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Factors affecting the current and the voltage efficiencies of the synthesis of quaternary ammonium hydroxides by electrolysis–electrodialysis

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Abstract

The applied voltage equation and the current density equation are formulated for the electrolysis of the anolyte, aqueous quaternary ammonium chloride, and the catholyte, aqueous quaternary ammonium hydroxide, separated with a cation exchange membrane. The two equations reveal the factors that affect the current efficiency and the voltage efficiency. The effects of the factors on the efficiencies were investigated experimentally. The results show that Nafion 901 is a suitable cation exchange membrane, and both the current efficiency and voltage efficiency increase with the decreasing size of the quaternary ammonium cation, and for the preparation of benzyltriethylammonium hydroxide, the current efficiency is well correlated as $\varepsilon_\mathrm{c} = 1.05(I/FC_\mathrm{a}u_\mathrm{c})^{-0.16}(I/FC_\mathrm{c}u_0)^{0.28}$, with r^2=0.96. The voltage efficiency is correlated as $\varepsilon_\mathrm{v}^{-1} - 1 = 3.78 + (-I\ell/\varepsilon^0\kappa_\mathrm{m}) + 1.56\ln(-I\ell/\varepsilon^0\kappa_\mathrm{m})$, with r^2=0.88. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Quaternary ammonium hydroxides; Electrolysis; Electrodialysis

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1. Introduction

The process of electrolysis–electrodialysis for the production of NaOH and Cl_2 has been successfully commercialized since 1975 [1]. A similar process can be applied for producing quaternary ammonium hydroxides. The hydroxides can be used for the titration of nonaqueous organic acid solution [2] and as cleaning and etching agents for IC boards [3]. Another important use of the hydroxides is to prepare quaternary ammonium salts (QY) as phase transfer catalysts by neutralization ($QOH+HY \rightarrow QY+H_2O$). In the electrolysis–electrodialysis process, a Nafion cation-exchange membrane is commonly used because the impurities in the product solution (aqueous QOH) are extremely low. However, there was a study of using anion exchange membranes for the production of the hydroxides with relatively large quaternary cations. In this case the raw material quaternary ammonium chlorides were used as initial catholyte, so the purity of the product could not be very high, and the current efficiency was lower than that using the cation-exchange membrane [4].

Although there were many patents [5–9] concerning the preparation of quaternary ammonium hydroxides, only a few theoretical studies are found [10,11], and the systematical studies for the economical production of the hydroxides by the ion exchange membrane process have not been found yet. In this study, the current density equation and the applied voltage equation of the electrolysis–electrodialysis system were inspected to figure out the factors that affect the current efficiency and the voltage efficiency. Then the effects of the various factors on the efficiencies were experimentally investigated, and the correlations between the efficiencies and the dimensionless groups of the operation variables were obtained by the method of least square. The correlations are basic to the determination of the suitable conditions for preparing quaternary ammonium hydroxides.

2. The current density equation and the applied voltage equation

The system for the production of quaternary ammonium hydroxides is as in Fig. 1. Initially, the catholyte is a dilute aqueous QOH solution and the anolyte is a concentrated aqueous QCl solution. When the system is in operation, a typical concentration profile can be shown as in Fig. 2. The

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Abbreviations: BTEAC, benzyltriethylammonium chloride; BTEAH, benzyltriethylammonium hydroxide; BTMAC, benzyltrimethylammonium chloride; BTMAH, benzyltrimethylammonium hydroxide; TMAC, tetramethylammonium chloride; TMAH, tetramethylammonium hydroxide

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Nomenclature

a_i	the activity of the species i in solution phase
$a_i^{(m)}$	the activity of the species i in membrane phase
C_a	anolyte concentration (M)
C_c	catholyte concentration (M)
C_i	molar concentration of species i (M)
E	the electrical energy required for producing QOH (W h)
F	the Faraday constant=96 484 C/eq
I	$\lvert\vec{I}\rvert$ (A/dm^2)
$\vec{I}$	current density (A/dm^2)
$\vec{J}_i$	Nernst–Planck flux of species i (mol/(cm^2 s))
ℓ	width of compartment (mm)
$\vec{N}_i$	molar flux of species i (mol/(cm^2 s))
n_i	mole number of species i (mol)
R	gas constant=8.314 J/(mol K)
T	absolute temperature (K)
t_i	transference number of the species i
U_i	ionic mobility of species i (cm/(s V))
u_a	anolyte linear flow velocity through anode compartment (cm/s)
u_c	catholyte linear flow velocity through cathode compartment (cm/s)
$\vec{v}$	flow velocity of bulk solution (cm/s)
x	distance from the cathode (cm)
x_j	distance of point j from the cathode (cm)
z_i	electric charge number of species i

Greek letters

ε	electromotive force of the cell (V)
ε^0	standard electromotive force of the cell (V)
ε_c	current efficiency
ε_E	energy consumption
ε_e	energy efficiency
ε_v	voltage efficiency
η_{ct}	change transfer overvoltage (V)
ϕ	electrical potential (V)
κ	specific conductance (μS/cm)
κ_a, κ_c	conductivity of anolyte and catholyte, respectively (μS/cm)
κ_m	mean conductivity
μ_i	chemical potential of species i (J/mol)
μ_i^0	standard chemical potential of species i (J/mol)
$\bar{\mu}_i$	electrochemical potential of species i (J/mol)

ionic molar flux can be expressed by Eq. (1).

$$\vec{N}_i = C_i\vec{v} - \frac{U_i}{|z_i|F}C_i\,\nabla\bar{\mu}_i \tag{1}$$

The first term on the right-hand side is the flux caused by the bulk flow and the second term is the flux ($\vec{J}_i$) caused by the electrochemical potential gradient. The expression $\vec{J}_i = -(U_i/(|z_i|F))C_i\,\nabla\bar{\mu}_i$ is known as the Nernst–Planck flux equation [12]. The electrochemical potential is defined as

$$\bar{\mu}_i = \mu_i + z_iF\phi \tag{2}$$

The activity is related to the chemical potential as

$$\mu_i = \mu_i^0 + RT\ln a_i \tag{3}$$

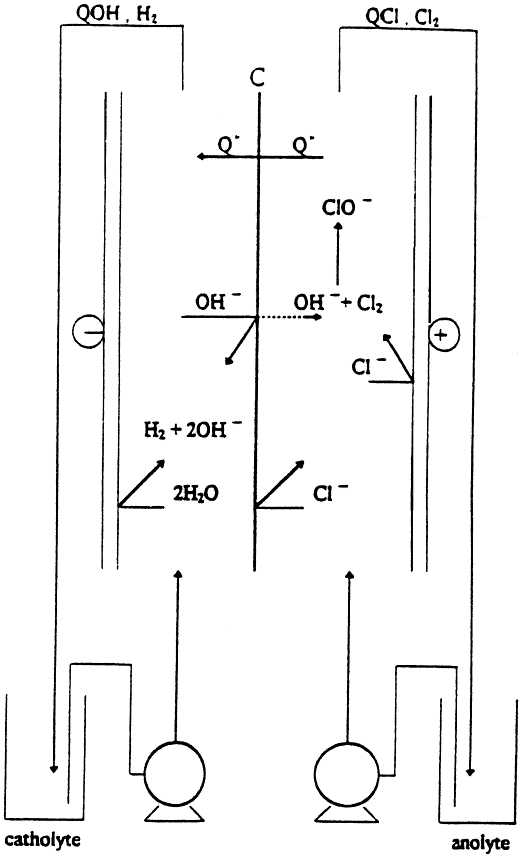

Fig. 1. The electrolysis–electrodialysis system for the synthesis of quaternary ammonium hydroxides. C is the cation exchange membrane.

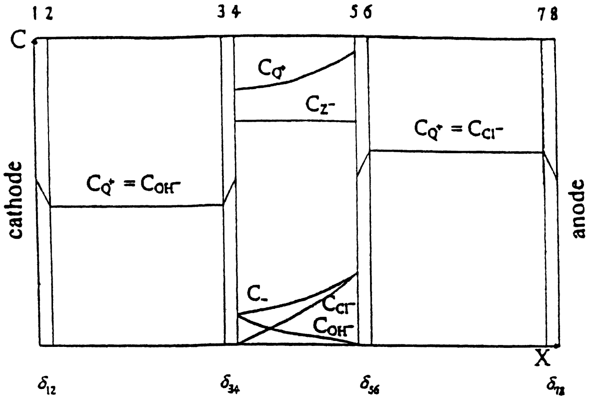

Fig. 2. A typical concentration profile in the operating system. δ_{12}, δ_{78}, δ_{34} and δ_{56} are the concentration boundary layers adjacent to the cathode, the anode and the two sides of the membrane, respectively.

Then the molar flux is expressed as

$$\vec{N}_i = C_i\vec{v} - \frac{U_i C_i}{|z_i|F} RT \ln a_i - \frac{z_i}{|z_i|} U_i C_i \nabla\phi \qquad (4)$$

The neutrality of the solution is expressed by the following equation:

$$\sum z_i C_i = 0 \qquad (5)$$

The relation between the current density and the ionic molar fluxes is

$$\vec{I} = F \sum_i z_i \vec{N}_i \qquad (6)$$

Substituting Eqs. (4) and (5) into Eq. (6), the current density equation is obtained as

$$\vec{I} = -RT \sum \frac{z_i}{|z_i|} U_i C_i \nabla \ln a_i - \sum |z_i| F U_i C_i \nabla\phi \qquad (7)$$

On the other hand, from Eq. (7), the potential gradient is expressed as

$$\nabla\phi = -\frac{\vec{I}}{\kappa} - \frac{RT}{F} \sum \frac{t_i}{z_i} \nabla \ln a_i \qquad (8)$$

where the conductivity, κ, and the transference number, t_i, are respectively defined as

$$\kappa = F \sum |z_i| U_i C_i \qquad (9)$$

$$t_i = \frac{|z_i| U_i C_i}{\sum |z_i| U_i C_i} \qquad (10)$$

Referring to Fig. 2, and considering the charge transfer overvoltages and the Donnan potentials, and integrating Eq. (8) from x_1 to x_8, the applied voltage is obtained as [13,14]

$$\Delta\phi = -\varepsilon + \eta_{\mathrm{ct}} - \frac{RT}{F} \sum_i \int_{x_1}^{x_8} \frac{t_i}{z_i}\, \mathrm{d} \ln a_{i,x} + \int_{x_1}^{x_8} \frac{I}{\kappa}\, \mathrm{d}x + \frac{RT}{z_i F} \ln \left[\left(\frac{a_{i,x_5}^{(\mathrm{m})}/a_{i,x_5}}{a_{i,x_4}^{(\mathrm{m})}/a_{i,x_4}} \right) \right] \qquad (11)$$

where ε is the equilibrium cell voltage, η_{ct} the charge transfer overvoltage, and the other terms on the right-hand side of Eq. (11) are the diffusion potentials, the Ohmic voltages, and the Donnan potentials, respectively.

3. The factors affecting the current efficiency and the voltage efficiency

The current efficiency is defined as the amount of the product, QOH, accumulated in the catholyte divided by the quantity of the electricity driven through the cell, that is

$$\varepsilon_{\mathrm{c}} = -\frac{F}{It} \int_0^t N_{\mathrm{Q}^+, x_3}\, \mathrm{d}t \qquad (12)$$

By inspecting Eqs. (4) and (7), one can see that the operating variables affecting the current efficiency include the current density, the linear velocities of the catholyte and the anolyte, and the concentrations of the catholyte and anolyte. By dimensional analysis, the correlation between the current efficiency and the dimensionless groups of the operating variables can be expressed as [15]

$$\varepsilon_{\mathrm{c}} = p \left(\frac{I}{FC_{\mathrm{a}} u_{\mathrm{c}}} \right)^q \left(\frac{I}{FC_{\mathrm{c}} u_{\mathrm{a}}} \right)^r \qquad (13)$$

Generally, the voltage efficiency is defined as the minimum voltage required to proceed the electrolysis divided by the average applied voltage, that is

$$\varepsilon_{\mathrm{v}} = -\frac{\varepsilon t}{\int_0^t \Delta\phi\, \mathrm{d}t} \qquad (14)$$

Since the partial pressures at the electrode surfaces are unknown, the voltage efficiency is defined as

$$\varepsilon_{\mathrm{v}} = -\frac{\varepsilon^0 t}{\int_0^t \Delta\phi\, \mathrm{d}t} \qquad (15)$$

Then, from Eqs. (11) and (15), the voltage efficiency is related to the dimensionless group of the operating variables as the form

$$\varepsilon_{\mathrm{v}}^{-1} - 1 = a + \left(\frac{I\ell}{-\varepsilon^0 \kappa_{\mathrm{m}}} \right) + b \ln \left(\frac{I\ell}{-\varepsilon^0 \kappa_{\mathrm{m}}} \right) \qquad (16)$$

where κ_{m} is defined as

$$\frac{1}{\kappa_{\mathrm{m}}} = \frac{1}{\kappa_{\mathrm{a}}} + \frac{1}{\kappa_{\mathrm{c}}} \qquad (17)$$

4. Experimental

4.1. Chemicals

The aqueous solutions of 40% benzyltrimethylammonium hydroxide, 45% trimethylamine, and 0.1 M sodium chloride were products of Merck. The chemicals of 98% tetramethylammonium chloride, 98% benzyl chloride, 99% trimethylamine, 25% aqueous tetramethylammonium hydroxide, 1 M hydrochloric acid, and 1 M sodium hydroxide were of Riedel-de Haen. The 10% aqueous solution of benzyltriethylammonium hydroxide was purchased from TCI. Silver nitrate of purity above 98% was from Nippon Reagents Industrial Co., Ltd. Benzyltriethylammonium chloride and benzyltrimethylammonium chloride were prepared in our laboratory [16].

4.2. Apparatus

A Du-ob electrodialyzer of Shibayama Scientific Company was used as the electrolysis–electrodialysis cell. Both the areas of the SUS-27 cathode and the Pt–Ti anode were

209 cm^2. A net-shaped spacer is inserted between the membrane and each electrode to avoid their contact and promote the turbulence of the electrolyte flow through the compartment. The tanks containing the electrolytes were immersed in a cooling bath for offsetting the temperature rise of the electrolytes due to the electrical energy dissipation. The potentiostat/galvanostat with maximum output voltage 100 V and maximum output current 50 A was manufactured by Song Jin Co., Ltd., Taiwan. The conductivity meter was of the type TOA CS-40S.

4.3. Procedure

Firstly, a suitable cation exchange membrane was to be used. The commercial membranes Asahi CMV, Ionac MC-3470, and Du Pont Nafion 901 were tested. The operating conditions were anolyte 1.4 M TMAC, initial catholyte 0.2 M TMAH, both flow rates 1.71 cm/s, current density 4.78 A/dm^2, temperature of the electrolytes 30°C, and widths of both compartments 16.8 mm. A catholyte sample was taken at a time interval of 30 min for analyzing the hydroxyl ion concentration. Then, the factors affecting the current and the voltage efficiencies were subsequently investigated. Take the effect of catholyte concentration as an illustration, the conditions were: cation exchanger membrane Nafion 901, anolyte 1.38 M BTEAC, initial concentration of BTEAH for the seven runs 0.085, 0.207, 0.45, 0.715, 0.935, 1.21, and 1.48 M, respectively, and the other conditions were as above. The data of voltage versus time were recorded, and the hydroxyl ion concentration was analyzed by the titration with standard aqueous HCl at a time interval of 5 min, and the conductivities of the electrolytes were measured at the start and the end of the run.

5. Results and discussion

5.1. Suitability of cation exchange membrane

Fig. 3 shows the performances of current efficiency versus time for CMV, MC-3470, and Nafion 901 under the conditions of Q=TMA, I=4.78 A/dm^2, u_a=u_c=1.71 cm/s, [TMAC]=1.35 M, and [TMAH]=0.2–1.05 M. During these experiments, no organics had been found by gas chromatography. So no side-reaction was considered to occur at the electrodes. For Nafion 901, the current efficiency decreases gradually with time, this is because more and more hydroxyl ions move across the membrane toward the anode when their concentration increases. The Cl ions in the catholyte could not be detected by the Mohr method. So the current efficiency being less than unit is almost due to leakage of OH ions across the membrane. For the other two membranes, the efficiencies decrease rapidly with time. The main reason may be the interactions of the quaternary ammonium cations with the membranes. After 5 h of operation there is little change in the appearance of Nafion 901, but the other two are seriously deteriorated. Their fabrics were loosed and could be torn by hand.

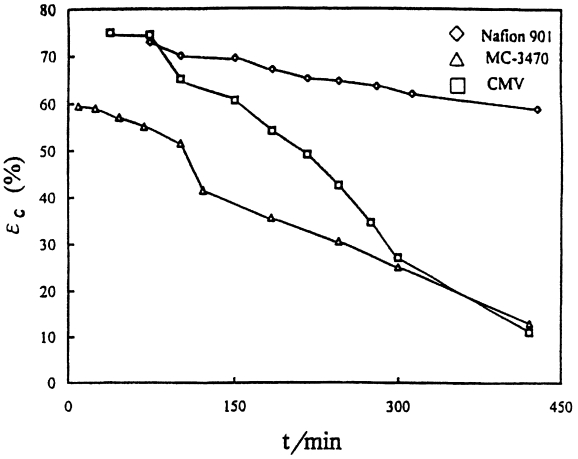

Fig. 3. The performances of current efficiency vs. time of the various cation exchange membranes. Q=TMA, I=4.78 A/dm^2, u_a=u_c=1.71 cm/s, [TMAC]=135 M, [TMAH]=0.2–1.05 M and ℓ=16.8 mm.

5.2. Effects of catholyte concentration

Under the conditions of Q=BTEA, M=Nafion 901, C_a=1.35 M, C_c=0.12–1.5 M, and other conditions the same as above, the effects of the concentration of catholyte on the current and the voltage efficiencies are shown in Fig. 4, where the current efficiency decreases with increasing catholyte concentration. However, the voltage efficiency increases with the increasing catholyte concentration. This is due to the decreasing resistance of the catholyte.

5.3. Effects of anolyte concentration

With the conditions of C_c=0.49 M and others as above, the variations of the efficiencies with anolyte concentration

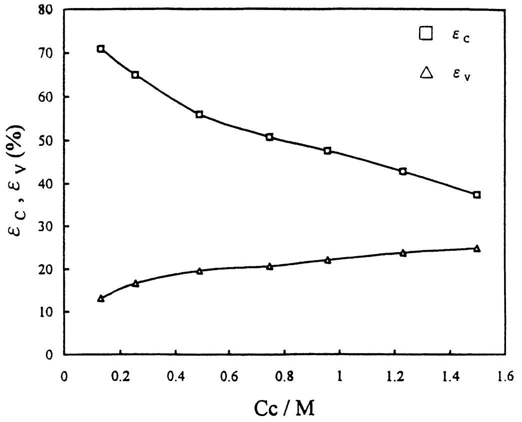

Fig. 4. The effects of catholyte concentration on the current and the voltage efficiencies. Q=BTEA, M=Nafion 901, C_a=1.35 M, I=4.78 A/dm^2, u_a=u_c=1.71 cm/s, ℓ=16.8 mm and C_c=0.12–1.5 M.

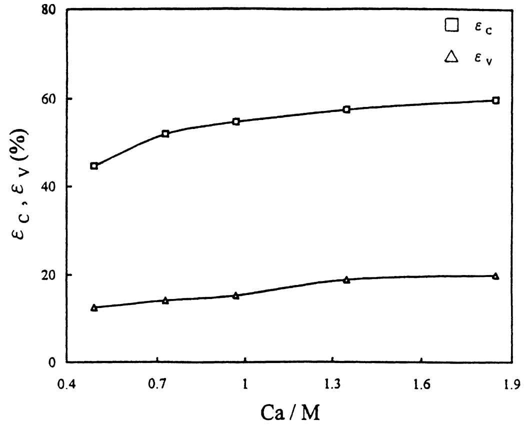

Fig. 5. Effects of anolyte concentration on the current and the voltage efficiencies. Q=BTEA, M=Nafion 901, I=4.78 A/dm^2, u_a=u_c=1.71 cm/s, ℓ=16.8 mm, C_a=0.45 N–1.85 M and C_c=0.49 M.

are as in Fig. 5. The figure shows that the dependence of the voltage efficiency on anolyte concentration is similar to that on the catholyte concentration shown in Fig. 4, but the dependence of the current efficiency on the anolyte concentration is opposite to that on the catholyte concentration. The ascending current efficiency shown in Fig. 5 is caused by the increasing flux of the quaternary ammonium ions toward the cathode.

5.4. Effects of current density

When C_a is 1.35 M and the others are not changed, the effects of current density on the efficiencies is shown in Fig. 6. The voltage efficiency decreases and the current efficiency increases when the current density increases. The lowering in the voltage efficiency is due to the increasing Ohmic voltage drop between the electrodes and the increasing activation overvoltages of the reactions at the electrodes and the reason for the promotion of the current efficiency can be explained using Eq. (8) and Fig. 2. The production rate of OH$^-$ per unit area of cathode, R_{OH^-}, by electrochemical reaction is proportional to the current density. However, Eq. (8) shows $\nabla\phi$ is not directly proportional to the current density, then the migration flux of the hydroxyl ions toward anode is not enhanced proportionally by the increasing current density. Moreover, the direction of the diffusion of OH$^-$ in the boundary layer δ_{34} is opposite to that of migration, so the current efficiency $(R_{OH^-} - J_{OH^-}|_{x_4})/(I/F)$, increases with the increasing current density.

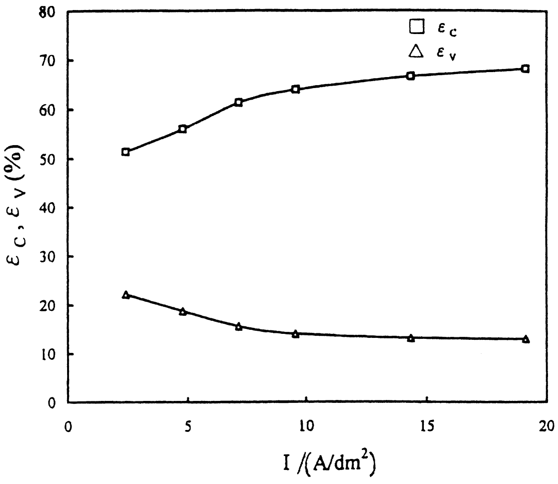

Fig. 6. Effects of current density on the current and the voltage efficiencies. Q=BTEA, M=Nafion 901, I=2.39–19.12 A/dm^2, C_c=0.49 M, C_a=1.35 M, u_a=u_c=1.71 cm/s and ℓ=16.8 mm.

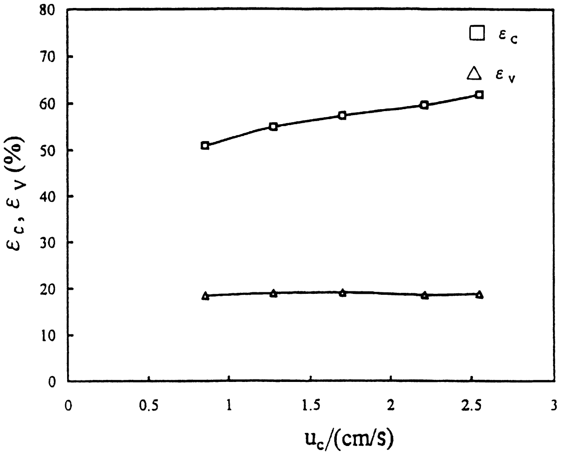

Fig. 7. Effects of catholyte flow velocity on the current and the voltage efficiencies. Q=BTEA, M=Nafion 901, C_a=1.35 M, C_c=0.49 M, ℓ=16.8 mm, u_a=1.71 cm/s, u_c=0.85–2.55 cm/s and I=4.78 A/dm^2.

5.5. Effects of catholyte flow velocity

When the conditions except the catholyte flow velocity are not changed, the effects of the catholyte flow velocity on the efficiencies is as in Fig. 7. It shows that the current efficiency is enhanced by increasing the catholyte flow rate, but the voltage efficiency is not affected. Fig. 2 shows that the thickness of the catholyte boundary layer adjacent to the membrane is reduced with the increasing velocity. Consequently, the mass transfer resistance to the hydroxyl ion diffusional flux backward to the bulk catholyte is also reduced. So the current efficiency is enhanced [11]. Since the volume of the boundary layer is negligible when compared to that of the bulk solution, the electrical resistance of the catholyte is nearly unchanged with varying boundary layer thickness. As a result, the voltage efficiency is also unchanged.

5.6. Effects of anolyte flow velocity

With other constant conditions, Fig. 8 shows the dependences of the current and the voltage efficiencies on the anolyte flow velocity. The voltage efficiency is not influenced by the flow velocity. But the current efficiency is slightly lowered by the increasing anolyte flow velocity.

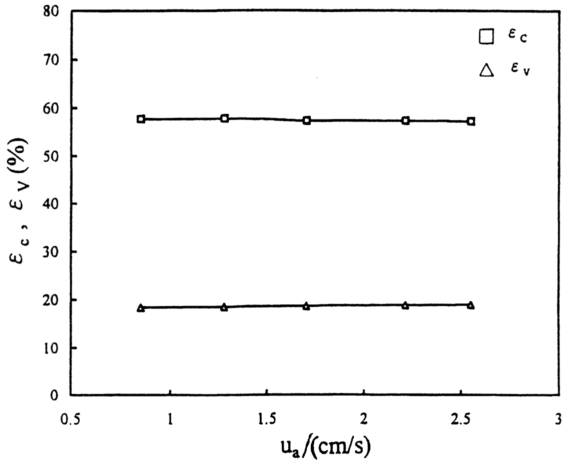

Fig. 8. Effects of anolyte flow velocity on the current and the voltage efficiencies. Q=BTEA, M=Nafion 901, I=4.78 A/dm^2, C_a=1.35 M, C_c=0.49 M, u_a=1.71 cm/s, u_c=0.85–2.55 cm/s and ℓ=16.8 mm.

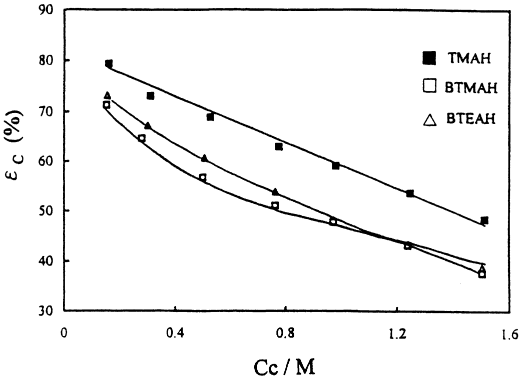

Fig. 10. Effects of size of quaternary ammonium cation on the current efficiency. M=Nafion 901, C_a=1.35 M, I=4.78 A/dm^2, C_c=0.12–1.5 M, u_a=u_c=1.71 cm/s and ℓ=16.765 mm.

The thickness of the anolyte boundary layer adjacent to the membrane is reduced by the increasing flow velocity. This enhanced the hydroxyl ion diffusional flux toward the bulk anolyte. However, the hydroxyl ion concentration in the anolyte is very low, so that the concentration difference across the boundary layer for driving the diffusion is very small. That is, the hydroxyl ion flux within the anolyte boundary layer is predominantly due to the electrical migration. Therefore, the current efficiency decreases slightly with increasing anolyte flow velocity [11].

5.7. *Effects of width of compartment*

When the compartments are of equal width and the other conditions are not changed, the effects of the width on the efficiencies are shown as in Fig. 9. The current efficiency is not influenced by the width of the compartments within the range of 9.77–20.8 mm. This means that with the aid of the spacer the boundary layer thickness is not varied by changing the width within the range. The voltage efficiency is reduced with the increasing width, because the width is proportional to electrical resistance of the electrolyte.

5.8. *Effects of varying quaternary ammonium cations*

With the same conditions as those in Fig. 4, Fig. 10 shows the relation of ε_c versus C_c for the hydroxides of TMAH, BTEAH and BTEAH, and Fig. 11 shows that of ε_v versus C_c for the same hydroxides. Since the ionic mobility of an ion is inversely proportional to its size, it is obvious that at the same catholyte concentration, both efficiencies are higher for the hydroxide with smaller cation than with larger cation [11].

5.9. *The dimensionless and the dimensional correlations of current efficiency, voltage efficient, and energy efficiency*

By examining the experimental results and Eq. (13), the current efficiency is correlated by the method of least

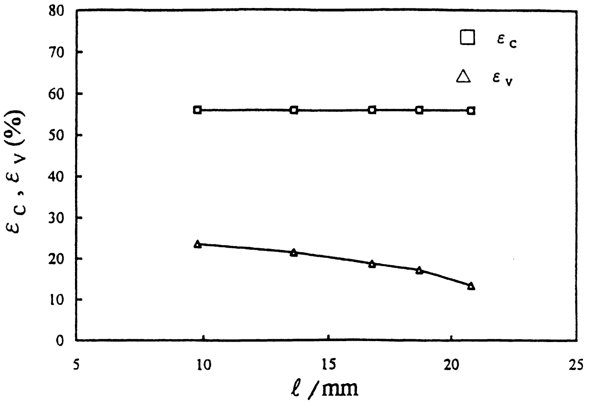

Fig. 9. Effects of width of compartment on the current and the voltage efficiencies. Q=BTEA, M=Nafion 901, I=4.78 A/dm^2, C_a=1.35 M, C_c=0.49 M, u_a=u_c=1.71 cm/s and ℓ=9.77–20.8 mm.

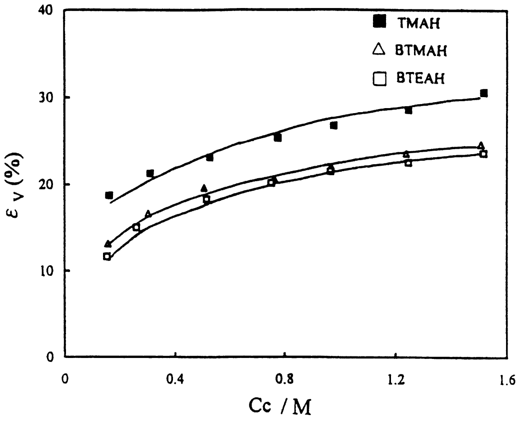

Fig. 11. Effects of size of quaternary ammonium cation on the voltage efficiency. M=Nafion 901, C_a=1.35 M, I=4.78 A/dm^2, C_c=0.12–1.5 M, u_a=u_c=1.71 cm/s and ℓ=16.765 mm.

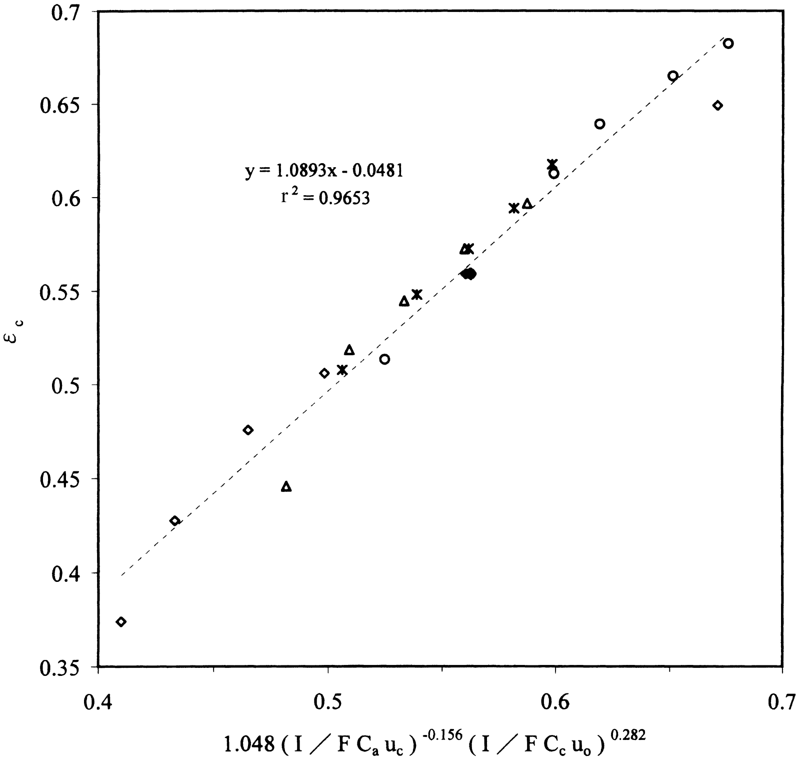

Fig. 12. The correlation between the current efficiency and the dimensionless groups of the operating variables. y=value of coordinate, x=value of abscissa and r^2=coefficient of correlation.

square as

$$\varepsilon_c = 1.05\left(\frac{1}{FC_a u_c}\right)^{-0.16}\left(\frac{1}{FC_a u_0}\right)^{0.28} \tag{18}$$

and the dimensional correlation obtained by multiple regression is given as

$$\varepsilon_c = 30.3\left(\frac{C_a}{C_c}\right)^{0.25} I^{0.14} u_c^{0.17} \tag{19}$$

It is seen that the exponents of I and u_c in the two equations are in good agreement, respectively. With ε_c as coordinate and the term on the right-hand side of Eq. (18) as the abscissa, the correlation is shown by Fig. 12, in which the square of the coefficient of correlation, r^2, equals 0.96. Similarly, the dimensionless and the dimensional correlations of the voltage efficiency are

$$\varepsilon_v^{-1} - 1 = 3.78 + \left(-\frac{I\ell}{\varepsilon^0\kappa}\right) + 1.56\ln\left(-\frac{I\ell}{\varepsilon^0\kappa}\right) \tag{20}$$

and

$$\varepsilon_v = 175 C_a^{0.39} C_c^{0.26} I^{-0.29} \ell^{0.62} \tag{21}$$

respectively. The correlation of Eq. (20) is shown by Fig. 13, in which, r^2 equals 0.88. The reason that this is not so good as those above is that the arithmetical mean of the initial and the final values of $\Delta\phi$, is used to calculate ε_v. However, $\Delta\phi$ does not vary with time linearly. The ranges of the operating variables for the above correlations are $0.491<C_a$ (M)<1.85, $0.147<C_c$ (M)<1.51, $2.39<I$ (A/dm^2)<19.1, $0.85<u_c$ (cm/s)<2.55, $9.77<\ell$ (mm)<20.8, and the reference velocity u_0=1 cm/s. The energy efficiency is defined as

$$\varepsilon_e = \varepsilon_c \varepsilon_v \tag{22}$$

From Eqs. (19) and (21), its dimensional correlation is

$$\varepsilon_e = 531 C_a^{0.64} C_c^{0.017} I^{-0.15} u_c^{0.17} \ell^{0.62} \tag{23}$$

Eq. (19) shows that the current efficiency depends mainly on C_a/C_c, but not on ℓ and u_a. While Eq. (23) shows that the energy efficiency depends predominately on C_a and ℓ, and slightly on I, but not on u_a, and the effect of C_c on ε_e is very small compared to that of C_a. The current density, I, has positive influence on the current efficiency, but it also has negative influence on the energy efficiency to the same extent as on the former. The production rate of QOH is proportional to the current density. However, when the current density is large, one must pay attention to the occurrence of the concentration polarization at the interface of the membrane and the anolyte [17].

5.10. Energy consumption under varying electrolyte concentrations

Here, the energy consumption is defined as the electrical energy required for accumulating an equivalent of the

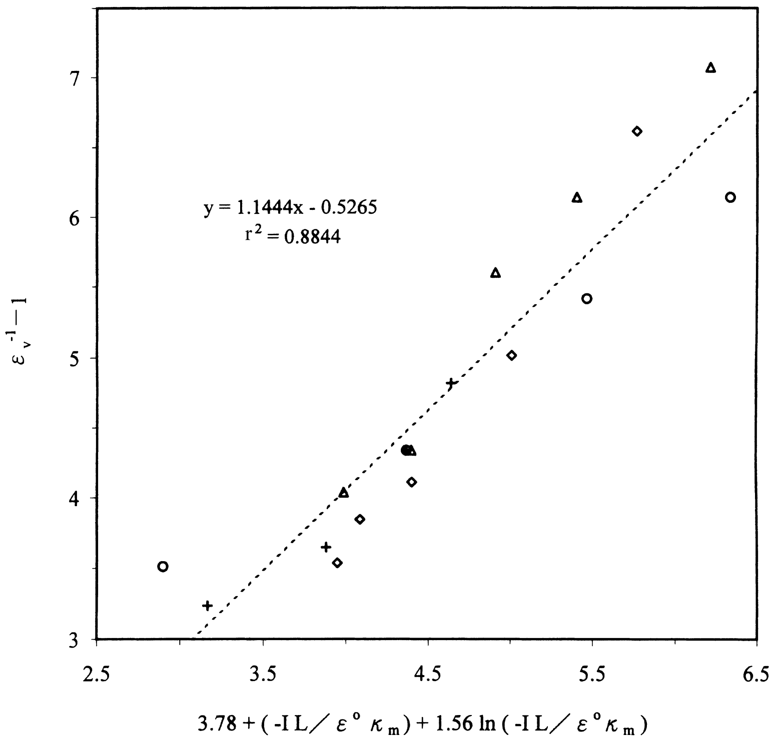

Fig. 13. The correlation between the voltage efficiency and the dimensionless groups of the operating variables. y=value of coordinate, x=value of abscissa and r^2=coefficient of correlation.

product, QOH, that is

$$\varepsilon_E = \frac{E}{n_{QOH}} \tag{24}$$

It is related to ε_c and ε_v as

$$\varepsilon_E = \frac{\varepsilon^0 F}{\varepsilon_c \varepsilon_v} \tag{25}$$

With the typical conditions, Fig. 14 shows that the energy consumption decreases rapidly with increasing anolyte concentration when C_c=0.49 M, and changes little within the range of the concentration ratio of $1.08<C_a/C_c<5.4$ when C_a=1.35 M. These results agree with the energy efficiency equation, which shows that $\varepsilon_e \propto C_a^{0.51} C_c^{0.017}$ for $0.9<C_a/C_c<11.2$. It also shows that the energy consumption increases quickly as the catholyte concentration falls below 0.25 M. This means that a considerable part of electrical energy dissipation is caused by the Ohmic resistance between the electrodes, and the resistance is predominately contributed by the catholyte. It is worthy to note that about 10% extra energy consumption (60 W h/eq) is required to keep C_c at 1.25 M instead of keeping at 0.5 M. While the corresponding heat required for the concentration by evaporation is about 752 W h/eq. So, in this case, it is much advantageous to operate with C_c= 1.25 M.

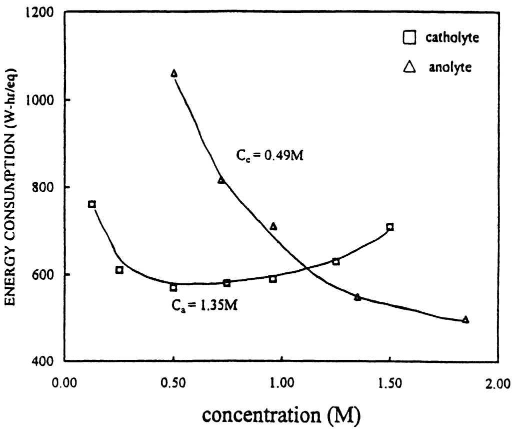

Fig. 14. Energy consumption under the varying electrolyte concentrations. Q=BTEA, M=Nafion 901, I=4.78 A/dm^2, C_a=0.45–1.85 M, C_c=0.12–1.5 M, u_a=u_c=1.71 cm/s and ℓ=16.8 mm.

6. Conclusion

The electrolysis–electrodialysis process with a Nafion cation exchange membrane is a suitable method for preparing quaternary ammonium hydroxides, especially, those used as cleaning and etching agents for IC boards. However, the current efficiency may fall below 50% when the concentration of the hydroxide is greater than 20 wt.%. This is because the mobility of hydroxyl ion is abnormally high, and the cation exchange membrane, Nafion

901, is still not satisfactory to prevent permeation of hydroxyl ions. From the experimental results and the equations of the current efficiency and the energy efficiency, a logical method of operation may be suggest as follows: (1) keep anolyte concentration as high as possible; (2) without resulting in serious flow resistance, make the electrolyte compartment as narrow as possible; (3) compare the pumping work with the energy consumption for selecting an appropriate electrolyte flow rate; (4) use a suitably high current density which does not cause concentration polarization for high production rate of QOH and (5) when the suitable set of C_a, ℓ, u_c and I is determined, the optimum value of C_c can be estimated by the dimensionless correlation for the current efficiency (Eq. (18)), the dimensionless correlation for the energy efficiency (Eq. (20)), and the equation for the energy consumption (Eq. (25)).

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