JMEPEG (2009) 18:1086–1090
DOI: 10.1007/s11665-008-9331-4

1059-9495/$19.00

Research on Electrochemical Behavior of Ti-Ir-Ru Anode Coating in Electrolytic Antifouling of Flowing Brine

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(Submitted January 17, 2008; in revised form November 9, 2008)

By electrochemical techniques, the electrochemical behavior of Ti-Ir-Ru anode coating was studied in electrolytic antifouling of flowing brine. The effect of the brine's flow rate and the anode/cathode interval on electrolysis was also considered. The results indicated that the brine's flow rate had remarkable effect on the characteristic of the Ti-Ir-Ru anode. The electrolytic voltage and the evolved active chlorine concentration of Ti-Ir-Ru anode increased with increasing flow rate. Its energy consumption displayed the same variable rule as the electrolytic voltage. But the current density reduced with increasing flow rate. Increasing flow rate favored attenuation of the thickness of mass-transfer control layer and expediting the oxygen's mass transfer, which accelerated the cathode polarization and the oxygen absorption reaction. The maximal current efficiency for Ti-Ir-Ru anode was obtained at the anode/cathode interval of 5 cm with the current density of 60 mA/cm^2. At this point, Ti-Ir-Ru anode also had relatively low electrolytic voltage. The above operating procedure was ideal for electrolyzing flowing brine using Ti-Ir-Ru anode coating.

Keywords ceramics, electrochemical properties, Ti-Ir-Ru anodic coatings

1. Introduction

Along with the development of the shipbuilding industry and ocean engineering, marine pest organisms have attracted interest from government agencies, scientific laboratories and industry. Electrolytic antifouling of brine is one of the most effective methods to inhibit marine pest organisms. Its mechanism involves electrolyzing brine to generate Cl^- ion and hypochlorous acid by special electrodes, which are all oxidizing agent and have toxicity to halobios.

During the electrolyzing process, the evolution of active chlorine, which is the main product of the anode side, is accompanied by oxygen emission. Thus, the used anode should have the following characteristic. The first is that the potential of releasing active chlorine on the anode is low. The second is the potential of oxygen reduction on the anode is high. The last is the anode should have excellent corrosion resistance and stability. In recent years, titanium-iridium-ruthenium (Ti-Ir-Ru) anode coating has been widely used in electrolytic antifouling of brine since it has many advantages such as low decomposition tension, higher current efficiency, lower energy consumption, and generating higher active chlorine concentration. Some researchers have reported the electrochemical characteristic and failure mechanism of Ti-Ir-Ru anode coating in electrolyzing seawater (Ref 1-4). But most of the results were obtained at the static condition, which were different from the practical situation.

In this article, the electrochemical behavior of Ti-Ir-Ru anode coating in electrolyzing flowing brine was studied by electrochemical techniques. At the same time, the effect of anode/cathode intervals on the electrolysis process was also studied.

2. Experimental

2.1 Electrode Materials

RuO_2, IrO_2, and TiO_2 ternary oxide coating (ab. Ti-Ir-Ru anode, Ru:Ir:Ti 17:13:70 in mole ratio) was presented by 725 Institute Qingdao Branch of CSIC. The coating's preparation process was as follows. The TiO_2 sol was obtained by adding $TiCl_3$ solution to a stirred boiling 5 mol/L HCl solution and keeping at the boiling temperature for 12 h. The RuO_2 sol was prepared by the addition of solid $RuCl_3$ to stirred boiling water to form dispersed solid phase. This solution was kept at the boiling temperature for 7 h. The IrO_2 sol was prepared by dissolving H_2IrCl_6 in 1:1 (v/v) ethanol and propanol mixed solvent. The obtained TiO_2, IrO_2, and RuO_2 sols, as well as their mixtures, were stable dispersions for some time, and then the solutions having corresponding oxides were painted to titanium plates which were previously etched in hot HCl solution and dipped into a NaOH-ethanol mixture to remove grease. The layer was calcined at 450 °C for 20 min. The procedure was repeated until the expected coatings were obtained. The samples were embedded in Shin-Etsu Silicone and 5 cm^2 areas were exposed to the test solution. The A3 iron was used as negative material, and its area was equal to that of titanium supported anode.

2.2 Electrochemical Experiment

Electrochemical measurements were conducted in a conventional three-electrode system by using HA-501

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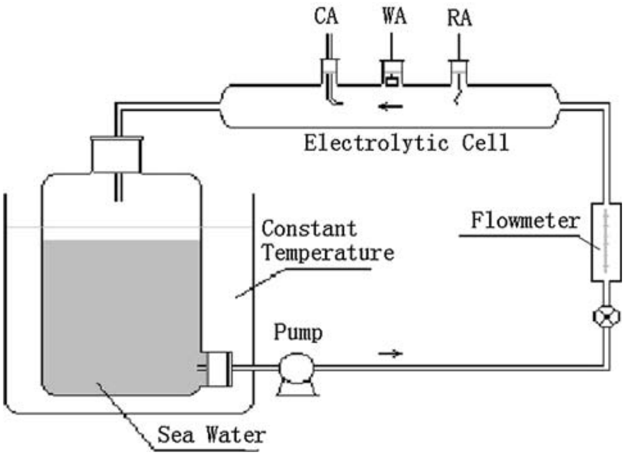

Fig. 1 The illustration of dynamic loop installation

POTENTIOSTAT/GALVANOSTAT, in which a platinum sheet acted as the counter electrode, titanium supported anode as the working electrode, and the saturated calomel (SCE) as the reference electrode. All potentials were recorded according to SCE. The solution was nature brine and its temperature was maintained around (25 ± 1) °C during testing. Figure 1 shows the dynamic loop installation used in the experiment. During testing, the brine's flow rate was set at 1.10, 2.11, and 10 cm/s, respectively. Cathodic polarization curves were obtained by sweeping from open circuit potential with a scanning rate of 50 mV/min after the specimens were immersed in the solution for about 20 min.

Anode electrolytic voltage was provided by steady transistor power (WYT-9B), and measured by numerical multimeter (DT-896). The constant current was obtained by adjusting resistance box (ZX38/10). Anode/cathode intervals were controlled at 2, 5, and 7 cm, respectively.

By o-tolidine light transmission, the active chlorine concentration in the brine was determined during electrolysis (Ref 5). The testing process was as follows. o-Tolidine was continuously added to the electrolyzed brine until the brine's color changed from yellow to yellow-brown. And then, the brine's transmittance was measured by spectrophotometer (type 72). The active chlorine concentration was determined according to the standard curve with known active chlorine concentration.

3. Results and Discussions

Figure 2 illustrates the curve of the current density versus the electrolytic voltage for Ti-Ir-Ru anode in electrolyzing the brine with a flowing velocity of 2.11 cm/s (ν = 2.11 cm/s). In the process, anode/cathode intervals were controlled at 2, 5, and 7 cm, respectively. As a result, the anode's electrolytic voltage increased with increasing current density. The reason was that the potential polarization degree and the brine's resistance were gradually raised during electrolyzing. At the same electrolytic voltage, the maximal current density all appeared at 7 cm interval.

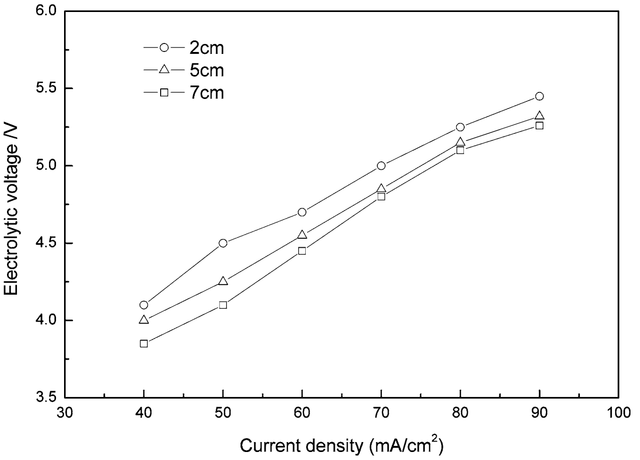

Fig. 2 The current density versus electrolytic voltage curve of Ti-Ir-Ru anode in flowing brine (ν = 2.11 cm/s)

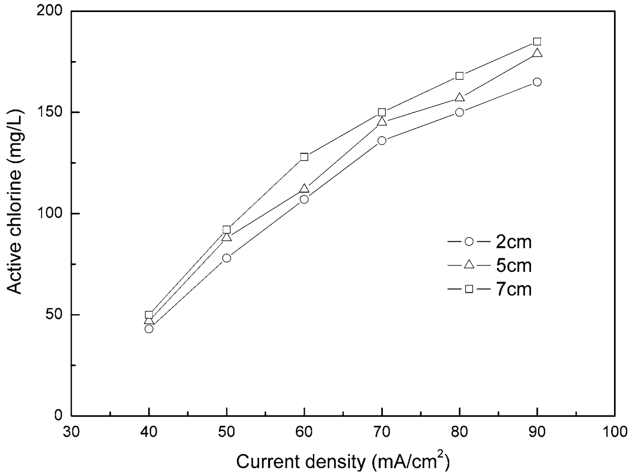

Fig. 3 The active chlorine concentration versus current density curve of Ti-Ir-Ru anode in flowing brine (ν = 2.11 cm/s)

The effect of Ti-Ir-Ru anode's electrolytic current density on the active chlorine concentrations in the brine with a velocity of 2.11 cm/s is shown in Fig. 3. From the figure it is seen that the active chlorine concentration increased with increasing current density. When the current density was 60 mA/cm^2, the active chlorine concentration was 128, 112, and 107 mg/L as the interval was 7, 5, and 2 cm, respectively. The maximal active chlorine concentration appeared at the interval 7 cm.

During electrolyzing, the current efficiency was evaluated by calculating the ratio of the actual active chlorine mole number to the theoretical active chlorine mole number. Figure 4 shows the effect of current density on the current efficiency and the energy consumption of Ti-Ir-Ru anode in the flowing brine (ν = 2.11 cm/s). According to the figure, the current efficiency and the energy consumption all increased with increasing current density. When the interval was set 2, 7, and 5 cm, the corresponding current efficiency was 47.6, 53.7, and 55.8%, respectively, with the current density of 60 mA/cm^2. The maximal current efficiency appeared at 5 cm interval. This manifested the interval had effect on the current efficiency. As a rule, the current efficiency of Ti-Ir-Ru anode in closed system is up to 90% (Ref 6). Since the electrolytic tests were done in an open system, the overflow and dissipation of chlorine was inevitable, which decreased the current efficiency. Kobayashi et al. (Ref 7) studied the electrochemical properties of activated

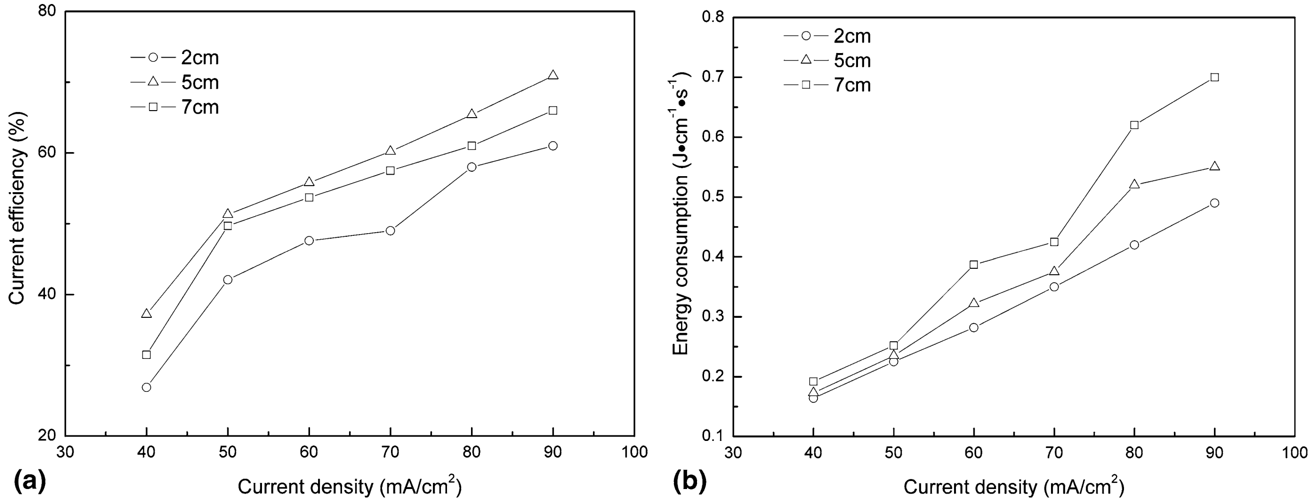

Fig. 4 The effect of current density on (a) the current efficiency and (b) the energy consumption of Ti-Ir-Ru anode in flowing brine (ν = 2.11 cm/s)

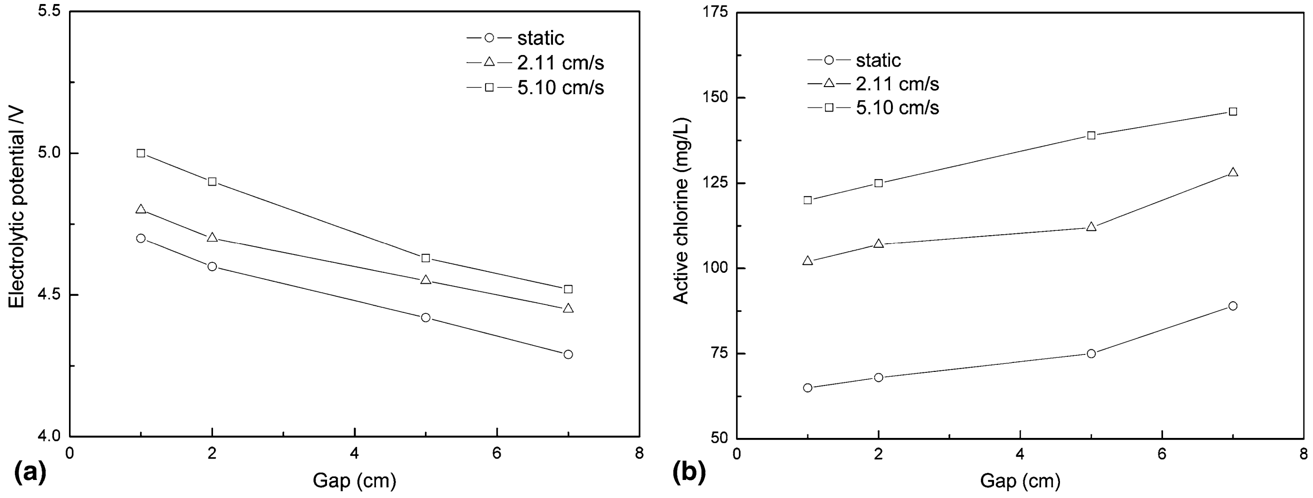

Fig. 5 The changes of (a) electrolytic voltage and (b) active chloride concentration with the anode/cathode interval for Ti-Ir-Ru anode in brine at 60 mA/cm^2 at different velocities

titanium anodes in electrolyzing dilute NaCl solution in an open system. Their results indicated that the maximal current efficiency was about 50%. Our results are in accordance with theirs. From Fig. 4(b), the larger the interval, the higher the energy consumption.

Figure 5 illustrates the changes of the active chloride concentration and the electrolytic voltage with the anode/cathode interval for Ti-Ir-Ru anode in the brine for different velocities at a current density of 60 mA/cm^2. As a result, the electrolytic voltage and the active chlorine concentration all increased with the increase of velocity. At a fixed flow rate, the electrolytic voltage decreased with the increase of anode/cathode interval (Fig. 5a). But the active chlorine concentration increased with the increase of anode/cathode interval (Fig. 5b). For example, the active chlorine concentration generated in the static brine was 75 mg/L. The value increased to 112 mg/L in the brine at the flow rate of 2.11 cm/s. It continued to build up to 139 mg/L while the brine's flow rate increased to 5.10 cm/s.

Figure 6 shows the effect of flow rate on the current efficiency and the energy consumption for Ti-Ir-Ru anode at 60 mA/cm^2. From Fig. 6(a), it is noted that the anode's current efficiency decreased with increasing flow rate, which indicated that the flow rate had some effect on the current efficiency. At a certain velocity, the anode's current efficiency gradually increased with increasing anode/cathode interval. The maximum was obtained when the interval was increased to 5 cm. And then, the current efficiency decreased with increasing interval. While anode/cathode interval was diminutive (such as 1 cm), $Mg(OH)_2$ and $Ca(OH)_2$ would accumulate on the cathode surface during the electrolytic process, which partially closed the cathode surface and inhibited the reduction of ClO^-. As a result, the current efficiency was decreased. However, as the interval exceeded 5 cm, the reduction of ClO^- on the cathode was accelerated, and oxygen was likely to release from the cathode, which reduced the current density. According to Fig. 6(b), the increase of the flow rate and the interval all resulted in increasing energy consumption (Ref 6).

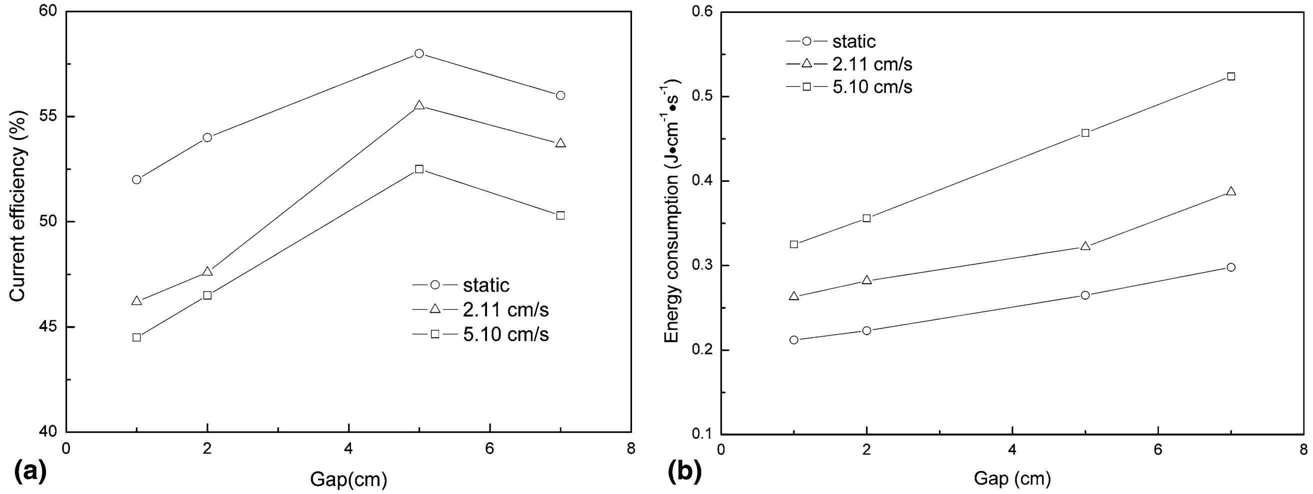

Fig. 6 The effect of the flow rate on (a) the current efficiency and (b) the energy consumption for Ti-Ir-Ru anode at various anode/cathode intervals at 60 mA/cm^2

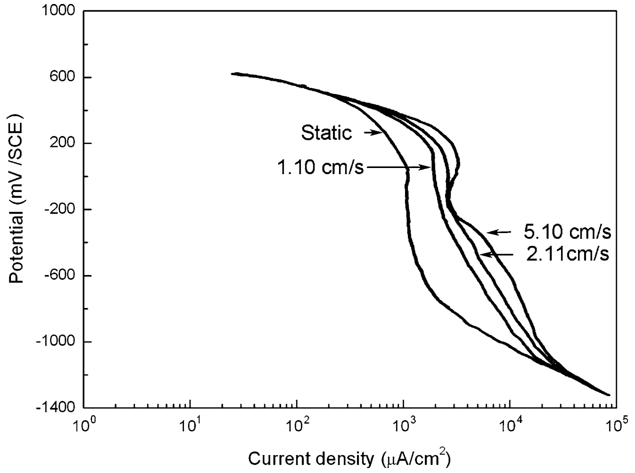

Fig. 7 The polarization curve of Ti-Ir-Ru anode at various flow rates of brine

The polarization curves of Ti-Ir-Ru anode in the brine with various flow rates are shown in Fig. 7. The flow rate had remarkable effect on the cathode reaction on the surface of Ti-Ir-Ru anode. The cathode polarization curve shifted right and the current density was augmented when the flow rate was increased. This indicated that the cathode polarization reaction was accelerated. Under static condition, the cathode polarization current density remained stable when the polarization potential was between 0.2 and 0.8 V. It was obvious that oxygen diffusion control was the rate controlling step under the flowing condition, the mass transfer velocity of oxygen is controlled by the laminar layer thickness (Eq 1),

$$N_A = \frac{D}{\delta} \times (C - C_1) \qquad \text{(Eq 1)}$$

where N_A is the mass transfer velocity in the phase, D the diffusion coefficient, and δ the thickness of laminar layer.

As δ is reduced, N_A increased. That is, the flowing of the solution attenuated the laminar layer's thickness. Oxygen could easily reach at the electrode surface (Ref 8). Thus, diffusion was no longer the rate controlling step. By now, oxygen absorption was controlled by the electrochemical reaction and the oxygen's diffusion. The polarization current density of oxygen absorption reaction increased with the potential shifting to negative values. At the same time, the cathode reaction was also accelerated while the flow rate increased. The evolution of hydrogen became the main reaction when the cathode polarization potential was negative to −1.2 V, which was controlled by electrochemical reaction and was not affected by the flow rate.

During the process of electrolyzing brine on Ti-Ir-Ru anode, the main electrode reaction was as follows (Ref 9).

$$\text{Anode:}\quad Cl^- \rightarrow \frac{1}{2}Cl_2 + e \qquad \text{(Eq 2)}$$

$$\text{Cathode:}\quad H_2O + \frac{1}{2}O_2 + 2e \rightarrow 2OH^- \qquad \text{(Eq 3)}$$

$$H_2O + e \rightarrow OH^- + \frac{1}{2}H_2 \qquad \text{(Eq 4)}$$

Anode side reaction

$$6ClO^- + 3H_2O \rightarrow 2ClO_3^- + 4Cl^- + 6H^+ + \frac{3}{2}O_2 + 6e \qquad \text{(Eq 5)}$$

Or

$$6HClO + 3H_2O \rightarrow 2ClO_3^- + 4Cl^- + 12H^+ + \frac{3}{2}O_2 + 6e \qquad \text{(Eq 6)}$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e \qquad \text{(Eq 7)}$$

$$4OH^- \rightarrow O_2 + 2H_2O + 4e \qquad \text{(Eq 8)}$$

$$ClO_3^- + H_2O \rightarrow ClO_4^- + 2H^+ + 2e \qquad \text{(Eq 9)}$$

Cathode side reaction

$$ClO^- + H_2O + 2e \rightarrow 2OH^- + Cl^- \qquad \text{(Eq 10)}$$

$$ClO_3^- + 3H_2O + 6e \rightarrow Cl^- + 6OH^- \qquad \text{(Eq 11)}$$

The other reaction

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \qquad \text{(Eq 12)}$$

$$Ca^{2+} + 2OH^- \rightarrow Ca(OH)_2 \qquad \text{(Eq 13)}$$

Sodium hypochlorite was the product of the mixed reaction of the anode and the cathode.

$$Cl_2 + 2NaOH \rightarrow NaOCl + NaCl + H_2O \qquad \text{(Eq 14)}$$

The above-mentioned anode side reaction (Eq 7 and 8) only took place while the Cl^- concentration in the vicinity of the anode decreased sharply. Since the potential of oxygen reduction on Ti-Ir-Ru anode was high, and the potential of active chlorine evolution on Ti-Ir-Ru anode was low, the electrode's polarization was obstructed. The reaction of Eq 2 became the preferred reaction, which restrained the evolution of oxygen and favored the emission of chlorine. That is, chlorine and hypochlorite ions were the main anode products.

During electrolysis, the electrolytic voltage was controlled by the concentration polarization of oxygen and the brine's resistance. When anode/cathode interval was diminutive, the electrolytic products were difficult to diffuse to the bulk solution, which resulted in an increase in the concentration polarization and the electrolytic voltage. As the gap and the current density were augmented, a great deal of bubbles evolved from the cathode, which agitated the brine and accelerated the diffusion process. As a result, the concentration polarization was eliminated. Thus, the electrolytic voltage with the anode/cathode interval of 7 cm was lower than that of 1 cm.

4. Conclusions

During the process of electrolyzing brine by Ti-Ir-Ru anode, the electrolytic voltage and the generated active chlorine concentration increased with increasing brine flow rate. The anode's energy consumption displayed the same variable rule as the electrolytic voltage. But the current density reduced with increasing flow rate. The brine's flow rate had remarkable effect on the oxygen absorption reaction. Raising flow rate could attenuate the thickness of mass-transfer control layer and expedite the oxygen's mass transfer, which accelerated the cathode polarization and the oxygen absorption reaction. In the flowing brine, the active chlorine concentration and the energy consumption increased with increasing anode/cathode interval. On the contrary, the electrolytic potential and the current efficiency decreased with increasing interval. The maximal current efficiency for Ti-Ir-Ru anode was obtained at the anode/cathode interval of 5 cm with current density of 60 mA/cm^2. At this point, Ti-Ir-Ru anode coating also had relatively low electrolytic voltage. The above was the ideal operating procedure for electrolyzing flowing brine using Ti-Ir-Ru anode coating.

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