Study on electrochemical properties of Al-Ga-Mn-Ca-Cu alloy electrode alkaline system

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Abstract. This study is aimed to study a new type of Al-Ga-Mn-Ca-Cu anode alloy. The corrosion behavior and electrochemical performance of the alloy in different concentrations of NaOH solution were studied. The micro-corrosion morphology of the alloy anode was observed. The conclusion is as follows: With the increase of the concentration of NaOH solution, the alloy anode film resistance $R_f$ and the pore resistance $R_{por}$ are reduced, so that the reaction rate of the anode of the reaction alloy is increased, the activity is improved, and the reaction of the alloy anode is facilitated; The main corrosion factor of alloy anode is hydrogen evolution corrosion. Therefore, inhibition of hydrogen evolution corrosion on the basis of maintaining anode activity is the next research focus of the alloy anode. When the alloy anode is continuously constant current discharge at different current densities, the voltage of 5mol/L NaOH solution the minimum drop is the most stable; the comprehensive performance is 4mol/L NaOH solution, and the discharge performance is the best, the Al-0.017Ga-0.885Mn-0.038Ca-0.048Cu (wt.%) alloy has a lower corrosion rate in the 4mol/L NaOH solution. The higher discharge voltage and the highest anode energy density are more suitable for continuous constant current discharge at different current densities; the constant current discharge and EIS results of the alloy agree well with the corrosion characteristics.

1. Introduction
Metal aluminum has the advantages of low cost, high volumetric capacity and low toxicity, and is an ideal anode material for the development of metal air batteries [1-3]. Its potential value is much higher than the use of zinc as anode material, but aluminum air battery is still not popular with zinc air battery [4]. The main reason is that the polarization and hydrogen evolution corrosion of the aluminum anode during the use of the battery are serious, resulting in the actual specific capacity and electrode efficiency of the aluminum air battery being much lower than the theoretical value; at the same time, the hydrogen generated by the corrosion brings the normal operation and safety of the battery. The effect is that aluminum loses the attractiveness of high-energy anode materials [5-6]. At present, there are two main methods for alleviating hydrogen evolution corrosion and polarization of aluminum anodes. One is anode alloying, that is, adding elements such as Ga, In, Sn, Zn, Mg, Ca, Pb or oxides thereof to aluminum to improve the corrosion resistance and activity of the anode [7-8]. The second is to change the nature of the electrolyte, that is, add a corrosion inhibitor to the electrolyte to slow the occurrence of hydrogen evolution corrosion [9-11].
At present, alkaline electrolytes used in aluminum air batteries have extremely high conductivity of NaOH and KOH [12]. When KOH is used as an electrolyte, it is impossible to recover alumina in the electrolyte by the industrial Hall-Heroult method, and it is not conducive to the recycling of electrolytes and electrode materials and the green production of batteries. [13] Therefore, NaOH is commonly used as an electrode solution in the industry. In addition, the concentration of NaOH also affects the electrochemical performance of the anode alloy. Only when the concentration of NaOH is first determined, the electrochemical performance of the anode alloy can be tested on this basis.

In this paper, Al-0.017Ga-0.885Mn-0.038Ca-0.048Cu was used as the anode to explore the surface activity, oxide film change, electrochemical performance, discharge performance and hydrogen evolution corrosion of the anode in 1mol/L~6mol/L NaOH electrolyte. And through analysis, select a suitable discharge system for the anode.

2. Experimental

2.1. Preparation of alloy anode
Industrial pure aluminum was melted in an intermediate frequency furnace at 760 °C, and then alloying elements Ga, Mn, Ca, and Cu wrapped with aluminum foil were added, and the mixture was thoroughly stirred and kept for 10 minutes. After that, the aluminum liquid was poured into a graphite mold and poured into a 10 mm aluminum plate, and then rolled into an alloy plate having a thickness of 2 mm, and kept at 300 °C for 8 hours for sample preparation. The chemical composition of the alloy is shown in Table 1.

| element | Ga  | Mn  | Ca  | Cu  | Al allowance |
|---------|-----|-----|-----|-----|--------------|
| Wt.%    | 0.016 | 0.883 | 0.036 | 0.048 |              |

2.2. Electrochemical performance test
This test was carried out using a three-electrode system using the PGSTAT204 electrochemical workstation from Metrohm. The auxiliary electrode was a 1.5 cm x 1.5 cm platinum plate electrode, and the reference electrode was a saturated calomel electrode (SCE). The working electrode is Al-0.017Ga-0.885Mn-0.038Ca-0.048Cu. Except for the working area of 1cm×1cm, all other parts are sealed with epoxy resin, and the part involved in the reaction is used (800-1000-1500-2000 mesh). Sandpaper is polished in sequence. The working electrodes were measured in open circuit potential, Nyquist curve and polarization curve in 1mol/L, 2mol/L, 3mol/L, 4mol/L, 5mol/L, 6mol/L NaOH solution system. The polarization curve voltage range is -2V~1V, and the scanning speed is 0.01mV/s. The impedance test range is from 0.1 Hz to 105 Hz, and the data fitting software is Metrohm Nova2.13.

2.3. Determination of hydrogen evolution corrosion rate
Six 1cm×1cm samples were cut out on the aluminum plate and numbered, sanded with sandpaper (800-1000-1500 mesh), and washed three times with distilled water to measure the mass of each sample, and then placed in 1mol/L, 2mol/L. In a conical flask of 3 mol/L, 4 mol/L, 5 mol/L, and 6 mol/L NaOH solution, after 2 h of corrosion reaction, the amount of hydrogen evolution was measured by a drainage gas collection method. Finally, the sample is taken out and concentrated with nitric acid to remove corrosion products, washed, blown dry, and weighed, and then the hydrogen evolution rate is calculated by formulas (1)-(3).

Calculation formula of corrosion rate:
\[ v_t = \frac{m_0 - m_1}{St} = \frac{m_0 - m_1}{2} \text{ (mg·cm}^{-2}·\text{h}^{-1}) \]  
\[ v_{\text{H}_2} = \frac{2PVM}{3RTSt} = 0.366V \text{ (mg·cm}^{-2}·\text{h}^{-1}) \]
\[ \omega = \frac{V_{H_2}}{V} \]  



\[ v_s \] is the weight loss corrosion rate; \( m_0 \) is the initial mass of the corrosion sample (mg); \( m_1 \) is the mass after the corrosion-like corrosion (mg); \( S \) the working area of the aluminum anode (cm\(^2\)); \( t \) the corrosion time (h); \( V \) the volume of the hydrogen evolution (mL); \( V_{H_2} \) hydrogen plate corrosion loss aluminum plate rate; \( P \) atmospheric pressure (Pa) during the experiment; molar mass of aluminum element (K∙mol\(^{-1}\)); \( R \) gas constant (J∙K\(^{-1}\)∙mol\(^{-1}\)) ; \( T \) absolute temperature (K), \( w \) the proportion of hydrogen evolution corrosion in the corrosion of aluminum sheets.

2.4. Discharge performance measurement

The anode of the battery is an alloy aluminum plate. The size and manufacturing method are the same as those used in the electrochemical performance test. The cathode is a special aluminum-air battery catalytic electrode, and the electrolyte is 1 mol/L, 2 mol/L, 3 mol/L, 4 mol/L, 5 mol/L, 6 mol/L NaOH solution, anode working area is 1 cm\(^2\), and effective area of cathode is 16 cm\(^2\). At room temperature, the battery was subjected to continuous constant current discharge test at different current densities using a blue electric test system CT2001, and the discharge voltage platform at each current density in different concentrations of NaOH solution was obtained. In addition, the amount of anode mass loss was measured, and the anodic corrosion rate and energy density at the time of continuous discharge were calculated. The calculation formula is as follows. The surface morphology of the sample after discharge was observed with an EPMA-1720 electron probe microscope of Shimadzu Corporation of Japan.

The calculation formula of anode corrosion rate and energy density is as follows:

\[ v_a = \frac{60W_0}{S \cdot t} \]  \hspace{1cm} (4)

\[ \eta = \frac{\sum U \cdot j \cdot S \cdot t}{60W_0} \]  \hspace{1cm} (5)

\( v_a \) is the corrosion rate (g·cm\(^{-2}\)·h\(^{-1}\)), \( \eta \) represents the energy density (W·h·kg\(^{-1}\)), \( j \) is the current density (mA·cm\(^{-2}\)), and \( W_0 \) is the actual loss mass (g), which is the corresponding current. \( U \) is the discharge voltage (V), \( S \) is the density is the effective area (cm\(^2\)), \( t \) is the anode plate and is the discharge time (min).

3. Results and discussion

3.1. Electrochemical properties

Figure 2 and Table 2 show the polarization curves and corresponding corrosion parameters of alloy aluminum plates in different concentrations of NaOH solution. It can be obtained from the graph that the corrosion potential (Ecorr) value does not change much with the fluctuation of the lye, the potential
fluctuates between 1.51V and 1.57V, and the corrosion potential is in order: Al (1mol/L NaOH) > Al (6mol/L NaOH)>Al (5mol/L NaOH)>Al (2mol/L NaOH)>Al (3mol/L NaOH)>Al (4mol/L NaOH). Corrosion rate and corrosion current density (Jcorr) trend are the same as follows: Al (5mol/L NaOH)>Al (3mol/L NaOH)>Al (4mol/L NaOH)>Al (6mol/L NaOH) >Al (2mol/L NaOH)>Al (1mol/L NaOH); the polarization resistance is opposite to the corrosion rate. In addition, although the fluctuation of the corrosion potential is not large, the corrosion rate fluctuates greatly, and the corrosion rate of the anode in the 5 mol/L NaOH solution is the largest, which causes the energy density of the anode to be seriously reduced, which affects the electrode efficiency.

Figure 3 and Table 3 are the Nyquist curve and circuit fitting data of the alloy aluminum plate in different concentrations of NaOH solution. The resistance at the beginning of the Nyquist curve for the aluminum alloy anode is the solution resistance (Rs), and the resistance value obtained by extrapolating the curve level is Polarization resistance (Rp). The polarization resistance (Rp) includes the sheet resistance Rf and the pore resistance caused by alkali corrosion Rpor = Rct (charge transfer resistance)+Rdl (diffusion layer resistance)+ Ra (all other types of accumulation (corrosion products, any existing molecules or ions, etc.)) [14-15]

Analysis of the Nyquist curve shows two capacitor rings. The first one is a high-frequency capacitor ring, which represents the sheet resistance Rf, which consists of a resistance value (R1) and a non-ideal capacitance (CEP1) formed by a thin film (due to the microscopic fluctuation of the surface of the alloy electrode during electrochemical reaction, Its dispersion effect, so the capacitor components in the circuit are all replaced by the constant phase angle component CEP, the correlation performance is characterized by the corresponding Y0 and dispersion index n parameters [17]); the second is the low frequency region capacitor ring, which represents The pore resistance Rpor is composed of a resistance value (R2) and a non-ideal capacitance formed by a thin film (CEP2) [16,17]. It can be seen that the pore resistance gradually decreases with the increase of the concentration of NaOH solution, and the lowest resistance of the solution in 5mol/L NaOH; the pore resistance is greater than 2mol/L and 3mol/L pore resistance at 4mol/L NaOH. The sheet resistance is to a large extent characterize the activity of the aluminum alloy anode during the reaction. The smaller the sheet resistance value, the thinner the film, the smaller the barrier of the electrode reaction, the smaller the polarization and the faster the reaction; the sheet resistance can be seen. As the concentration of NaOH solution increases, the film resistance decreases in 5mol/L NaOH. The aluminum anode has the highest activity in the reaction of 5mol/L NaOH solution, the internal resistance is the smallest, and the maximum size of n is also proved. The film layer is most uniform at this lye concentration. The pore resistance reflects the material exchange and conversion between the aluminum alloy anode alloy and the electrolyte. The trend of the pore resistance is consistent with the trend of the sheet resistance.

Figure 2. potential polarization curves of alloy anode in NaOH solution of different concentrations
Table 2. Measurement data of potential polarization curves of alloy anodes in NaOH solutions of different concentrations

| NaOH(mol/L) | Ecorr (V vs Hg/HgO) | Jcoor (A·cm⁻²) | Corrosion rate (mm·year⁻¹) | R_P (Ω·cm⁻²) |
|-------------|---------------------|---------------|-----------------------------|---------------|
| 1           | -1.5291             | 0.07698       | 2295.3                      | 8.2117        |
| 2           | -1.5436             | 0.11019       | 3604                        | 2.8279        |
| 3           | -1.5334             | 0.22589       | 7388                        | 1.3598        |
| 4           | -1.5163             | 0.17168       | 5615                        | 1.4301        |
| 5           | -1.5645             | 0.71823       | 23318                       | 1.0399        |
| 6           | -1.5608             | 0.17021       | 5567                        | 1.9500        |

Figure 3. Nyquist plots of alloy anodes in NaOH solutions of different concentrations

Table 3. Nyquist plots of alloy anodes in NaOH solutions of different concentrations

| NaOH(mol/L) | Rs (Ω·cm⁻²) | CEP₁ Y₀(10⁻⁴Ω⁻¹·cm⁻²·sn) | n | R₁ (Ω·cm⁻²) | CEP₂ Y₀(10⁻⁴Ω⁻¹·cm⁻²·sn) | n | R₂ (Ω·cm⁻²) |
|-------------|-------------|----------------------------|---|-------------|----------------------------|---|-------------|
| 1           | 2.192       | 4.759                      | 0.936 | 1.561       | 1032.4                     | 1.062 | 0.647      |
| 2           | 1.087       | 4.873                      | 0.905 | 1.101       | 1430.3                     | 1.077 | 0.385      |
| 3           | 0.565       | 13.348                     | 0.921 | 0.487       | 1438.7                     | 1.074 | 0.168      |
| 4           | 0.735       | 38.543                     | 0.912 | 0.401       | 722.7                      | 1.030 | 0.184      |
| 5           | 0.516       | 28.382                     | 0.942 | 0.281       | 1174.8                     | 0.985 | 0.116      |
| 6           | 1.250       | 9.451                      | 0.933 | 0.473       | 1415.1                     | 0.876 | 0.240      |

3.2. Hydrogen evolution corrosion

Figure 4 and Table 4 show the self-corrosion rate of the anode at the open circuit potential. It can be seen that the self-corrosion rate of the alloy anode increases with the increase of NaOH concentration, but the growth rate of the corrosion rate in the 4mol/L NaOH solution decreases significantly. This corresponds to the corrosion rate in Table 2. In addition, it can be found that the self-corrosion reaction of the anode at the open circuit potential is mainly hydrogen evolution corrosion, and the hydrogen evolution corrosion accounts for about 90% of the anode corrosion.
Figure 4. self-corrosion rate of anode under open circuit potential, 1: Weight loss corrosion rate, 2: Corrosion rate of hydrogen developing aluminum plate.

| NaOH (mol/L) | 1   | 2   | 3   | 4   | 5   | 6   |
|--------------|-----|-----|-----|-----|-----|-----|
| $V_s$ (g·cm$^{-2}$·h$^{-1}$) | 0.0092 | 0.0148 | 0.0195 | 0.0213 | 0.0247 | 0.0277 |
| $V_{H^2}$ (g·cm$^{-2}$·h$^{-1}$) | 0.0084 | 0.0136 | 0.0186 | 0.0200 | 0.0236 | 0.0256 |
| $\omega$ (%) | 91.33 | 89.68 | 93.23 | 91.84 | 93.38 | 90.16 |

3.3. Discharge performance

Figure 5. lower potential of alloy anode with different current densities in NaOH solution of different concentrations.
Table 5. Test results of constant current discharge at different current densities of alloy anode

| Current density (mA/cm²) | NaOH 浓度(mol/L) |
|--------------------------|-----------------|
|                          | 1   | 2   | 3   | 4   | 5   | 6   |
| Current density          |     |     |     |     |     |     |
| 0                        | 1.4326 | 1.4816 | 1.4512 | 1.4475 | 1.5027 | 1.4745 |
| 40                       | 0.8349 | 0.9403 | 1.1375 | 1.1511 | 1.1787 | 1.1558 |
| 60                       | 0.4173 | 0.6166 | 1.0330 | 1.0686 | 1.1130 | 1.0807 |
| 80                       | 0.0202 | 0.2096 | 0.9245 | 0.9942 | 1.0668 | 1.0190 |
| 100                      | 0.0202 | 0.1055 | 0.6820 | 0.9025 | 1.0246 | 0.9415 |
| 120                      | 0.0189 | 0.0905 | 0.0552 | 0.7134 | 0.9905 | 0.3013 |
| 0                        | 1.3446 | 1.5241 | 1.5408 | 1.5858 | 1.3266 | 1.4841 |
| Voltage (V)              |     |     |     |     |     |     |
| 0.053 (g)                | 0.0163 | 0.0125 | 0.0286 | 0.0149 | 0.0299 | 0.0267 |
| \(\nu\) (g cm⁻² h⁻¹)    | 0.0122 | 0.0094 | 0.0215 | 0.0112 | 0.0224 | 0.0201 |
| \(\eta\) (Wh kg⁻¹)      | 701.69 | 1789.28 | 1929.42 | 6056.06 | 3578.1 | 2829.0 |

Figure 5 is showing constant current discharge performance of an Al-Ga-Mn-Ca-Cu aluminum alloy anode in a 1 mol/L-6 mol/L NaOH electrolyte. The specific data is shown in Table 5. It can be seen that the current density decreases and the voltage drop of the alloy anode is the smallest at 5 mol/L, followed by 4 mol/L. When discharged in different concentrations of NaOH solution, the integrated discharge energy density of the alloy anode becomes larger as the concentration of the NaOH solution increases, reaching a maximum at 4 mol/L. Then, as the concentration of the NaOH solution increases, its energy density gradually decreases. This is because the discharge potential of the alloy anode in the 4 mol/L lye is high, and the corrosion rate is much less than 5 mol/L, so the utilization of the anode is high and the energy density is high. At the same time, the self-corrosion rate of the anode of the alloy anode of Table 2 and Table 4 is lower in 4mol/L than in the 5mol/L NaOH solution.

3.4. Micro-structure and corrosion morphology

Figure 6. Surface morphologies of alloy anode under different current densities in NaOH solution with different concentrations: a:1mol/L NaOH; b:2mol/L NaOH; c:3mol/L NaOH; d:4mol/L NaOH; e:5mol/L NaOH; f:6mol/L NaOH
As shown in figure 6, it can be seen that the surface of the alloy anode has different degrees of corrosion in different alkali liquids, and the roughness of the surface of figure b is increased compared with the surface of figure a, and the corrosion pit becomes deeper and the number becomes larger. When it is shown in figure c, the surface of the anode is cracked, and the anode is divided into numerous small pieces to accelerate the corrosion rate. At the same time, the morphology tends to cause corrosion on the anode surface and reduce the energy density of the anode. The surface pores of figure d are enlarged but relatively flat, which can reduce the corrosion rate to a certain extent, but because of the large concentration of alkali, the activity is higher, resulting in better discharge performance. The surfaces of figure e and figure f are also corroded. Figure e is mainly composed of corrosion pits and cracks. Figure a dense hole, which is also caused by corrosion of alkali concentration, which leads to a decrease in energy density.

4. Conclusion
In this paper, the electrochemical properties of alloy anodes at different lye concentrations were investigated, and the micro-corrosion morphology of alloy anodes was observed. The following conclusions were drawn:

1) With the increase of the concentration of NaOH solution, the alloy anode film resistance $R_f$ and the pore resistance $R_{por}$ are reduced, so that the reaction rate of the anode of the reaction alloy is accelerated, and the activity is improved, which is favorable for the reaction of the alloy anode.

2) The main corrosion factor of the alloy anode during the open circuit is hydrogen evolution corrosion. The next research focus of the aluminum-air battery of the alloy anode should be based on the inhibition of hydrogen evolution corrosion on the basis of the anode activity.

3) When the alloy anode is continuously constant current discharge at different current densities, the voltage drop of 5mol/L NaOH solution is the smallest and most stable; the comprehensive performance is 4mol/L NaOH solution system.

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