Delta H_{298} = -1830.04 \text{ kJ}$).

**EXPERIMENTS AND RESULTS**

This problem is solved by us by creating a hydronic chemical current source (CCS). This is an electrochemical cell consisting of an aluminum anode, a cathode made of an inert material such as nickel or molybdenum and an electrolyte between them. Consumable substances in the hydronic CCS are aluminum anode and water. The reaction products are hydrogen, aluminum hydroxide $\text{Al(OH)}_3$, and electricity [1].

During the operation of the hydronic CCS with an aluminum anode in an aqueous alkaline electrolyte, an anode current-forming reaction is as follow:

$$\text{Al} - 3e + 4\text{OH}^- \rightarrow [\text{Al(OH)}_4^-].$$

(1)

At the cathode hydrogen is reduced from water according to the reaction:

$$2\text{H}_2\text{O} + 2e \rightarrow 2\text{H}_2 \uparrow + 2\text{OH}^-.$$

(2)

The total current-forming reaction in a hydronic CCS with an alkaline electrolyte can be represented by the following equation:

$$2\text{Al} + 6\text{H}_2\text{O} + 2\text{OH}^- \rightarrow 2[\text{Al(OH)}_4^-]^- + 3\text{H}_2 \uparrow.$$

(3)
Since aluminum is thermodynamically unstable in water, the anode is consumed at the same time in current-forming and corrosion reactions described by exactly the same summary equation (3). The only difference that hydrogen is released in the cathode sections of corrosive aluminum.

The aluminate solution formed during the dissolution of aluminum in alkali is extremely prone to supersaturation. But after reaching a certain degree of supersaturation it decomposes with the release of solid aluminum hydroxide, which crystallizes in the form of gibbsite:

\[
Na[Al(OH)_4] \rightarrow NaOH + Al(OH)_3 \downarrow. \quad (4)
\]

In a neutral salt electrolyte, the current-forming reaction and the corrosion reaction are expressed by the summary equation:

\[
2Al + 6H_2O \rightarrow 2Al(OH)_3 \downarrow + 3H_2 \uparrow. \quad (5)
\]

As follows from equations (4) and (5), the processes in alkaline and neutral electrolytes lead to the same reaction products: \( Al(OH)_3 \) и \( H_2 \). But in a neutral electrolyte aluminum hydroxide precipitates as a gel. Thus, as mentioned earlier, aluminum and water are consumable substances in a hydronic CCS with an aluminum anode.

We made experimental investigations of the electrochemical parameters for the hydronic CCS: current-voltage characteristics (CVC) of the anodes from various aluminum alloys (A99 aluminum, protector alloys AP4N, AP2, AP3 (AP4H, AP2, AP3), and A995 alloy + 0.6 wt.% In ) and inert metal cathodes (Ni, Mo, Ti, steels Kh18N10T (X18H10T) and St.3 (Cr.3)) in a pure alkaline electrolyte (4M NaOH), alkali-stannate (4M NaOH +, 0.6 mol/l Na\(_2\)SnO\(_3\)) and salt (4M NaCl) and the corrosion rates of the aluminum anode in these electrolytes. According to the results of the joint assessment of the obtained polarization and corrosion characteristics for the anodic and cathodic materials, it was found that the best composition of working components for the hydronic CCS is 4M NaOH + 0.06M Na\(_2\)SnO\(_3\) electrolyte, molybdenum cathode and Al-In alloy anode. The AP4N protector alloy has a close complex of properties. For this composition, the range of current densities at which the hydronic CCS can work as a source of current increases to 2500-3000 A/m\(^2\). Hydronic CCS with salt electrolyte due to high polarization losses at the cathodes can operate as a current source only at low current densities (short circuit mode 300-500 A/m\(^2\)), what leads to large dimensions of the hydrogen generator. For the salt electrolyte, the best composition of working components for the hydronic CCS is the cathode of steel St.3 and the anode of the protector alloy AP4N [1].

However, our further studies have shown that the addition of stannate-ion \( SnO_3^{2-} \), significantly affects the CVC of any cathode materials for the hydronic
CCS. CVC for all electrodes of the above-mentioned metals in alkali-stannate electrolyte significantly deteriorated compared to CVC obtained in pure alkali (Fig. 1 and 2).

To explain this phenomenon, experiments were made to study the film on the cathodes formed in the process of CCS operation. The same nickel cathode was repeatedly investigated in the alkaline-stannate electrolyte and it was found that its CVC deteriorated significantly with each new experiment (Fig. 3).

Figure 1. Current-voltage characteristics of various metal cathodes in 4M NaOH at 333K.

Figure 2. Current-voltage characteristics of a nickel cathode in the electrolyte 4M NaOH + 0.06M Na₂SnO₃, at T=333K.
Seems the reason for the varying degrees of potential decrease in cathodes made of different materials, when operating in an alkaline-stannate electrolyte, is the nature of the film formed on the cathode during the discharge of a CCS. The structure of this film (coating) was studied by us by X-ray structural analysis and scanning electron microscopy (SEM). The results of X-ray structural analysis of the coating on the nickel electrode are shown in a diffractogram (figure 4).

The diffractogram clearly shows the peaks of tin and tin compounds with indium In$_{0.2}$Sn$_{0.8}$. But the peaks of the nickel substrate are rather weak, which characterizes a rather large coating thickness (more than 15-20 microns). Indium is also presents in the coating in a rather large percentage, which is an activating element of the anodic Al-In alloy and formed a crystalline compound with tin in the ratio indicated above.
Photographs of the surface obtained with an electron microscope with different degrees of magnification showed that the surface structure is volumeporous with a high visual porosity, which is estimated to be about 50%, especially with prolonged and/or repeated cathode use. This confirms the assumption put forward earlier by us that the coating is porous due to the release of gaseous hydrogen on it.

The formation of a porous tin coating on the cathode, firstly, worsens the CVC, and, secondly, explains the difference in the CVC of cathodes from different metals due to the release of hydrogen both on the substrate surface (base material) and on the surface of the coating.

CONCLUSION

Thus, we have shown that the use of stannate-ion additives to the alkaline electrolyte of the hydronic CCS is undesirable, since this leads to a deterioration in the characteristics of the cathodes. Therefore, in order to inhibit the corrosion process of the aluminum anode and, thereby, increase its useful life, it is necessary to use additives of organic inhibitors in the alkaline electrolyte for a hydronic CCS.

Preliminary experiments with a number of organic inhibitors showed that, with the addition of tartrate ion (tartaric acid anion) in 4M NaOH, the working range of the hydronic CCS current density reaches 2000 A/m². This is
approximately in 4 times higher than using the previously proposed electrolyte 4M NaOH + 0.06M Na₂SnO₃ [6].

REFERENCES