

## Effect of different anions back-diffusion through cation-exchange membrane at different cathodes: anode sodium concentration ratio

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### ABSTRACT

In the progress of integrating alkaline recovery of valuable metals from the waste catalyst and the regeneration of alkali liquor by electro-dialysis processes, the back-diffusion of anions through the cation-exchange membrane is one of the key issues that limit the effect of electro-dialysis. Parameters of current efficiency and desalination rate reveal that the back-diffusion quantity of hydroxide ions ( $\text{OH}^-$ ) enhanced along with the change of cathode: anode sodium concentration ratio. The presence of  $\text{CO}_2$  can decrease the back-diffusion quantity of  $\text{OH}^-$  owe to  $\text{OH}^-$  had been transformed into carbonate ions ( $\text{CO}_3^{2-}$ ). Ionic coefficient also showed that their ionic concentration difference in concentration polarization layers. Therefore, the back-diffusion of  $\text{CO}_3^{2-}$  is more difficult than  $\text{OH}^-$  because of their different interactions with the functional groups of membrane. Different back-diffusion quantity of two anions ( $\text{OH}^-$  and  $\text{CO}_3^{2-}$ ) through cation-exchange membrane may be owe to their different ionic diffusion capacity and interactions with the functional groups of membrane.

*Keywords:* Electro dialysis; Back diffusion of anions; Oxometallate sodium; Current efficiency; Carbon dioxide

### 1. Introduction

Membrane technology has obtained a wide range of applications in the industry and in research centers for recent years. Improved ionic selectivity, stability, and non fouling property have made ion-exchange membranes (IEMs) to be an important method in chemical and waste treatment applications, such as the desalination of brackish water, the recovery of valuable metals from the effluents industry, and application in the food and pharmaceutical industry [1–4]. As a separation process of IEMs, the selectivity of ion transport has been improved in order to obtain better performance of the process which is compatible with the technical and economic conditions. The different percentage of individual ion removal made ion-exchange membrane with various applications, such as mono- and di-valent perm selective membrane [5].

However, the influential factors of electro-dialysis separation performance are various, such as polymer composite

of the membrane, water content, specific surface area, surface hydrophilicity, ion exchange capacity, ionic permeability, conductivity, type of electrode, solvent flux and so on. Gohil et al. investigated different type inter polymer films of cation-exchange membrane (CEM) and concluded that electrochemical transport properties of the homogeneous type of CEMs are superior to those of the heterogeneous type of CEMs [6]. Their research was also observed that due to the coating of PPY for 2 h, membrane perm selectivity of CEM for NaCl (0.907) had changed [7]. The effect of electrolyte concentration and environmental pH variations on membranes illustrated that CEM had higher potential, transport number, and selectivity at specific pH and membrane resistance was decreased due to the increase of electrolyte concentration [8]. N. Tzanetakis et al. investigated the comparative performance of flat membrane and corrugated membrane for electro dialysis showed that the membrane structure had also related to current efficiency [9].

Meanwhile, a factor that influences the effect of electro-dialysis is ion back-diffusion through membrane, both

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for CEM and anion-exchange membrane (AEM). IEMs absorbed water are swollen polymeric ion exchangers and ions can back-diffuse through membrane accompany with water. In AEM, the proton transports by a mechanism which is fundamentally different from that of other ions: its mobility is abnormally high [10]. Losses of current efficiency, especially Nafion membrane, caused by the back-diffusion of OH<sup>-</sup> have been found for many years. In the classical Grotthus mechanism, the OH<sup>-</sup> migrates from one water molecule to another, and the classical co-ion leakage is associated with the transport of the sorbed electrolyte. The solution of this problem mainly focuses on changing the properties of CEM or increasing the acid concentration in the anodic compartment. A large quantity of H<sup>+</sup> migrate from the cation-selective membrane to inhibit OH<sup>-</sup> ions back-diffusion that can enhance the current efficiency of the membrane, but it will decrease the life of membrane [11]. Considering the selective mono-valent ion properties of Nafion membrane, OH<sup>-</sup> selective back-diffusion to anodic compartment may influence the electro-dialysis performance.

Meanwhile, roasting of spent catalysts with sodium salts significantly enhanced the solubility of some metals in water from where they could be recovered, such as recovering vanadium and tungsten from selective catalyst reduction (SCR) catalyst [12]. However, the step of separating and recovering metals from alkali recycling liquor of SCR catalyst demands acid to control the pH value of the solution. Recovering vanadium from recycling solution should be adjusted pH of solution around zero to four [13]. Compared to traditional methods of adding acid to decrease pH, utilizing CEM electrolysis process to deal with valuable metal recovered solution had few attentions. Meanwhile, the aqueous alkaline solution in the cathodic compartment can be recycled to dissolve the precious metal of waste catalysts. However, dealing with back-diffusion of OH<sup>-</sup> in the cathodic compartment to enhance electro-dialysis efficiency will become one of the key issues to this technique.

Therefore, the objective of this novelty work is to utilize recovering metals process from SCR catalyst alkali recycling liquor to demonstrate the relationship between electrolysis performance and the back-diffusion of different anions through CEM in sodium solution. In order to consider compose of SCR catalyst recycling alkaline solution, the anolyte of sodium metavanadate (NaVO<sub>3</sub>) and sodium tungstate (Na<sub>2</sub>WO<sub>4</sub>) have been discussed in this research. By investigating ionic coefficient *K* of two different anions, the reason that influence electrolysis effectiveness was discussed. In this research, we present one of the possible explanation of the practical back-diffusion phenomenon for system, and we show how to reduce influence of electrolysis resulting from anions back-diffusion.

## 2. Materials and methods

The solution applied to CEM electrolysis experiment was prepared with analytical grade chemicals. Sodium metavanadate dihydrous (NaVO<sub>3</sub>·2H<sub>2</sub>O), the source of pentavalent vanadium and sodium tungsten oxide dihydrous (Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O), the source of hexavalent tungsten were all supplied by Kermel, Tianjin. The compositions of the baths used in the experiment were defined as representatives

of an industrial bath. Additionally, NaOH and Na<sub>2</sub>CO<sub>3</sub>, supplied by Kermel, Tianjin, were catholyte to explain the experimental phenomenon of anions back-diffusion through CEM.

The CEM used for electro-dialysis is a new perfluorinated proton exchange membrane (PFSAPEM) of DF988 (Shandong Dongyue Polymer Material Co., Ltd., China). The whole area of the membrane was 0.675 d m<sup>2</sup>. The peristaltic pumps used to control the feed solution flow rates (0.86 L/min) of cathode and anode were provided by Chuang Xing Co., Ltd., China. Two pieces of the electrodes were made of titanium coated with ruthenium.

A previous report showed that the membrane should be filled with feed solution and deionized water initially for two hours to reach equilibrium [14]. Each test of our experiments began after 2 h when the electro migration of Na<sup>+</sup> under electric field and free diffusion reached a dynamic equilibrium state. The tests were operated under pre-designed operational conditions, and samples were taken after steady state condition subsequently. All the experiments were conducted at an ambient temperature around 25°C. In addition to taking into consideration of pH influence of anolyte deposition, electrolysis time was set for 100 min to obtain the optimum membrane state of electro dialysis. The samples were diluted by the cooling ultrapure water, then filtered by 0.22 μm micro filtration membrane. The PXSJ-216F ion meter measured the concentration of sodium ions was provided by Leici instrument Co., Ltd., China. The curve correlation coefficient was greater than 0.999. The corresponding concentration of OH<sup>-</sup> in the cathodic compartment was determined by auto-titrator. CO<sub>3</sub><sup>2-</sup> content of sodium carbonate aqueous solution could be measured by an inorganic carbon analyzer (Shimadzu TOC-V CSH/TNM-1). The electric energy was provided by stabilized voltage supply APS3005S which is made from ATEN Co., Ltd., China. The pH of the anode aqueous solution was determined by the Mettler Toledo pH meter, which was supplied by Keli Co., Ltd., China.

## 3. Results and discussion

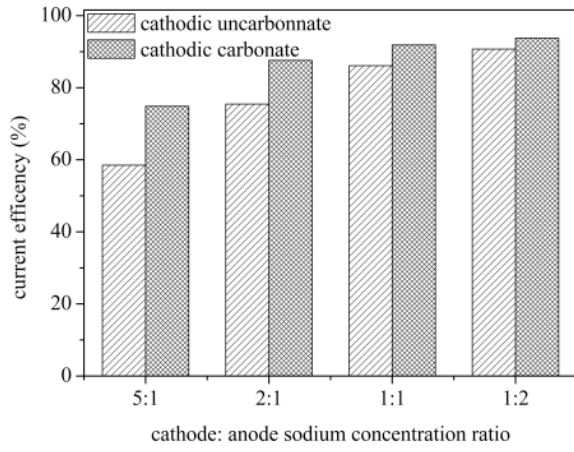
### 3.1. Effect of back-diffusion on current efficiency

The results of the 2-h experiment of the difference of sodium concentration between cathode and anode are seen in Fig. 1. The current efficiency is a key parameter to investigate the effect of electro-dialysis.  $C_{eff,ca}$  can be expressed as Eq. (1):

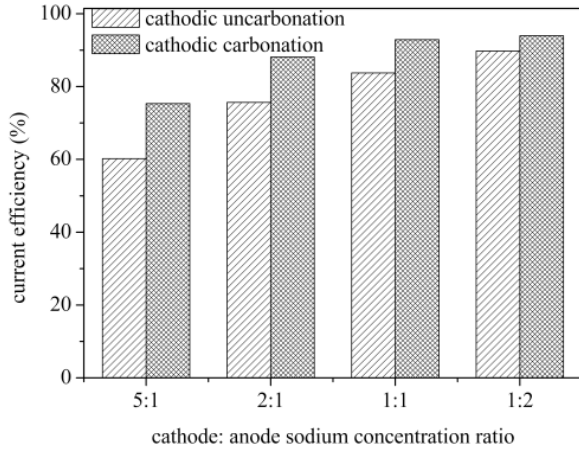
$$C_{eff,ca} = Z_{ca} \cdot \frac{dC_{ca} / C_{ca,0}}{dn_F / n_{ca,0}} \quad (1)$$

$C_{ca}$ , based on the concentration changes of the cathode, was calculated to fit the instantaneous current efficiency. The current efficiency only takes into account the Na<sup>+</sup> transport, so  $C_{effm,ca}$  was calculated as well. The relationship between two different efficiencies can be expressed as follow: the concentration of cathodic solution at given time *t*:

$$C_{ca} = \frac{V_{ca,0}C_{ca,0} + S_m \int_0^t J_1 dt}{V_{ca,0} + S_m \int_0^t J_v dt} \quad (2)$$



(a)



(b)

Fig. 1. Effects of carbon dioxide on the performance of current efficiency at different cathode: anode sodium concentration ratio. (a) Na<sub>2</sub>WO<sub>4</sub> aqueous solution, (b) NaVO<sub>3</sub> aqueous solution.

To investigate the influence factor of  $C_{effn,ca}$  we defined  $y$  as a factor that related to  $t$ :

$$y = \frac{n_F}{n_{ca,0}} = \frac{S_m j}{C_{ca,0} V_{ca,0} F} t \quad (3)$$

So we can get:

$$\frac{C_{ca}}{C_{ca,0}} = \frac{1 + \frac{F}{j} \int_0^y J_1 dy}{1 + C_{ca,0} \frac{F}{j} \int_0^y J_v dy} \quad (4)$$

After the transformation of Eq. (5):

$$C_{effn,ca} = \frac{dn_1}{dn_F} = \frac{FJ_1}{j} \quad (5)$$

$$= \frac{d}{dy} \left( \frac{C_{ca}}{C_{ca,0}} \left( 1 + \frac{F}{j} C_{ca,0} \int_0^y J_v dy \right) - 1 \right) \Big|_{J_v = const}$$

$$= \frac{d}{dy} \left( \frac{C_{ca}}{C_{ca,0}} \right) \left( 1 + \frac{F}{j} C_{ca,0} \int_0^y J_v dy \right) + \frac{FJ_v}{j} C_{ca}$$

$$= C_{eff,ca} \left( 1 + \frac{FJ_v}{j} C_{ca,0} y \right) + \frac{FJ_v}{j} C_{ca}$$

According to comparison results between Eq. (1) and Eq. (5),  $C_{effn,ca}$  was higher than  $C_{eff,ca}$  because it does not take into account the diluting effect of osmotic flows and electro-osmotic [15]. In our experiments, the diluting effect of osmotic flows and electro-osmotic is not obvious (ca. 5%). Therefore,  $C_{effn,ca}$  can be regarded as the upper limit of  $C_{eff,ca}$  if there is no solution volume changes during the concentration process. In these experiments, current efficiency  $C_{effn,ca}$  of NaVO<sub>3</sub> could be assumed as a constant volume of cathodic solution, which gave concentration difference of Na<sup>+</sup> between cathode and anode for 100 min at a current density of 1.5 A/dm<sup>2</sup>. Effects of carbon dioxide on the performance of current efficiency  $C_{effn,ca}$  can be calculated from Eq. (6) as followed:

$$C_{effn,ca} = \frac{(C_t - C_0)VF}{It} \quad (6)$$

The influence of the cathodic OH<sup>-</sup> back-diffusion on current efficiency may be obviously. As could be seen in the figure, the current efficiency shows a sharp decrease as the cathode: anode sodium concentration ratio changed. With the ratio of sodium concentration on both sides of the membrane of 5:1 for NaVO<sub>3</sub> aqueous solution, the current efficiency is only 60.18%. However, the current efficiency is 89.78% when the sodium concentration on both sides of the membrane is 1:2. Similar phenomenon can be obtained in other concentration difference of Na<sub>2</sub>WO<sub>4</sub>.

The current efficiency increased from only 60.18% reaching up to 75.33% with the ratio of sodium concentration on both sides of the membrane of 5:1 by adding CO<sub>2</sub> to the cathodic aqueous solution. The real reason may be the different interactions of the negatively charged with negatively charged membrane [16]. The similar phenomenon can be found in the Na<sub>2</sub>WO<sub>4</sub> solution of different concentration difference. Therefore, we can assume that CO<sub>2</sub> can make a contribution to electro-dialysis efficiency of the membrane.

In the model of ionic transport through the membrane, the concentration polarization layers (CPLs) should be taken into account. The ionic transport equation can be expressed as Eqs. (7), (8):

$$J_i = -D_i \left( \frac{dC_i}{dx} + Z_i C_i \frac{F}{RT} \cdot \frac{d\phi}{dx} \right) + C_i J_v \quad i = 1, 2; \text{CPLs} \quad (7)$$

$$J_i = -k_{DV\theta,i} \frac{\bar{C}_i}{C_i} D_i \left( \frac{dC_i}{dx} + Z_i C_i \frac{F}{RT} \cdot \frac{d\phi}{dx} \right) + \bar{C}_i J_v \quad i = 1, 2; \text{membrane} \quad (8)$$

The parameter  $k_{DV\theta,i}$  is defined as Eq. (9):

$$k_{DV\theta,i} = \frac{V_p}{\theta^2} \cdot \frac{\bar{D}_i}{D_i} \quad (9)$$

In our experiments, it can be assumed that the diffusion coefficient ratio is the same for the both ions as  $k_{DV\theta,1} = k_{DV\theta,2}$ . Meanwhile,  $\text{Na}^+$  concentrations  $C = C_1 = C_2$  is assumed. The ion concentration inside the membrane,  $\bar{C}_i$ , is given by the electro-neutrality condition:

$$\bar{C}_1 - \bar{C}_2 + Z_m \bar{C}_m = 0 \quad (10)$$

and the ideal Donnan equilibrium equation:

$$\bar{C}_1 \bar{C}_2 = C^2 \quad (11)$$

This results from the equality of electrochemical potentials of ions inside and outside the membrane. It is also assumed that the fluxes of ions are the same in both the CPLs and the membrane:

$$J_i(\text{CPL, left}) = J_i(\text{membrane}) = J_i(\text{CPL, right}) \quad (12)$$

Therefore the concentration difference of CPL for electrolyte is as follows:

$$\frac{dc}{dx} = \frac{cJ_v - J_2 - t_2j/F}{D_s} \quad (13)$$

The electrolyte concentrations at the membrane surfaces can be integrating over the thickness of CPL under the assumption  $J_2, J_v, D_i = \text{constant}$ :

$$C'^m = C' \exp(J_v/k) + (1 - \exp(J_v/k)) \frac{J_2 + t_2j/F}{J_v} \quad \text{left CPL} \quad (14)$$

$$C''^m = C' \exp(-J_v/k) + (1 - \exp(-J_v/k)) \frac{J_2 + t_2j/F}{J_v} \quad \text{right CPL} \quad (15)$$

where  $k = 2D_1D_2/(D_1+D_2)$ ;  $t_2 = D_2/(D_1+D_2)$ ; In these experiments,  $D_1$  represents diffusion coefficient of  $\text{Na}^+$ ,  $D_2$  represents diffusion coefficient of  $\text{OH}^-$  or  $\text{CO}_3^{2-}$ .

The migration increment of  $\text{Na}^+$  to cathode at electric current density ( $i$ ) can be expressed as follows:

$$dm_e = \bar{t}_{\text{Na}^+} \cdot \frac{i \cdot dt \cdot A}{F} \quad (16)$$

where  $\bar{t}_{\text{Na}^+}$  represents transference number of  $\text{Na}^+$  through cation-exchange membrane;

$\text{Na}^+$  and  $\text{OH}^-$  or  $\text{CO}_3^{2-}$  of cathode may be back-diffused to anode owe to cathode: anode sodium concentration ratio. The back-diffusion quantity of  $\text{Na}^+$  and  $\text{OH}^-$  or  $\text{CO}_3^{2-}$  can be expressed as follows:

$$J_i = P_s \cdot \Delta C \quad (17)$$

$$dm_d = -A \cdot J_i \cdot dt \quad (18)$$

The parameter  $K_s$  is defined as Eq. (18):

$$K_s = A \cdot P_s \quad (19)$$

$$dm_d = -(K_s^A + K_s^C) \cdot \Delta C \cdot dt = -K_s \cdot \Delta C \cdot dt \quad (20)$$

So

$$dm_1 = dm_e + dm_d = (\bar{t}_{\text{Na}^+} \cdot \frac{i \cdot A}{F} - K_s \cdot \Delta C) dt \quad (21)$$

$$dm_2 = \frac{i \cdot A \cdot dt}{F} \quad (22)$$

Current efficiency can be expressed as:

$$C_{\text{eff,ca}} = \frac{dm_1}{dm_2} = \bar{t}_{\text{Na}^+} - K_s \cdot \Delta C \cdot \frac{F}{i \cdot A} \quad (23)$$

Influences of  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  back-diffuse under the electro-dialysis equipment without electric field were measured. The process includes two steps: first, the diffusing quantity of  $\text{CO}_3^{2-}$  was measured with a  $\text{Na}_2\text{CO}_3$  cathodic solution at different ratio of sodium concentration on both sides of the membrane in 100 min by using  $\text{NaVO}_3$  or  $\text{Na}_2\text{WO}_4$  aqueous solution as the anodic solution, respectively. Second, the diffusing quantity of  $\text{OH}^-$  was measured with  $\text{NaOH}$  solution at different ratio of sodium concentration on both sides of the membrane in 100 min in a similar case. Ionic coefficient  $K_s^A$  ( $\text{m} \cdot \text{s}^{-1}$ ) of  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  can be determined according to curve slope and described as following:

$$K_{\text{sw,OH}^-}^A = 1.1178 \times 10^{-5} \text{ m} \cdot \text{s}^{-1} \quad (24)$$

$$K_{\text{sw,CO}_3^{2-}}^A = 1.7412 \times 10^{-6} \text{ m} \cdot \text{s}^{-1} \quad (25)$$

$K_{\text{sw,OH}^-}^A$  and  $K_{\text{sw,CO}_3^{2-}}^A$  are ionic coefficient of  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  in  $\text{NaVO}_3$  aqueous solution.

$$K_{\text{sw,OH}^-}^A = 1.3354 \times 10^{-5} \text{ m} \cdot \text{s}^{-1} \quad (26)$$

$$K_{\text{sw,CO}_3^{2-}}^A = 2.7213 \times 10^{-6} \text{ m} \cdot \text{s}^{-1} \quad (27)$$

$K_{\text{sw,OH}^-}^A$  and  $K_{\text{sw,CO}_3^{2-}}^A$  are ionic coefficient of  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  in  $\text{Na}_2\text{WO}_4$  aqueous solution.

As we can see, the ionic coefficient of  $\text{OH}^-$   $K_{\text{sw,OH}^-}^A$  is always larger than the ionic coefficient of  $\text{CO}_3^{2-}$   $K_{\text{sw,CO}_3^{2-}}^A$  whatever in  $\text{NaVO}_3$  or  $\text{Na}_2\text{WO}_4$  solution, that results in  $k_{\text{NaOH}}$  is larger  $k_{\text{Na}_2\text{CO}_3}$ . Therefore, the  $\text{NaOH}$  concentration of polarization layers  $C''_{\text{m,NaOH}}$  is larger than the  $\text{Na}_2\text{CO}_3$  concentration of polarization layers  $C''_{\text{m,Na}_2\text{CO}_3}$ . According to Fick's law of diffusion, the back-diffusion quantity of  $\text{NaOH}$  is larger than  $\text{Na}_2\text{CO}_3$ .

### 3.2. Effect of back-diffusion on desalination rate

The experimental results are shown in Figs. 3a and 3b for  $\text{NaVO}_3$  and  $\text{Na}_2\text{WO}_4$  aqueous solution, respectively. The desalination rate  $\eta$  was calculated as Eq. (28) [17]:

$$\eta = \frac{C_{\text{an},0} - C_{\text{an},t}}{C_{\text{an},0}} \quad (28)$$

where  $C_{\text{an},t}$  and  $C_{\text{an},0}$  ( $\text{mol/L}$ ) were the sodium ion concentrations of  $\text{Na}_2\text{WO}_4$  solution or  $\text{NaVO}_3$  solution at time  $t$  and  $0$  in the anodic compartment, respectively.



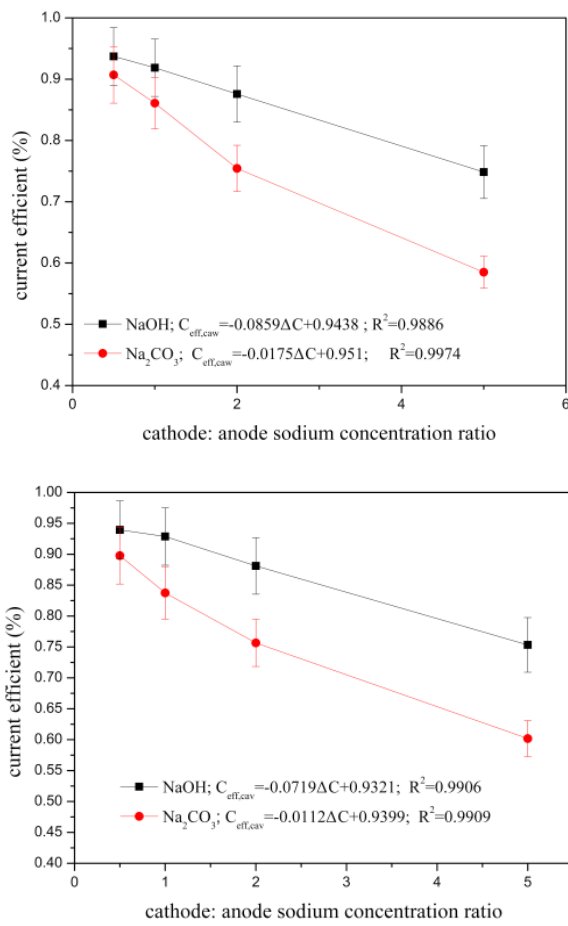


Fig. 2. The curve slope of current efficiency at different cathode: anode sodium concentration ratio. (a) Na<sub>2</sub>WO<sub>4</sub> aqueous solution, (b) is NaVO<sub>3</sub> aqueous solution.

From these figures, the desalination rate also increased along with CO<sub>2</sub> added into cathodic solution. This demonstrated desalination rate of NaVO<sub>3</sub> aqueous solution and Na<sub>2</sub>WO<sub>4</sub> aqueous solution were both obviously influenced by OH<sup>-</sup> back-diffuse through membrane.

### 3.3. Effect of back-diffusion on energy consumption

As one of the important factors that determine the feasibility of cathodic solution carbonate process, the energy consumption should be evaluated.

The energy consumption  $E$  (kW·h·kg<sup>-1</sup>) was calculated as Eq. (29) [17]:

$$E = \int \frac{UI dt}{C_{ca,t} VM} \quad (29)$$

where  $C_{ca,t}$  and  $C_{ca,0}$  (mol/L) were the concentrations of NaOH or Na<sub>2</sub>CO<sub>3</sub> at time  $t$  and 0, respectively;  $t$  was the duration time (h);  $V$  (L) was the circulated volume of solution in the cathode;  $F$  stood for the Faraday constant (96485 C·mol<sup>-1</sup>);  $I$  (A) was the current and  $U$  (V) was the voltage drop across the membrane electrolysis reactor, and  $M$  (g·mol<sup>-1</sup>) was the molar mass of NaOH or Na<sub>2</sub>CO<sub>3</sub>.

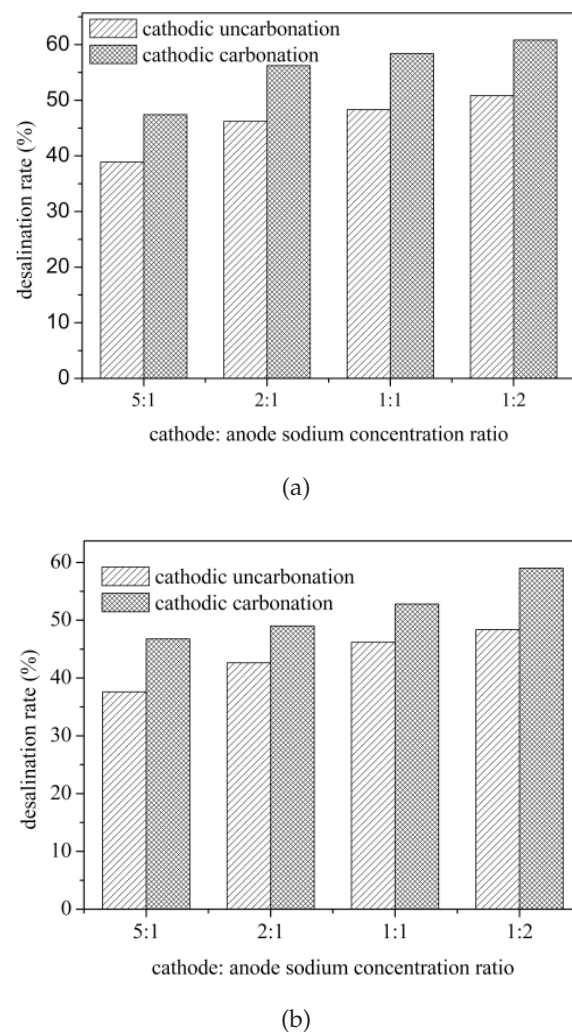


Fig. 3. Effects of carbon dioxide on performance of desalination rate at different cathode: anode sodium concentration ratio. (a) Na<sub>2</sub>WO<sub>4</sub> aqueous solution, (b) NaVO<sub>3</sub> aqueous solution.

The energy consumption based on the lab-scale experiments is displayed in Table 1. It is well known that the energy requirements mainly result from water dissociation, ion migration through IEM and solution. From Table 1, energy consumption reduced due to the CO<sub>2</sub> addition to cathodic compartment. For Na<sub>2</sub>WO<sub>4</sub> solution, energy consumption decreased from 3.97 to 2.85 kW·h·kg<sup>-1</sup> after adding CO<sub>2</sub> to cathode with the ratio of sodium concentration on both sides of the membrane of 5:1. While the energy consumption decreased from 3.55 to 2.87 kW·h·kg<sup>-1</sup> after adding CO<sub>2</sub> to cathode at same condition for NaVO<sub>3</sub> solution. Although technology of NaOH generates Na<sub>2</sub>CO<sub>3</sub> is diseconomy that does not spread widely in IEM electrolysis industry, Na<sub>2</sub>CO<sub>3</sub> can act as a by-product in vanadium and tungsten recovering process from SCR catalyst. By applying diffusion dialysis, Na<sup>+</sup> contained in the electrode solution can be recycled and energy consumption can decrease in the flow scheme by CO<sub>2</sub> addition. It is not difficult to understand that this is beneficial to reduce investment cost.

Table 1  
Effect of carbonation to energy consumption E (kW·h·kg<sup>-1</sup>) of different cathode: anode sodium concentration ratio

Anodic aqueous solution	Different cathode: anode sodium concentration ratio			
	5:1	2:1	1:1	1:2
Na <sub>2</sub> WO <sub>4</sub>	3.97	3.21	2.87	2.79
Na <sub>2</sub> WO <sub>4</sub> (carbonation)	2.85	2.52	2.16	1.97
NaVO <sub>3</sub>	3.55	3.32	3.04	2.86
NaVO <sub>3</sub> (carbonation)	2.87	2.82	2.74	2.43

Therefore, it is necessary to add CO<sub>2</sub> to cathodic aqueous solution after a comprehensive consideration.

#### 4. Conclusions

Based on the experiments conducted in this research, we have elucidated the back-diffusion of OH<sup>-</sup> and CO<sub>3</sub><sup>2-</sup> through CEM is strongly affected by different cathode: anode sodium concentration ratio in equilibrium conditions. The difference of back-diffusion of free anions (OH<sup>-</sup> and CO<sub>3</sub><sup>2-</sup>) may due to strong interactions of CO<sub>3</sub><sup>2-</sup> with negatively charged CEM. In the case of Na<sub>2</sub>WO<sub>4</sub> and NaVO<sub>3</sub> solutions respectively, an unexpected performance of the current efficiency and energy consumption of the membrane system can be observed through adding CO<sub>2</sub> at different cathode: anode sodium concentration ratio.

Additionally, the desalination rate of Na<sub>2</sub>WO<sub>4</sub> and NaVO<sub>3</sub> solutions demonstrated the influence of the back-diffusion of free anions (OH<sup>-</sup> and CO<sub>3</sub><sup>2-</sup>) to Na<sup>+</sup> transport through membrane. Charge balance between both sides of CPLs and free anions (OH<sup>-</sup> and CO<sub>3</sub><sup>2-</sup>) interactions with membrane may decide the desalination rate of solutions.

Integration of alkali leaching and CEM electro-dialysis can avoid adding acid to satisfy pH of valuable metals extraction, and make alkali recover. This process made a contribution to the separation and purification of the valuable metals from waste catalysts and realized resource utilization.

#### Symbols

$\eta$	— Desalination rate
$E$	— Energy consumption
$C_t$	— Concentration at time $t$ (mol·m <sup>-3</sup> )
$C_0$	— Concentration at time 0 (mol·m <sup>-3</sup> )
$V$	— Volume of NaVO <sub>3</sub> or Na <sub>2</sub> WO <sub>4</sub> solution (m <sup>3</sup> )
$t$	— Time (s)
$I$	— Current (A)
$U$	— Voltage drop across the membrane (V)
$M$	— Molar mass (g·mol <sup>-1</sup> )
$C$	— Current efficiency of cathode
$Z_{i,\alpha}^{eff,ca}$	— Charge number of $i$ -th ion
$n_F$	— Molar charge (mol)
$n_{\alpha,0}$	— Molar quantity at time 0 (mol)
$V_{\alpha,0}$	— Volume (m <sup>3</sup> )

$S_m$	— Membrane area (m <sup>2</sup> )
$J_i$	— Flux of $i$ -th species (mol·s <sup>-1</sup> ·m <sup>-2</sup> )
$j$	— Current density (A·m <sup>-2</sup> )
$F$	— Faraday constant (C·mol <sup>-1</sup> )
$J_v$	— Volume flux (mol·s <sup>-1</sup> ·m <sup>-2</sup> )
$R$	— Gas constant (J·K <sup>-1</sup> ·mol <sup>-1</sup> )
$\phi$	— Electric potential (V)
$x$	— $x$ -coordinate
$\bar{C}_i$	— Concentration in the pore solution (mol·m <sup>-3</sup> )
$D_i$	— Diffusion coefficient of $i$ -th ion (m <sup>2</sup> ·s <sup>-1</sup> )
$k_{D^{Vn,i}}$	— Tortuosity-porosity parameter
$V^p$	— Volume fraction of pores
$\theta^p$	— Tortuosity coefficient
$Z_m$	— Charge number of membrane
$t_i$	— Transport number of $i$ -th ion
$D$	— Diffusion coefficient of electrolyte (m <sup>2</sup> ·s <sup>-1</sup> )
$C^s$	— Membrane concentration (mol·m <sup>-3</sup> )
$C$	— CPLs concentration (mol·m <sup>-3</sup> )
$t_{Na^+}$	— Sodian transport number of CEM
$dm_e$	— Enrichment cathodic compartment of Na <sup>+</sup> amount (mol)
$dm_d$	— Decreasing cathodic compartment of Na <sup>+</sup> or OH <sup>-</sup> amount (mol)
$P_s$	— Coefficient of diffusion flux (m·s <sup>-1</sup> )
$A$	— Membrane area (m <sup>2</sup> )
$dm_1$	— Migration amount of $i$ -th ion (mol)
$dm_2$	— Migration amount of electron (mol)
$K_s^C$	— Cationic coefficient
$K_s^A$	— Anionic coefficient
$K_s$	— Ionic coefficient
$\Delta C$	— Change of concentration (mol·m <sup>-3</sup> )

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