Comparison of Electrosynthesis of Ammonium Persulfate by Membrane Electrolytic Cells with Shared Catholyte and with Separate Catholyte

Junbo ZHOU, a Yutong WU, a Chao WANG, a,b,* and Liping GAOC

a College of Mechanical and Electrical Engineering, Beijing University of Chemical Technology, No. 15, Beisianhu East Road, Chaoyang District, Beijing, 100029, China
b Beijing Key Laboratory for Emerging Organic Contaminants Control, School of Environment, Tsinghua University, Beijing, 100084, China
c College of Biochemical Engineering, Beijing Union University, No. 18, Fatou Xili 3 Qu, Chaoyang District, Beijing, 100023, China

* Corresponding author: wangchaobuct@163.com

ABSTRACT

To investigate the effect of catholyte shared by different membrane electrolytic cells on electrosynthesis of ammonium persulfate, the equivalent circuit models of two electrolytic cells with shared catholyte and separate catholyte were established and the pilot experiments were carried out with a cation exchange membrane (named PGN membrane) and the Al2O3 ceramic membrane. The model results showed that there appeared the bias ionic current from the low resistance electrolytic cell to the high resistance electrolytic cell with shared catholyte. The experimental results showed that the cathode current of the PGN membrane electrolytic cell was 56 A lower than its anode current with shared catholyte while the cathode current of the ceramic membrane electrolytic cell was 56 A higher than its anode current at the supply voltage of 5.3 V. And the current efficiency of PGN membrane and the ceramic membrane declined with their energy consumption increasing compared with those with separate catholyte. The model results showed a good agreement with those of the experiments. Therefore, it is necessary to consider the effect of shared catholyte by different membrane electrolytic cells on industrial electrosynthesis of ammonium persulfate.

Keywords : Shared Catholyte, Electrosynthesis, Ammonium Persulfate, Equivalent Circuit

1. Introduction

Ammonium persulfate ((NH4)2S2O8) exhibiting strong oxidizing properties has been widely used in the chemical engineering, the light industry, the electronics, petroleum and the food industries and as an initiator in organic synthesis industry and a detergent in the wastewater treatment and so on.1 At present, ammonium persulfate is mostly produced by the ion exchange membrane electrolysis of ammonium sulfate at the industrial scale:4

Anode reaction:

$$2\text{SO}_4^{2-} \rightarrow \text{S}_2\text{O}_7^{2-} + 2e^- \quad E^0 = 2.01 \text{ V vs. SHE}$$

Cathode reaction:

$$2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \quad E^0 = 0 \text{ V vs. SHE}$$

Mainly anodic side reaction:

$$2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4e^- \quad E^0 = 1.23 \text{ V vs. SHE}$$

Nowadays, the ceramic membrane is the main membrane used in the industrial electrosynthesis of ammonium persulfate. Although the electrical resistance of the ceramic membrane is higher with higher energy consumption compared with ion exchange membranes, it is still used by some factories in the industrial electrosynthesis of ammonium persulfate due to its lower price, easy installation and longer lifespan.5,6 The research on the electrosynthesis of ammonium persulfate mainly involves anode materials, cathode materials, additives, membranes and the cell structure.7–10 In past decades, ion exchange membranes have been widely used in the vanadium flow battery, the water electrolysis, the electrosynthesis and other production processes.6–10 In recent years, ion exchange membranes have played an important role in improving current efficiency and reducing energy consumption in the electrosynthesis of ammonium persulfate.13 At present, ion exchange membranes applied in the production of caustic soda have been extensively studied in the electrosynthesis of ammonium persulfate, such as Nafion® 424 membrane,14 Nafion® 117 membrane15 and the like. In the meanwhile, a lot of attention has been paid to the development and the research of novel ion membranes.16 The PGN membrane has the highest current efficiency and the lowest energy consumption in the electrosynthesis of ammonium persulfate compared with JCM-II® membrane, Nafion® 324 membrane and CMI-7000® membrane in our previous work.17

The plate-frame membrane electrolytic cell has been widely used in the industrial electrosynthesis of ammonium persulfate,18 the membrane of which can be ion exchange membranes or the ceramic membrane. Many plate-frame membrane electrolytic cells may be placed in a common catholyte to make full advantage of the catholyte and make the electrolytic cell compact in the industrial electrosynthesis of ammonium persulfate. During the technical transformation of some factories, the ion exchange membranes or the ceramic membrane will be put in the same electrolytic cell with shared catholyte to compare the performance of the different membranes, which is thought to ensure the same electrolytic conditions of the membranes. In regard to the cell structure with shared catholyte, the electrolytic performance of the membrane electrolytic cells may be affected when the performance of their membranes changed or the membrane performances are different, however, the corresponding experimental research has not been reported.

The equivalent circuit model has been used in the aluminum electrolysis industry19 and the battery industry.20 Although the equivalent circuit of the electrolytic cell has been studied,21 the equivalent circuit model of the electrolytic cells with the shared catholyte has not been reported in the literature.
In this paper, in order to study the effect of the shared catholyte by two electrolytic cells with different membranes, the equivalent circuit models were established and the pilot experiments with a cation exchange membrane (named PGN membrane) and the ceramic membrane were carried out to investigate the effect of shared catholyte on the electrolytic performances of the two electrolytic cells in the industrial electrosynthesis of ammonium persulfate.

2. Equivalent Circuit Model of Electrosynthesis of Ammonium Persulfate

2.1 Experimental electrolytic cell

Three dimensional diagram of the electrolytic cell with separated catholyte used in the experiment was shown in Fig. 1.

As shown in Fig. 1, the anode and the cathode were placed in a polypropylene cuboid electrolytic cell. The internal surface size of the polypropylene electrolytic tank was 60 cm $\times$ 130 cm $\times$ 35 cm. The cathode was made from lead antimony alloy orifice plate and the temperature of the catholyte was adjusted by a coil heat exchanger surrounding the cathode. The average distance between the membrane and the titanium plates of the anode was 1 cm and the average distance between the membrane and the cathode plate was 1 cm.

In Fig. 1, the positive junction and the negative junction were made from aluminium rods connected to anode and cathode by bolts, respectively. The current from the power supply to the positive junction of the anode flowed to the platinum wire and then to the cathode plate, negative junction in order and back to the power supply.

The anode, the membrane and the anode frame comprised an anode chamber, as shown in Fig. 2. The five anodic cuboid cavities were connected by circular titanium pipes as a heat exchanger with cooling water flowing to adjust the temperature of the anolyte. The membrane with an effective surface area of 0.57 m$^2$ was mounted on both sides of the anode frame, which was supported by the polypropylene rib plate.

The cross-sectional diagram of the electrolytic cell on the left membrane of Fig. 1 was shown in Fig. 3. As was shown in Fig. 3, the platinum wire with a total surface area of 1071.45 cm$^2$ welded onto the both side of the anode worked as the electrode and the five anodic titanium plates were connected as an anode body by two aluminium rods. The dimensions of anodic titanium plate was 18 cm $\times$ 28 cm and the thickness of the titanium plate was 2 mm. The red arrows illustrated the flow direction of the anolyte, which was set by the hole of the node frame near the arrows.

Three dimensional diagram of the electrolytic cells with shared catholyte used in the experiment was shown in Fig. 4.

As was shown in Fig. 4, two electrolytic cells were placed in a polypropylene cuboid electrolytic cell. One membrane of the two electrolytic cells was the PGN membrane and the other was the Al$_2$O$_3$ ceramic membrane. The two electrolytic cells shared the
catholyte between the two membranes and had their separate catholyte between the membrane and the wall of polypropylene cuboid electrolytic cell. And the other experimental devices were the same as shown in Fig. 1.

In Fig. 4, the two electrolytic cells were connected to the same power supply in parallel. The current from the power supply to the two positive junctions of the anode flowed to the platinum wire and then to the two cathode plates, negative junctions in order and back to the power supply.

2.2 The equivalent circuit model of one membrane electrolytic cell

The cell voltage of the electrolytic cell in the electrosynthesis of ammonium persulfate can be described using Eq. (1):22

\[
E_{\text{cell}} = E_\text{eq} + |A\Delta \varphi_\text{a}| + |A\Delta \varphi_\text{c}| + IR_{\text{Al}} + IR_{\text{Cl}} + IR_M + IR_a + IR_c
\]

where \(E_\text{eq}\) is the balance voltage, \(V\); \(A\Delta \varphi_\text{a}\) is the anodic overvoltage, \(V\); \(A\Delta \varphi_\text{c}\) is the cathodic overvoltage, \(V\); \(I\) is the working current, \(A\); \(R_{\text{Al}}\) is the ionic resistance of the anolyte, \(\Omega\); \(R_{\text{Cl}}\) is the ionic resistance of the catholyte, \(\Omega\); \(R_M\) is the electrical resistance of the membrane, \(\Omega\); \(R_a\) is the electrical resistance of the anode electrode, \(\Omega\); \(R_c\) is the electrical resistance of the cathode electrode, \(\Omega\).

In a steady electrosynthesis system of ammonium persulfate, it can be assumed that the value of the ionic resistance of anolyte \(R_{\text{Al}}\), the ionic resistance of catholyte \(R_{\text{Cl}}\), the electrical resistance of the membrane \(R_M\), the electrical resistance of the anode electrode \(R_a\) and the electrical resistance of the cathode electrode \(R_c\) are constant. The anodic overvoltage and the cathodic overvoltage are mainly affected by the electrode materials and the current density. In order to simplify the circuit model, the anodic overvoltage and the electrical resistance of the anode electrode are regarded as the product of one electrical resistance \(R_a\) and the working current \(I\). And the cathodic overvoltage and the electrical resistance of the cathode electrode are regarded as the product of one electrical resistance \(R_c\) and the working current \(I\). The balance voltage is mainly affected by the temperature and the electrolyte activity so the balance voltage can be regarded as the theoretical decomposition voltage \(E_\text{0}^0\). Therefore, the equivalent circuit model of one electrolytic cell in the electrosynthesis of ammonium persulfate can be simplified as shown in Fig. 5. 21

2.3 The equivalent circuit model of the electrolytic system with shared catholyte

In the equivalent circuit model of the electrolytic system of the electrosynthesis of ammonium persulfate, the electrical resistance of the electrolytic system in series with the electrolytic cell can be seen as one constant electrical resistance. When two electrolytic cells operate with separate catholyte and are connected to the same power supply \(E\) in parallel with the same anode interface and the same cathode interface, the equivalent circuit model of the electrolytic system can be shown in Fig. 6(a), where the physical quantities with the subscript of ‘1’ belong to the No. 1 electrolytic cell and the physical quantities with the subscript of ‘2’ belong to the No. 2 electrolytic cell. And \(R_{\text{CL1}}\) and \(R_{\text{CL2}}\) are the electrical resistance of the electrolytic system in series with No. 1 electrolytic cell and No. 2 electrolytic cell, respectively; \(E_{1\text{b}}^0\) and \(E_{2\text{b}}^0\) are the theoretical decomposition voltage of the No. 1 electrolytic cell and No. 2 electrolytic cell, respectively.

When two electrolytic cells operate with shared catholyte and are connected to the same power supply \(E\) in parallel with the same anode interface and the same cathode interface, the equivalent circuit model of the electrolytic system can be shown in Fig. 6(b), where the physical quantities with the subscript of ‘1’ belong to the No. 1 electrolytic cell and the physical quantities with the subscript of ‘2’ belong to the No. 2 electrolytic cell. And \(R_{\text{D1b}}\) and \(R_{\text{D2b}}\) are the electrical resistance of the electrolytic system in series with No. 1 electrolytic cell and No. 2 electrolytic cell, respectively; \(R_{\text{CL1b}}\) and \(R_{\text{CL2b}}\) are the ionic resistance of the separate catholyte of the No. 1 electrolytic cell and the No. 2 electrolytic cell, respectively. The electrolytic system in series with No. 1 electrolytic cell and No. 2 electrolytic cell, respectively, named the bias ionic resistance; \(E_{1b}^0\) and \(E_{2b}^0\) are the theoretical decomposition voltage of the No. 1 electrolytic cell and the No. 2 electrolytic cell, respectively.

Some assumptions in Fig. 6 are as follows:

\[
E_{1\text{a}}^0 = E_{2\text{a}}^0 = E_{1\text{b}}^0 = E_{2\text{b}}^0 = E^0
\]

\[
R_{\text{Al1}} = R_{\text{Al2}} = R_{\text{Alb}} = R_{\text{Alb}}
\]

\[
R_{\text{AL2a}} = R_{\text{AL1b}} = R_{\text{AL2b}}
\]

\[
R_{\text{CL1a}} = R_{\text{CL2a}}
\]

\[
R_{\text{CL1b}} = R_{\text{CL2b}}
\]

\[
R_{\text{CL1b}} = R_{\text{CL2b}}
\]

\[
R_{\text{CL1a}} = R_{\text{CL2a}} = R_{\text{CL1b}} = R_{\text{CL2b}}
\]

\[
R_{\text{M1a}} = R_{\text{M1b}}
\]

\[
R_{\text{M2a}} = R_{\text{M2b}}
\]

In addition, for the two electrolytic cells in Fig. 6, it can be assumed that the ionic resistance of the catholyte in Fig. 6(a) is equal to that of the separate catholyte plus that of the shared catholyte in Fig. 6(b). Therefore we have Eq. (11) and Eq. (12):

\[
R_{\text{CL1a}} = R_{\text{CL1b}} + R_{\text{b}}
\]

\[
R_{\text{CL2a}} = R_{\text{CL2b}} + R_{\text{b}}
\]
As shown in Fig. 6(a), when the two electrolytic cells operate with separate catholyte, the electric current of the No. 1 electrolytic cell \( I_{b1} \) and the electric current of the No. 2 electrolytic cell \( I_{b2} \) are calculated using Eq. (13) and Eq. (14), respectively:

\[
I_{b1} = \frac{E - E^0}{(R_{A1b} + R_{A1fb}) + R_{Di1} + (R_{C1b} + R_{C1fb} + R_{Di1})}
\]

(13)

\[
I_{b2} = \frac{E - E^0}{(R_{A2b} + R_{A2fb}) + R_{Di2} + (R_{C2b} + R_{C2fb} + R_{Di2})}
\]

(14)

As shown in Fig. 6(b), when the two electrolytic cells operate with shared catholyte, the anode current of the No. 1 electrolytic cell \( I_{a1} \), the anode current of the No. 2 electrolytic cell \( I_{a2} \), and the electric current of the No. 2 electrolytic cell \( I_{b2} \), the bias ionic current \( R_{Is} \) are calculated using Eqs. from (15) to (19):

\[
I_{a1} - I_{b1} - I_{11b} = 0
\]

(15)

\[
I_{a2} + I_{b2} - I_{21b} = 0
\]

(16)

\[
E^0 + (R_{A1b} + R_{A1fb})I_{b1} + R_{Di1}I_{b1} + (R_{C1b} + R_{C1fb} + R_{Di1})I_{11b} - E = 0
\]

(17)

\[
E^0 + (R_{A2b} + R_{A2fb})I_{b2} + R_{Di2}I_{b2} + (R_{C2b} + R_{C2fb} + R_{Di2})I_{21b} - E = 0
\]

(18)

\[
E^0 + (R_{A2b} + R_{A2fb})I_{b2} + R_{Di2}I_{b2} + (R_{C2b} + R_{C2fb} + R_{Di2})I_{21b} - E = 0
\]

(19)

where \( I_{ab} \) is named the bias ionic current, \( A; I_{1a} \) is the cathode current of the No. 1 electrolytic cell, \( A; I_{2a} \) is the cathode current of the No. 2 electrolytic cell, \( A \).

3. Experimental

3.1 Materials and chemicals

The pilot experiment was carried out in a company producing ammonium persulfate in Hebei province. The cation exchange membrane named PGN membrane was investigated in our previous work. Both PGN membrane and the ceramic membrane were purchased from Beijing University of Chemical Technology. Ammonium sulfate \((\text{NH}_4)_2\text{SO}_4\), sulfuric acid \((\text{H}_2\text{SO}_4)\), and ammonium persulfate \((\text{NH}_4\text{HS}_2\text{O}_8)\) were provided by the company. Chemicals for volumetric titration analysis (ferrous sulfate \((\text{FeSO}_4)\) and potassium permanganate \((\text{KMnO}_4)\)) were used of analytical grade and were purchased from Tianjin Hongyan Chemical Reagent Factory.

3.2 Physical characterization of PGN membrane and \(\text{Al}_2\text{O}_3\) ceramic membrane

The PGN membrane was fabricated by solution coating technology. First, a proper amount of perfluorinated sulfonic acid resin (Shandong Dongyue Group Shenzhen New Material Co., Ltd.) was dissolved in NaOH solution and then in isopropyl alcohol-water solution. And the structure of the perfluorinated sulfonic acid resin was shown in Fig. 7. Then mixture of the resin solution and pyrrolidone solution was heated at a certain temperature to produce the resin solution with high boiling point. And the solution was casted onto the clean strip surface with polytetrafluoroethylene reinforced mesh and transferred at a certain temperature after removing bubble. Afterward, the prepared membranes were immersed in diluted hydrochloric acid and then washed by deionized water to obtain the PGN membrane finally.

The \(\text{Al}_2\text{O}_3\) ceramic slurry was produced by quadratic ball mill process with \(\text{Al}_2\text{O}_3\) powder as the aggregate, polyvinyl butyral (PVB) as binder, phthalate butyl ester (DBP) as the plasticizer and ethanol as the solvent. Then the porous \(\text{Al}_2\text{O}_3\) ceramic membrane was formed through flow-casting, dumping, pore-forming, sintering the \(\text{Al}_2\text{O}_3\) ceramic slurry.

The two membranes’ cross-section surface morphologies were characterized by a scanning electron microscope (SEM) (S-4700, HITACHI). And the cross-section surface of PGN membrane was obtained by brittle failure using liquid nitrogen.

Fourier-transform infrared (FTIR) spectra of PGN membrane was recorded on a TENSOR 27 spectrometer (Bruker, Germany) between 4000 cm\(^{-1}\) and 525 cm\(^{-1}\) with a resolution of 1 cm\(^{-1}\).

The properties of the PGN membrane and the \(\text{Al}_2\text{O}_3\) ceramic membrane were shown in Table 1 and Table 2, respectively. From Table 1 and Table 2, it can be seen that the electrical conductivity of the PGN membrane is higher than that of the \(\text{Al}_2\text{O}_3\) ceramic membrane and the thermal stability range of the two membranes can meet the demand of the temperature of 20°C–40°C in the industrial electrosynthesis of ammonium persulfate.

3.3 Experimental design

The diagram of the experimental apparatus for an electrolytic cell in the pilot electrosynthesis of ammonium persulfate was shown in Fig. 8. A power converter (KGD1-1000 A/30 V) from (Beijing Chunshu Rectifier Co., Ltd.) was used in the experiment with separate catholyte and the experiment with shared catholyte used the power supply of the company producing ammonium persulfate. As for the experiment with separate catholyte and shared catholyte, the experimental apparatus that both of the electrolytic cells were equipped with consisted of two plastic rotor flowmeters (ZN-LZS-15) from Jiangsu Instrument Technology Co., Ltd. and two flow regulating valves (Q11F-10S) from Ningbo Arkema Pipe Valve

---

**Table 1.** The properties of the PGN membrane.

| Membrane | Thickness (µm) | Electrical conductivity (S/cm) | Ion exchange capacity (meq/g) | Water Content (%) | Thermal stability range (°C) | Burst strength (MPa) |
|----------|----------------|-------------------------------|-----------------------------|-------------------|-----------------------------|---------------------|
| PGN      | 320            | 0.13                          | 1.3                         | 30                | 5–80                        | 0.5                 |

**Table 2.** The properties of the \(\text{Al}_2\text{O}_3\) ceramic membrane.

| Membrane | Thickness (mm) | Average pore size (µm) | Porosity (%) | Electrical conductivity (S/cm) | Thermal stability range (°C) | Compressive strength (MPa) |
|----------|----------------|------------------------|--------------|-------------------------------|-------------------------------|---------------------------|
| Ceramic  | 4              | 10                     | 35           | 0.03                          | 0–300                         | 10                        |
Figure 8. Diagram of the experimental apparatus for an electrolytic cell.

Technology Co., Ltd. The anode current and the cathode current were measured by a clamp type DC ammeter (BM2000B) from Shenzhen Riverside Electronic Technology Co., Ltd. When two electrolytic cells operate with shared catholyte, the anodes of the two electrolytic cells in parallel are connected to the same anode interface of the power converter with their cathodes connected to the same cathode interface.

The electrochemical reaction in the electrolytic cell was operated using the anolyte with a mixture of 90 g L\(^{-1}\) (NH\(_4\))\(_2\)SO\(_4\) and 460 g L\(^{-1}\) (NH\(_4\))\(_2\)SO\(_4\) and the catholyte with a mixture of 49 g L\(^{-1}\) H\(_2\)SO\(_4\) and 400 g L\(^{-1}\) (NH\(_4\))\(_2\)SO\(_4\) at a temperature of 35°C at an electrolyte flow rate of 2 L min\(^{-1}\). All experiments were conducted using constant voltage method with the electrolytes continually pumped from the inlet reservoir to the electrolytic cell and then flowing into the outlet reservoir. Afterwards, the anolyte was cooled and crystallized to produce ammonium persulfate particles and the catholyte was recycled to prepare the inlet catholyte again. The electrolyte flow was regulated by the valve at the inlet pipe of the electrolyte. Samples were extracted at the anolyte outlet for analysis when the ammonium persulfate concentration of the anolyte outlet remained unchanged.

3.4 Analytical methods

The amount of the ammonium persulfate generated was determined using the potassium permanganate method. Samples of solutions were treated by excess 0.2 mol L\(^{-1}\) standard FeSO\(_4\) solution, which generated Fe\(_2\)(SO\(_4\))\(_3\) with surplus FeSO\(_4\). The surplus FeSO\(_4\) was measured using 0.01 mol L\(^{-1}\) standard KMnO\(_4\) solution that could be used as an indicator to determine the end point of the titration.

The titration reaction:

\[
2\text{FeSO}_4 + (\text{NH}_4)_2\text{S}_2\text{O}_8 = \text{Fe}_2(\text{SO}_4)_3 + (\text{NH}_4)_2\text{SO}_4
\]

The concentration of the ammonium persulfate \((c, \text{ moL}^{-1}\) \) was calculated using Eq. (20) according to the titration reaction above:

\[
c = \frac{(c_1 V_1 - 5c_2 V_2)}{nV_0} \tag{20}
\]

where \(c_1\) and \(c_2\) were the concentration of the FeSO\(_4\) solution and the KMnO\(_4\) solution, respectively, \(\text{mol} L^{-1}\); \(V_0, V_1\) and \(V_2\) were the titration volume of samples, FeSO\(_4\) solution and KMnO\(_4\) solution, respectively; \(L\); \(n\) was the charge of S\(_2\)O\(_8^{2-}\) that was equal to 2.

The experimental current efficiency \((\eta, \text{ %})\) was calculated using Eq. (21):

\[
\eta = \frac{nFV(c_4 - c_3)}{I} \times 100\% \tag{21}
\]

where \(c_3\) and \(c_4\) were the concentration of ammonium persulfate before electrolysis and after electrolysis, respectively, \(\text{moL} L^{-1}\); \(V\) was the total volume of the anolyte flowing through the anode chamber; \(I\) was the Faraday constant, 96485 C mol\(^{-1}\); \(I\) was the working current; \(A\); \(t\) was the total time of the constant cell voltage applied; \(s\); \(n\) was the number of electrons involved in the anode reaction that was equal to 2.

The experimental energy consumption per ton of the ammonium persulfate generated \((W, \text{kWh} t^{-1})\) is calculated using Eq. (22):

\[
W = \frac{UI/t/3600/1000}{V_0(c_4 - c_3)M/10^6} \tag{22}
\]

where \(U\) was the constant cell voltage applied; \(V\); \(M\) was the molar mass of ammonium persulfate, g mol\(^{-1}\).

4. Results and Discussion

4.1 The effect of the power supply on the current of the equivalent circuit

In the experiment of the electrosynthesis of ammonium persulfate where \(E^0 = 2.01\) V, the experimental current results at the power supply of 5.5 V are as follows: \(I_{1a} = 602\) A, \(I_{2a} = 447\) A, \(I_1 = 619\) A, \(I_{2b} = 441\) A, \(I_{1tb} = 533\) A and \(I_{2tb} = 527\) A, so \(I_{fb} = I_{1b} - I_{1tb} = I_{2b} - I_{2tb} = 86\) A. Using equations from Eq. (15) to Eq. (19) with the current value at the power supply of 5.5 V, we can get the values of resistance as follows: \(R_{41b} + R_{42tb} = 4\) m\(\Omega\), \(R_{MA} = 1\) m\(\Omega\), \(R_{MB} = 3\) m\(\Omega\), \(R_{3b} = 0.05\) m\(\Omega\), \(R_{CL1b} + R_{CL2b} = 0.8\) m\(\Omega\) in Fig. 6. Then Matlab was used to calculate \(I_1ab, I_2ab, I_1tb, I_2tb, I_{1b}, I_{1tb}\) and \(I_{2b}, I_{2tb}\) at different supply voltages in Fig. 6.

As shown in Fig. 9, when the No. 1 electrolytic cell and the No. 2 electrolytic cell shared the same catholyte, the bias ionic current \(I_{fb}\) increased with the increase of the power supply, which suggested that the voltage of the cathode electrode of the No. 1 electrolytic cell was higher than that of the cathode electrode of the No. 2 electrolytic cell and there existed the bias ionic current flowed from the cathode electrode of the No. 1 electrolytic cell to that of the No. 2 electrolytic cell.

As shown in Fig. 10, with respect to the No. 1 electrolytic cell, its anode current \(I_{1b}\) with shared catholyte was higher than that with...
catholyte was lower than that with separate catholyte the No. 2 electrolytic cell. The electrolytic cell with separate catholyte lower than the anode current of the No. 1 electrolytic cell increased the ionic supply voltages in the equivalent circuit. The current of the No. 1 electrolytic cell, the interelectrode gap of which was much higher than that of the No. 1 electrolytic cell. The higher interelectrode gap of the No. 1 electrolytic cell increased the ionic resistance of its electrode reactions, which could decline its current efficiency of anode corresponding to the part of cathodic reaction of the No. 1 electrolytic cell reacted on the cathode surface of the No. 2 electrolytic cell. On the other hand, compared with operating with separate catholyte, there were two cathodes for the anodic reaction of the No. 1 electrolytic cell, which increased its anode current on the whole.

In addition, the part of the cathodic reaction of the No. 1 electrolytic cell reacted on the cathode surface of the No. 2 electrolytic cell caused the bias ionic current, which increased cathode current of the No. 2 electrolytic cell but reduced its active cathode surface and the mass transfer rate for the anode reaction of the No. 2 electrolytic cell resulting in the decline of its cathode current and current efficiency. According to the law of conservation of charge, the decline of the cathode current of the No. 2 electrolytic cell caused the decline of its corresponding anode current. Therefore, the shared catholyte exerted an effect on the current and the current efficiency of the two electrolytic cells.

4.2 The effect of the ionic resistance on the bias ionic current

As shown in Fig. 4.2, when the power supply was 5 V in the equivalent circuit shown in Fig. 6(b), the bias ionic current \( I_{1b} \) increased with the increase of the bias ionic resistance \( R_{3b} \) and other condition remaining constant. When the bias ionic resistance \( R_{3b} \) increased from \( 10^{-3} \) Ω to \( 10^{-4} \) Ω, the bias ionic current declined slowly from 75.1 A to 72.4 A. When the bias ionic resistance increased from \( 10^{-4} \) Ω to \( 10^{-1} \) Ω, the bias ionic current declined quickly from 72.4 A to \( 5.0 \times 10^{-3} \) A. When the bias ionic resistance increased from \( 10^{-1} \) Ω to \( 10^{3} \) Ω, the bias ionic current declined slowly from \( 5.0 \times 10^{-3} \) A to \( 4.8 \times 10^{-5} \) A.

As the electrolytic cells with the shared catholyte, on one hand, it can be seen from Fig. 12 that the bias ionic current was high and remained almost constant when the bias ionic resistance was low than one value, which should be considered in the electrosynthesis of ammonium persulfate. On the other hand, when the bias ionic resistance was high than one value, the bias ionic current was very low and changed a little, where the bias ionic current could be neglected. When the two electrolytic cells shown in Fig. 4 was separated by a plastic film, the bias ionic resistance was high and the bias ionic current was low and could be neglected and when there was even a little leakage with the bias ionic resistance high than one value, the corresponding bias ionic current may be low causing a little effect on the current and the current efficiency of the electrolytic cells, which could be neglected in the industrial electrosynthesis of ammonium persulfate.

**Figure 10.** The current of the No. 1 electrolytic cell at different supply voltages in the equivalent circuit.

**Figure 11.** The current of the No. 2 electrolytic cell at different supply voltages in the equivalent circuit.

**Figure 12.** The effect of the bias ionic resistance on the bias ionic current.
4.3 The characterization of PGN membrane and Al₂O₃ ceramic membrane

The presence of sulfonic acid groups (SO₃H) of PGN membrane is confirmed by FTIR spectra (shown in Fig. 13). The peak at 3193 cm⁻¹ is due to the vibration of water free H₃O⁺ and the peak at 1700 cm⁻¹ is caused by the presence of the weakly-hydrated H₂O⁺(H₂O)₂. The peak at 1468 cm⁻¹ is assigned as S=O stretching bands of the -SO₃H group. The peaks at 1222 cm⁻¹ and 1153 cm⁻¹ are attributed to vibration of -CF₂ symmetric stretching vibration and -CF₂ asymmetric stretching vibration, respectively. The peak at 1054 cm⁻¹ is characteristic of -SO₃H stretching vibration, strongly indicating the presence of SO₃H group. A peak at 979 cm⁻¹ is due to the -C-O-C- symmetric stretching vibration and the peaks at 632 cm⁻¹ and 524 cm⁻¹ are due to the -CF₂ wagging vibration and -CF₂ twisting vibration, respectively.

The cross-section surface morphology of the PGN membrane was presented in Fig. 14. As shown in Fig. 14, there was a good bond between the perfluorinated sulfonic acid resin and the reinforced mesh. The cross-section morphology of the Al₂O₃ ceramic was depicted in Fig. 15. The Al₂O₃ ceramic membrane had a porous cross-section surface with different pore sizes, which facilitated to entrap the aqueous liquid electrolyte upon soaking the membrane into it.

4.4 The bias ionic current in the experiment of the electro-synthesis of ammonium persulfate

Table 3 showed the electrolytic parameters of the PGN membrane electrolytic cell and the Al₂O₃ ceramic membrane electrolytic cell with separate catholyte and with shared catholyte at the supply voltage of 5.3 V at an electrolyte flow rate of 2 L min⁻¹. As was seen in Table 3, the anode current of the PGN membrane electrolytic cell was 540 A that was equal to its cathode current with separate catholyte. When it came to the shared catholyte, the anode current of the PGN membrane electrolytic cell increased to 541 A and its cathode current declined to 485 A. And the anode current of the ceramic membrane electrolytic cell was 444 A that was equal to its cathode current with separate catholyte, whereas its anode current declined to 440 A while its cathode current increased to 496 A with shared catholyte. It can be seen from Table 3 that there appeared the bias ionic current from the cathode electrode of the PGN electrolytic cell to the cathode electrode of the ceramic membrane electrolytic cell and the bias ionic current reached 56 A at the supply voltage of 5.3 V. In addition, as could be seen from Table 3, compared with operating with separate catholyte, the current efficiency of the two electrolytic cells declined with their energy consumption increased with shared catholyte.

Because the electrical resistance of the PGN membrane was lower than that of the ceramic membrane, the electrical resistance of the PGN membrane electrolytic cell was lower than that of the ceramic membrane electrolytic cell in the experiment. According to the equivalent circuit shown in Fig. 4, the PGN membrane electrolytic cell and the ceramic membrane electrolytic cell could be regarded as the No. 1 electrolytic cell and the No. 2 electrolytic cell in the equivalent circuit, respectively. Besides, the appearance of the bias ionic current in the experiment was in agreement with that of the bias ionic current in the equivalent circuit model in Fig. 6.

According to the analysis of the equivalent circuit model, compared with shared catholyte, the increase of the cathode current

| Membrane type | Catholyte state | Cell voltage (V) | Anode current (A) | Cathode current (A) | Current efficiency (%) | Energy consumption (kWh t⁻¹) |
|---------------|----------------|-----------------|-------------------|---------------------|------------------------|-----------------------------|
| PGN membrane  | Separate       | 5.0             | 540               | 540                 | 93.87                  | 1250                        |
|               | Shared         | 5.05            | 541               | 485                 | 85.89                  | 1380                        |
| Ceramic membrane | Separate    | 5.0             | 444               | 444                 | 66.6                   | 1762                        |
|               | Shared         | 4.9             | 440               | 496                 | 62.4                   | 1843                        |
of the ceramic membrane electrolytic cell and the decline of the cathode current of the PGN membrane electrolytic cell resulted from that the part of cathodic reaction of the PGN membrane electrolytic cell reacted on the cathode surface of the ceramic membrane electrolytic cell, which caused the bias ionic current. Moreover, the bias ionic current increased the interelectrode gap of the part reaction of the PGN membrane electrolytic cell increasing the ionic resistance of its electrode reactions, which declined its current efficiency of anode corresponding to the part of cathodic reaction of the PGN membrane electrolytic cell reacted on the cathode surface of the ceramic membrane electrolytic cell. In the meanwhile, with respect to the ceramic membrane electrolytic cell, the bias ionic current reduced its active cathode surface and the mass transfer rate on its cathode surface resulting in the decline of its current efficiency the corresponding anode current, which increased its energy consumption.

5. Conclusions

The investigation results of the equivalent circuit model of the two electrolytic cells showed that the bias ionic current appeared when the two electrolytic cells with different electrical resistance shared the same catholyte. The bias ionic current occurred from the electrolytic cell with lower cell resistance to that with higher cell resistance, which changed the electrode current and the current efficiency of the electrolytic cells. Besides, when the bias ionic resistance increased, the bias ionic current first declined slowly, then declined rapidly, and then declined slowly, which was valuable in the industrial electro synthesis of ammonium persulfate.

The experimental results revealed that the bias ionic current caused by catholyte shared reached 56 A from the cathode of the PGN electrolytic cell with lower cell resistance to the cathode of the Al2O3 ceramic membrane electrolytic cell with lower cell resistance at a supply of 5.3 V and at an electrolyte flow rate of 2 L min⁻¹ using the anolyte with a mixture of 90 g L⁻¹ (NH4)2S2O8 and 460 g L⁻¹ (NH4)2SO4 and the catholyte with a mixture of 49 g L⁻¹ H2SO4 and 400 g L⁻¹ (NH4)2SO4 in the pilot electro synthesis of ammonium persulfate. Because of the bias ionic current, the cathode current of the PGN membrane electrolytic cell was 56 A lower than its anode current and the cathode current of the ceramic membrane electrolytic cell was 56 A higher than its anode current, which reduced their current efficiency and increased their energy consumption. The bias ionic current in the experiment was in agreement with that of the bias ionic current in the equivalent circuit model. Therefore, it should be taken into account that the effect of the bias ionic current on the industrial electro synthesis of ammonium persulfate when the two electrolytic cells operated with the shared catholyte.

References

1. S. Wachnow, H. V. Latze, K. Grübel, V. T. Padil, M. Černík, and D. D. Dionysiou, *Chem. Eng. J.*, **330**, 44 (2017).
2. L. Rozenberga, L. Vikele, L. Vecbiskena, I. Sable, M. Laka, and U. Grinfelds, *Key Eng. Mater.*, **674**, 21 (2016).
3. L. R. Bernedsen, *In situ chemical oxidation: The Mechanisms and Applications of Chemical Oxidants for Remediation Purposes*, Elsevier B.V., Amsterdam, p. 13 (2014).
4. K. K. Hii, K. Hellgardt, G. H. Kelsall, J. B. Brazier, and L. A. Adrio, International Patent, WO/2016/193738A1 (2016).
5. X. Cheng and H. Liang, *J. Harbin Inst. Technol.*, **48**, 1 (2016).
6. S. K. Amin, M. H. Roushdy, S. A. El-Sherbiny, and H. A. M. Abdallah, *Int. J. Appl. Eng. Res.*, **11**, 7708 (2016).
7. J. R. Davis, J. C. Baygents, and J. Farrell, *J. Appl. Electrochem.*, **44**, 841 (2014).
8. V. Brieaga-Martos, E. Herrero, and J. M. Feliz, *Electrochim. Acta*, **241**, 497 (2017).
9. A. Lim, K. C. Min, S. Y. Lee, H. J. Kim, S. J. Yoo, Y. E. Sung, J. H. Jang, and H. S. Park, *J. Electrochem. Sci. Technol.*, **8**, 265 (2017).
10. C. Kim, P. Sehnuk, J. Lee, M. Asla, and V. Presser, *Desalin.*, **425**, 104 (2018).
11. H. Luo, C. Li, X. Sun, and B. B. Ding, *J. Electroanal. Chem.*, **792**, 110 (2017).
12. D. Chen, X. Chen, L. Ding, and X. Li, *J. Membr. Sci.*, **553**, 25 (2018).
13. N. Xu, *Guangdong Chem. Ind. (Natural Science Edition)*, **42**, 114 (2015).
14. J. Zhu, K. K. Hii, and K. Hellgardt, *J. Appl. Surf. Chem. Eng.*, **4**, 2027 (2016).
15. Y. Wang, Y. Xiong, and J. Zhang, *J. Southeast Univ.*, **45**, 738 (2015).
16. H. Nan and Y. Wang, *Chem. Ind. Eng.*, **30**, 53 (2013).
17. C. Wang, J. Zhou, and L. Gao, *J. Electrochem. Sci. Technol.*, **9**, 37 (2018).
18. G. Zhang and Y. Chen, *Guangzhou Chin. Ind.*, **40**, 19 (2012).
19. Y. Wang, J. Tie, G. Tu, S. Sun, R. Zhu, and Z. Zhang, *Trans. Nonferrous Met. Soc. China*, **25**, 335 (2015).
20. J. Xu, L. Pei, B. Xu, G. Wu, and C. Zhu, *Electr. Meas. Instrum.*, **54**, 1 (2017).
21. C. H. Hamann, A. Hamnett, and W. Vielstich, *Electrochemistry: Second edition*, Chemical industry press, Beijing, p. 59 (2016).
22. D. Xie, S. Tong, and B. Lou, *Fundamental Knowledge of Industrial Electrochemistry*, Chemical industry press, Beijing, p. 224 (2009).
23. A. Grucher, A. Régis, T. Schmatko, and P. Colomban, *Vib. Spectrosc.*, **26**, 215 (2001).
24. M. Ludvigsson, J. Lindgren, and J. Tegenfeldt, *Electrochim. Acta*, **45**, 2267 (2000).
25. Y. Zhang and Y. Chen, *Guangzhou Chin. Ind.*, **40**, 19 (2012).
26. S. Xu, R. Jiang, and Y. Gao, *J. Membr. Sci.*, **507**, 63 (2016).