

**REMOVAL OF PERCHLORATE FROM DILUTE AQUEOUS SOLUTIONS:  
SYNTHESIS, CHARACTERIZATION AND TESTING OF  
PERCHLORATE SELECTIVE AND PERMSELECTIVE MEMBRANES  
AND BIMETALLIC CATALYSTS**

by

Po-Yen Wang

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Civil Engineering

Fall 2015

© 2015 Po-Yen Wang  
All Rights Reserved

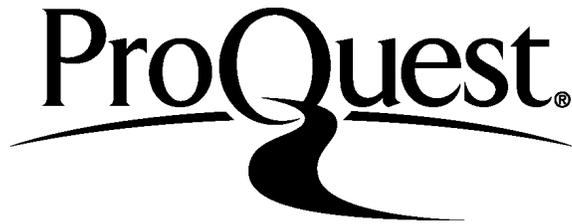
ProQuest Number: 10014767

All rights reserved

INFORMATION TO ALL USERS

The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.



ProQuest 10014767

Published by ProQuest LLC (2016). Copyright of the Dissertation is held by the Author.

All rights reserved.

This work is protected against unauthorized copying under Title 17, United States Code  
Microform Edition © ProQuest LLC.

ProQuest LLC.  
789 East Eisenhower Parkway  
P.O. Box 1346  
Ann Arbor, MI 48106 - 1346

**REMOVAL OF PERCHLORATE FROM DILUTE AQUEOUS SOLUTIONS:  
SYNTHESIS, CHARACTERIZATION AND TESTING OF  
PERCHLORATE SELECTIVE AND PERMSELECTIVE MEMBRANES  
AND BIMETALLIC CATALYSTS**

by

Po-Yen Wang

Approved: \_\_\_\_\_  
Harry W. Shenton III, Ph.D.  
Chair of the Department of Civil and Environmental Engineering

Approved: \_\_\_\_\_  
Babatunde A. Ogunnaike, Ph.D.  
Dean of the College of Engineering

Approved: \_\_\_\_\_  
Ann L. Ardis, Ph.D.  
Interim Vice Provost for Graduate & Professional Education

I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed:

---

Chin-Pao Huang, Ph.D.  
Professor in charge of dissertation

I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed:

---

S. Ismat Shah, Ph.D.  
Member of dissertation committee

I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed:

---

Daniel K. Cha, Ph.D.  
Member of dissertation committee

I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed:

---

Pei C. Chiu, Ph.D.  
Member of dissertation committee

## ACKNOWLEDGMENTS

First of all, I would like to start by expressing my sincere gratitude to my advisor Dr. C.P. Huang for his invaluable guidance and consistent mentoring through all these years of my being a graduate student. For providing me with comments and suggestions to improve this work I would also like to thank my dissertation committee: Dr. Ismat Shah, Dr. Daniel Cha and Dr. Pei Chiu.

I would like to acknowledge lab members, Minghua, Steve, Soohoon, Tommy, Jenn-Fang, Xuesong, Yangang, Lu, Arason, Daniel and Mary for collaboration during these years. I also want to thank several visiting scholars, Albert, Jimmy, Ben, and Wen-Pin and Emma, for their beneficial advice and suggestions. I am grateful to Dr. Rovshan Mahmudov and Mr. Michael Davidson for their help in my experimental work. Without their help this work would not be what it is.

Moreover, the research work would not have been possible without funding support; I must thank the funding sources, University of Delaware graduate research assistantship and National Science Foundation, grant No. 0965984 under the Environmental Engineering Program, Division of Chemical, Bioengineering, Environmental, and Transport Systems.

Finally, I want to express my most sincere gratitude to my family for their encouragement, love and support during these years. I owe a great debt of gratitude to my parents, sister and parents-in-law. Last but not the least; I would like to thank my wife, Joannie, for her love, patience, and support, and my two little girls Livie and Maisie for their love and smiles.

## TABLE OF CONTENTS

LIST OF TABLES.....	ix
LIST OF FIGURES .....	x
ABSTRACT .....	xvi

### Chapter

1	INTRODUCTION.....	1
	1.1 Perchlorate Contamination Issue .....	1
	1.2 Regulations for Perchlorate .....	2
	1.3 Objectives.....	4
	REFERENCES .....	7
2	LITERATURE REVIEW .....	9
	2.1 Sources of Perchlorate in Environment .....	9
	2.2 Chemical and Physical Properties of Perchlorate .....	11
	2.3 Toxicity / Health Effects of Perchlorate .....	12
	2.4 Current Remediation Methods .....	13
	2.4.1 Separation Methods.....	14
	2.4.2 Transformation Methods.....	15
	2.5 Electrocatalytic Reaction.....	17
	2.6 Hypothesis .....	18
	REFERENCES .....	21
3	A POLYMERIC MEMBRANE ELECTRODE FOR THE DETECTION OF PERCHLORATE IN WATER AT THE SUB-MICRO-MOLAR LEVEL.....	25
	3.1 Abstract.....	25
	3.2 Introduction .....	25
	3.3 Materials and Methods .....	27
	3.3.1 Chemicals and Reagents .....	27

3.3.2	Electrode Preparation .....	28
3.3.3	Electrode Characterization .....	30
3.3.4	Apparatus and Potentiometric Measurements .....	31
3.4	Results and Discussion .....	32
3.4.1	Perchlorate ISE with MTOAC .....	32
3.4.2	Perchlorate Ion Selectivity .....	36
3.4.3	Response Time .....	40
3.4.4	Influence of pH .....	42
3.4.5	Response in Natural Water .....	44
3.4.6	Aging .....	46
3.5	Summary .....	48
	REFERENCES .....	50
4	<b>PREPARATION AND CHARACTERIZATION OF FUNCTIONALIZED MEMBRANE FOR THE SELECTIVE SEPARATION OF PERCHLORATE FROM OTHER ANIONS IN WATER .....</b>	<b>54</b>
4.1	Abstract.....	54
4.2	Introduction .....	55
4.3	Materials and Methods .....	57
4.3.1	Chemicals and Reagents .....	57
4.3.2	Preparation of Membranes .....	58
4.3.3	Chemical and Physical Characterization .....	58
4.3.4	Perchlorate and Other Anions Separation Studies .....	61
4.4	Results and Discussion .....	63
4.4.1	Membrane Thickness .....	63
4.4.2	Polymer Mass Content .....	65
4.4.3	Chemical Property .....	68
4.4.4	Surface Hydrophilicity .....	79
4.4.5	Surface Morphology.....	81
4.4.6	Perchlorate Separation .....	86
4.4.7	Perchlorate Permselective Membrane.....	93
4.5	Summary .....	100
	REFERENCES .....	102

5	CATALYTIC ELECTROCHEMICAL REDUCTION OF PERCHLORATE WITH METALLIC DOPED ELECTRODE .....	106
5.1	Abstract.....	106
5.2	Introduction .....	107
5.3	Materials and Methods .....	107
5.3.1	Chemicals and Reagents .....	107
5.3.2	Preparation of Metallic Catalysts .....	108
5.3.3	Cyclic Voltammetry Experiments .....	108
5.3.4	Surface Characterization .....	109
5.3.5	Electrochemical Reduction System.....	110
5.3.6	Analytical Method.....	111
5.4	Results and Discussion .....	111
5.4.1	Reduction of Perchlorate.....	111
5.4.2	Electrode Characterizations .....	116
5.4.3	CV Scan Rate Selection .....	122
5.4.4	CV Study on Perchlorate Reduction with Rh-Cu/SS Electrode	125
5.4.5	Perchlorate Reduction with Rh-Cu/SS Electrode at Different pH .....	128
5.4.6	Perchlorate Reduction with Rh-Cu/SS Electrode at Different Concentration and Temperature .....	130
5.4.7	Proposed Perchlorate Reduction Mechanism .....	133
5.5	Summary .....	139
	REFERENCES .....	140
6	INTEGRATED ELECTRODIALYSIS AND CATALYTIC ELECTROCHEMICAL REDUCTION (CECR) PROCESS FOR THE REMOVAL OF PERCHLORATE .....	142
6.1	Abstract.....	142
6.2	Introduction .....	142
6.3	Materials and Methods .....	143
6.3.1	Chemicals and Reagents .....	143
6.3.2	Preparation of Metallic Catalysts .....	144
6.3.3	Perchlorate Separation and Reduction system.....	144
6.4	Results and Discussion .....	145

6.4.1	Effect of Anion Concentration .....	145
6.4.2	Effect of ED Current .....	146
6.4.3	Effect of ED Current on Perchlorate Reduction .....	148
6.4.4	Separation and Reduction of Perchlorate in ED-CECR System	150
6.4.5	Proposed Model for Perchlorate Reduction with Bimetallic Catalysts .....	152
6.5	Summary .....	155
	REFERENCES .....	157
7	CONCLUSION AND SUGGESTIONS .....	166
7.1	Conclusion .....	166
7.2	Suggestions for Future Works .....	168
Appendix		
A	POLYMERIC MEMBRANE ELECTRODE FOR THE DETECTION OF PERCHLORATE IN WATER AT THE SUB-MICRO-MOLAR LEVEL ...	169
A.1	Internal Solution .....	169
A.2	Thickness of ISE Membrane .....	171
B	COPYRIGHT PERMISSIONS .....	174
B.1	Permission for Chapter 3 .....	174
B.2	Permission for Chapter 4 .....	175

## LIST OF TABLES

Table 1.1.	Advisory levels for perchlorate in drinking water in 24 states (ASTSWMO 2011).....	3
Table 3.1.	The linearity range and the Nernstian slope of both electrodes were affected. Comparison of the potentiometric perchlorate selectivity coefficients ( $K_{ClO_4^-,B}$ ) and working pH range of various perchlorate ion specific electrodes. ....	38
Table 3.2.	Perchlorate detection in various natural and tap waters. ....	46
Table 4.1.	Chemical Structure of quaternary ammonium salts. ....	69
Table 4.2.	Characterization of various membranes. ....	78
Table 4.3.	Rate constants of anions passed through various membranes in electro dialysis separation (n = 3). ....	92
Table 4.4.	Values of electrochemical parameters obtained by fitting the experimental impedance data. ....	99
Table 5.1.	Elements composition of various electrodes.....	115
Table 5.2.	Rh <sub>0.11</sub> -Cu <sub>0.89</sub> /SS XRD analysis.....	122
Table 5.3.	Electrochemical parameters (slope, $\alpha$ , and n) of perchlorate reduction on Rh <sub>0.11</sub> -Cu <sub>0.89</sub> /SS electrode.....	127
Table A1.	Effect of ionophore and presence of perchlorate in the internal solution on the performance of the PVC-only and the PVC+ionophore electrodes. Experimental conditions: Perchlorate concentration = 10 <sup>-8</sup> to 0.1 M; Temperature = 21 ~ 23 °C; pH = 5 ~7; Reference electrode = SCE. ....	172
Table A2.	Chemical composition of water samples studied.....	173

## LIST OF FIGURES

Figure 2.1.	Perchlorate distribution in the United State. (GAO 2010).....	10
Figure 2.2.	Comparison of perchlorate detection with known release sites.(Brandhuber and Clark 2005).....	11
Figure 3.1.	Effect of the membrane chemical composition on the Nernstian slope response of the electrodes in the presence of $10^{-3}$ M of nitrate. Experimental conditions: perchlorate concentration: $10^{-8}$ or $10^{-6}$ to 0.1 M; temperature: 21 ~ 23 °C; pH = 5 ~7. Symbols: (□) PVC with DBP, (○) PVC with MTOAC, (△) PVC with Ni(DBM) <sub>2</sub> , (●) PVC with DBP and MTOAC, (▲) PVC with DBP, MTOAC and Ni(DBM) <sub>2</sub> .....	33
Figure 3.2.	Competitive adsorption isotherms of ClO <sub>4</sub> <sup>-</sup> and (a) NO <sub>3</sub> <sup>-</sup> (b) HCO <sub>3</sub> <sup>-</sup> (c) SO <sub>4</sub> <sup>-2</sup> with different membranes. (■) PVC membrane without ionophore, (●) PVC membrane with 0.1g Ionophore, (▲) AMI 7001S, (◆) Ionac MA-3475. Experimental conditions: Membrane: 0.01g; [ClO <sub>4</sub> <sup>-</sup> ]: 0 to 10 ppm; [NO <sub>3</sub> <sup>-</sup> ], [HCO <sub>3</sub> <sup>-</sup> ] and [SO <sub>4</sub> <sup>-2</sup> ]: 0 to 10 ppm; pH = 5 ~7. ....	35
Figure 3.3.	Effect of humic acid (HA) on the potentiometric response of PVC-electrode and PVC+Ni(DBM) <sub>2</sub> electrode. Experimental conditions: perchlorate concentration = $10^{-6}$ to 0.1 M; temperature = 21 ~ 23 °C; pH = 5 ~7. The dashed line represents the theoretical Nernstian slope of 58.4 mV/log. ....	39
Figure 3.4.	Practical response time of PVC-electrode (●) and PVC+Ni(DBM) <sub>2</sub> electrode (○). Experimental conditions: perchlorate concentration = $10^{-5}$ to $10^{-4}$ M; temperature = 21 ~ 23 °C; pH = 5 ~7. The dashed line represents the theoretical Nernstian slope of 58.4 mV/log. ....	42
Figure 3.5.	Effect of pH on the potentiometric response of the PVC-electrode (○) and the PVC+Ni(DBM) <sub>2</sub> electrode (●). Experimental conditions: perchlorate concentration = $10^{-5}$ M; temperature= 21 ~ 23 °C. ....	44

Figure 3.6.	Effect of aging on the potentiometric response of (a) PVC-electrode (○), PVC+Ni(DBM) <sub>2</sub> electrode (●); (b) PVC-electrode with Ni(DBM) <sub>2</sub> in the internal solution (△), PVC+Ni(DBM) <sub>2</sub> with Ni(DBM) <sub>2</sub> in the internal solution (▲). Experimental conditions: perchlorate concentration = 10 <sup>-8</sup> to 0.1 M; temperature = 21 ~ 23 °C; pH = 5 ~7. The dashed line represents the theoretical Nernstian slope of 58.4mV/log. ....	48
Figure 4.1.	(a) Perchlorate permselectivity as affected by membrane thickness. (b) Perchlorate permselectivity as affected by PVC weight content (%). Experimental conditions: [MTBA] = 0.1 g; [TBOAC] = 1.04 g; THF = 10 mL; ED Current = 1 mA; pH = 6.8; temperature = 22 ± 1 °C; I = 0.13 mM NaCl. ....	65
Figure 4.2.	Voltage drop of membrane of different PVC weight percentage. Experimental Conditions: [MTBA] = 0.1 g; [TBOAC] = 1.04 g; THF = 10mL; ED Current = 1 mA; pH = 6.8; temperature = 22±1 °C; I = 0.13 mM (NaCl). ....	67
Figure 4.3.	Voltage drop of membrane of different thickness. Experimental Conditions: [MTBA] = 0.1 g; [TBOAC] = 1.04 g; THF = 10mL; ED Current = 1 mA; pH = 6.8; temperature = 22±1 °C; I = 0.13 mM (NaCl). ....	68
Figure 4.4.	Perchlorate permselectivity with respect to nitrate, sulfate (left y-axis) and bicarbonate (right y-axis) of different membranes as a function of chain length or carbon number: (a) symmetric amines; (b) amines with one long chain group, and (c) amines with benzyl group. Experimental conditions: [PVC] = 34.5 %(wt); [TBOAC] = 59.8%(wt); [R <sub>4</sub> N <sup>+</sup> X <sup>-</sup> ] = 5.7%(wt); THF = 10 mL; ED Current = 1 mA; pH = 6.8; temperature = 22 ± 1 °C; I = 0.13 mM NaCl. ....	74
Figure 4.5.	FTIR spectra of different membranes functionalized with different quaternary ammonium salts. Experimental conditions; [PVC] = 34.5 %(wt); [TBOAC] = 59.8% (wt); [R <sub>4</sub> N <sup>+</sup> X <sup>-</sup> ] = 5.7%(wt); THF = 10 mL. ....	76

Figure 4.6.	Hydrophobicity of different membranes as a function of molecular weight of quaternary ammonium salts. (a) Contact angle ( $\theta$ ) of the PVC- membranes before and after perchlorate exchange experiments; (b) change of contact angle after ion exchange experiments. Experimental conditions: [PVC] = 34.5%; [R <sub>4</sub> N <sup>+</sup> X <sup>-</sup> ] = 5.7%; [TBOAC] = 59.8%; THF = 10 mL; ED current = 1 mA; pH = 6.8; temperature = 22 ± 1 °C; I = 0.13 mM.....	80
Figure 4.7.	SEM images of (a) PVC only; (b) TMA; (c) CTMA; (d) BTMA; (e) MTOA and (f) MTBA membranes. Experimental Condition: [PVC] = 34.5%; [R <sub>4</sub> N <sup>+</sup> X <sup>-</sup> ] = 5.7%; [TBOAC] = 59.8%; THF = 10 mL.....	83
Figure 4.8.	SEM images of (a) TEA; (b) TPA; (c) OTMA; (d) DDTMA; (e) BTBA and (f) BDMHA membranes. Experimental Condition: [PVC] = 34.5%; [R <sub>4</sub> N <sup>+</sup> X <sup>-</sup> ] = 5.7%; [TBOAC] = 59.8%; THF = 10 mL.....	84
Figure 4.9.	Cross-sectional view of MTBA membrane . Experimental Condition: [PVC] = 34.5%; [MTBA] = 5.7%; [TBOAC] = 59.8%; THF = 10 mL. ....	85
Figure 4.10.	Kinetics of ion transport across different membranes. (a) Change of ion concentrations in the dilute and the concentrate streams as a function of time across the MTBA membrane. (b-d) k <sub>1</sub> , rate constant of anions transport from the diluate to the membrane (n = 3). Experimental conditions: [Alkalinity] = 15 mg/L as CaCO <sub>3</sub> ; [NO <sub>3</sub> <sup>-</sup> ] = 10 mg/L; [SO <sub>4</sub> <sup>2-</sup> ] = 4.3 mg/L; [ClO <sub>4</sub> <sup>-</sup> ] = 1.0 mg/L. Temperature = 21 ~ 23 °C; pH = 5 ~7; ED current = 1 mA. ....	88
Figure 4.11.	Electrodialytic separation of perchlorate from water containing major anions, namely NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> and HCO <sub>3</sub> <sup>-</sup> with different membranes.(a)TMA; (b)TEA; (c)TPA; (d) HTMA; (e)OTMA, (f)DDTMA; (g)CTMA; (h)BTMA; (i)BTBA; (j) BDMHA and (k)MTOA. [Alkalinity] = 15 mg/L as CaCO <sub>3</sub> (3 mg/L); [NO <sub>3</sub> <sup>-</sup> ] = 10 mg/L; [SO <sub>4</sub> <sup>2-</sup> ] = 4.3 mg/L; [ClO <sub>4</sub> <sup>-</sup> ] = 1.0 mg/L. Experimental conditions: Temperature = 21 ~ 23 °C; pH = 5 ~7; ED current = 1mA. ....	91

Figure 4.12.	Relationship between permselective constant of major anions with respective to perchlorate and (a) maximum adsorption constant and (b) monolayer adsorption capacity corresponding major anions of various [PVC-R <sub>4</sub> N <sup>+</sup> X <sup>-</sup> ] membranes. Experimental Conditions: [PVC] = 34.5%; [R <sub>4</sub> N <sup>+</sup> X <sup>-</sup> ] = 5.7%; [TBOAC] = 59.8%; THF = 10 mL; ED Current = 1 mA; pH = 6.8; temperature = 22±1 °C; I = 0.13 mM (NaCl). The numbers in the plot represents different quaternary ammonium salts [R <sub>4</sub> N <sup>+</sup> X <sup>-</sup> ]: (1)=MTBA; (2)=TPA; (3)=BTMA; (4)=HTMA; (5)=BTBA; (6)=OTMA; (7)=BDMHA; (8)=TMA; (9)=DDTMA; (10)=CTMA; (11)=TEA; (12)=MTOA. ....	94
Figure 4.13.	(a) Nyquist plots of the impedance spectrums for PVC-MTBA membrane in 0.1 M of NaNO <sub>3</sub> , Na <sub>2</sub> SO <sub>4</sub> , NaHCO <sub>3</sub> and NaClO <sub>4</sub> electrolyte, respectively. (b) The equivalent circuit of PVC-MTBA membrane based o EIS data. Experimental Conditions: Scan frequency = 0.1 to 5×10 <sup>5</sup> Hz; membrane area = 38.48 cm <sup>2</sup> . ....	98
Figure 5.1.	Electrocatalytic reactor for reduction of perchlorate. ....	110
Figure 5.2.	(a) Electrochemical reduction of perchlorate and (b) formation of chloride with various catalytic electrodes. Experimental conditions: [ClO <sub>4</sub> <sup>-</sup> ] = 10 mM; catalytical cathode =various metals, anode = graphite; current = 20 mA; T = 298K; pH = 3.4. ....	114
Figure 5.3.	SEM images on the surface of various metals doped electrodes. (a)stainless steel; (b) Rh/SS; (c) Cu/SS; (d) Pd/SS; (e) Ru/SS; (f) Mo/SS; (g) Rh-Ru/SS and (h) Rh <sub>0.11</sub> -Cu <sub>0.89</sub> /SS. ....	117
Figure 5.4.	XPS patterns of Rh <sub>0.11</sub> -Cu <sub>0.89</sub> /SS catalysts (a) full; (b)Cu; (c) Rh spectra and (d) XRD patterns of Rh <sub>0.11</sub> -Cu <sub>0.89</sub> /SS catalysts. ....	121
Figure 5.5.	Cyclic voltammograms on Rh <sub>0.11</sub> -Cu <sub>0.89</sub> /SS electrode recorded at different scan rate (from 0.05 to 0.20 V/s) in 20 mM NaClO <sub>4</sub> solution; (b) The peak currents versus the square root of the scan rate ( $v^{0.5}$ ) extracted from Fig. 5.5(a). Experimental condition: counter electrode = Pt; reference electrode = SCE; T = 298K; pH =5.0. ....	124

Figure 5.6.	(a) Cyclic voltammograms on Rh <sub>0.11</sub> -Cu <sub>0.89</sub> /SS electrode recorded at different concentration (from 5 mM to 29 mM ) of NaClO <sub>4</sub> solution; (b) The fitting results from cycle voltammetric curve in 29 mM NaClO <sub>4</sub> solution (Fig. 5.6(a)) on Rh <sub>0.11</sub> -Cu <sub>0.89</sub> /SS electrode; and (c) The corresponding Nicholson and Shain plot at R <sub>1</sub> , R <sub>2</sub> , and R <sub>3</sub> peaks. Experimental condition: scan rate = 0.05 V/s; counter electrode = Pt; reference electrode = SCE; T = 298K; pH =5.0. ....	126
Figure 5.7.	Reduction of perchlorate (a) at different pH and (b) reaction kinetic. Experimental conditions: [ClO <sub>4</sub> <sup>-</sup> ] = 1 mM; catalytical cathode = Rh <sub>0.11</sub> -Cu <sub>0.89</sub> /SS metals, anode = graphite; current = 20.0 mA, T = 298K. ....	129
Figure 5.8.	Reduction of perchlorate (a) at different concentration of perchlorate and (b) the Langmuir-Hinshelwood plot. Experimental conditions: [ClO <sub>4</sub> <sup>-</sup> ] = 1 mM; catalytical cathode = Rh <sub>0.11</sub> -Cu <sub>0.89</sub> /SS metals, anode = graphite; current = 20 mA, T = 298K; pH =5.0. ....	131
Figure 5.9.	Reduction of perchlorate (a) at different temperature and (b) Arrhenius plot of the observed first-order rate constant as a function of 1/T. Experimental conditions: [ClO <sub>4</sub> <sup>-</sup> ] = 1 mM; catalytic cathode = Rh <sub>0.11</sub> -Cu <sub>0.89</sub> /SS metals, anode = graphite; current = 20.0 mA, T = 283 to 343K; pH =5.0. ....	133
Figure 5.10.	The mechanistic model fit to Figure 5.2 (a) and (b) obtained over the Rh <sub>0.11</sub> -Cu <sub>0.89</sub> /SS electrode. . Experimental conditions: [ClO <sub>4</sub> <sup>-</sup> ] = 10 mM; catalytical cathode =various metals, anode = graphite; current = 20 mA; T = 298K; pH = 3.4. ....	138
Figure 6.1.	Integrated electro dialytic separation and catalytic electrochemical reduction system (ES-CERs) for perchlorate. ....	145
Figure 6.2.	Separation rate constant of perchlorate and other anions (nitrate, sulfate and bicarbonate) with MTBA membrane at different initial concentration. Experimental conditions: each anion = 10 <sup>-5</sup> M to 2×10 <sup>-3</sup> M; ED cathode and anode = graphite, current = 1 mA; temperature = 295K. ....	146
Figure 6.3.	Separation rate constant of perchlorate and other anions (nitrate, sulfate and bicarbonate) with MTBA membrane at different ED current. Experimental conditions: each anion = 10 <sup>-4</sup> M; ED cathode and anode = graphite, current = 1 to 60 mA; temperature = 295K. ...	147

Figure 6.4.	Separation of perchlorate with MTBA membrane. Experimental conditions: $[\text{ClO}_4^-] = 10^{-4} \text{ M}$ ; ED cathode and anode = graphite, current = 1 mA; temperature = 295K; pH = 5.5 in dilute stream; pH = 4.5 in concentrate stream. ....	148
Figure 6.5.	Mass balance of $[\text{ClO}_4^-]$ and $[\text{Cl}^-]$ in integrated separation and reduction of the perchlorate by Rh-Cu/SS bimetallic catalysts under (a) 1 mA and (b) 2 mA ED current. Experimental conditions: $[\text{ClO}_4^-] = 10^{-5} \text{ M}$ ; catalytical cathode = Rh-Cu/SS, anode = graphite; reduction current = 20 mA; ED cathode and anode = graphite, ED current = 1 and 2 mA; temperature = 295K; pH = 5.5 in dilute stream; pH = 4.5 in concentrate stream. ....	150
Figure 6.6.	Integrated separation and reduction of the perchlorate by different bimetallic catalysts. (a) Rh-Ru/SS and (b) Rh-Cu/SS. Experimental conditions: $[\text{ClO}_4^-] = 10^{-4} \text{ M}$ ; catalytical cathode = various metals, anode = graphite; current = 20 mA; ED cathode and anode = graphite, current = 1 mA; temperature = 295K; pH = 5.5 in dilute stream; pH = 4.5 in concentrate stream. ....	152
Figure 6.7.	Model fitted separation and reduction of perchlorate by different bimetallic catalysts. (a) Rh-Ru/SS and (b) Rh-Cu/SS. Experimental conditions: $[\text{ClO}_4^-] = 10 \text{ mg/L}$ ; catalytical cathode = various metals, anode = graphite; current = 20 mA; ED cathode and anode = graphite, current = 1 mA; temperature = 295K; pH = 5.5 in dilute stream; pH = 4.5 in concentrate stream. ....	155
Figure A1.	Effect of internal perchlorate concentration on the potentiometric response of (a) PVC, (b) PVC+Ni(DBM) <sub>2</sub> electrode and (c) changes of Nernstian slope. Experimental conditions: temperature = 21 ~ 23 °C; pH = 5 ~ 7. Symbols: (□) 0.1 mM, (○) 1.0 mM, (△) 10 mM, (▽) 100 mM. The dashed line represents the theoretical Nernstian slope of 58.4 mV/log. ....	170
Figure A2.	Effect membrane thickness on the (a) potentiometric response and (b) Nernstian slope of PVC-only electrodes. Experimental conditions: temperature = 21~23 oC; pH = 6 ~7. Thickness: (■) 0.29 mm; (◆) 0.70 mm and (△) 1.08 (mm). ....	171

## ABSTRACT

Perchlorate is an emerging inorganic contaminant in the United States. The Environmental Protection Agency (EPA) expects to issue a national primary drinking water regulation (NPDWR) for perchlorate in March 2017. Therefore, methods that are effective in eliminating perchlorate from water are needed. The objective of this study is to synthesize a perchlorate selective and permselective membrane for detection and separation of perchlorate and to integrate electro dialysis and catalytic electrochemical techniques for the simultaneous separation and reduction of perchlorate.

First, a highly sensitive polymeric membrane electrode was synthesized for the detection of perchlorate in water. The membrane electrode exhibited favorable selectivity toward perchlorate over interfering anions such as chloride, nitrate, sulfate, and bicarbonate in water and had a response time of *ca.* 5 s over the perchlorate concentration (activity) range of  $10^{-6}$  to  $10^{-1}$  M and a Nernstian slope of  $58.5 \pm 0.4$  mV at room temperature. The potentiometric response of the electrode was pH independent in the range of 3.0 to 11.0 and had a perchlorate detection limit of  $7.0 \times 10^{-7}$  M (or 70 ppb). The polymeric membrane electrode was able to detect perchlorate ion at the sub-micro-molar level under conditions mimicking those of natural water systems.

Next, perchlorate permselective membranes were synthesized and characterized in this study. A membrane with a thickness of  $\sim 300\mu\text{m}$  was prepared with polyvinyl chloride (PVC) and quaternary ammonium salts in solvent under room

temperature. Among 12 different quaternary ammonium salts, methyltributylammonium chloride (MTBA) showed superior perchlorate permselectivity due in part to the favorable steric effect of the alkyl chain length. In addition, results from contact angle measurements indicated that modification with quaternary ammonium salts rendered the membranes hydrophobic. Results from Fourier transform infrared (FTIR) spectrum analysis showed that the functional groups responsible for ion exchange were incorporated in the membrane matrix successfully. The surface roughness, averaged pore radius, and ion exchange capacity of the MTBA membrane were  $3.23 \pm 2.58$  (nm), 83.6 (Å), and 0.12 (meq/g), respectively. In the presence of an electric field, about 60% of perchlorate ions were separated from the solution while only less than 9% of other anions, specifically, nitrate, sulfate and bicarbonate passed through the membrane under otherwise identical operation conditions simultaneously.

After the membranes were prepared for the separation of perchlorate, catalysts for the reduction of perchlorate were also examined. Monometallic and bimetallic catalysts were prepared for perchlorate reduction in the study. The electrodes were characterized for surface structure and chemical composition using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The results showed that with applying the same current and pH in the system, perchlorate reduction efficiency of monometallic-doped electrodes were in the order of Rh>Cu>Ru>Mo>Pd. For bimetallic-doped electrodes, Rh-Cu (75% reduction) was found to be more effective than Rh-Ru (60% reduction). The mass balance of chlorine species (chloride and perchlorate) in the system can be up to 95%. The imbalance part of chlorine species mass would be due to the adsorption of perchlorate by the electrode. The

testing results of the catalytic electrochemical technique showed its suitability for reduction of perchlorate. X-ray photoelectron spectroscopy (XPS) analysis of the bimetallic catalyst indicated the presence of metal oxide and elemental metals. X-ray diffraction (XRD) spectra showed the presence of both crystalline and amorphous metallic catalysts.

Finally, an integrated process for the separation and reduction of perchlorate from water was constructed. With the perchlorate permselective membrane, perchlorate can be exclusively separated and concentrated from water in presence of other anions. Followed by using perchlorate reduction electrodes, perchlorate can be reduced to chloride. A proposed model for perchlorate reduction was developed and successfully used to calculate the rate constants of anions passing through the membranes. Thus, it has been shown that 80% of perchlorate could be separated by MTBA membrane in electro dialysis process and up to 95% of separated perchlorate can be readily reduced to chloride within 6 hours. No other oxyanions of chlorine, such as  $\text{ClO}_3^-$ ,  $\text{ClO}_2^-$  or  $\text{ClO}^-$  was detected as the intermediates during the reduction process. This integrated ED-CECR process can be applied for the removal of low concentrations of perchlorate from drinking water sources.

## Chapter 1

### INTRODUCTION

#### 1.1 Perchlorate Contamination Issue

During the past few decades, perchlorate ( $\text{ClO}_4^-$ ) has become a national concern due to high concentrations found in groundwater and surface waters. Perchlorate has been widely used as oxidizer in solid propellant for rocket, missile, firework, and explosives during the past decades. In 1964, the California Department of Water Resources first recorded that groundwater in east Sacramento contained perchlorate in 34 wells at levels of up to 1.8 mg/L (Fisher, Brown et al. 1964). Later in 1985, perchlorate was also found at Superfund sites in San Gabriel Valley in California (USEPA 1998). In 2005, public drinking water supplies serving more the 11 million people in the United States contained a detectable perchlorate concentration (NRC 2005). In addition, perchlorate has been detected in breast milk, dairy milk (Kirk, Martinelango et al. 2005; Kirk 2006), and produce (Sanchez, Krieger et al. 2005) mainly caused by using perchlorate containing water. As of 2010, perchlorate has been detected at private and federal facilities in 45 States, three United States territories, and the District of Columbia (GAO 2010).

Outside of the United States, perchlorate has been detected in rivers in Korea (Quiñones, Oh et al. 2007) and in lakes in Canada (Backus, Klawuun et al. 2005). In Japan, perchlorate concentration was found in the range of hundreds to thousands of ppb in drinking water sources of metropolitan areas (Kosaka, Asami et al. 2007). Besides in water, perchlorate is also found in fresh and canned food, and in wine and

beer samples from more than 20 countries at low part-per-trillion levels (El Aribi, Le Blanc et al. 2006). In China, perchlorate has been reported in sewage sludge, rice, bottled drinking water, and milk (Shi, Zhang et al. 2007). Therefore, perchlorate contamination in water can be regarded as a global problem.

The United States Environmental Protection Agency (USEPA) considers perchlorate as a contaminant of concern for several reasons, (i) the potential of perchlorate to cause human health problems when present at low concentrations in water; (ii) likely common presence of perchlorate in groundwater, surface waters, soils, and crops; (iii) lack of cost-effective treatment technologies for removal of perchlorate from water; (iv) and the impact of the fate of perchlorate in the environment on the whole ecological system (USEPA 1998).

## **1.2 Regulations for Perchlorate**

A National Primary Drinking Water Regulation (NPDWR) for perchlorate does not currently exist in the United States. The USEPA added perchlorate to the drinking water contaminant candidate list (CCL) in 1998 (USEPA 1998). In the following year, the USEPA put perchlorate under the federal Unregulated Contaminant Monitoring Rule (UCMR), with monitoring beginning in January of 2001. The minimum detection level of perchlorate for data collected under UCMR was 4 ppb. The National Academy of Science has recommended a reference dose (RfD) of 0.7  $\mu\text{g}/\text{kg}\text{-day}$  for perchlorate, which is equivalent to 24.5  $\mu\text{g}/\text{L}$  of perchlorate in drinking water based on the assumption of daily water consumption of 2000 mL by an adult of 70 kg average weight at a cancer risk of  $10^{-6}$  (Kirk, Dyke et al. 2007). In February 2011, the USEPA expressed the government's intend to establish a national primary drinking water regulation (NPDWR) for perchlorate (USEPA 2011).

The USEPA had anticipated issuing a proposal at the end of 2014 and a notice of proposed rulemaking (NPRM) in 2017 (Greenhaw 2014; USEPA 2015).

Table 1.1. Advisory levels for perchlorate in drinking water in 24 states (ASTSWMO 2011).

<b>State</b>	<b>Advisory Levels / MCLs (ppb)</b>
<b>Alabama</b>	24.5
<b>Alaska</b>	26
<b>Arizona</b>	14
<b>California</b>	6
<b>Florida</b>	4
<b>Hawaii</b>	26
<b>Iowa</b>	4.9
<b>Kansas</b>	10.9
<b>Maine</b>	1
<b>Maryland</b>	1
<b>Massachusetts</b>	2
<b>Missouri</b>	10.9
<b>Nebraska</b>	0.91
<b>Nevada</b>	18
<b>New Jersey</b>	5
<b>New Mexico</b>	1
<b>New York</b>	5
<b>North Carolina</b>	2
<b>Texas</b>	17
<b>Vermont</b>	2
<b>Virginia</b>	15
<b>Washington</b>	11
<b>Wisconsin</b>	1

Due to the lack of national regulatory standards for perchlorate, 24 states have developed their own regulations or advisory cleanup levels for perchlorate in drinking water, groundwater, soils or sediments (ASTSWMO 2011). Table 1.1 shows that the advisory concentrations of perchlorate are in the range of 0.91 ppb to 24.5 ppb.

Among the 24 states, Massachusetts is the first state in the U.S. to set a drinking water standard for perchlorate at 2 ppb in 2006 (MDEP 2006). In 2007, California set the maximum contaminant level (MCL) for perchlorate in drinking water at 6 ppb according to the public health goal (PHG) of 6 ppb established by the Office of Environmental Health Hazard and Assessment (OEHHA) in 2004. In 2015, PHG for perchlorate in drinking water was reduced from 6 ppb to 1 ppb. Accordingly, California is in the process of modifying the MCL for perchlorate (CDPH 2015).

### **1.3 Objectives**

The overall goal of the research is to develop an integrated detection, separation, and reduction method for the removal and transformation of perchlorate from water under ambient pressure and temperature conditions. To approach this goal, several objectives were designed, (1) to develop a simple, environmentally benign method to synthesize a perchlorate ion exchange membrane for selective detection and permselective separation of perchlorate; (2) to develop a perchlorate reduction catalytic electrode; and (3) to optimize the separation and reduction process for the removal and transformation of perchlorate.

The background of the research is reviewed in Chapter 2. This includes discussion about the source of perchlorate in the environment, chemical and physical properties of perchlorate, and health effects of perchlorate. Current remediation methods are compared and discussed. Basic concepts of electrodialytic separation and electrocatalytic reaction are introduced. The hypothesis of the research is also postulated in the end of Chapter 2.

Chapter 3 focuses on the development of the perchlorate selective membrane for detection of perchlorate in water. The membranes were characterized for thickness,

potentiometric responses, and response time. Factors such as interfering anions, humic acid, and pH that may affect the performance of the electrode were investigated. The polymeric membrane electrode was found to be able to detect perchlorate ion at the sub-micro-molar level under conditions mimicking those of natural water systems.

Chapter 4 discusses preparation and characterization of the perchlorate permselective membranes. Different quaternary ammonium salts cooperated membranes were examined under an electric field. The mechanism of how membrane can have perchlorate permselectivity is also discussed in this chapter.

Chapter 5 concentrates on monometallic and bimetallic catalytic electrodes for perchlorate reduction. The electrodes were characterized for surface structure and chemical composition using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Test results of the catalytic electrochemical technique showed its suitability for the reduction of perchlorate. X-ray photoelectron spectroscopy (XPS) analysis of the bimetallic catalyst indicated the presence of metal oxide and elemental metals. X-ray diffraction (XRD) spectra showed the presence of both crystalline and amorphous metallic catalysts. Finally, the chapter also elaborates on the mechanism of perchlorate reduction in the electrocatalytic electrode system.

Chapter 6 is devoted to integrate the electrodialytic separation and electrochemical reduction of perchlorate, ED-CECR systems. Catalytic material was prepared by electroplating of metals onto conductive metal mesh. Atomic hydrogen was produced to reduce perchlorate with the aid of metallic catalysts, and the ED current was found to influence the reduction products.

Chapter 7 summarizes how perchlorate can be detected, removed and reduced in the integrated processes. Future works are discussed with recommendations on

areas that require further understanding of the process and to improve the performance of the membrane. This proposed research will develop an innovative technology for the monitoring, removal and reduction of perchlorate in drinking water under ambient conditions.

## REFERENCES

- ASTSWMO (2011). Perchlorate policy update, Federal Facilities Research Center - Emerging Issues Focus Group.
- Backus, S. M., P. Klawuun, et al. (2005). "Determination of perchlorate in selected surface waters in the Great Lakes Basin by HPLC/MS/MS." Chemosphere **61**(6): 834-843.
- CDPH. (2015). "Perchlorate in Drinking Water." Retrieved July 3rd, 2015, from [http://www.waterboards.ca.gov/drinking\\_water/certlic/drinkingwater/Perchlorate.shtml](http://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/Perchlorate.shtml).
- El Aribi, H., Y. J. C. Le Blanc, et al. (2006). "Analysis of perchlorate in foods and beverages by ion chromatography coupled with tandem mass spectrometry (IC-ESI-MS/MS)." Analytica Chimica Acta **567**(1): 39-47.
- Fisher, H., E. G. Brown, et al. (1964). Folsom-East Sacramento ground water quality investigation, California Department of Water Resources. **Bulletin no. 133**.
- GAO (2010). Perchlorate: Occurrence Is Widespread But At Varying Levels; Federal Agencies have Taken Some Actions to Respond to and Lessen Releases, Government Accounting Office. **GAO-10-769**.
- Greenhaw, K. (2014). "Rules to Watch (and Wait) for in 2014." Retrieved March 3rd, 2014, from <http://www.foreffectivegov.org/rules-watch-and-wait-2014>.
- Kirk, A. B. (2006). "Environmental perchlorate: Why it matters." Analytica Chimica Acta **567**(1): 4-12.
- Kirk, A. B., J. V. Dyke, et al. (2007). "Temporal patterns in perchlorate, thiocyanate, and iodide excretion in human milk." Environmental Health Perspectives **115**(2): 182-186.
- Kirk, A. B., P. K. Martinelango, et al. (2005). "Perchlorate and Iodide in Dairy and Breast Milk." Environmental Science & Technology **39**(7): 2011-2017.
- Kosaka, K., M. Asami, et al. (2007). "Occurrence of perchlorate in drinking water sources of metropolitan area in Japan." Water Research **41**(15): 3474-3482.
- MDEP. (2006). "Drinking Water Standard for Perchlorate." Retrieved March 3rd, 2014, from <http://www.mass.gov/eea/docs/dep/water/laws/i-thru-z/perchlorate-310cmr22-07282006.pdf>.
- NRC (2005). Health Implications of Perchlorate Ingestion. Washington, D. C., National Academies Press.
- Quiñones, O., J.-E. Oh, et al. (2007). "Perchlorate assessment of the Nakdong and Yeongsan watersheds, Republic of Korea." Environmental Toxicology and Chemistry **26**(7): 1349-1354.
- Sanchez, C. A., R. I. Krieger, et al. (2005). "Accumulation and perchlorate exposure potential of lettuce produced in the Lower Colorado River region." Journal of Agricultural and Food Chemistry **53**(13): 5479-5486.
- Shi, Y. L., P. Zhang, et al. (2007). "Perchlorate in sewage sludge, rice, bottled water and milk collected from different areas in China." Environment International **33**(7): 955-962.

- USEPA (1998). "Announcement of the Drinking Water Contaminant Candidate List; Notice." Federal Register **63**(40): 10273.
- USEPA (1998). Perchlorate Environmental Contamination: Toxicological review and risk characterization based on emerging information, Environmental Protection Agency.
- USEPA. (2011). "Drinking Water: Regulatory Determination on Perchlorate." Retrieved March 3rd, 2014, from <http://www.gpo.gov/fdsys/pkg/FR-2011-02-11/pdf/2011-2603.pdf>.
- USEPA. (2015). "National Primary Drinking Water Regulations: Regulation of Perchlorate." Retrieved June, 2015, from <http://yosemite.epa.gov/opei/rulegate.nsf/byRIN/2040-AF28#1>.

## Chapter 2

### LITERATURE REVIEW

#### 2.1 Sources of Perchlorate in Environment

Many states in the USA have reported the contamination of perchlorate in water (See Fig. 2.1). Natural and anthropogenic origins are important contributing sources of perchlorate in the environment. Naturally occurring perchlorate in terrestrial soils is observed in a few locations of West Texas (Dasgupta, Martinelango et al. 2005). Low levels of perchlorate exist in the atmosphere by a heterogeneous reaction between ozone and volatile chlorine species and enter into the groundwater through wet deposition (Rajagopalan, Anderson et al. 2009), although other alternative pathways are also being investigated. Perchlorate salts, namely ammonium perchlorate and potassium perchlorate have been widely used as oxidizers in solid propellants for rockets, missiles, fireworks, and explosives since the late 1940s because of their high stability and consistent performance. Department of Defense (DoD) and National Aeronautics and Space Administration (NASA) used large amounts of perchlorate as the ingredient in composite propellants and munitions. Perchlorate contamination in military-related places can be dated back to the 1940s when large amounts of perchlorate salts were used by DoD or NASA facilities. For example, one-third of all perchlorate used in the United States is used in California and 90% of California's use is related to the aerospace industry. Most of the locations where perchlorate has been detected are associated with facilities that have manufactured or tested solid rocket fuel for the DoD and NASA. Fig. 2.2 maps out

locations of perchlorate known releases. From Figure 2.2, most sites of perchlorate detection are related to human application or manufacture of perchlorate-containing materials.

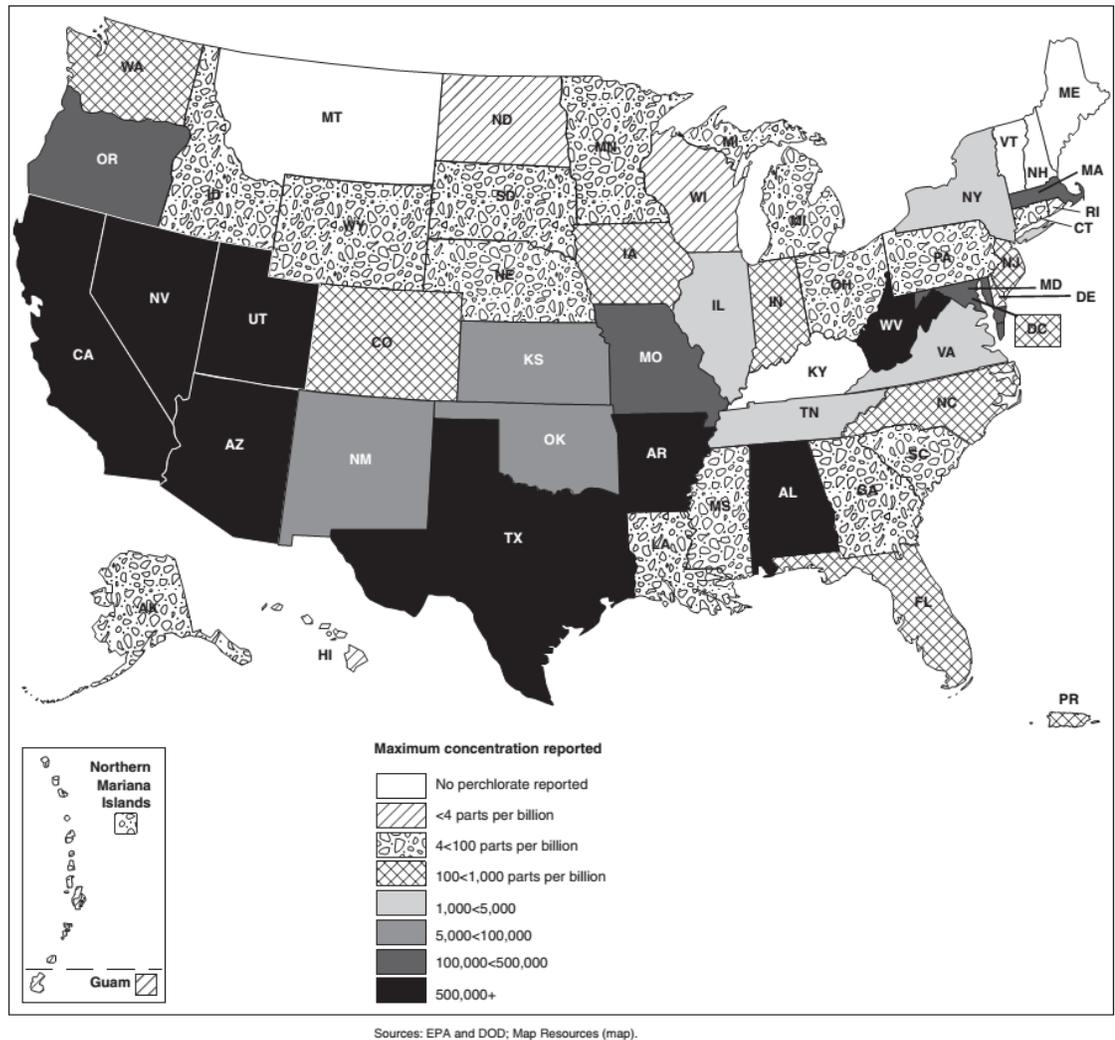


Figure 2.1. Perchlorate distribution in the United State. (GAO 2010)

Also, perchlorate has been discovered in the range of 0.065 to 0.4 % (wt) as an impurity in Peruvian and Chilean  $\text{NaNO}_3$  fertilizers that have been extensively used in

agricultural activities between 1830 and 1980 (Dasgupta, Martinelango et al. 2005). As a result, large amounts of the perchlorate-containing compounds or residuals have been released into the environment. Due to the high degree of solubility and inertness of perchlorate salts, these compounds contribute perchlorate ions which can be transported freely in the aqueous phase.

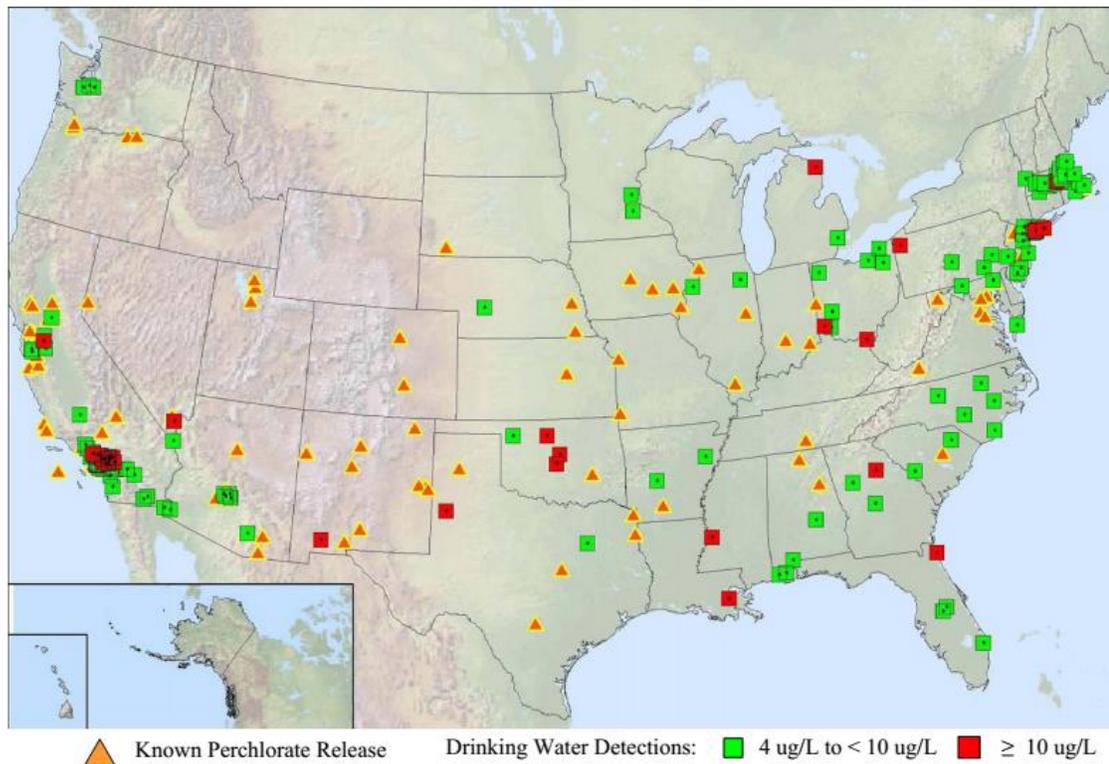


Figure 2.2. Comparison of perchlorate detection with known release sites.(Brandhuber and Clark 2005)

## 2.2 Chemical and Physical Properties of Perchlorate

Perchlorate ion ( $\text{ClO}_4^-$ ) is an anion with one chlorine atom in the center and four oxygen atom bonded to it at the corners. The whole ion is negative one charged and the charge is distributed evenly among four oxygen atoms due to the symmetric

geometry. The chemical structure of perchlorate is  $sp^3$  hybrid tetrahedron with an angle of 109.5 degree between chlorine and oxygen bonding. The radius of the perchlorate ion is about 5.5 Å. The length of Cl-O bond is about 1.44 Å. Perchlorate is a strong oxidant due to having the highest oxidizing state (+VII) of the central chlorine atom. It is also the conjugate base of perchloric acid. Perchloric acid is one of the strongest acids with pKa value of about -10. Concentrated perchloric acid is in the concentration of 70% to 72%. Perchlorate salts have high solubility in water. For example, the solubilities of potassium, ammonium, or sodium perchlorate are 15, 200, and 2096 g/L at 298K, respectively. Therefore, due to the properties of the high dissociation constant of perchloric acid and high solubility of perchlorate salts, perchlorate always exists in the ionic form in water. In addition to the properties of perchlorate stated above, perchlorate ion is also poorly hydrated due to the even distribution of the negative charge. The hydration energy of perchlorate (about 205 kJ/mol) is among the lowest in common ions in natural waters. Therefore, these unique properties of perchlorate ion contribute the property of being weakly adsorbed to organic or mineral surface (Urbansky 1998; Urbansky and Brown 2003).

### **2.3 Toxicity / Health Effects of Perchlorate**

The interference of perchlorate on thyroid function has been reported (Wolff 1998). The perchlorate ion (0.240 nm) is comparable in size to the iodide ion (0.210 nm) which is the key component of thyroid hormones. This allows perchlorate ions to be transported into the thyroid gland of mammals through ingestion of perchlorate contaminated waters or food products. Consequently, thyroid hormone production decreases and may cause adverse effects on the metabolism and growth of newborns, hypothyroidism, thyroid cancer, and neurological dysfunction associated with other

thyroid disorders. Through bioaccumulation and food chain transfers, perchlorate has been detected at much higher concentrations in produce and dairy products. The National Academy of Science has established the recommended reference dose (RfD) for perchlorate to be 0.7  $\mu\text{g}/\text{kg}\text{-day}$ . While most adults do not exceed perchlorate uptake at this amount in their diets, the full effect of perchlorate at any concentration is yet to be learned (Parker 2009) and therefore it is difficult to determine the true significance of the recently suggested reference dose (RfD) for perchlorate. For example, hypothyroidism is not solely caused by perchlorate in the thyroid gland. Hundreds of thousands of people in U.S. suffer from hypothyroidism, and only a handful of correlations reported pertaining to perchlorate contamination. Furthermore, in comparison to the average population, special populations such as infants or pregnant women may be more sensitive to the toxicity of perchlorate and require a larger safety factor. Accordingly decisions on the drinking water standards should take into account the safety of these special populations.

#### **2.4 Current Remediation Methods**

The conventional filtration, sedimentation, or air stripping process in drinking or wastewater treatment plants cannot remove perchlorate from water due to the high soluble and nonvolatile natures of perchlorate. Many efforts have been put on developing more efficient methods to separate or to transform perchlorate from water. Separation has often focused on the transfer of perchlorate from one phase to another phase, such as from water to solid. Transformation requires reducing the perchlorate compound to other chlorine species, such as chloride. These technologies can be further subcategorized as physical, biological, chemical, or electrochemical treatments.

### 2.4.1 Separation Methods

Among the various chemical and physical processes, granular activated carbon (GAC) (Chen, Cannon et al. 2005; Chen, Cannon et al. 2005; Parette and Cannon 2005; Mahmudov and Huang 2010; Mahmudov and Huang 2011) and ion exchange resins (Gu, Ku et al. 2005; Gu, Brown et al. 2007) have received much attention as methods for perchlorate removal. Proper functionalization of GAC or ion exchange resins can improve the perchlorate adsorption capacity and selectivity of these materials. It has been reported that GAC modified with cationic quaternary ammonium surfactants (Parette and Cannon 2005) and ammonium (Chen, Cannon et al. 2005) can increase its perchlorate adsorption capacity by 8 and 4 folds, respectively. Gu et al. (Gu, Brown et al. 2007) have used bifunctional anion resins (WBR109 and Purolite A530E.), which showed significant perchlorate selectivity and reaction kinetics in the presence of 0.1 to 10 mM of sulfate solution. Xiong et al. (Xiong, Zhao et al. 2007) have studied perchlorate adsorption and regenerability of five different ion exchange materials, including strong-base anion (SBA), weak-base anion (WBA), bifunctional resin, polymeric ligand exchangers (PLEs), and an ion-exchange fiber (IXF). They concluded that IXF resins exhibited rapid removal of perchlorate (equilibrium time 90 min) and efficient regeneration (about 85% of exchange capacity can be recovered). Kim et al. (Kim, Jang et al. 2008) used ammonium mono- or bifunctionalized mesoporous molecular sieve (MMS) to study perchlorate removal and reported that the quaternary ammonium bifunctionalized MMS exhibited 1.14 to 1.88 times higher adsorption capacity and faster removal of perchlorate than other mono-functionalized MMS. Granular ferric hydroxide (GFH) has been reported to enhance perchlorate removal from aqueous solutions at room temperature. They found that the maximum adsorption capacity of GFH for

perchlorate was about 20 mg/g at pH 6.0 to 6.5 (Kumar, Bhatnagar et al. 2010). Fang and Chen (Fang and Chen 2012) compared the performance of raw and oxidized carbon nanotubes (CNTs) on perchlorate adsorption. The 8-hour oxidized CNTs showed better perchlorate adsorption capacity (3.55 mg/g) than raw CNTs (1.50 mg/g) due to the presence of oxygen-containing functional groups, which provide additional adsorption sites. Recently, Lakshmi and Vasudevan studied the adsorption of perchlorate on graphene and reported that graphene achieved 99.2% perchlorate removal in the pH range between 6.0 and 8.0.(Lakshmi and Vasudevan 2013) Although these adsorption processes are effective for the removal of perchlorate at trace concentration in water, the processes still need to address the regeneration of the adsorbents or ultimate disposal of perchlorate laden spent adsorbent materials. Furthermore competitive and inhibitory adsorption of other anions against perchlorate may limit the practical use of these adsorption processes in natural waters.

#### **2.4.2 Transformation Methods**

Unlike physical or physicochemical adsorption methods, biological, chemical or electrochemical reduction can be categorized as destruction technologies to treat perchlorate ion polluted waters. From the thermodynamics point of view, perchlorate is a strong oxidizing agent and not stable at hot conditions. The unstable reaction can occur when hot concentrated perchloric acid is mixed with organic compounds such as organic ligands. However, when perchlorate salts dissolve in the water, its reaction with the strongest reductants (such as Cr, Sn) is very sluggish even in the presence of transition metals as catalysts or direct electron donors. Therefore, the reduction of perchlorate in perchlorate contaminated waters has represented a challenge for

chemical and environmental engineers for decades. In recent years, many catalysts have been reported to reduce perchlorate in remediation methods.

Transformation of perchlorate into harmless chloride by biological approach has been widely reported. Biodegradation of perchlorate occurs under anaerobic conditions which bacteria utilize perchlorate as an electron acceptor for cellular respiration and perchlorate completely to chloride ion (Bender, Shang et al. 2005). The major types of bacteria that reduce perchlorate can be categorized as (i) perchlorate reducing bacteria; (ii) high chlorate accumulating perchlorate reducing bacteria; and (iii) denitrifying bacteria (Bardiya and Bae 2011). Xu et al. (Xu, Trimble et al. 2004) examined the effect of nitrate on perchlorate and chlorate reduction by perchlorate-respiring bacteria and concluded that bacteria that were grown in the presence of both nitrate and perchlorate had higher perchlorate reduction when compared to bacteria that were grown only in the presence of either perchlorate or nitrate. An effluent re-circulated plug-flow reactor was studied in perchlorate reduction with fixed bed biofilm and the results indicated that within 8 hours perchlorate at 400 and 10 ppb was completely reduced to chloride (Choi, Li et al. 2008). However, further studies (Choi and Silverstein 2008) also indicated that competition for electrons by nitrate is a factor in the inhibition of perchlorate reduction. Therefore, microbial perchlorate reduction has shown a lot of promising applications. Several parameters including the amount of sludge, the concentration of acetate and dissolved oxygen, pH, salinity, the C/N ratio and the reaction temperature have been shown to affect perchlorate removal efficiencies (Wu, He et al. 2008; Bardiya and Bae 2011).

Thrash et al.(Thrash, Van Trump et al. 2007) combined electrochemical and microbial method to study a bioelectrical reactor for perchlorate reduction with

removal rate at 60mg/L reactor volume per day. Hurely et al. used heterogeneous Pd/Re-C catalyst for perchlorate reduction under low pH (pH = 3) and high hydrogen gas pressure condition. And the catalytic efficient of rhenium(VII) can be further improved by the addition of ligands (Hurley and Shapley 2007; Hurley, Zhang et al. 2009). Wang et al. used monometallic catalysts and hydrogen gas to reduce perchlorate ions (Wang, Huang et al. 2007; Wang, Shah et al. 2008). However, these perchlorate reduction techniques only showed satisfactory reduction rate at higher perchlorate concentration conditions (about 10 to 100 ppm level).

## 2.5 Electrocatalytic Reaction

Electrochemical reduction is an easy process and has high public recognition. Electrochemical reduction of perchlorate is practically attractive. The reduction of perchlorate is 1.38 V (Eq.1) which indicates the reaction is thermodynamically favorable.



However, perchlorate reduction to chloride by this reaction does not occur spontaneously at ambient temperatures due to the chemical inertness of perchlorate makes the reaction rate extremely slow. The whole reduction process at the electrode surface requires several steps, (i) the adsorption of perchlorate on the metal surface of electrode; (ii) indirect electron transfer through oxygen atom transfer reaction and (iii) final product desorption from the electrode surface site. The catalytic electrochemical reduction of perchlorate has been widely studied using different electrode materials. These electrochemical reactions could be classified (Láng and Horányi 2003) as those occurring at noble metal electrode materials such as Pt (Horányi and Vértes 1975), Rh (Láng, Sas et al. 2008) and Ru (Colom and González-

Tejera 1985), at non-noble electrodes such as Re (Horányi and Bakos 1994), and as perchlorate reduction occurring in conjunction with the corrosion of metals such as Ti (Brown 1986) or Al (Paoinot and Augustynski 1975). Wang et al. (Wang and Huang 2008) developed an electrodiallytically assisted catalytic reduction (EDACR) system, where electro dialysis facilitated movement of perchlorate towards a stainless steel cathode coated with nanometallic catalysts that eventually reduces perchlorate. A total of 18 metallic catalysts were examined and the results indicated that the perchlorate reduction rate followed the order,  $Cd > Pt > Cr > Mo > Sc > Rh > Ru \sim Sn > Pd > V \sim Ti > Zn > Mn > Ni > Zr > Co > Cu > Pb$  (Wang, Huang et al. 2007). Wang et al. also used indirect electrochemical method for removal of perchlorate and nitrate at the Ti–water interface. Within 8 hours of reaction, both perchlorate and nitrate at initial concentration of 200 and 1000 ppm individually were reduced to the concentration of <20 and <200 ppb, respectively (Wang, Lin et al. 2009).

Many efforts have been made on electrochemical reduction of perchlorate with various monometallic catalyst electrodes, but only a few have examined the bimetallic catalysts for perchlorate electrochemical reduction. Wang et al. showed that using different type of bimetallic catalysts, such as Co–Rh, Co–Cr, and Co–Ru in perchlorate electrochemical reduction system would lead to different end products (chlorite or chloride) (Wang and Huang 2008).

## **2.6 Hypothesis**

The overall goal of the research is to study the electrochemical reduction of perchlorate in dilute aqueous solutions and under ambient pressure and temperature conditions. From above reviews, it is found that an efficient separation method plays an important role on perchlorate reduction from waters. Ion exchange membrane has

been used in the electro-dialysis technique for the desalination of brackish water to generate portable water and for the production of table salts, acids or bases in the chemical or food industry (Strathmann 2010). Electrodialysis techniques are regarded as a mature tool for separation. The separated and concentrated perchlorate ion solution can be further reduced to chloride ion via catalytic electrochemical reduction process which was established by Wang et al (Wang, Huang et al. 2007; Wang and Huang 2008).

In addition, many efforts have been made to find appropriate ion carriers for ion selective electrodes (ISE). By incorporating suitable selective ion receptors (ionophores) in the sensors, the detection limit of an ISE can reach the sub-nanomolar levels (Bakker and Pretsch 2007). Several polymeric perchlorate-selective membrane electrodes with different metal complexes, such as cobaloxime cobalt(III) (Zanjanchi, Arvand et al. 2006; Rezaei, Meghdadi et al. 2009), bis(dibenzoyllemethanato)cobalt(II) (Rezaei, Meghdadi et al. 2009), nickel(II)-hexaazamacrocyclic (Ganjali, Norouzi et al. 2007; Rezaei, Meghdadi et al. 2009), bis(dibenzoylmethanato) nickel(II) (Rezaei, Meghdadi et al. 2007) or platinum(II) complexes (Soleymanpour, Asl et al. 2007; Soleymanpour, Garaili et al. 2008) have been demonstrated to detect perchlorate ion at the micromolar and submicromolar levels. Another study by Okeke et al. (Okeke, Ma et al. 2007) who used perchlorate reductase with Nafion membrane to construct an amperometric biosensor which measured perchlorate levels ranging from 25 to 100  $\mu\text{g/L}$ .

Results of the above literatures showed that the membrane electrodes may be applied to selective separation of perchlorate. However, these electrodes still use organo-metallic compounds such as ionophores which potentially can have negative

impacts to the environment due mostly to potential metal hazards. Furthermore, it has been suggested that ionic additives, another common components of membrane ISE electrode, not only can lower the electrical resistance of the membrane but also play a role of ion exchanger that induces selective response (Bakker, Buhlmann et al. 1997).

In brief, with modification of polymeric membrane from current perchlorate ion selective electrodes, a better perchlorate selective ion exchange membrane could be fabricated. On the other hand, electrochemical reduction of perchlorate with metallic catalysts could be further improved via combination of multimetallic catalysts. Hence, it is hypothesized that

(1) due to unique characteristics of ion additives, it is possible to prepare a perchlorate ion selective membrane without using ionophores (i.e., charge carrier) which are mostly metallic complexes;

(2) perchlorate ion selective membrane without using ionophores can also be applied to selective separation and analysis of perchlorate;

(3) to have a membrane with good perchlorate ion separation efficiency, the strong binding between anion and membrane may not favor anion transport across the membrane in electrostatic field.

(4) bimetallic catalysts could show better reduction efficiencies of perchlorate than the monometallic catalysts

This proposed research will develop an innovative technology for the reduction of perchlorate in drinking water.

## REFERENCES

- Bakker, E., P. Buhlmann, et al. (1997). "Carrier-Based Ion-Selective Electrodes and Bulk Optodes. 1. General Characteristics." Chem. Rev. **97**(8): 3083-3132.
- Bakker, E. and E. Pretsch (2007). "Modern Potentiometry." Angew. Chem. Int. Ed. **46**(30): 5660-5668.
- Bardiya, N. and J.-H. Bae (2011). "Dissimilatory perchlorate reduction: A review." Microbiological Research **166**(4): 237-254.
- Bender, K. S., C. Shang, et al. (2005). "Identification, characterization, and classification of genes encoding perchlorate reductase." Journal of Bacteriology **187**: 5090-5096.
- Brandhuber, P. and S. Clark (2005). "Perchlorate Occurrence Mapping " American Water Works Association.
- Brown, G. M. (1986). "The reduction of chlorate and perchlorate ions at an active titanium electrode." Journal of Electroanalytical Chemistry and Interfacial Electrochemistry **198**(2): 319-330.
- Chen, W., F. S. Cannon, et al. (2005). "Ammonia-tailoring of GAC to enhance perchlorate removal. I: Characterization of NH<sub>3</sub> thermally tailored GACs." Carbon **43**(3): 573-580.
- Chen, W., F. S. Cannon, et al. (2005). "Ammonia-tailoring of GAC to enhance perchlorate removal. II: Perchlorate adsorption." Carbon **43**(3): 581-590.
- Choi, H. and J. Silverstein (2008). "Inhibition of perchlorate reduction by nitrate in a fixed biofilm reactor." Journal of hazardous materials **159**(2-3): 440-445.
- Choi, Y. C., X. Li, et al. (2008). "Chemisorption of oxygen onto activated carbon can enhance the stability of biological perchlorate reduction in fixed bed biofilm reactors." Water Research **42**(13): 3425-3434.
- Colom, F. and M. J. González-Tejera (1985). "Reduction of perchlorate ion on ruthenium electrodes in aqueous solutions." Journal of Electroanalytical Chemistry and Interfacial Electrochemistry **190**(1-2): 243-255.
- Dasgupta, P. K., P. K. Martinelango, et al. (2005). "The origin of naturally occurring perchlorate: The role of atmospheric processes." Environmental Science & Technology **39**(6): 1569-1575.
- Fang, Q. and B. Chen (2012). "Adsorption of perchlorate onto raw and oxidized carbon nanotubes in aqueous solution." Carbon **50**(6): 2209-2219.
- Ganjali, M. R., P. Norouzi, et al. (2007). "Perchlorate-selective membrane sensors based on two nickel-hexaazamacrocyclic complexes." Sensors and Actuators B: Chemical **120**(2): 494-499.
- GAO (2010). Perchlorate: Occurrence Is Widespread But At Varying Levels; Federal Agencies have Taken Some Actions to Respond to and Lessen Releases, Government Accounting Office. **GAO-10-769**.
- Gu, B., Y.-K. Ku, et al. (2005). "Sorption and Desorption of Perchlorate and U(VI) by Strong-Base Anion-Exchange Resins." Environmental Science & Technology **39**(3): 901-907.

- Gu, B. H., G. M. Brown, et al. (2007). "Treatment of perchlorate-contaminated groundwater using highly selective, regenerable ion-exchange technologies." Environmental Science & Technology **41**(17): 6277-6282.
- Horányi, G. and I. Bakos (1994). "Investigation of the electrodeposition and behaviour of Re layers by coupled radiochemical and electrochemical methods." Journal of Electroanalytical Chemistry **378**(1-2): 143-148.
- Horányi, G. and G. Vértes (1975). "Catalytic and electrochemical reduction of perchlorate ions on platinum in aqueous solution." Journal of Electroanalytical Chemistry and Interfacial Electrochemistry **64**(2-3): 252-254.
- Hurley, K. D. and J. R. Shapley (2007). "Efficient heterogeneous catalytic reduction of perchlorate in water." Environmental Science & Technology **41**(6): 2044-2049.
- Hurley, K. D., Y. X. Zhang, et al. (2009). "Ligand-Enhanced Reduction of Perchlorate in Water with Heterogeneous Re-Pd/C Catalysts." Journal of the American Chemical Society **131**(40): 14172-3.
- Kim, T.-H., M. Jang, et al. (2008). "Bifunctionalized mesoporous molecular sieve for perchlorate removal." Microporous and Mesoporous Materials **108**(1-3): 22-28.
- Kumar, E., A. Bhatnagar, et al. (2010). "Perchlorate removal from aqueous solutions by granular ferric hydroxide (GFH)." Chemical Engineering Journal **159**(1-3): 84-90.
- Lakshmi, J. and S. Vasudevan (2013). "Graphene - a promising material for removal of perchlorate ( $\text{ClO}_4^-$ ) from water." Environmental Science and Pollution Research **20**(8): 5114-5124.
- Láng, G. G. and G. Horányi (2003). "Some interesting aspects of the catalytic and electrocatalytic reduction of perchlorate ions." Journal of Electroanalytical Chemistry **552**: 197-211.
- Láng, G. G., N. S. Sas, et al. (2008). "The kinetics of the electrochemical reduction of perchlorate ions on rhodium." Electrochimica Acta **53**(25): 7436-7444.
- Mahmudov, R. and C. P. Huang (2010). "Perchlorate removal by activated carbon adsorption." Separation and Purification Technology **70**(3): 329-337.
- Mahmudov, R. and C. P. Huang (2011). "Selective adsorption of oxyanions on activated carbon exemplified by Filtrasorb 400 (F400)." Separation and Purification Technology **77**(3): 294-300.
- Okeke, B. C., G. Y. Ma, et al. (2007). "Development of a perchlorate reductase-based biosensor for real time analysis of perchlorate in water." Journal of Microbiological Methods **68**(1): 69-75.
- Paoinot, J. and J. Augustynski (1975). "Etude potentiostatique et spectroscopique de l'aluminium recouvert par une couche d'oxyde: effet de différents anions." Electrochimica Acta **20**(10): 747-752.
- Parette, R. and F. S. Cannon (2005). "The removal of perchlorate from groundwater by activated carbon tailored with cationic surfactants." Water Research **39**(16): 4020-4028.

- Parker, D. R. (2009). "Perchlorate in the environment: the emerging emphasis on natural occurrence." Environ. Chem. **6**: 10-27.
- Rajagopalan, S., T. Anderson, et al. (2009). "Perchlorate in Wet Deposition Across North America." Environmental Science & Technology **43**(3): 616-622.
- Rezaei, B., S. Meghdadi, et al. (2009). "Perchlorate-selective polymeric membrane electrode based on bis(dibenzoylmethanato)cobalt(II) complex as a neutral carrier." Journal of Hazardous Materials **161**(2-3): 641-648.
- Rezaei, B., S. Meghdadi, et al. (2007). "Fast response and selective perchlorate polymeric membrane electrode based on bis(dibenzoylmethanato) nickel(II) complex as a neutral carrier." Sensors and Actuators B: Chemical **121**(2): 600-605.
- Soleymanpour, A., E. H. Asl, et al. (2007). "Perchlorate selective membrane electrodes based on synthesized platinum(II) complexes for low-level concentration measurements." Sensors and Actuators B: Chemical **120**(2): 447-454.
- Soleymanpour, A., B. Garaili, et al. (2008). "Perchlorate selective membrane electrodes based on a platinum complex." Monatshefte Fur Chemie **139**(12): 1439-1445.
- Strathmann, H. (2010). "Electrodialysis, a mature technology with a multitude of new applications." Desalination **264**(3): 268-288.
- Thrash, J. C., J. I. Van Trump, et al. (2007). "Electrochemical stimulation of microbial perchlorate reduction." Environmental Science & Technology **41**(5): 1740-1746.
- Urbansky, E. T. (1998). "Perchlorate Chemistry: Implications for Analysis and Remediation." Bioremediation Journal **2**(2): 81 - 95.
- Urbansky, E. T. and S. K. Brown (2003). "Perchlorate retention and mobility in soils." Journal of Environmental Monitoring **5**(3): 455-462.
- Wang, D. M. and C. P. Huang (2008). "Electrodialytically assisted catalytic reduction (EDACR) of perchlorate in dilute aqueous solutions." Separation and Purification Technology **59**(3): 333-341.
- Wang, D. M., C. P. Huang, et al. (2007). "Reduction of perchlorate in dilute aqueous solutions over monometallic nano-catalysts: Exemplified by tin." Separation and Purification Technology **58**(1): 129-137.
- Wang, D. M., H. Y. Lin, et al. (2009). "Indirect electrochemical reduction of perchlorate and nitrate in dilute aqueous solutions at the Ti-water interface." Separation and Purification Technology **67**(2): 127-134.
- Wang, D. M., S. I. Shah, et al. (2008). "Catalytic reduction of perchlorate by H<sub>2</sub> gas in dilute aqueous solutions." Separation and Purification Technology **60**(1): 14-21.
- Wolff, J. (1998). "Perchlorate and the thyroid gland." Pharmacological Reviews **50**(1): 89-105.

- Wu, D., P. He, et al. (2008). "The effect of various reaction parameters on bioremediation of perchlorate-contaminated water." Journal of Hazardous Materials **150**(2): 419-423.
- Xiong, Z., D. Zhao, et al. (2007). "Sorption and Desorption of Perchlorate with Various Classes of Ion Exchangers: A Comparative Study." Industrial & Engineering Chemistry Research **46**(26): 9213-9222.
- Xu, J., J. J. Trimble, et al. (2004). "Chlorate and nitrate reduction pathways are separately induced in the perchlorate-respiring bacterium *Dechlorosoma* sp. KJ and the chlorate-respiring bacterium *Pseudomonas* sp. PDA." Water research **38**(3): 673-680.
- Zanjanchi, M. A., M. Arvand, et al. (2006). "Perchlorate-selective polymeric membrane electrode based on a cobaloxime as a suitable carrier." Sensors and Actuators B: Chemical **113**(1): 304-309.

## Chapter 3

### **A POLYMERIC MEMBRANE ELECTRODE FOR THE DETECTION OF PERCHLORATE IN WATER AT THE SUB-MICRO-MOLAR LEVEL**

#### **3.1 Abstract**

A highly sensitive polymeric membrane electrode was synthesized for the detection of perchlorate in water. The membranes were characterized for thickness, potentiometric responses, and response time. Factors such as interfering anions, humic acid, and pH that may affect the performance of the electrode were investigated. The membrane electrode exhibited favorable selectivity toward perchlorate over interfering anions such as chloride, nitrate, sulfate, and bicarbonate in water and had a response time of *ca.* 5 s over the perchlorate concentration (activity) range of  $10^{-6}$  to  $10^{-1}$  M and a Nernstian slope of  $58.5 \pm 0.4$  mV at room temperature. The potentiometric response of the electrode was pH independent in the range of 3.0 to 11.0 and had a perchlorate detection limit of  $7.0 \times 10^{-7}$  M (or 70 ppb). The polymeric membrane electrode was able to detect perchlorate ion at the sub-micro-molar level under conditions mimicking those of natural water systems.

#### **3.2 Introduction**

Recently, methods such as Raman spectroscopy (Levitskaia, Sinkov et al. 2007), liquid chromatography mass spectrometry (LC-MS), ion chromatography (IC) equipped with conductivity detection (Barron, Nesterenko et al. 2006; Lamb, Simpson et al. 2006), mass spectrometry (IC-MS) or electro-spray ionization MS (IC-ESI-MS)

(El Aribi, Le Blanc et al. 2006; Martinelango, Gumus et al. 2006; Martinelango and Dasgupta 2007) have been developed for perchlorate ion analysis. These methods have a detection limit (MDL) in the ppb and even the ppt levels. However, these methods require extensive sample preparation, lack real time monitoring ability and need high cost instrumentation systems to operate, which may limit their potential for field deployment.

On the contrary, ion-selective electrode (ISE) requires little sample preparation, has excellent field portability, short response time, and real time detection possibility. ISE, in the form of solid state or liquid membrane, has already been used widely for detecting various ions in water or soil samples (Hecht, Kounaves et al. 2009). Recently, membrane type ISE has attracted much attention due to durability, ease for operation, and low cost. Typically, a membrane type ISE can be made of polymer, ionophore, and additive. There were membrane electrodes developed for perchlorate detection (Bakker, Buhlmann et al. 1997; Bakker and Pretsch 2007). In order to lower the detection limits, metallic ionophores, such as cobaloxime cobalt(III) (Zanjanchi, Arvand et al. 2006), bis(dibenzoylmmethanato)cobalt(II) (Rezaei, Meghdadi et al. 2009), nickel(II)-hexaazamacrocyclic (Ganjali, Norouzi et al. 2007), bis(dibenzoylmethanato) nickel(II) (Rezaei, Meghdadi et al. 2007) or platinum(II) complexes (Soleymanpour, Asl et al. 2007; Soleymanpour, Garaili et al. 2008) have been added to the polymer matrix. These membrane electrodes were indeed capable of detecting perchlorate in the concentration range of  $10^{-7}$  or  $10^{-6}$  to 0.1 M.

The objective of this research was to synthesize and evaluate a PVC (polyvinyl chloride) membrane electrode using quaternary amines as ion carriers. The performance of the electrode prepared was compared with those reported in the

literature (Rezaei, Meghdadi et al. 2007). Factors such as the thickness of the membrane, chemical composition of the internal solution, pH of the external solution, and the presence of humic acid that may affect the performance of the perchlorate electrode were investigated. Finally, the electrode was used to detect perchlorate concentration in rain, creek, and tap water samples.

### **3.3 Materials and Methods**

#### **3.3.1 Chemicals and Reagents**

All chemicals were of analytical or reagent grade, or the highest purity available from suppliers. Dibutyl phthalate (DBP, 99 %, Acros Organics, Morris Plains, NJ, USA), methyltriethylammonium chloride (MTOAC, Acros Organics), tetrahydrofuran (THF, HPLC grade, Fisher Scientific, Fair Lawn, NJ, USA) and high molecular mass polyvinyl chloride (PVC, MP Biomedicals, Solon, OH, USA) were used for synthesizing the membrane.

The certified standard anion solutions (1000 mg/L) of nitrate ( $\text{NO}_3^-$ ), perchlorate ( $\text{ClO}_4^-$ ) and sulfate ( $\text{SO}_4^{2-}$ ) were purchased from SPEX CertiPrep (Metuchen, NJ, USA). Sodium bicarbonate (analytical grade ACS, 99.7 %, Acros Organics), sodium chloride (reagent grade ACS, >99 %, Acros Organics), sodium carbonate (HPLC grade, Fisher Scientific), sodium sulfate (certified ACS, Fisher Scientific), sodium nitrate (analytical grade ACS, >99 %, Acros Organics) and humic acid (Technical grade, Sigma-Aldrich, St. Louis, MO, USA) were individually dissolved into deionized water to prepare stock solutions for studying the interference of anions on perchlorate determination. Perchlorate stock solution (1.0 M) was dissolved from solid  $\text{NaClO}_4$  (ACS reagent, >98 %, Sigma-Aldrich, St. Louis, MO,

USA). Different perchlorate concentrations ( $1.0 \times 10^{-8}$  to  $1.0 \times 10^{-1}$  M) were daily prepared in each bottle. All aqueous solutions were prepared with de-ionized, distilled water (DIW).

### 3.3.2 Electrode Preparation

Polymer (polyvinyl chloride) serves the physical framework, ionophore provides the ion selectivity, and additives give the necessary dielectric characteristics of the membrane electrode. Metal complex, bis(dibenzoylmethanato)nickel(II) or  $\text{Ni}(\text{DBM})_2$ , was synthesized according to the procedure of Soldatov et al. (Soldatov and Ripmeester 2001).

Two types of electrode, (i) PVC (or type I) and (ii)  $\text{PVC} + \text{Ni}(\text{DBM})_2$ , (or type II), were prepared in this study. Type I membrane electrode was synthesized by dissolving PVC, plasticizer (DBP), and additive (MTOAC) in THF solvent. Type II membrane electrode was prepared with  $\text{Ni}(\text{DBM})_2$  in addition to all chemicals for type I membrane electrode. The optimum composition for the  $\text{PVC} + \text{Ni}(\text{DBM})_2$  membrane was: 49.36 wt% of PVC, 42.90 wt% of DBP, 3.62 wt% of MTOAC and 4.12 wt% of  $\text{Ni}(\text{DBM})_2$ . The optimum composition of the PVC membrane was 51.55 wt% of PVC, 44.67 wt% of DBP, and 3.78 wt% of MTOAC. The above chemical composition was followed for the preparation of the PVC or the  $\text{PVC} + \text{Ni}(\text{DBM})_2$  electrode throughout the entire study. It is interesting to note that the percentage of plasticizer used in our study was smaller than that of others (66 % of plasticizer) (Moody, Oke et al. 1970; Craggs, Moody et al. 1974; Bakker, Buhlmann et al. 1997). However, with less plasticizer, both type I and type II electrodes still gave good Nernstian response.

When the mixture was completely dissolved, a glass tube with 0.6 cm o.d. was dipped into the membrane mixture for *ca.* 5 s and then slightly pulled out of the liquid; the glass tube coated with the membrane material was dried overnight at room temperature to evaporate the solvent. To control the membrane thickness, the glass tube was dipped repeatedly for several times into the synthesis liquid. After solidified, the membrane electrode was conditioned by filling and soaking with  $10^{-4}$  M of perchlorate solution as internal / external solution prior to experiment (Fig. A1, and Table A1, Appendix A). A copper wire was inserted into the internal solution for signal transfer, e.g., mV readings. Top of the glass tube was wrapped with parafilm. When not in use, the electrode was kept immersing in  $10^{-4}$  M of  $\text{ClO}_4^-$  solution. All experiments were performed at ambient temperature ( $22 \pm 1$  °C).

The thickness,  $x$ , was calculated from the electrode geometry and mass, that is:

$$x = \frac{(W_2 - W_1)}{\rho \pi r^2} \quad (3.11)$$

where  $x$  is the thickness (cm);  $W_1$  and  $W_2$  is the weight (g) of electrode before and after dipping in the polymeric solution, respectively;  $\rho$  is the density of polymeric mixture ( $1.23 \text{ g/cm}^3$ ) and  $r$  is the radius (cm) of the tubular glass electrode.

The thickness of ISE membrane may influence the ion flux across the membrane. Ceresa et al. reported that the major factors affecting the Nernstian slope and electrodes response were the thickness and conductivity of the membrane which are related to the ion flux across the membrane (Ceresa, Sokalski et al. 2001).

However, the influence of the ISE membrane thickness on electrode response was rarely discussed in the literature. According to Fig. A2 (Appendix A), dipping once

yielded a membrane thickness of about 0.3 mm which was thus chosen for all following experiments.

### 3.3.3 Electrode Characterization

The membrane electrodes were characterized for selectivity constant, linearity, Nernstian slope, and dynamic response time. The selectivity constant,  $K_{A,B}$ , can be calculated using the following equation (Bard and Faulkner 2000; Bobacka, Ivaska et al. 2008):

$$K_{A,B} = \frac{\exp\left[(\phi'_T - A) \frac{z_A F}{RT}\right]}{(a_B^\alpha)^{z_A/z_B}} \quad (3.2)$$

where the term,  $\frac{RT}{F}$ , is the Nernstian slope;  $A = -\frac{RT}{z_A F} \ln(K_{A,B}^{\beta,m_2} a_B^\beta + a_A^\beta)$ ;  $z_A$  and  $z_B$  are the charge numbers of the primary ion (A) and the interfering ion (B), respectively;  $a_A^\alpha$  is the activity of the primary ion in the solution (the  $\alpha$  phase);  $\phi'_T$  is the electro  $\varphi$  de potential. The electrode potential was measured at various perchlorate concentrations,  $C_i$ . The voltage was plotted as a function of the perchlorate activity,  $a_i$ . A  $K_{A,B}$  value of less than unity indicates that the electrode responds to the primary ion more selectively than to the interfering ion .

The potentiometric response (electrode potential) of ISE is derived from the primary ion in equilibrium between the hydrated layer and the adjacent solution. The electrode response time is also important to the performance of ISE. We used the IUPAC version of practical response time according to which “the length of time that

elapses between the instant at which an ISE and a reference electrode are brought into contact with sample solution (or the time at which the concentration of the ion of interest in a solution is changed on contact with an ISE and a reference electrode) and the first instant at which the potential of the cell becomes equal to its steady-state value within  $\pm 1$  mV” (IUPAC 1976). By monitoring the potentiometric response of the electrode as a function of time, the relaxation time,  $\tau$ , can be calculated by the following equation:

$$\phi(t) = \phi_{eq} \left( 1 - \exp\left(-\frac{t}{\tau}\right) \right) \quad (3.3)$$

where  $\phi_{eq}$  is the potential at equilibrium,  $t$  is time, and  $\tau$  is the relaxation time.

### 3.3.4 Apparatus and Potentiometric Measurements

The ISE potentials were measured with a potentiostat (Pine Instrument, Grove City, PA, USA; Model AFRDE4) connected to a computer via an analogue-to-digital converter (DATAQ Instruments, Akron, OH, USA; Model DI710-UL) to provide the reading outputs. A saturated calomel electrode (SCE) (Analytical Sensors Inc., Sugar Land, Texas, USA) was used as the reference electrode. The data acquisition was carried out using WinDaq Data Acquisition Software v.3.03 software (DATAQ Instruments) and a personal computer. To minimize the electrical interference, all the coaxial cable and copper wire, connecting to the potentiostat were properly grounded. The solutions were stirred constantly at fixed rate using a magnetic bar during measurements. When the electrode potentiometric response was stable in solution, the reading was recorded. After uses, electrode was rinsed with DIW and wiped gently

with Kim-Wipes paper. The electrode potentials returned to the starting values when they were placed once again in the first solution.

### **3.4 Results and Discussion**

#### **3.4.1 Perchlorate ISE with MTOAC**

Fig. 3.1 shows the response of perchlorate ion specific membrane electrodes prepared by the combination of polymer, Ni(DBM)<sub>2</sub>, and MTOAC in the presence of 10<sup>-3</sup> M of nitrate. Results showed good Nernstian response (to 10<sup>-5</sup> or 10<sup>-7</sup> M) as long as MTOAC was present in the electrode membranes. Membrane electrode made of poly(vinyl) chloride (PVC)/dibutylphthalate (DBP) and PVC/ Ni(DBM)<sub>2</sub> showed erratic Nernstian response toward perchlorate ion. The Nernstian slope for the Ni(DBM)<sub>2</sub>-only membrane electrode was smaller than the theoretical value of 58.4 mV/log (at 21 °C). Only the electrodes composed of MTOAC demonstrated the theoretical Nernstian slope, implying that MTOAC was capable of bringing about selectivity for perchlorate ion. Therefore, even without Ni(DBM)<sub>2</sub> in the membrane phase, PVC membrane electrode was still capable of detecting perchlorate ion selectively when MTOAC was present.

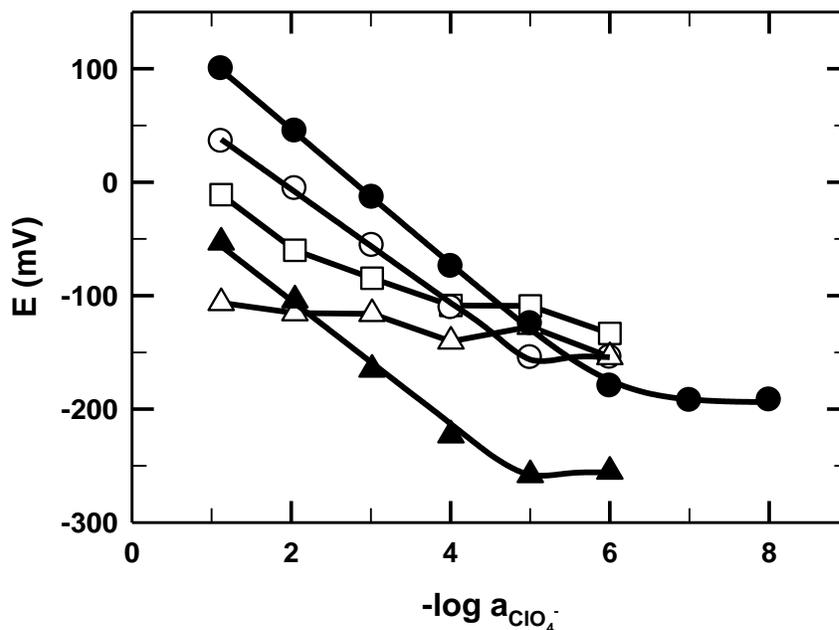
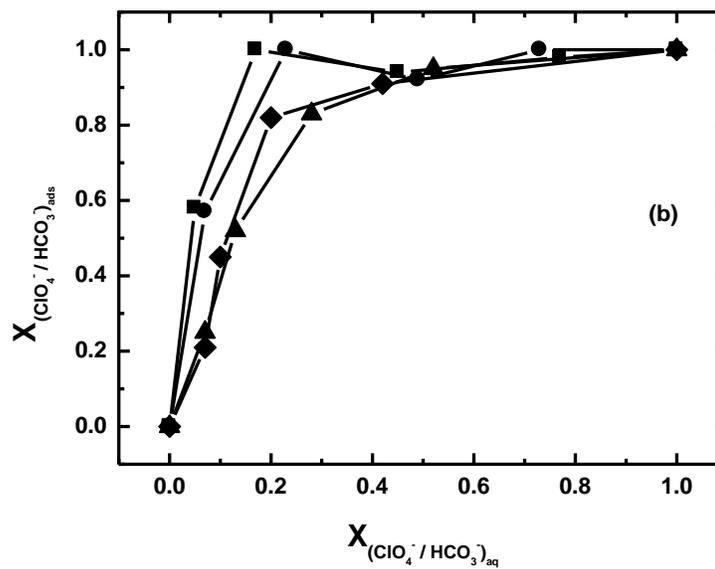
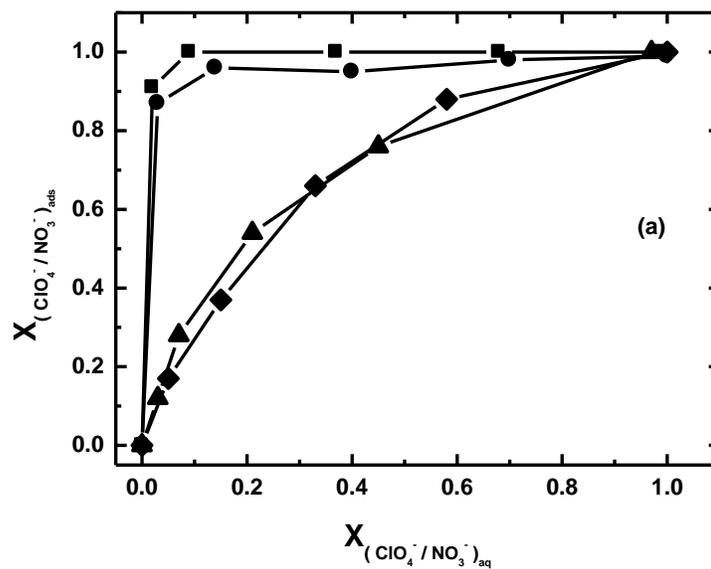


Figure 3.1. Effect of the membrane chemical composition on the Nernstian slope response of the electrodes in the presence of  $10^{-3}$  M of nitrate. Experimental conditions: perchlorate concentration:  $10^{-8}$  or  $10^{-6}$  to 0.1 M; temperature: 21 ~ 23 °C; pH = 5 ~ 7. Symbols: (□) PVC with DBP, (○) PVC with MTOAC, (△) PVC with Ni(DBM)<sub>2</sub>, (●) PVC with DBP and MTOAC, (▲) PVC with DBP, MTOAC and Ni(DBM)<sub>2</sub>.

Soleymanpour et al. (Soleymanpour, Garaili et al. 2008) reported that without metal complexes, the membrane electrode had a very limited Nernstian slope and linear range due to lipophilic nature of the perchlorate ions. Separate experiments were conducted to study the adsorption of perchlorate on various membranes in the presence of anions, namely, nitrate, sulfate, or bicarbonate. Results revealed that the perchlorate adsorption followed the order: PVC membrane > PVC+Ni(DBM)<sub>2</sub>

membrane > AMI 7001S  $\approx$  Ionac MA-3475. Both AMI 7001S and Ionac MA-3475 were commercial anion exchange membrane (Fig. 3.2).



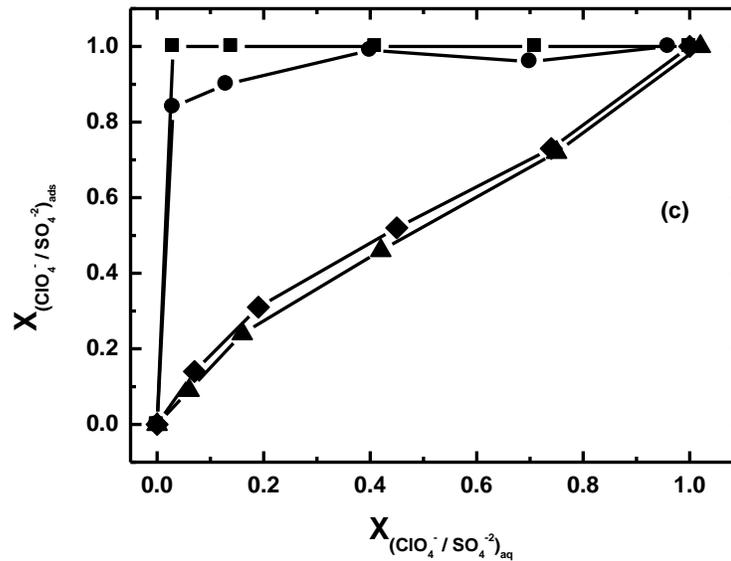
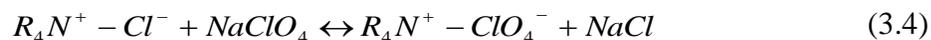


Figure 3.2. Competitive adsorption isotherms of  $\text{ClO}_4^-$  and (a)  $\text{NO}_3^-$  (b)  $\text{HCO}_3^-$  (c)  $\text{SO}_4^{2-}$  with different membranes. (■) PVC membrane without ionophore, (●) PVC membrane with 0.1g Ionophore, (▲) AMI 7001S, (◆) Ionac MA-3475. Experimental conditions: Membrane: 0.01g;  $[\text{ClO}_4^-]$ : 0 to 10 ppm;  $[\text{NO}_3^-]$ ,  $[\text{HCO}_3^-]$  and  $[\text{SO}_4^{2-}]$ : 0 to 10 ppm; pH = 5 ~7.

It is noted that all four membranes (PVC, PVC+Ni(DBM)<sub>2</sub>, AMI 7001S and Ionac MA-3475) contained quaternary amines. Quaternary amines have been used to prepare ion-exchange resin for enhancing the perchlorate adsorption capacity in groundwater treatment. Bonnesen et al. (Bonnesen, Brown et al. 2000) reported that it was possible to synthesize perchlorate ion selective electrode of high selectivity using suitable non-metallic ion carriers and showed that the large tri-alkylammonium site of quaternary amines could enhanced the selectivity of the anion-exchange resin for

poorly hydrated large anions such as  $TcO_4^-$  and  $ClO_4^-$  ions according to the following reaction,



where R= alkyl group

The lipophilic quaternary amines were used in the membrane electrodes (Hara, Ohkubo et al. 1993; Ozawa, Miyagi et al. 1996; Egorov, Rakhman'ko et al. 2004). The quaternary amines function as dissociated ion exchangers, equilibrium anion extraction into membranes is exclusively based on the difference between the free energy of solvation for an anion in the aqueous solution and organic membrane. Polymeric membrane electrodes prepared with quaternary amine exhibited potentiometric anion selectivity patterns in accordance with the Hofmeister series, e.g.,  $ClO_4^- > SCN^- > I^- > NO_3^- > Cl^- > SO_4^{2-}$ , which means that the membrane selectivity is controlled by the free energy of hydration of the ions involved. (Smirnova, Tarasevitch et al. 1994). Therefore, the additive, methyltrioctylammonium chloride (MTOAC), a quaternary amine salt, used in the synthesis of polymeric membranes would also show the selectivity toward perchlorate. While primarily MTOAC was supposed to lower the dielectric constant of the electrode membrane (Rezaei, Meghdadi et al. 2007), the trioctylammonium group of MTOAC also showed to function as charge carrier. Bakker et al. suggested that ionic additives, such as MTOAC, could lower the electrical resistance of the membrane and induce selective response (Bakker, Buhlmann et al. 1997).

### 3.4.2 Perchlorate Ion Selectivity

The selectivity of an ISE is its most significant characteristics. By keeping the concentration of competing anions at 0.01 M, the performance of the membrane

electrodes was examined in perchlorate concentration in the range of  $10^{-8}$  to  $10^{-1}$  M. The selectivity coefficients were calculated according to eq. (3.2) (Bakker, Pretsch et al. 2000). Table 3.1 summarizes the results of the potentiometric selectivity coefficients of other anions, such as chloride, nitrate, sulfate and bicarbonate in water. Table 3.1 also compares the potentiometric responses of other perchlorate ion selective electrodes reported by various researchers (Zanjanchi, Arvand et al. 2006; Ganjali, Norouzi et al. 2007; Rezaei, Meghdadi et al. 2007; Soleymanpour, Asl et al. 2007; Soleymanpour, Garaili et al. 2008; Rezaei, Meghdadi et al. 2009). Results indicated that the selectivity coefficients obtained for both the PVC membrane and the PVC+Ni(DBM)<sub>2</sub> membrane electrodes followed the orders:  $\text{ClO}_4^- > \text{NO}_3^- > \text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ , which again was in good agreement with what would be predicted by the Hofmeister series. Overall, the PVC electrode exhibited greater capability for the detection of perchlorate ion in the presence of interfering/competing ions. Without Ni(II) complexes, the performance of the membrane electrode was comparable with those containing Ni(DBM)<sub>2</sub>.

Natural organic matters (NOMs) are ubiquitous in natural water. The response of the PVC electrode was tested using humic acid as surrogate NOM. To the best of our knowledge, no study on the influence of NOM on the response of perchlorate ion specific electrode has been made ever. As shown in Fig. 3.3, the responses of both electrodes were affected by the presence of humic acid, especially when the concentration of the humic acid was increased from 0 to 25 mg/L.

Table 3.1. The linearity range and the Nernstian slope of both electrodes were affected. Comparison of the potentiometric perchlorate selectivity coefficients ( $K_{ClO_4^-,B}$ ) and working pH range of various perchlorate ion specific electrodes.

$\log K_{ClO_4^-,B}$				Working pH range	Ion Carrier or Ionophore	References
Interfering anion						
$Cl^-$	$NO_3^-$	$SO_4^{2-}$	$HCO_3^-$			
-3.01	-1.60	-4.07	-2.93	3.0 – 11.0	MTOAC	This Study (PVC)
-2.13	-1.69	-3.47	-2.12	3.0 – 9.0	[Ni(DBM) <sub>2</sub> ]	This Study (PVC+Ni(DBM) <sub>2</sub> )
-3.5	--	-2.1	--	3.0 – 10.0	[Co(dmgh) <sub>2</sub> pph <sub>3</sub> Cl]	Zanjanchi et al. 2006
-3.12	-1.70	-2.74	-3.65	2.0 – 9.0	[Co(DBM) <sub>2</sub> ]	Rezaei et al. 2009
-4.6	-4.1	-4.1	-4.3	3.0 – 11.0	Ni(II) complexes	Ganjali et al. 2007
-2.89	-1.95	-2.86	-3.01	1.2 – 12.5	[Ni(DBM) <sub>2</sub> ]	Rezaei et al. 2007
-4.0	-3.5	-4.2	-2.8	2.5 – 9.5	[PtR <sub>2</sub> (NN)]	Soleymanpour et al. 2007
-3.5	-3.4	-3.9	-3.0	2.0 – 9.0	[Pt(X) <sub>2</sub> (dppm)]	Soleymanpour et al. 2008

[Ni(DBM)<sub>2</sub>]: bis(dibenzoylmethanato) nickel(II)

[Co(dmgh)<sub>2</sub>pph<sub>3</sub>Cl]: [chlorobis(dimethylglyoximateo)(triphenylphosphine)] cobalt(III)

[Co(DBM)<sub>2</sub>]: bis(dibenzoylmethanato) cobalt(II)

Ni(II) complexes: (1) Nickel(II) 1,3,6,8,10,13-hexaazacyclotetradecane perchlorate; (2) Nickel(II) 1,8-ditertbutyl-1,3,6,8,10,13-hexaazacyclotetradecane perchlorate,

[PtR<sub>2</sub>(NN)]: platinum(II) complexes, [PtR<sub>2</sub>(NN)] (R=Me, *p*-MeC<sub>6</sub>H<sub>4</sub> and *p*-MEOC<sub>6</sub>H<sub>4</sub>; NN=2,2' bipyridy)

[Pt(X)<sub>2</sub>(dppm)]: platinum(II) complexes, [Pt(X)<sub>2</sub>(dppm)] (X=Me, *p*-MeC<sub>6</sub>H<sub>4</sub> and Cl; dppm=Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)

The Nernstian slope deviated from theoretical value (58.4 mV/log at 21°C) for both electrodes when the humic acid concentration increased (Fig. 3.3). The Nernstian slopes of the PVC electrode were 57.5, 63.2, 63.9 and 64.9 mV/log, respectively, in the presence of 0, 5, 10 and 25 mg/L of humic acid. The super Nernstian behavior indicated that the surface of the type I electrode established a potential across the membrane with humic acid via complex reaction (Amemiya, Bühlmann et al. 2003).

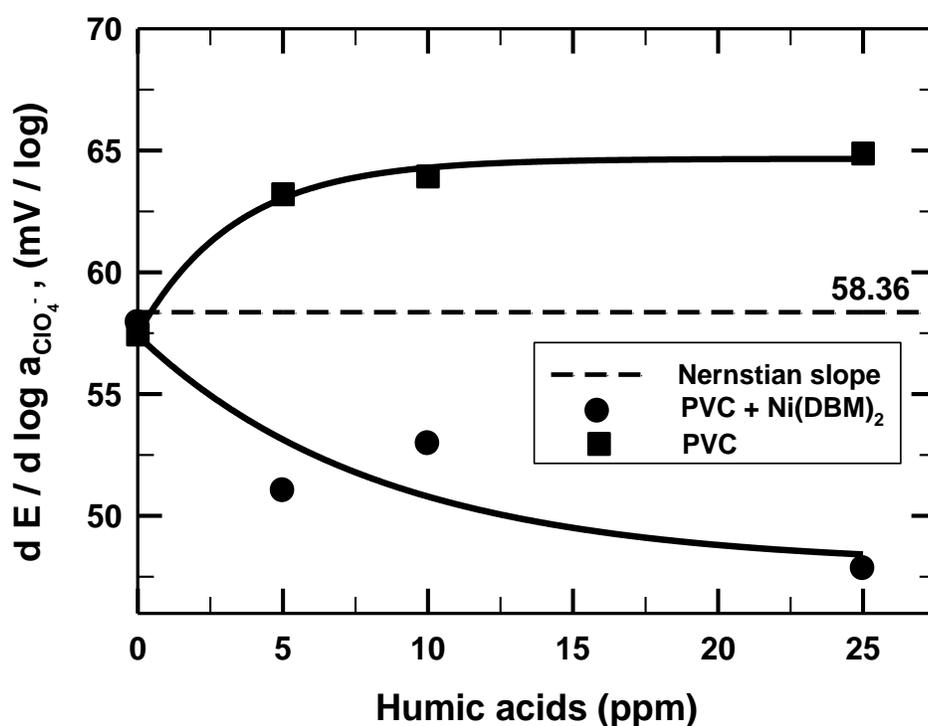


Figure 3.3. Effect of humic acid (HA) on the potentiometric response of PVC-electrode and PVC+Ni(DBM)<sub>2</sub> electrode. Experimental conditions: perchlorate concentration = 10<sup>-6</sup> to 0.1 M; temperature = 21 ~ 23 °C; pH = 5 ~7. The dashed line represents the theoretical Nernstian slope of 58.4 mV/log.

Unlike the PVC electrode, the Nernstian slopes of the PVC+Ni(DBM)<sub>2</sub> (type II) electrode were 57.9, 51.0, 52.9 and 47.8 mV/log, respectively, in the presence of 0, 5, 10 and 25 ppm of humic acid. The Nernstian slope of the PVC+Ni(DBM)<sub>2</sub> electrode decreased (sub Nernstian behavior) significantly when the humic acid concentration increased. Since humic acid have multiple-functional groups such as carboxylic (COO<sup>-</sup>) and phenolic (C<sub>6</sub>H<sub>5</sub>O<sup>-</sup>), it is likely that humic acid would form complex with Ni(II), the center atom of the metal complexes, i.e., Ni(DBM)<sub>2</sub>. Adsorption of humic acid on the membrane surface would modify the membrane surface charge which will interfere with the response of perchlorate ion to the membrane electrode. Based on above results, it is clear that the performance of both electrodes was affected by the presence of humic acid. However, the PVC electrode was more tolerant to humic acid than the PVC+Ni(DBM)<sub>2</sub> electrode.

### 3.4.3 Response Time

Dynamic response time of ISE is an important factor indicating time for the membrane to reach equilibrium with sample solutions and attain stable and reliable potentiometric response (Maccà 2004). In this study, the response time of both PVC and PVC+Ni(DBM)<sub>2</sub> electrodes were evaluated over perchlorate concentration range from 10<sup>-5</sup> to 10<sup>-4</sup> M. Fig. 3.4 shows the potentiometric response versus time. The relaxation time ( $\tau$ ) was calculated based on eq. (3.3) as mentioned above. Fig. 3.4 shows that both electrodes reached the equilibrium within about 5 s. Very similar order of the response time values were also observed in other perchlorate ISE studies (Bakker, Buhlmann et al. 1997; Rezaei, Meghdadi et al. 2007). The  $\tau$  value of the PVC and the PVC+Ni(DBM)<sub>2</sub> electrodes were 0.36 and 1.27 s, respectively. Our results

were in the same order of magnitude as that predicted by Ganjali et al. who gave a  $\tau$  value of 3.49 s (Ganjali, Norouzi et al. 2007).

With the relaxation time ( $\tau$ ), it is possible to estimate the thickness of the hydrated layer or diffusion layer of the membrane according to the following equation (Ozawa, Miyagi et al. 1996):

$$\tau = \frac{4d_h^2}{\pi^2 D_h} \quad (3.5)$$

where  $d_h$  is the thickness (m) of the hydrated or diffusion layer, and  $D_h$  is the diffusion constant ( $\text{m}^2\text{s}^{-1}$ ). Assuming a  $D_h$  value of  $10^{-12} \text{ m}^2\text{s}^{-1}$  (Kumar, Singh et al. 2010), the calculated  $d_h$  values of the PVC and the PVC+Ni(DBM)<sub>2</sub> electrodes were 0.94 and 1.77  $\mu\text{m}$ , respectively. The PVC+Ni(DBM)<sub>2</sub> membrane appeared to be more hydrated than the PVC membrane due to the existence of the metal complexes. Since the theoretical thickness of the PVC electrode membrane is about 0.30 mm. It can be seen that the thickness of the hydrated layer was only about 0.31% of the membrane thickness.

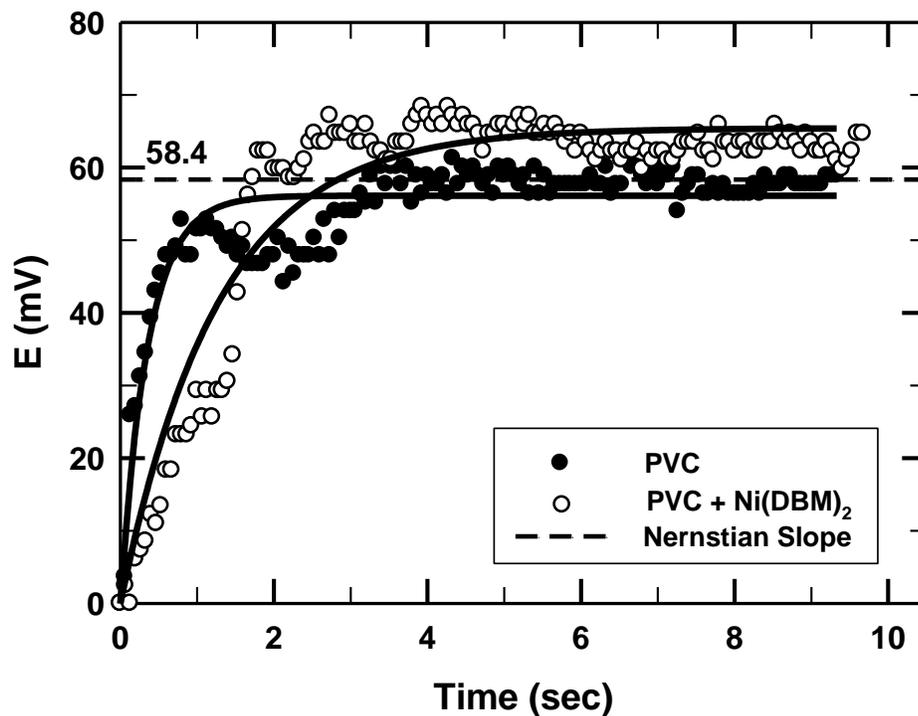


Figure 3.4. Practical response time of PVC-electrode (●) and PVC+Ni(DBM)<sub>2</sub> electrode (○). Experimental conditions: perchlorate concentration =  $10^{-5}$  to  $10^{-4}$  M; temperature = 21 ~ 23 °C; pH = 5 ~7. The dashed line represents the theoretical Nernstian slope of 58.4 mV/log.

#### 3.4.4 Influence of pH

The pH value can alter the surface characteristics of the membrane which in turn will affect the ISE response. The pH of the perchlorate containing solution ( $10^{-4}$  M) was adjusted with H<sub>2</sub>SO<sub>4</sub> or NaOH. Fig. 3.5 shows that the potentiometric responses of the PVC (type I) and the PVC+Ni(DBM)<sub>2</sub> (type II) electrodes were relatively constant over the pH range of 3.0 to 11.0 and 3.0 to 9.0, respectively. Apparently, the PVC only (type I) electrode had the wider working pH range than the PVC+Ni(DBM)<sub>2</sub> electrode (type II). Other researchers have reported various pH

working ranges of 3.0 to 10.0 for cobaloxime carrier (Zanjanchi, Arvand et al. 2006), 2.5 to 9.5 for platinum(II) complexes (Soleymanpour, Asl et al. 2007) and 2.0 to 9.0 for platinum or cobalt complexes (Soleymanpour, Garaili et al. 2008; Rezaei, Meghdadi et al. 2009). Results showed that our PVC only (type I) electrode was extremely comparable with other perchlorate ISEs with respect to working pH range. Apparently, the chemical composition of a membrane controls its working pH range. Results showed drastic decrease in potentiometric values at pH >11 for the PVC (type I) electrode and at pH > 9.0 for the PVC+Ni(DBM)<sub>2</sub> (type II) electrode. This can be attributed to the interference from high concentration of hydroxide ion that competes with perchlorate ion. Hydroxide ion, especially at high concentration, can form complex with the metal ions or ion carriers of the membrane (Soleymanpour, Garaili et al. 2008). Conversely, at low pH (< 3) the potentiometric response of both electrodes increased sharply. This can be attributed to the ion exchange reaction between sulfate and the membrane (Rezaei, Meghdadi et al. 2007). However, the working pH range (3.0 to 11.0) of PVC (type I) electrode is ideal for in-situ perchlorate detection of natural waters. In addition, it must be noted that the PVC electrode has a wider working pH range than the PVC+Ni(DBM)<sub>2</sub> electrode. It can be concluded in addition to the Ni(II) complexes, the other membrane components, specifically, PVC, plasticizer (DBP) and additives (MTOAC) are also in controlling the working pH range of the membrane electrode.

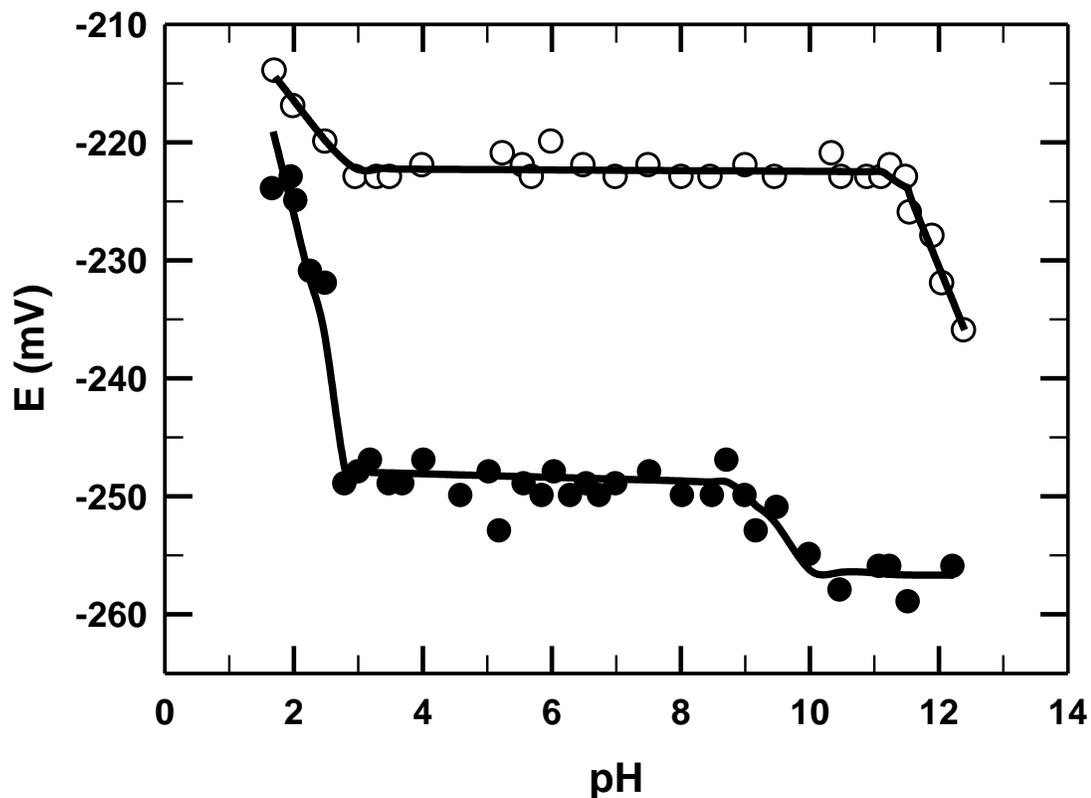


Figure 3.5. Effect of pH on the potentiometric response of the PVC-electrode (○) and the PVC+Ni(DBM)<sub>2</sub> electrode (●). Experimental conditions: perchlorate concentration = 10<sup>-5</sup> M; temperature= 21 ~ 23 °C.

### 3.4.5 Response in Natural Water

One of the major advantages of ISE is its ability for direct sample measurements. Based on results obtained above, we have fabricated a desired perchlorate selective electrode for test with natural water without any pretreatment of the water samples. Table A2 (Appendix A) shows the chemistry of the water samples studied. Local tap water, rain water and creek water were spiked with 0.5, 1.0 and 5.0

mg/L of perchlorate, respectively, and the perchlorate concentration of the water samples was measured using the PVC electrode. Results indicated that the recovery of perchlorate of the tap water, rain water and creek water was in the range of 92.6 to 109.3 %, 97.7 to 123.9% and 106.1 to 128.1 %, respectively (Table 3. 2). Rezaei et al. (Rezaei, Meghdadi et al. 2007) and Soleymanpour et al. (Soleymanpour, Garaili et al. 2008) reported the recovery from 96.3 to 101 % and 96 to 104.1 %, respectively using perchlorate ion specific electrode containing metal complexes. In addition, it is worthy of mention that PVC electrode still exhibited excellent performance on the analysis of creek water sample which contained anions such as chloride (at 160 mg/L), bicarbonate (at 178 mg/L), sulfate (at 25.3 mg/L) and nitrate (at 4 mg/L) (results from ion chromatography conductivity analysis). The pH values of the examined samples are between 5.88 and 6.60. The concentration of cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Cu}^{2+}$ ) and anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ) in the water samples were also in the range from 0.05 to 8.02 meq/L as summarized in Table A2 (Appendix A). Results clearly demonstrated that the PVC membrane electrode can be directly applied to natural water samples for the determination of perchlorate ion at the sub-mg/L or mg/L levels without interference from the other anions.

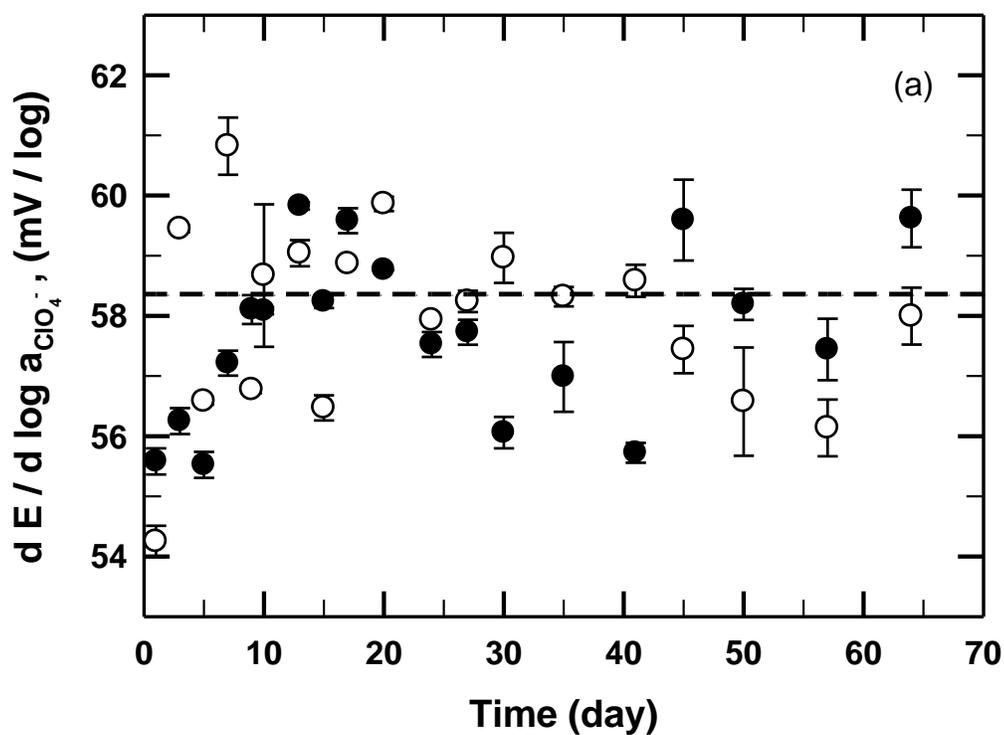
Table 3.2. Perchlorate detection in various natural and tap waters.

Samples	Perchlorate added (mg/L)	Perchlorate detected (mg/L)	Relative Standard Deviations (%)	Recovery (%)
Brandywine creek watershed (Wilmington, DE) (2010/3/21)	0.50	0.53 ± 0.04	8	106.1
	1.00	1.20 ± 0.05	4	119.7
	5.00	6.40 ± 0.16	3	128.1
Rain water (Wilmington, DE) (2010/3/24)	0.50	0.62 ± 0.04	6	123.9
	1.00	1.02 ± 0.02	2	101.8
	5.00	4.89 ± 0.11	2	97.7
Tap water (Newark, DE) (2010/3/25)	0.50	0.54 ± 0.01	2	109.3
	1.00	0.94 ± 0.02	2	94.3
	4.98	4.61 ± 0.12	3	92.6

### 3.4.6 Aging

Another important characteristic of ISE is its aging process or service time. Intuitively, the leaching of compositional chemicals from the membrane would shorten the lifetime of an ISE. The selectivity, sensitivity or slope response would be changed when the membrane deteriorates (Bakker, Buhlmann et al. 1997). The durability of the membrane electrode was tested by monitoring the electrode potential at pH = 5 ~ 7, in the presence of perchlorate at concentration in the range of  $10^{-8}$  to  $10^{-1}$  M for sixty days and the decadal slopes were recorded during the course of the experiment. Four types of the membrane electrode were examined, namely, PVC (electrode A), PVC+Ni(DBM)<sub>2</sub> (electrode B), PVC with Ni(DBM)<sub>2</sub> in the internal solution (electrode C), and PVC+Ni(DBM)<sub>2</sub> with Ni(DBM)<sub>2</sub> in the internal solution (electrode D). The average Nernstian slope (obtained in the linear range of  $10^{-5}$  to  $10^{-1}$

M of perchlorate) over 60 days were  $58.0 \pm 1.5$ ,  $57.7 \pm 1.4$ ,  $58.5 \pm 1.7$  and  $57.8 \pm 0.8$  mV for electrodes A, B, C, and D, respectively (Fig. 3.6). Among the four types of electrode, electrode D had relative smaller standard deviation of measurements over 60 days than the other electrodes. The existing of  $\text{Ni}(\text{DBM})_2$  in internal solution might limit the loss of Ni(II) complexes of the membrane phase in electrode D. However, the results demonstrated that the simplest type of membrane electrode (i.e., PVC membrane) exhibited a constant Nernstian slope over the entire test period. In addition, the detection limit of the electrode A was  $7.0 \times 10^{-7}$  M. The life time (>2 months) of the optimized PVC membrane electrode was comparable to those reported by other researchers (Rezaei, Meghdadi et al. 2007; Soleymanpour, Garaili et al. 2008; Rezaei, Meghdadi et al. 2009). In summary, the proposed PVC electrode functioned well for at least sixty days.



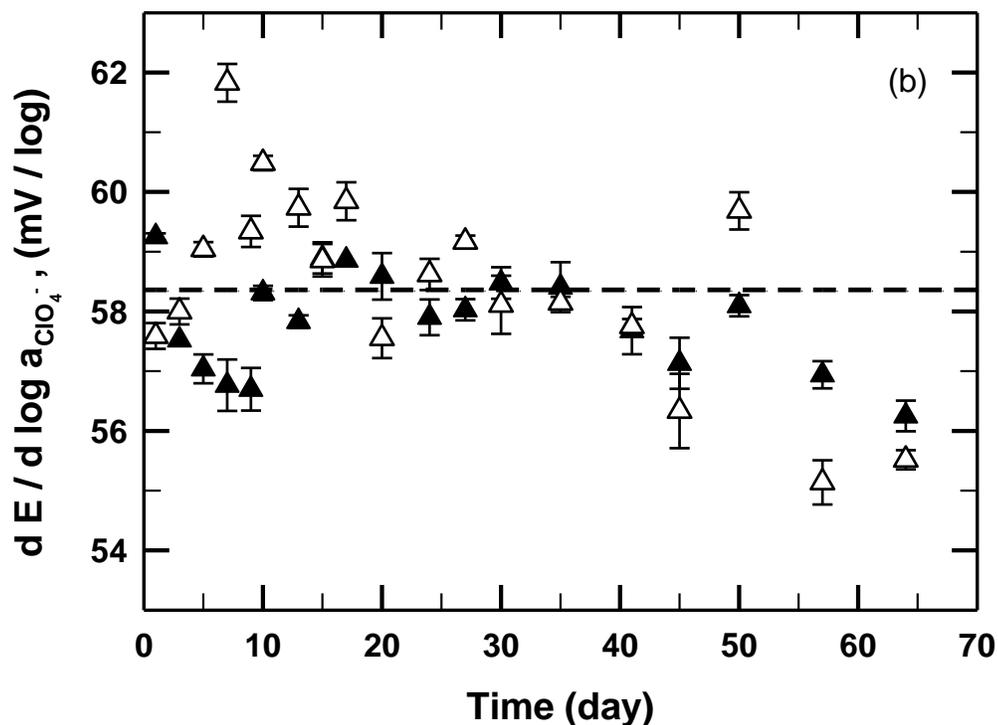


Figure 3.6. Effect of aging on the potentiometric response of (a) PVC-electrode ( $\circ$ ), PVC+Ni(DBM)<sub>2</sub> electrode ( $\bullet$ ); (b) PVC-electrode with Ni(DBM)<sub>2</sub> in the internal solution ( $\Delta$ ), PVC+Ni(DBM)<sub>2</sub> with Ni(DBM)<sub>2</sub> in the internal solution ( $\blacktriangle$ ). Experimental conditions: perchlorate concentration =  $10^{-8}$  to 0.1 M; temperature = 21 ~ 23 °C; pH = 5 ~7. The dashed line represents the theoretical Nernstian slope of 58.4mV/log.

### 3.5 Summary

In this study, a PVC based membrane electrode was synthesized easily to quantify perchlorate ion in water at the sub-micro-molar level. It is believed that the quaternary amine (MTOAC) that was added as ion additive contributed surface sites necessary for specific perchlorate adsorption in lieu of other anions. Ionic additives would increase the conductivity as well as selectivity of the electrode membrane.

The perchlorate selective electrode functioned well in the presence of common interfering anions such as chloride, sulfate, nitrate, bicarbonate. The membrane electrode had a wide application pH range (3.0 to 11.0), low detection limit ( $7.0 \times 10^{-7}$  M) and favorable potentiometric selectivity coefficients over other interfering anions in natural water thereby making it a great convenience for field perchlorate analysis. The membrane electrode can be made cheaply; it has rapid response and durability that offers water suppliers a valuable device with instant onsite water quality information.

## REFERENCES

- Amemiya, S., P. Bühlmann, et al. (2003). "A Generalized Model for Apparently "Non-Nernstian" Equilibrium Responses of Ionophore-Based Ion-Selective Electrodes. 1. Independent Complexation of the Ionophore with Primary and Secondary Ions." *Analytical Chemistry* 75(14): 3329-3339.
- Bakker, E., P. Bühlmann, et al. (1997). "Carrier-Based Ion-Selective Electrodes and Bulk Optodes. 1. General Characteristics." *Chem. Rev.* 97(8): 3083-3132.
- Bakker, E. and E. Pretsch (2007). "Modern Potentiometry." *Angew. Chem. Int. Ed.* 46(30): 5660-5668.
- Bakker, E., E. Pretsch, et al. (2000). "Selectivity of potentiometric ion sensors." *Analytical Chemistry* 72(6): 1127-1133.
- Bard, A. J. and L. R. Faulkner (2000). *Electrochemical methods: fundamentals and applications*. Hoboken, NJ, John Wiley & Sons, Inc.
- Barron, L., P. N. Nesterenko, et al. (2006). "Rapid on-line preconcentration and suppressed micro-bore ion chromatography of part per trillion levels of perchlorate in rainwater samples." *Analytica Chimica Acta* 567(1): 127-134.
- Bobacka, J., A. Ivaska, et al. (2008). "Potentiometric Ion Sensors." *Chem. Rev.* 108(2): 329-351.
- Bonnesen, P. V., G. M. Brown, et al. (2000). "Development of Bifunctional Anion-Exchange Resins with Improved Selectivity and Sorptive Kinetics for Perchlorate: Batch-Equilibrium Experiments." *Environmental Science & Technology* 34(17): 3761-3766.
- Ceresa, A., T. Sokalski, et al. (2001). "Influence of key parameters on the lower detection limit and response function of solvent polymeric membrane ion-selective electrodes." *Journal of Electroanalytical Chemistry* 501(1-2): 70-76.
- Craggs, A., G. J. Moody, et al. (1974). "PVC matrix membrane ion-selective electrodes. Construction and laboratory experiments." *J. Chem. Educ.* 51(8): 541.

- Egorov, V., E. Rakhman'ko, et al. (2004). "Novel Anion Exchangers for Electrodes with Improved Selectivity to Divalent Anions." *Electroanalysis* 16(17): 1459-1462.
- El Aribi, H., Y. J. C. Le Blanc, et al. (2006). "Analysis of perchlorate in foods and beverages by ion chromatography coupled with tandem mass spectrometry (IC-ESI-MS/MS)." *Analytica Chimica Acta* 567(1): 39-47.
- Ganjali, M. R., P. Norouzi, et al. (2007). "Perchlorate-selective membrane sensors based on two nickel-hexaazamacrocyclic complexes." *Sensors and Actuators B: Chemical* 120(2): 494-499.
- Hara, H., H. Ohkubo, et al. (1993). "Nitrate ion-selective coated-wire electrode based on tetraoctadecylammonium nitrate in solid solvents and the effect of additives on its selectivity." *Analyst* 118(5): 549-552.
- Hecht, M. H., S. P. Kounaves, et al. (2009). "Detection of Perchlorate and the Soluble Chemistry of Martian Soil at the Phoenix Lander Site." *Science* 325(5936): 64-67.
- IUPAC (1976). "Recommendations for Nomenclature of Ion-Selective Electrodes." *Pure and Applied Chemistry* 48(1): 127-132.
- Kumar, M., S. Singh, et al. (2010). "Cross-Linked Poly(vinyl alcohol)-Poly(acrylonitrile-co-2-dimethylamino ethylmethacrylate) Based Anion-Exchange Membranes in Aqueous Media." *J. Phys. Chem. B* 114(1): 198-206.
- Lamb, J. D., D. Simpson, et al. (2006). "Determination of perchlorate in drinking water by ion chromatography using macrocycle-based concentration and separation methods." *Journal of Chromatography A* 1118(1): 100-105.
- Levitskaia, T. G., S. I. Sinkov, et al. (2007). "In situ perchlorate determination on Purolite A850 ion exchange resin via Raman spectroscopy." *Vibrational Spectroscopy* 44(2): 316-323.
- Maccà, C. (2004). "Response time of ion-selective electrodes: Current usage versus IUPAC recommendations." *Analytica Chimica Acta* 512(2): 183-190.

- Martinelango, P. K. and P. K. Dasgupta (2007). "Dicationic ion-pairing agents for the mass spectrometric determination of perchlorate." *Analytical Chemistry* 79(18): 7198-7200.
- Martinelango, P. K., G. Gumus, et al. (2006). "Matrix interference free determination of perchlorate in urine by ion association-ion chromatography-mass spectrometry." *Analytica Chimica Acta* 567(1): 79-86.
- Moody, G. J., R. B. Oke, et al. (1970). "A calcium-sensitive electrode based on a liquid ion exchanger in a poly(vinyl chloride) matrix." *Analyst* 95(1136): 910-918.
- Ozawa, S., H. Miyagi, et al. (1996). "Anion-Selective Electrodes Based on Long-Chain Methyltrialkylammonium Salts." *Analytical Chemistry* 68(23): 4149-4152.
- Rezaei, B., S. Meghdadi, et al. (2009). "Perchlorate-selective polymeric membrane electrode based on bis(dibenzoylmethanato)cobalt(II) complex as a neutral carrier." *Journal of Hazardous Materials* 161(2-3): 641-648.
- Rezaei, B., S. Meghdadi, et al. (2007). "Fast response and selective perchlorate polymeric membrane electrode based on bis(dibenzoylmethanato) nickel(II) complex as a neutral carrier." *Sensors and Actuators B: Chemical* 121(2): 600-605.
- Smirnova, A. L., V. N. Tarasevitch, et al. (1994). "Some properties of sulfate ion-selective PVC membranes based on a neutral carrier and ion-exchanger." *Sensors and Actuators B: Chemical* 19: 392-395.
- Soldatov, D. V. and J. A. Ripmeester (2001). "Modified metal dibenzoylmethanates and their clathrates part III - Novel 4-vinylpyridine-extended metal-dibenzoylmethanate host frameworks: Structure, polymorphism, and inclusion properties." *Chemistry A European Journal* 7(14): 2979-2994.
- Soleymanpour, A., E. H. Asl, et al. (2007). "Perchlorate selective membrane electrodes based on synthesized platinum(II) complexes for low-level

concentration measurements." *Sensors and Actuators B: Chemical* 120(2): 447-454.

Soleymanpour, A., B. Garaili, et al. (2008). "Perchlorate selective membrane electrodes based on a platinum complex." *Monatshefte Fur Chemie* 139(12): 1439-1445.

Zanjanchi, M. A., M. Arvand, et al. (2006). "Perchlorate-selective polymeric membrane electrode based on a cobaloxime as a suitable carrier." *Sensors and Actuators B: Chemical* 113(1): 304-309.

## Chapter 4

### **PREPARATION AND CHARACTERIZATION OF FUNCTIONALIZED MEMBRANE FOR THE SELECTIVE SEPARATION OF PERCHLORATE FROM OTHER ANIONS IN WATER**

#### **4.1 Abstract**

Perchlorate permselective membranes were synthesized and characterized in this study. The membrane with a thickness of  $\sim 300\mu\text{m}$  was prepared with polyvinyl chloride (PVC) and quaternary ammonium salts in solvent under room temperature. Among the 12 different quaternary ammonium salts, methyltributylammonium chloride (MTBA) showed superior perchlorate permselectivity due to in part to the favorable steric effect of the alkyl chain length. In addition, results from contact angle measurements indicated that modification with quaternary ammonium salts rendered the membranes hydrophobic. Results from Fourier transform infrared (FTIR) spectrum analysis showed that the functional groups responsible for ion exchange were incorporated in the membrane matrix successfully. The surface roughness, averaged pore radius and ion exchange capacity of the MTBA membrane were  $3.23\pm 2.58$  (nm),  $83.6$  (Å) and  $0.12$  (meq/g), respectively. In the presence of an electric field, about 60% of perchlorate were separated from the solution while only less than 9% of other anions, specifically, nitrate, sulfate and bicarbonate passed through the membrane under otherwise identical operation conditions simultaneously.

## 4.2 Introduction

Membrane technology such as ultrafiltration (UF) and nanofiltration (NF) has been used to remove perchlorate from water. Yoon et al. (Yoon, Amy et al. 2002; Yoon, Amy et al. 2005) reported that increase in pH and conductivity can render NF and UF membrane surface negatively charged, which led to greater perchlorate rejection. The UF membrane modified with cationic surfactants also showed enhancement in perchlorate rejection from synthetic water due to the decrease in pore size of the membrane. (Yoon, Yoon et al. 2003) Roach et al. (Roach and Tush 2008; Roach, Lane et al. 2011) studied the removal of perchlorate from aqueous solution by colloid-enhanced ultrafiltration (CEUF) method in the presence of poly(4-vinylpyridine) and poly(diallyldimethylammonium) chloride and reported that greater than 95% of perchlorate (initial concentration of 10.3 ppm) removal in the presence of competition anions. Xie et al. (Xie, Li et al. 2011) studied the effect of chitosan on the separation of perchlorate using UF process and reported 92% perchlorate removal at pH 4.3 and initial perchlorate concentration of 10 mg/L. However, lacking of selectivity and use of chemicals (polymers) makes the method unattractive.

Electrodialysis (ED) technique is a promising alternative for ion separation from water since the technology requires no or low addition of chemical reagents while maintaining high degree of robustness toward mass loading rate and other operational conditions. ED has been used for brackish and sea water desalination and the production of table salts, acids and bases in the chemical and food industry. (Strathmann 2010) Sata and Wang studied the removal of perchlorate at high silica concentrations using a pilot electrodialysis reversal (EDR) process and reported percent removal of 70-97% depending on the initial perchlorate concentration and system configuration, i.e., number of treatment stage. (Roquebert, Booth et al. 2000)

However, competition against perchlorate by other major anions in water is inevitable using conventional ED process. Therefore, there is need to improve the selectivity and effectiveness of the membranes during conventional ED applications.

There have studies on improving the membrane selectivity toward cations(Sata, Sata et al. 2002) or anions(Sata 2000). Eyal and Kedem attempted to improve the nitrate permselectivity of membranes by incorporating polyfunctional groups such as tertiary and quaternary ammonium groups.<sup>35</sup> Sata et al.(Sata, Yamaguchi et al. 1995) developed ion exchange membranes with anion exchange groups of different hydrophobicities for nitrate ion removal from groundwater by electrodialysis. The permselectivity of membrane for nitrate increases with increasing chain length of the alkyl groups of the anion exchange groups. Kesore et al.(Kesore, Janowski et al. 1997) used carboxylic group modified anion exchange membrane for enhancement of nitrate selectivity. To the best of our knowledge, no study has been done on developing perchlorate permselective ion exchange membrane.

In order to selectively separate perchlorate from water, it is necessary to prepare membranes that are permselective to perchlorate. It is hypothesized that by modifying the ion exchange characteristics of membrane with different types of functional groups, specifically quaternary ammonium salts, and by manipulating the chemical composition and the physical properties such as thickness and hydrophobicity, it is possible to enhance the permselectivity of perchlorate over that of other major anions in water such as nitrate, bicarbonate, and sulfate. The objective of this study was to synthesize and test plastic membranes modified with quaternary ammonium salts in terms of perchlorate permselectivity.

### 4.3 Materials and Methods

#### 4.3.1 Chemicals and Reagents

All chemicals were either of analytical or reagent grade, or the highest purity available from suppliers. All aqueous solutions were prepared with de-ionized, distilled water. Tetrahydrofuran (THF, HPLC grade, Fisher Scientific, Fair Lawn, NJ, USA), Polyvinyl chloride (PVC, molecular weight is around 60,000-150,000 g/mol, MP Biomedicals, Solon, OH, USA) and Tributyl *O*-acetyl citrate (TBOAC, 98%, Aldrich, St. Louis, MO, USA) were used for the synthesis of the membrane. Tetramethylammonium chloride (TMA, 98+%) tetraethylammonium chloride (TEA, 99%), tetrapropylammonium chloride (TPA, 94%), benzyl dimethylhexadecylammonium chloride (BDMHA, 97%), benzyl tributylammonium chloride (BTBA, 98+%), methyl tributylammonium chloride (MTBA, 98%) and methyl trioctylammonium chloride (MTOA) were purchased from Acros organics (NJ, USA). (n-Octyl)trimethylammonium bromide (OTMA, 97%), (1-hexyl)trimethylammonium bromide (HTMA, 98%) and (1-Dodecyl)trimethylammonium bromide (DDTMA, 97%) were purchased from Alfa Aesar (Ward Hill, MA, USA). Cetyltrimethylammonium bromide (CTMA, 98-101%) and benzyltrimethylammonium bromide (BTMA) were obtained from Avocado Research Chemicals (Heysham, UK).

The certified standard anions solution (1000 mg/L) of nitrate ( $\text{NO}_3^-$ ), perchlorate ( $\text{ClO}_4^-$ ) and sulfate ( $\text{SO}_4^{2-}$ ) were purchased from SPEX CertiPrep (Metuchen, NJ, USA). Sodium perchlorate (ACS reagent, >98 %, Sigma-Aldrich, St. Louis, MO, USA), sodium bicarbonate (analytical grade ACS, 99.7 %), sodium chloride (reagent grade ACS, >99 %), sodium nitrate (analytical grade ACS, >99 %)

from Acros Organics, sodium carbonate (HPLC grade), sodium sulfate (certified ACS) from Fisher Scientific were individually dissolved into deionized water to prepare stock solutions. NaOH (50% w/w, Fisher Scientific, Fair Lawn, NJ, USA) was used as mobile phase solution in ion chromatography analysis.

#### **4.3.2 Preparation of Membranes**

Membranes were prepared by dissolving a given amount of polyvinyl chloride (PVC), TBOAC, and quaternary ammonium salts in 10 mL of tetrahydrofuran (THF) solvent under room temperature at weight percentage of 34.5 59.8 and 5.7%, respectively. TBOAC is regarded as a relatively nontoxic material than phthalate plasticizer and is therefore the widely phthalate substitute plasticizer in PVC polymer. Total of 12 different quaternary ammonium salts, namely, TMA, TEA, BDMHA, TPA, BTBA, MTBA, MTOA, BTMA, HTMA, OTMA, DDTMA and CTMA were studied as to identify the membrane with the best perchlorate selectivity. K Hand Coater (40, 100, 150, 300  $\mu\text{m}$ , RK PrintCoat Instrument Ltd., UK) was used to control the thickness of the membrane. The membrane solution was poured on a substrate (100 circles, diameter 9cm), followed by drawing the bar coater with both hands at a steady speed to coat a layer of solvent on the surface of the substrate. After the solvent evaporated under room temperature, the membrane was formed on the surface of the substrate.

#### **4.3.3 Chemical and Physical Characterization**

The membranes were characterized for pertinent chemical and physical properties, including permselectivity, ion exchange capacity, functional groups, contact angle, surface roughness, pore size and specific surface area.

The performance of preferential permeation of specific ions by membrane separation can be evaluated by permselectivity constant,  $K_{A,B}$ , between two ions (A and B) defined as the following (Sata 2000):

$$K_{A,B} = \frac{\mu_A \bar{C}_A C_B}{\mu_B \bar{C}_B C_A} \quad (\text{Eq. 4.1})$$

where  $\mu_A$ ,  $\mu_B$  are the mobility of ion A and B in the membrane phase ( $\text{cm}^2/(\text{V}\cdot\text{s})$ );  $\bar{C}_A$ ,  $\bar{C}_B$  and  $C_A$ ,  $C_B$  are the concentration of ion A and B in the membrane phase ( $\text{eq}/\text{cm}^3$ ) and in the solution phase of the desalting side ( $\text{eq}/\text{cm}^3$ ), respectively. If the value of  $K_{A,B}$  is greater than unity, it implies that the membrane is more permeable to ion A than to ion B. In this study, the permselectivity constants between ions through the membrane were measured in 2-compartment cell with electro dialysis. The membrane was placed between the two compartments, and the two compartments were filled with the appropriate mixed salt solutions (for example, sodium perchlorate and sodium nitrate solution). Electro dialysis was then carried out at a constant current density for a given period of time (about 4 hours) to reach steady-state transport condition at a constant temperature. The solutions were vigorously stirred during the electro dialysis to avoid the effect of diffusion. The concentrations of the anions in the both compartments were analyzed in the beginning, middle and the end of electro dialysis. The concentration of the anions in the membrane can also be calculated from the mass balance relationship. The permselectivity constants can be determined.

The ion exchange capacity of the membrane was determined with back titration method (Hwang and Ohya 1998) (Supporting information) and calculated by following equation:

$$q = (N \cdot V) / W \quad (\text{Eq. 4.2})$$

where  $q$  is the ion exchange capacity (eq/g dry wt),  $N$  is the normality of titrant, NaOH (eq/L),  $V$  is volume (L) of the titrant added to the membrane-containing solution at the end point, and  $W$  is the dry weight of membrane (g).

A contact angle goniometer (Ramé-hart instrument co. NJ, USA) was used to characterize the wettability of the membranes by the sessile drop method (Sobolev, Starov et al. 2003). Contact angles of different types of membrane were measured before and after perchlorate exchange experiments. The membranes were (area about  $0.5 \text{ cm}^2$ ) placed under the microscope. A droplet ( $\sim 5 \mu\text{L}$ ) of DIW was placed on the membranes to measure the angle between the liquid and membrane interface. Contact angles ( $\theta$ ) were determined by taking the average of five measurements.

The pore size of membrane was determined with nitrogen adsorption/desorption method using a BET pore size analyzer (NOVA 2000, Quantchrome Corp., USA). Three grams of each membrane sample were pretreated under nitrogen purging and vacuum environment in a glass cell at 303K for 24 h. The sample with glass cell was then placed in liquid nitrogen bottle to initiate nitrogen gas adsorption and desorption from the pressure of 38 to 760 mmHg. Based on the volume of nitrogen gas adsorbed the average pore size,  $r_p$ , of membrane was calculated according to the following equations (Barrett, Joyner et al. 1951):

$$V_{\text{liq}} = \frac{P_a V_{\text{ads}} \tilde{V}_m}{R T} \quad (\text{Eq. 4.3})$$

$$r_p = \frac{2 V_{\text{liq}}}{\Sigma} \quad (\text{Eq. 4.4})$$

where  $V_{\text{liq}}$  is the volume ( $\text{cm}^3/\text{g}$ ) of liquid nitrogen occupying the pores,  $P_a$  and  $T$  are pressure and temperature, respectively,  $\tilde{V}_m$  is the molar volume of the liquid

adsorbate (i.e.,  $34.7 \text{ cm}^3/\text{mol}$  for nitrogen),  $V_{\text{ads}}$  is the volume of nitrogen adsorbed ( $\text{cm}^3/\text{g}$ ), and  $\Sigma$  is the specific surface area ( $\text{cm}^2/\text{g}$ ).

The morphology of membrane surface was studied using atomic force microscope (AFM, Bioscope Catalyst, Bruker Corp., USA). The membranes were (area about  $2 \text{ cm}^2$ ) placed under the microscope without fluid and the tip of probe (ScanAsyst-Air, Bruker Corp.) was engaged to the samples in direct contact mode. The surface roughness ( $\delta$ ) of each membrane sample was determined by taking the average of three measurements.

The surface functional groups of membrane were detected with Fourier transform infrared (FTIR) spectrometer (Thermo Nicolet NEXUS 670, Thermo Scientific Inc., USA) coupled with attenuated total reflectance (ATR) method from wavenumber  $600$  to  $3500 \text{ cm}^{-1}$  of each membrane sample. The membrane images were obtained by scanning electron microscope (JSM 7400F, JEOL Ltd., USA JSM7400). Metal (Pd, Au) sputtering deposition on the surface of membrane samples under vacuum were carried out before imaging. Electro impedance spectroscopy (EIS) of membrane was conducted in potentiostatic mode where a sinusoidal potential signal of amplitude  $10 \text{ mV}$  was imposed with potentiostat (VersaSTAT3, PAE, USA).

#### **4.3.4 Perchlorate and Other Anions Separation Studies**

The synthesized membranes were placed in an electrodialysis device for perchlorate separation studies. The concentration of perchlorate and other anions, namely, chloride, sulfate, bicarbonate, carbonate, and nitrate were analyzed by ion chromatography. A Dionex DX500 (CA, USA) ion chromatography system equipped with Dionex AS40 auto-sampler and the guard column (IonPac AG16,  $50\text{mm}\times 4\text{mm}$ ) and analytical column (IonPac AS16,  $250\text{mm}\times 4\text{mm}$ ).

The transport kinetics of anions across the membrane can be expressed by following equations:

$$\frac{d[A_d]}{dt} = -k_1[A_d] \quad (\text{Eq. 4.5})$$

$$\frac{d[A_m]}{dt} = k_1[A_d] - k_2[A_m] \quad (\text{Eq. 4.6})$$

$$\frac{d[A_c]}{dt} = -k_2[A_m] \quad (\text{Eq. 4.7})$$

where  $[A_d]$ ,  $[A_m]$ ,  $[A_c]$  is the mass of the anion in the diluate, membrane phase and concentrate chamber, respectively.  $k_1$  is the rate constant of anion transport from the diluate to the membrane surface and  $k_2$  is the rate constant of anion transport from the membrane surface to the concentrate chamber. In the absence of other chemical reactions involving the anions of interest, the following mass balance equation can be written as:

$$[A_d] + [A_m] + [A_c] = [A_T] \quad (\text{Eq. 4.8})$$

where  $[A_T]$  is the total mass of ion in the system. By combining eq. (4.5) through eq. (4.8), and upon integration, one has:

$$[A_d] = [A_T]e^{-k_1t} \quad (\text{Eq. 4.9})$$

$$[A_m] = [A_T] \times \frac{k_1}{k_2 - k_1} (e^{-k_1t} - e^{-k_2t}) \quad (\text{Eq. 4.10})$$

$$[A_c] = [A_T] \times \left(1 + \frac{(k_1e^{-k_2t} - k_2e^{-k_1t})}{(k_2 - k_1)}\right) \quad (\text{Eq. 4.11})$$

By monitoring the ion concentration in the diluate and concentrate streams, it is possible to obtain the rate constants of ion transport,  $k_1$  and  $k_2$ .

## 4.4 Results and Discussion

### 4.4.1 Membrane Thickness

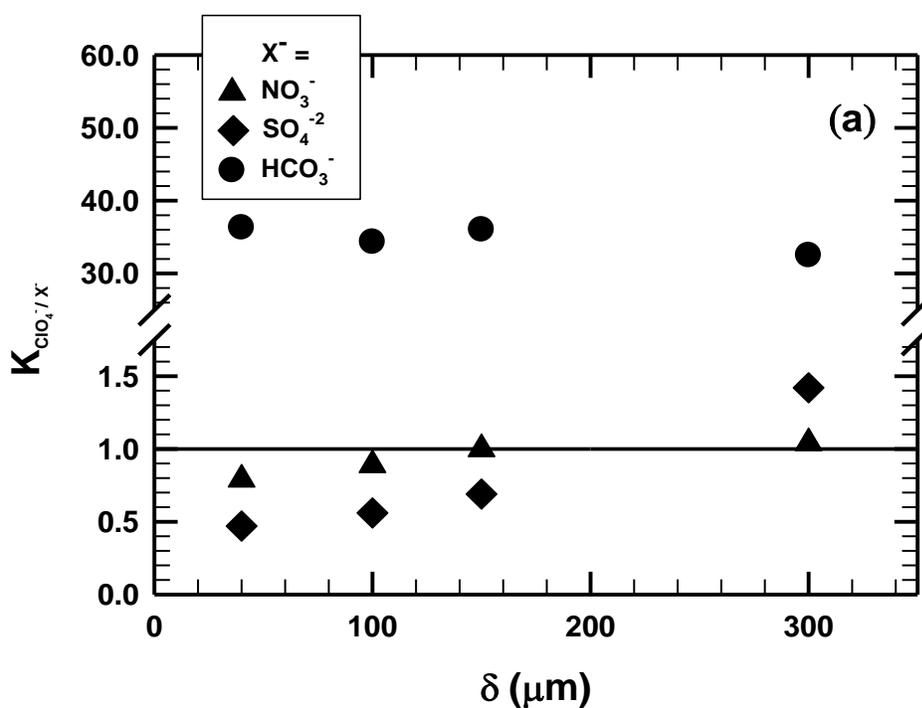
PVC membrane was synthesized in this study due to its flexibility and durability. The thickness of ion exchange membrane would influence the ion flux across the membrane. It is expected that thinner membrane would facilitate ion flux due to smaller resistance. The thickness of PVC membranes was controlled by the amount of polymeric solution used. Fig. 4.1(a) shows that the  $K_{\text{ClO}_4^-, \text{HCO}_3^-}$  value remained large at  $\sim 30$  and independent of the membrane thickness whereas both the  $K_{\text{ClO}_4^-, \text{NO}_3^-}$  and  $K_{\text{ClO}_4^-, \text{SO}_4^{2-}}$  values increased from  $<1$  to  $>1$  with the thickness of the membrane. Sata et al. (Sata, Teshima et al. 1996) showed that large anions such as sulfate, in general, were difficult to permeate through the membrane especially those have high crosslinkage structure. Although PVC polymer used here was of linear structure without crosslinkage, thicker membrane still could hamper the transport of ions. It is worthy of noting that perchlorate permselectivity versus bicarbonate ( $K_{\text{ClO}_4^-, \text{HCO}_3^-}$ ) remains almost constant over the range of membrane thickness studied, which indicates that other factors might affect the transport of the ions as well. The mobility ( $u$ ) of a ion at infinite dilution can be calculated via the following equation (Vanýsek 2002):

$$u = \frac{ZeD}{k_B T} \quad (4.12)$$

where  $Z$  is the valence of the ion,  $e$  is the charge of the electron ( $1.62 \times 10^{-19}$  C),  $D$  is the diffusion coefficient of the ion ( $\text{cm}^2 \text{s}^{-1}$ ),  $k_B$  is Boltzmann constant ( $1.38 \times 10^{-23}$   $\text{m}^2 \text{kg s}^{-2} \text{K}^{-1}$ ), and  $T$  is temperature (K). The calculated mobility of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$  and  $\text{HCO}_3^-$  is 8.29, 7.40, 6.98 and 4.61 ( $10^{-8} \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$ ), respectively at 298K.

Consequently the mobility of bicarbonate ion will be relatively smaller than that of all

other ions. Therefore, the slow-moving bicarbonate ion would pass through the membrane at slower rate. However, in order to maintain appropriate structural strength, a certain thickness is necessary. Most of commercial anion exchange membranes have typical thickness in the range from 0.12 to 0.60 mm (Nagarale, Gohil et al. 2006). Hence, a thickness around 0.3 mm was selected. Since at this thickness, both the  $K_{\text{ClO}_4^-/\text{NO}_3^-}$  and  $K_{\text{ClO}_4^-/\text{SO}_4^{2-}}$  values were greater than unity favoring the permselectivity of perchlorate over that of nitrate and sulfate.



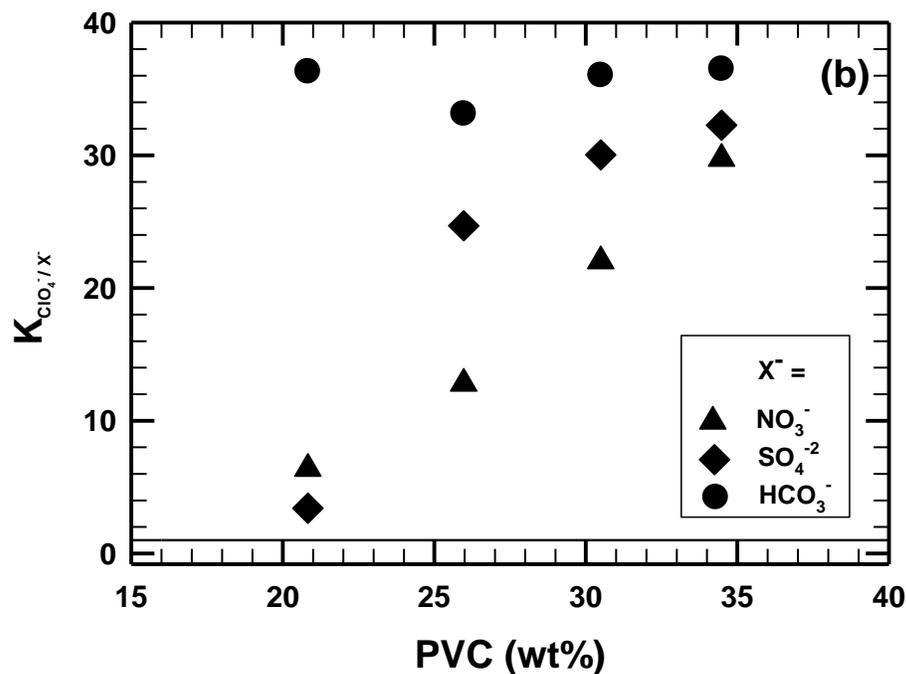


Figure 4.1. (a) Perchlorate permselectivity as affected by membrane thickness. (b) Perchlorate permselectivity as affected by PVC weight content (%). Experimental conditions: [MTBA] = 0.1 g; [TBOAC] = 1.04 g; THF = 10 mL; ED Current = 1 mA; pH = 6.8; temperature =  $22 \pm 1^\circ\text{C}$ ;  $I = 0.13 \text{ mM NaCl}$ .

#### 4.4.2 Polymer Mass Content

Altering the amount of PVC polymer is believed to closely relate to the ion selectivity. Therefore, the effect of chemical composition of the membrane on perchlorate permselectivity was examined in terms of polymer mass content.

Membranes were prepared by mixing different amounts of PVC (e.g., 20.83, 25.97, 30.5 and 34.5 wt %) while keeping the quaternary ammonium salt (MTBA) and TBOAC at 0.1 and 1.04 g, respectively. The results were plotted with perchlorate permselectivity against other anions,  $X = NO_3^-, SO_4^{2-}, HCO_3^-$ , ( $K_{ClO_4/X}$ ) versus the

PVC weight percentage, PVC (wt%). Fig. 4.1(b) shows that the perchlorate permselectivity against nitrate ( $K_{\text{ClO}_4^-, \text{NO}_3^-}$ ) and sulfate ( $K_{\text{ClO}_4^-, \text{SO}_4^{2-}}$ ) reached ~30 as the amount of PVC was increased from 20.83 to 34.5 wt%. Again, the value of  $K_{\text{ClO}_4^-, \text{HCO}_3^-}$  almost remained unchanged (~35) due to kinetically slow-moving bicarbonate ion. The results indicated that PVC has favorable perchlorate permselectivity characteristics and that the amount of polymer did control the perchlorate permselectivity of the membrane. It has been reported that ion exchange membranes of denser texture would be more ion-selective. (Klaysom, Moon et al. 2011) Furthermore, comparing the hydration radius of the anions studied, i.e.,  $\text{ClO}_4^-$  (2.40 Å) >  $\text{SO}_4^{2-}$  (2.30 Å) >  $\text{NO}_3^-$  (1.96 Å) >  $\text{HCO}_3^-$  (1.56 Å) (Moyer and Bonnesen 1997), it is seen that structurally dense membranes are more effective in hindering the direct transport of ions. Yoon et al. (Yoon, Yoon et al. 2003) reported that decreasing the UF membrane pore size led to lowering the ion flux across the membrane and increasing overall perchlorate rejection. Therefore, structurally dense membrane would prevent the smaller ions, e.g., nitrate from passing through the membrane. The transport of the ion of interest, e.g., perchlorate could be exclusively driven by its affinity toward the functional groups on the membrane structure.

Membrane prepared with optimum amount of PVC and thickness could have homogeneous structure, which enables effective transport of ions through the membrane via ion exchange process. However, the electrical conductivity of the membrane also decreased as the amount of polymer and membrane thickness increased. Under constant current operation in the electrodialysis experiments, voltage drop across the membrane was increased from 31.4 to 112.4V when the membrane thickness was increased from 0.04 to 0.3 mm (Fig. 4.2 and Fig. 4.3). Therefore,

membranes were prepared with 34.5 wt% of PVC polymer and a thickness of 0.3 mm in the present research.

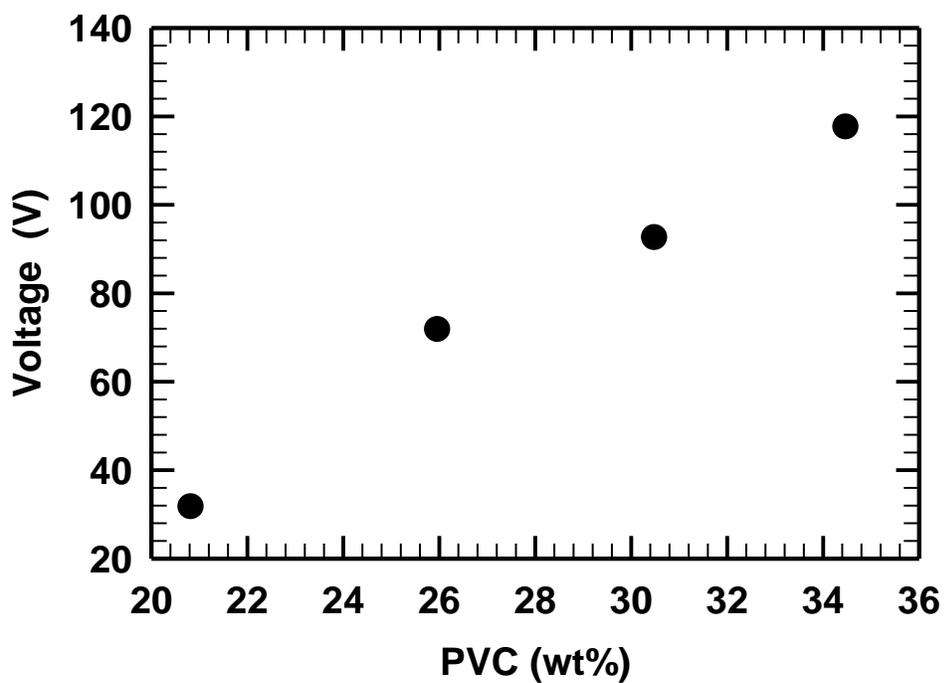


Figure 4.2. Voltage drop of membrane of different PVC weight percentage.  
Experimental Conditions: [MTBA] = 0.1 g; [TBOAC] = 1.04 g; THF = 10mL; ED Current = 1 mA; pH = 6.8; temperature = 22±1 °C; I = 0.13 mM (NaCl).

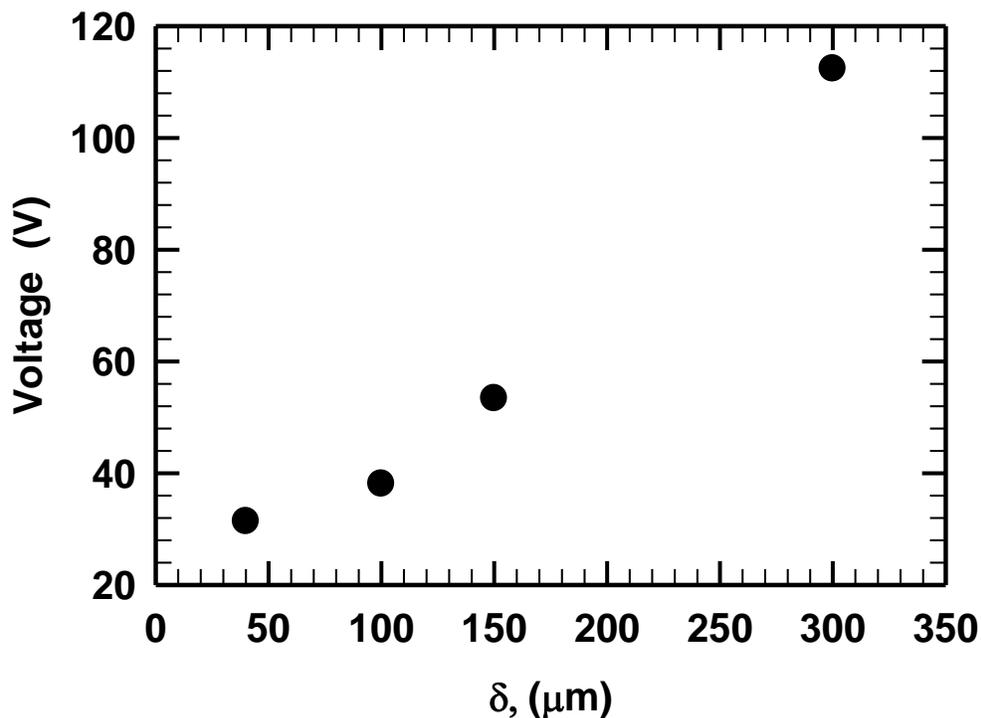
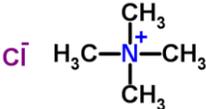
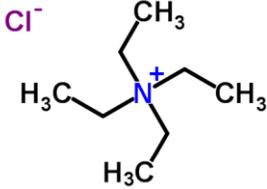
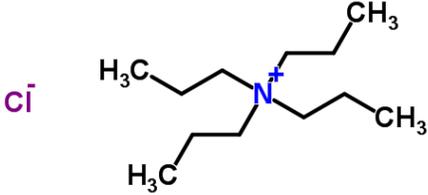
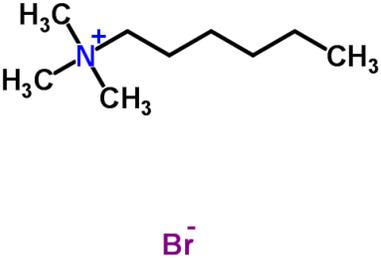
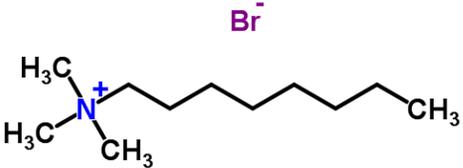


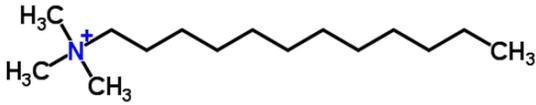
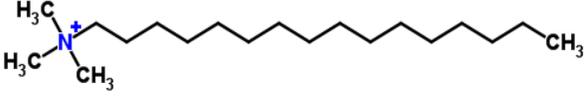
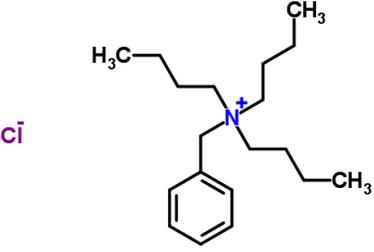
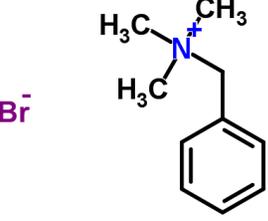
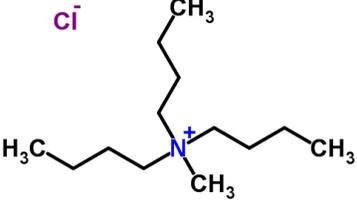
Figure 4.3. Voltage drop of membrane of different thickness. Experimental Conditions: [MTBA] = 0.1 g; [TBOAC] = 1.04 g; THF = 10mL; ED Current = 1 mA; pH = 6.8; temperature =  $22 \pm 1$  °C; I = 0.13 mM (NaCl).

#### 4.4.3 Chemical Property

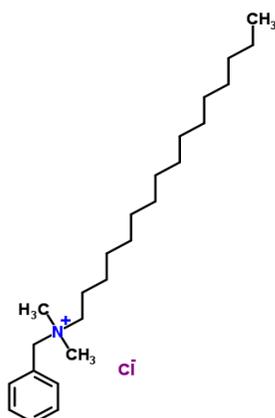
Fig. 4.4 shows perchlorate permselectivity versus major anions such as nitrate, sulfate (left y-axis) and bicarbonate (right y-axis) as a function of the carbon number of various quaternary ammonium salts (total 12). The 12  $\text{R}_4\text{N}^+\text{X}^-$  functionalized membranes were divided into three distinct groups for purpose of comparison (Table 4.1): (i)  $\text{R}_4\text{N}^+\text{X}^-$  with 4 identical short-chain methyl groups, e.g., TMA (chain length =

Table 4.1. Chemical Structure of quaternary ammonium salts.

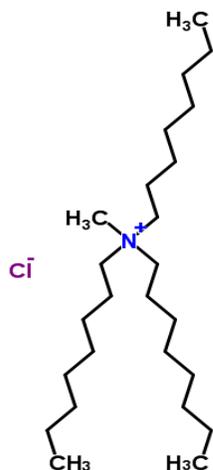
Name	Chemical Structure
Tetramethylammonium chloride (TMA)	
Tetraethylammonium chloride (TEA)	
Tetrapropylammonium chloride (TPA)	
(1-hexyl)trimethylammonium bromide (HTMA)	
(n-Octyl)trimethylammonium bromide (OTMA)	

<p>(1-Dodecyl)trimethylammonium bromide (DDTMA)</p>	<p><math>\text{Br}^-</math></p> 
<p>Cetyltrimethylammonium bromide (CTMA)</p>	<p><math>\text{Br}^-</math></p> 
<p>Benzyltributylammonium chloride (BTBA)</p>	<p><math>\text{Cl}^-</math></p> 
<p>Benzyltrimethylammonium bromide (BTMA)</p>	<p><math>\text{Br}^-</math></p> 
<p>Methyltributylammonium chloride (MTBA)</p>	<p><math>\text{Cl}^-</math></p> 

Benzyldimethylhexadecylammonium chloride (BDMHA)

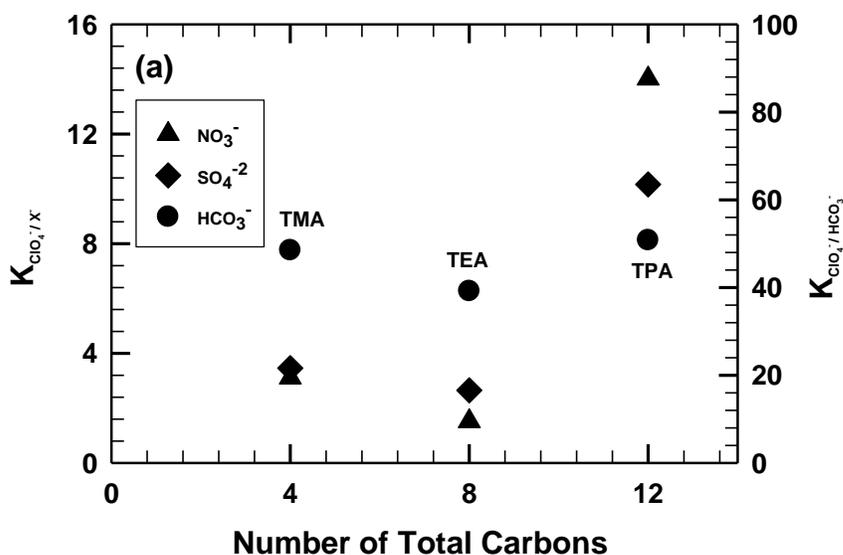


Methyltrioctylammonium chloride (MTOA)



$0,0,0,0)_M$ , TEA (chain length =  $1,1,1,1)_M$  and TPA (chain length =  $2,2,2,2)_M$  (Fig. 4.4a); (ii)  $R_4N^+X^-$  with one long-chain R group plus three short-chain methyl group, e.g., HTMA (chain length =  $0,0,0,5)_M$ , OTMA (chain length =  $0,0,0,7)_M$ , DDTMA chain length =  $0,0,0,11)_M$ , CTMA (chain length =  $0,0,0,15)_M$  (Fig. 4.4b); and (iii)  $R_4N^+X^-$  with one short-chain benzyl group plus one to three short-chain methyl groups, e.g., BTMA  $(0,0,0)_M(1)_B$ , BDMHA  $(0,0,15)_M(1)_B$  and BTBA  $(3,3,3)_M(1)_B$  (Fig. 4.4c). (Note: The figure in the parentheses stands for the number of carbon between  $N^+$  and functional group such as methyl group, M, and benzyl group, B.) Fig. 4.4(a) showed that the  $K_{ClO_4^-,NO_3^-}$  and  $K_{ClO_4^-,SO_4^{2-}}$  values of TPA-membrane were larger than that of the TMA- and the TEA- membranes due in part to the increase in steric effect contributed from the long-chain group, which promoted affinity between the membrane and the perchlorate. Although the chain length of TEA-membrane is longer than that of TMA-membrane, the perchlorate permselectivity of TEA-membrane is not better than that of TMA-membrane. Therefore, it is suggested that not only steric effect contributed from the long-chain group of amines would influence the perchlorate permselectivity. However, when the modifying  $R_4N^+X^-$  compounds had one long tail (Fig. 4.4b) the affinity of perchlorate toward the membrane decreased due mainly to the unique structure of the quaternary ammonium salts, which contain 3 short-chain and 1 long-chain methyl groups. Fig. 4.4c shows the permselectivity of perchlorate as affected by the presence of benzyl group in the quaternary ammonium salts. It is noted that one of the three hydrogen atoms of the methyl group in TMA, CTMA and MTBA is replaced by a benzyl structure to become BTMA, BDMHA, and BTBA, respectively. Both TMA and BTMA have four short chains, both CTMA and BDMHA have has one long and three short chains and both MTBA and BTBA have

one short and three medium-length chains. Based on perchlorate permselectivity versus nitrate and sulfate, two most competing anions, results showed that the perchlorate selectivity of BTMA and BDMHA were greater than that of TMA and CTMA, respectively; whereas, the perchlorate permselectivity of BTBA was smaller than that of MTBA. The benzyl group, slightly electron withdrawing relative to hydrogen being replaced, will contribute to the positive charge of the nitrogen center and enhance the electrostatic interaction between perchlorate and the membrane structure. However, in the presence of medium-length chains, namely, BTBA and MTBA, steric effect takes effect to inhibit the interaction between perchlorate and the nitrogen center. It is also worth of mention that MTOA which was used to prepare perchlorate selective electrode (Wang, Shah et al. 2013) showed insignificant  $K_{ClO_4^-,NO_3^-}$  and  $K_{ClO_4^-,SO_4^{2-}}$  values ( $\ll 1$ ) indicating small perchlorate permselectivity.



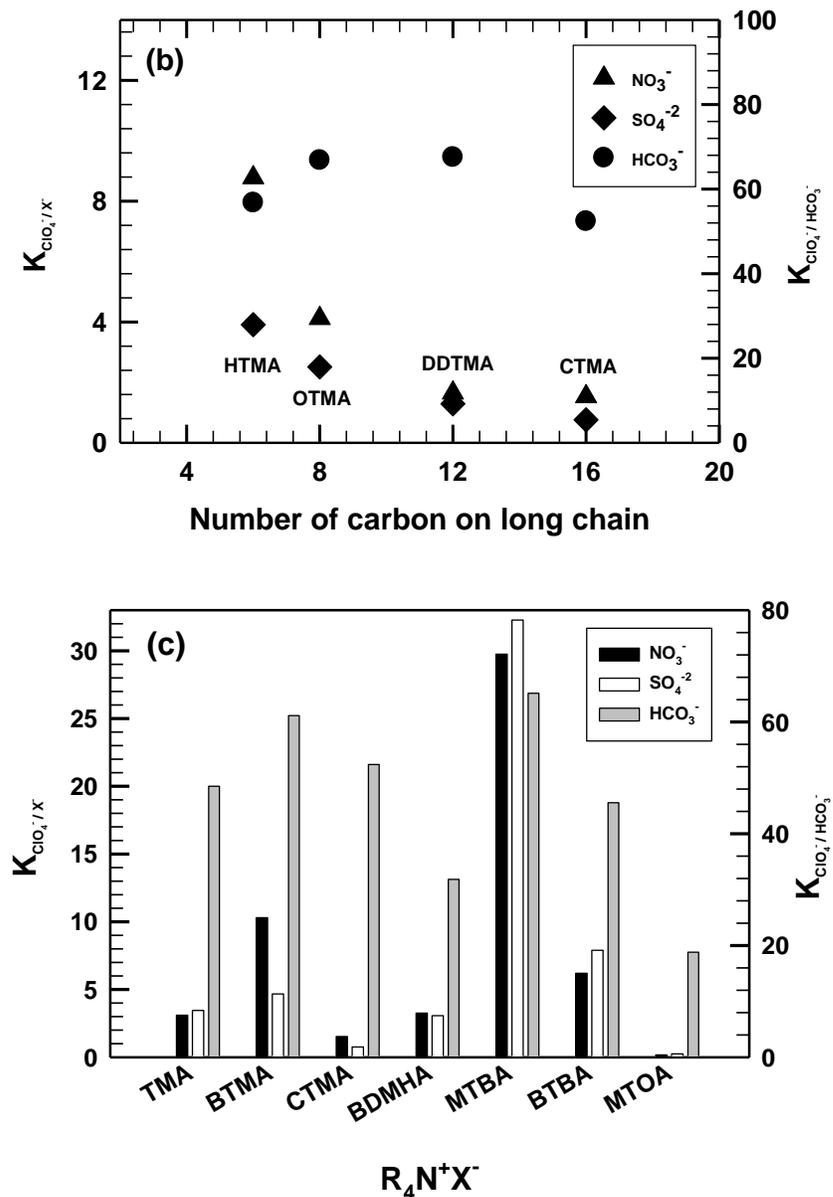


Figure 4.4. Perchlorate permselectivity with respect to nitrate, sulfate (left y-axis) and bicarbonate (right y-axis) of different membranes as a function of chain length or carbon number: (a) symmetric amines; (b) amines with one long chain group, and (c) amines with benzyl group. Experimental conditions: [PVC] = 34.5 % (wt); [TBOAC] = 59.8% (wt); [ $\text{R}_4\text{N}^+\text{X}^-$ ] = 5.7% (wt); THF = 10 mL; ED Current = 1 mA; pH = 6.8; temperature =  $22 \pm 1^\circ\text{C}$ ; I = 0.13 mM NaCl.

MTBA membrane showed significantly superior perchlorate permselectivity than BTBA membrane as shown in Fig. 4.4(c). It was found that neither the longest chain (CTMA) nor the shortest chain (TMA)  $R_4N^+X^-$  functionalized membranes exhibiting the maximum perchlorate permselectivity against nitrate and sulfate. Comparable results were also observed in ion exchange resins modified with quaternary amine for perchlorate adsorption. (Gu, Brown et al. 2007) The long-chain group of amine increased the selectivity for perchlorate but reduced the reaction kinetics, while the short-chain group showed the contrary behavior. The results can be attributed to the steric hindrance in the reaction of bulky amines group, which was also observed in the nitrate selective membrane. (Sata, Yamaguchi et al. 1995) Only amines with moderate chain length could offer sufficient steric effect for perchlorate separation and balance both the selectivity and the kinetic rate on adsorption and desorption of the perchlorate.

Table 4.2 summarizes ion exchange capacity (q) of different types of membranes. PVC-only membrane (as control) showed the lowest exchange capacity for lacking of ion exchange group. The q values of membranes prepared with quaternary ammonium salts were in the range from 0.06 to 0.15 meq/g. The increase in ion exchange capacity by incorporation of  $R_4N^+X^-$  into the PVC membrane was further confirmed by the results of FTIR analysis. From FTIR spectra (Fig. 4.5), several functional groups, such as carbonyl (C=O), methyl (-CH<sub>3</sub>) and butyl (-C<sub>4</sub>H<sub>9</sub>) were observed.

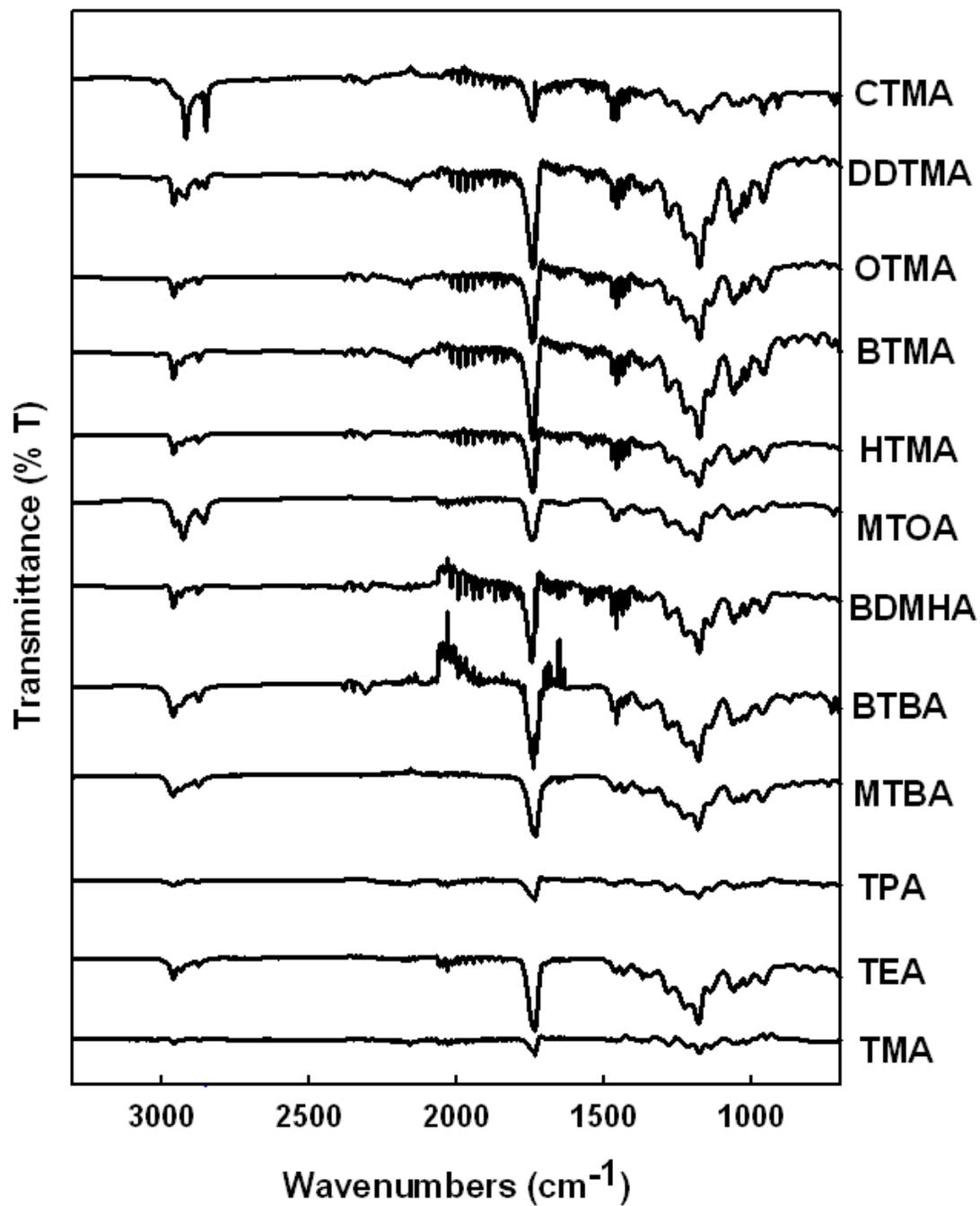


Figure 4.5. FTIR spectra of different membranes functionalized with different quaternary ammonium salts. Experimental conditions; [PVC] = 34.5 % (wt); [TBOAC] = 59.8% (wt);  $[\text{R}_4\text{N}^+\text{X}^-]$  = 5.7% (wt); THF = 10 mL.

Since the methyl group is present in all quaternary ammonium salts, the  $\text{-CH}_3$  asymmetric stretching signal at wavenumber from 2917 to 2958  $\text{cm}^{-1}$  support the evidence that quaternary ammonium salts were successfully incorporated in the polymer structure. The shift in quaternary ammonium group peaks (e.g.,  $\text{-CH}_3$ ) can be attributed in part to structural change of the amine compound in the PVC matrix. The stretching from 1728 to 1744  $\text{cm}^{-1}$  was assigned to the  $\text{C=O}$  group present in the TBOAC used for the synthesis of the membrane. Similar FTIR spectra of PVC membranes have been observed. (Ramesh, Leen et al. 2007; Rajendran, Prabhu et al. 2008) It has been reported (Soman and Kelkar 2009) that the shift of the vibration signals from the organic acids functionalized PVC membrane were resulted from the interaction between the organic acids and PVC .

Table 4.2. Characterization of various membranes.

Types of Membrane	q	$\theta$	$\delta$	$r_p$	$\Sigma$
PVC only	0.03±0.01	73.6±1.1	3.21±0.06	40.3	0.23
TMA	0.09±0.02	73.8±0.6	4.49±0.63	87.7	0.60
TEA	0.10±0.00	77.1±0.7	4.03±0.47	82.9	0.79
TPA	0.08±0.00	52.6±2.5	3.32±1.73	77.7	0.49
MTBA	0.12±0.00	77.4±1.1	3.23±2.58	83.6	0.51
BTBA	0.11±0.01	74.4±0.8	4.60±0.39	83.3	0.46
BDMHA	0.10±0.02	74.1±0.9	3.79±1.04	78.8	0.52
MTOA	0.06±0.01	39.0±2.4	11.07±1.79	79.8	0.55
BTMA	0.15±0.00	71.8±3.4	3.18±1.34	90.6	0.35
HTMA	0.08±0.01	47.6±3.6	21.30±5.76	79.5	0.61
OTMA	0.09±0.01	62.6±2.7	41.28±4.48	79.6	0.54
DDTMA	0.09±0.00	54.4±3.4	3.72±0.70	81.7	0.51
CTMA	0.13±0.01	3.7±0.5	17.07±4.72	86.7	0.48
q : Ion exchange capacity (meq/g) $\theta$ : Contact angle (degree) $\delta$ : Roughness (nm) $r_p$ : Average pore radius (Å) $\Sigma$ : Specific Surface Area (m <sup>2</sup> /g)					

#### 4.4.4 Surface Hydrophilicity

Membrane surfaces noticeably exhibited affinity toward water. Sata et al. (Sata, Mine et al. 1998) concluded that the permeation of halogen ions through the ion exchange membrane in electrodialysis can be altered by controlling the hydrophilicity of the membranes. Therefore, the surface hydrophilicity of the membrane controls the permselectivity. Table 4.2 summarizes the contact angle value of 13 fresh membranes. The contact angles of eight membranes (i.e., PVC, TMA, TEA, BTMA, OTMA, MTBA, BTBA and BDMHA) were between 60 and 80 deg, while the rest of the other five membranes (i.e., HTMA, TPA, DDTMA, CTMA and MTOA) were  $\leq$  ca. 50 deg. The higher the contact angle the more hydrophobic the surface is. It is worthy of mention that CTMA membrane has the smallest contact angle value (i.e., 3.7 deg) among all membranes studied and is thus the most hydrophilic. The contact angle of all, except the PVC-only, membranes (a control) was increased (i.e., becoming more hydrophobic) upon application for the treatment of perchlorate containing solution (Fig. 4.6 (a) and (b)). Obviously, perchlorate adsorption membrane rendered the membrane surface hydrophobic. In general, the change of contact angle before and after use of most membranes was less than 10 deg indicating the adsorption of a small amount of perchlorate. It must be noted that MTOA-membrane displayed the greatest change of contact angle ( $> 30$  deg) among all 13 membranes studied, which implied strong perchlorate adsorption onto the membrane. That is, the MTOA-membrane attracted perchlorate molecule strongly but barely released it to the bulk solution. In contrast, the contact angle of MTBA- membrane only increased by 5.6 deg, which implied effective passage of perchlorate molecule across the membrane as reflected by  $K_{ClO_4^-, X^-}$  value larger than that of all other functionalized membranes.

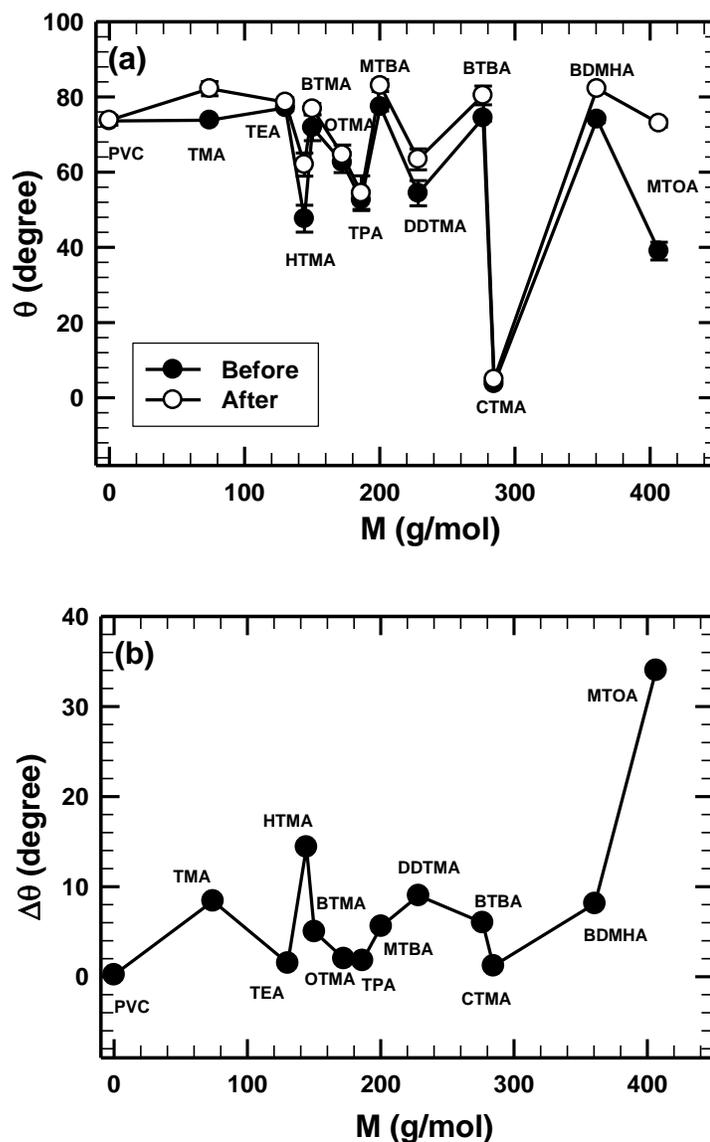


Figure 4.6. Hydrophobicity of different membranes as a function of molecular weight of quaternary ammonium salts. (a) Contact angle ( $\theta$ ) of the PVC-membranes before and after perchlorate exchange experiments; (b) change of contact angle after ion exchange experiments. Experimental conditions: [PVC] = 34.5%; [ $R_4N^+X^-$ ] = 5.7%; [TBOAC] = 59.8%; THF = 10 mL; ED current = 1 mA; pH = 6.8; temperature =  $22 \pm 1^\circ\text{C}$ ;  $I = 0.13$  mM.

#### 4.4.5 Surface Morphology

Klaysom et al.(Klaysom, Moon et al. 2011) reported that the surface morphology could influence the salt separation efficiency of membrane. Therefore, several morphology related factors such as surface roughness ( $\delta$ ), pore radius ( $r_p$ ) and specific surface area,  $\Sigma$ , were examined (Table 4.2) in addition to surface images using scanning electron microscope (SEM). The surface roughness ( $\delta$ ) of PVC-only membrane was  $3.21 \pm 0.06$  nm, which surface was considered smooth as seen in Fig. 4.7(a). Incorporation of inorganic or organic salts into the membrane structure increased the surface roughness from 3.2 to 41.3nm (Table 4.2). Incomplete incorporation of the organic salts in the structure of the polymer membranes could lead to increase in surface roughness. Similarly incorporation of quaternary amine salts increased the membrane pore size. PVC-only membrane showed the smallest average pore radius ( $r_p$ ) at 40.3 Å, whereas average pore radius of functionalized membranes was in the range of 77.7 to 90.6 Å. The quaternary ammonium salts would occupy the intermolecular space in the polymer structure, thereby hindering the polymerization process. Therefore, the uncompleted polymerization of the polymer molecules would generate more loose structure which would also increase the chance to have large porous structures. It is noted that the although the pore size of all membranes was relatively greater than the hydration radius of all anions studied, functionalized membranes still demonstrated superior perchlorate permselectivity. Hence, the pore size seemed to play a minor role in determining perchlorate permselectivity. The specific surface area ( $\Sigma$ ) of all membranes was in the range of 0.12 to 0.79 m<sup>2</sup>/g, which was small compared to most perchlorate adsorbents such as activated carbon(Mahmudov and Huang 2010). Therefore, specific surface could not

be major factor controlling perchlorate adsorption capacity, which is closely related to permselectivity.

Fig. 4.7 (a) to (f) showed the SEM images of PVC-, TMA-, CTMA-, BTMA-, MTOA- and MTBA- membrane surfaces. The features of the membrane surface changed as modification with different types of quaternary amines salts. For example, for the  $R_4N^+X^-$  with 4 identical short-chain groups, TMA membrane (Fig. 4.7(b)) showed several layers of porous structure which is not observed in TEA and TPA membrane (Fig. 4.8 (a) and (b)). For  $R_4N^+X^-$  with one long-chain R group plus three short-chain group, CTMA (Fig. 4.7(c)), OTMA and DDTMA (Fig. 4.8 (c) and (d)) all showed dent-like features. And the size of dents is in the range of c.a. 1 to 10  $\mu\text{m}$ . When  $R_4N^+X^-$  has one benzyl group, the surface of membrane (BTMA, Fig. 4.7(d); BTBA and BDMHA, Fig. 4.8 (e) and (f)) showed relative smooth without obvious dents or pores. In addition, MTOA membrane (Fig. 4.7(e)) showed tiny bumps (<1  $\mu\text{m}$ ) on the surface. As shown in Fig. 4.7(f), the surface of the MTBA-membrane showed numeral nodules-like features with the size in the range of c.a. 2 to 6  $\mu\text{m}$ . However, no such nodules-like features were observed in other membranes (Fig. 4.7 (b)-(e) and Fig. 4.8 (a) to (b)). It is also interesting to note that the variation of the surface roughness of the MTBA-membrane ( $\delta = 3.23 \pm 2.58 \text{ nm}$ ) was larger than that of most of the other membranes. Therefore, it is suggested that the nodules-like features were responsible for attributing to large surface roughness.

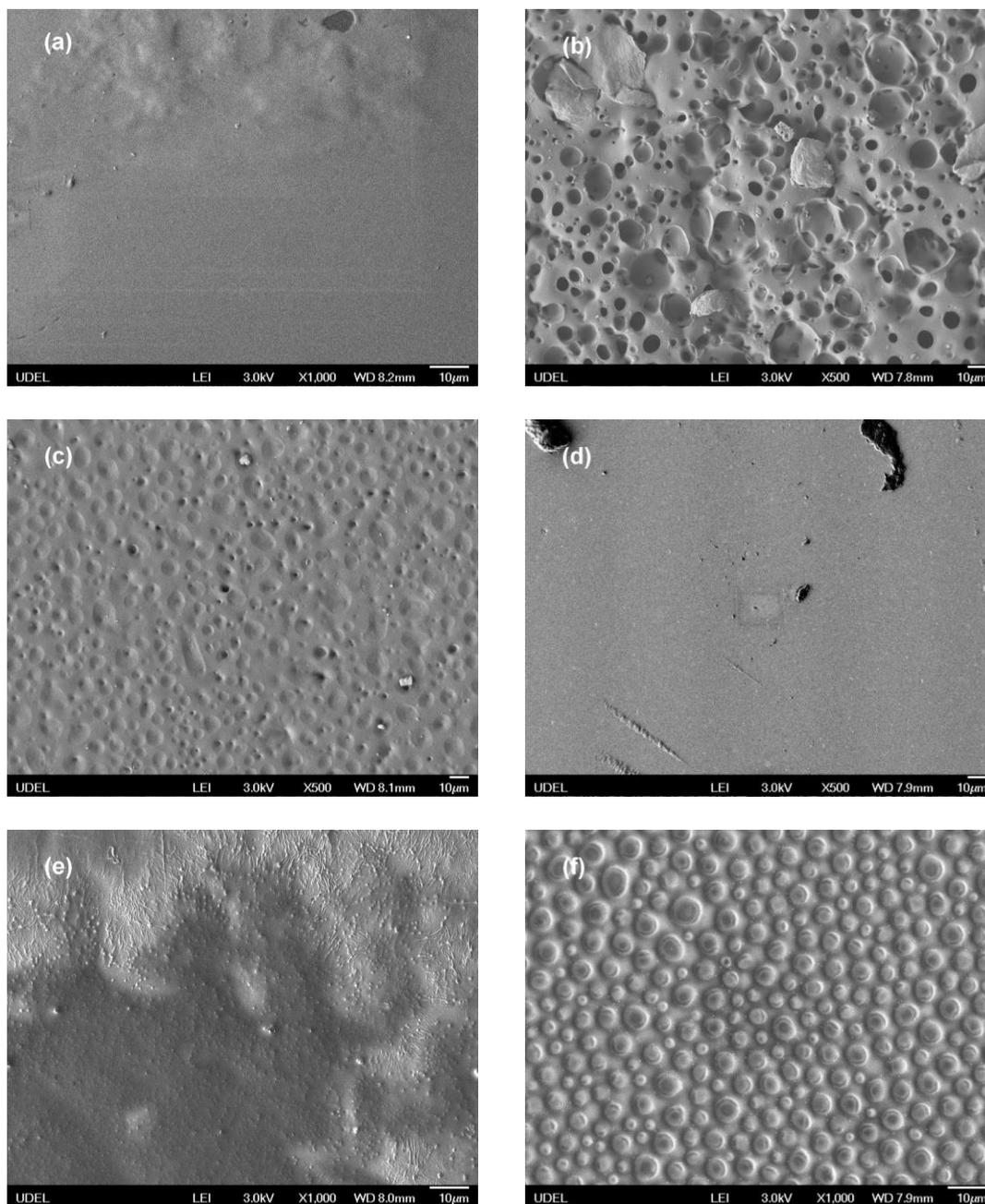


Figure 4.7. SEM images of (a) PVC only; (b) TMA; (c) CTMA; (d) BTMA; (e) MTOA and (f) MTBA membranes. Experimental Condition: [PVC] = 34.5%;  $[R_4N^+X^-]$  = 5.7%; [TBOAC] = 59.8%; THF = 10 mL.

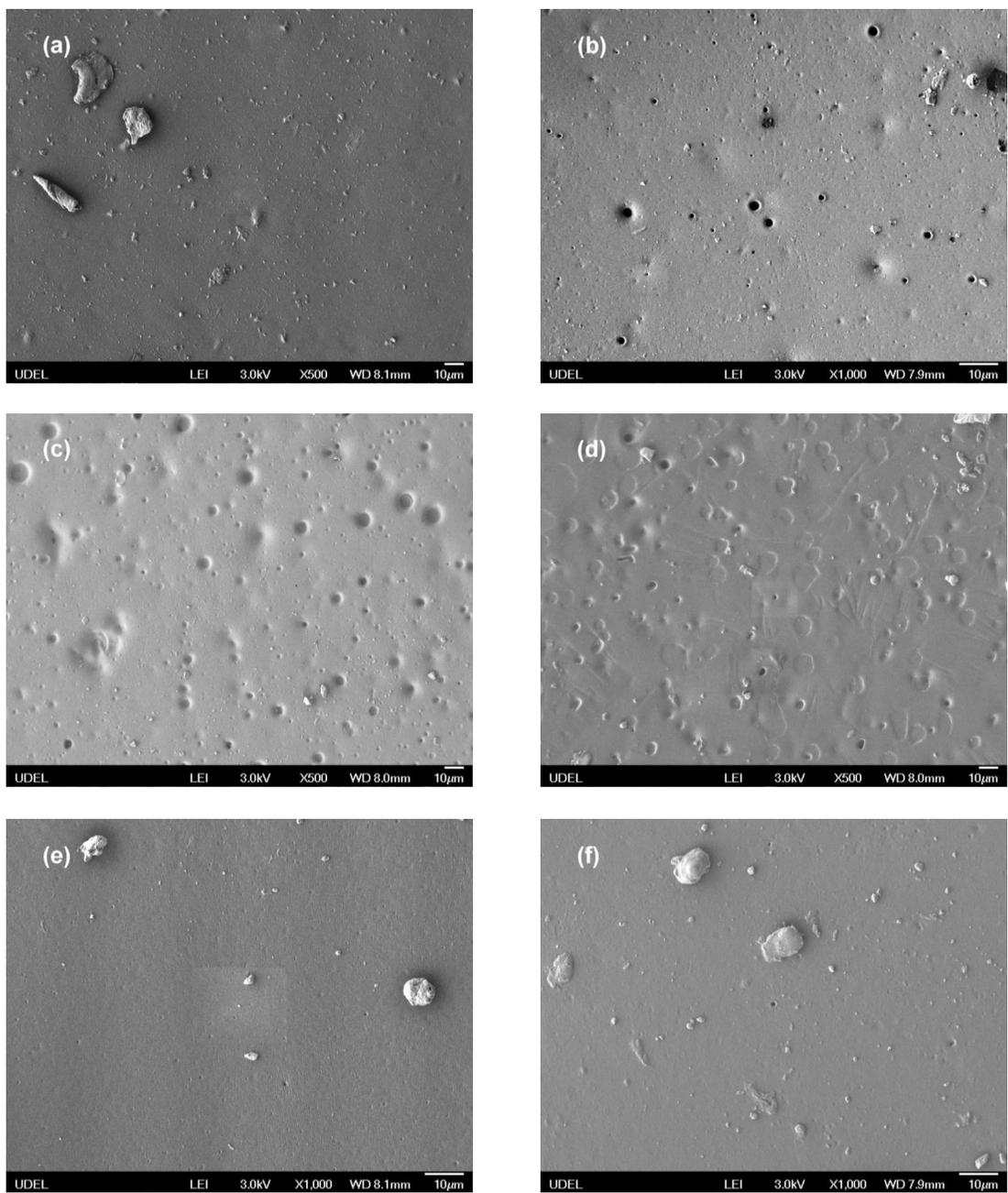


Figure 4.8. SEM images of (a) TEA; (b) TPA; (c) OTMA; (d) DDTMA; (e) BTBA and (f) BDMHA membranes. Experimental Condition: [PVC] = 34.5%; [R<sub>4</sub>N<sup>+</sup>X<sup>-</sup>] = 5.7%; [TBOAC] = 59.8%; THF = 10 mL.

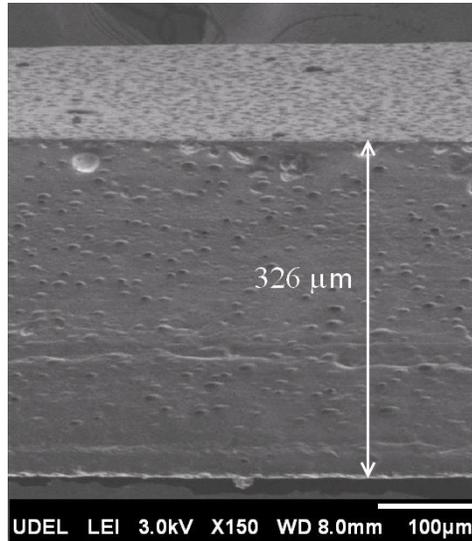
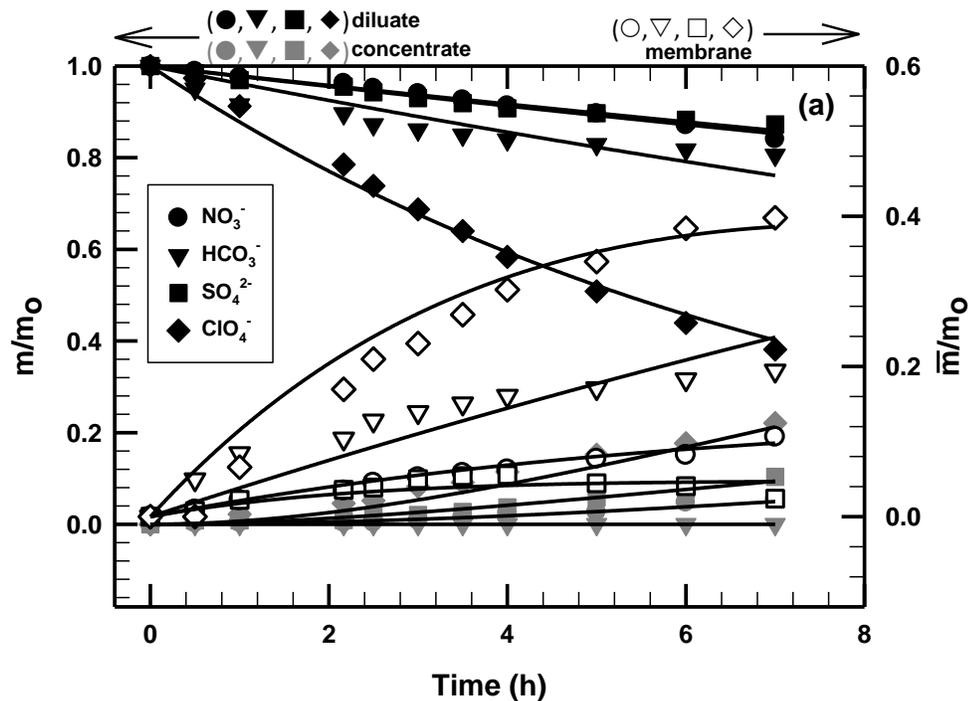


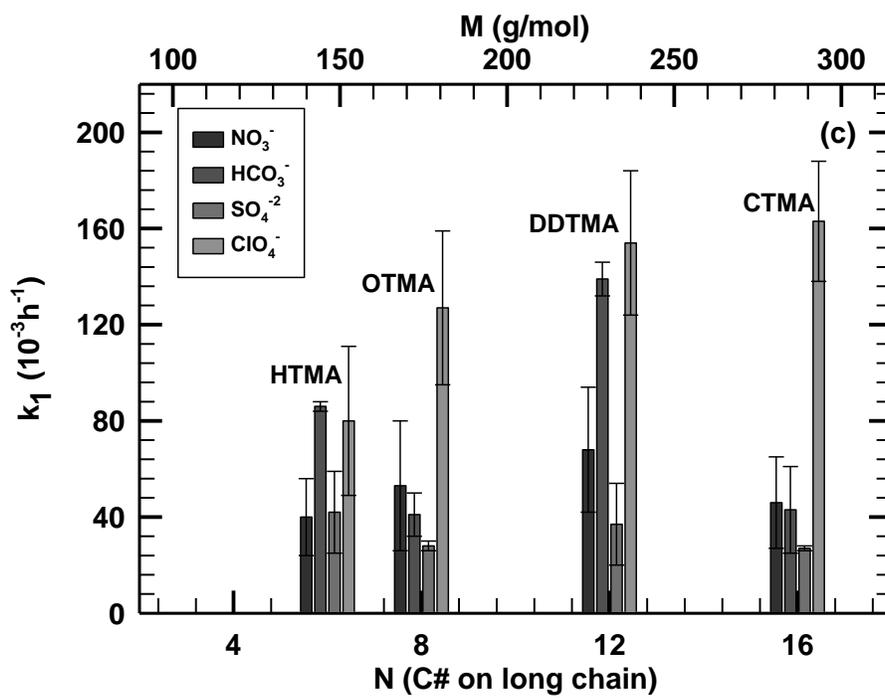
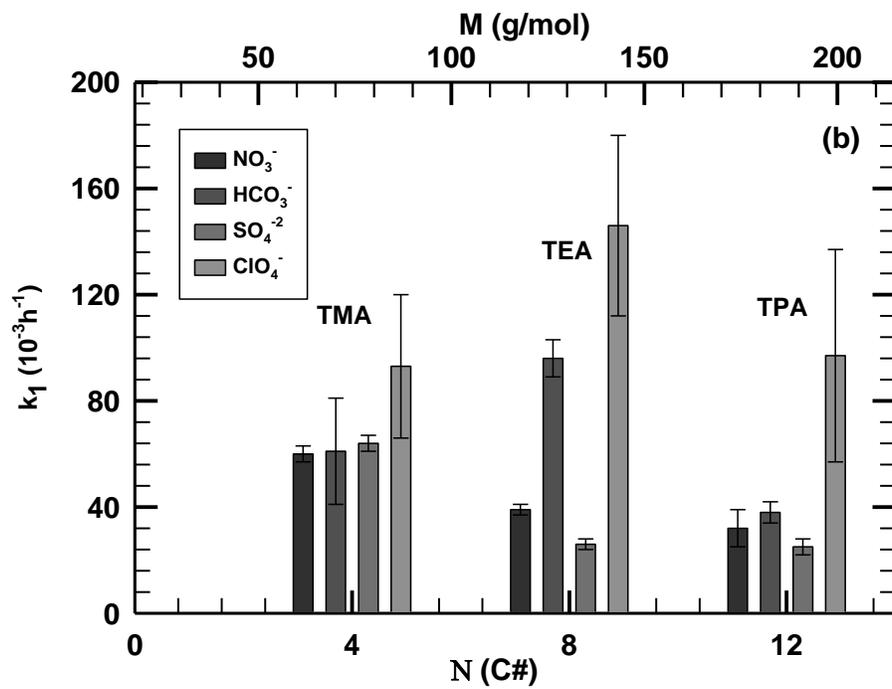
Figure 4.9. Cross-sectional view of MTBA membrane . Experimental Condition: [PVC] = 34.5%; [MTBA] = 5.7%; [TBOAC] = 59.8%; THF = 10 mL.

The cross sectional structure of the membrane was observed using scanning electron microscope (SEM) exemplified by the MTBA-membrane. Fig. 4.9 shows the cross-sectional view of the MTBA-membrane; again this membrane had nodules-like features inside of its structure. Consequently, it is compelled to speculate that it is these inner nodules-like features that not only were responsible for the ion exchange process of anion transport across the membrane under electrostatic field. Further investigation is needed to characterize the chemical composition of nodules-like features. Fig. 4.9 shows the thickness of the membrane, measured to be about 326 μm, which was close to the value obtained from the amount of materials used in the preparation of the membrane (300 μm).

#### 4.4.6 Perchlorate Separation

Fig. 4.10(a) shows electrodialytic separation (constant current operation) of perchlorate (noted as diamond) from water containing major anions, namely  $\text{NO}_3^-$  (noted as circle),  $\text{SO}_4^{2-}$  (noted as square) and  $\text{HCO}_3^-$  (noted as inverted triangle) with MTBA membranes. The black, gray and the open symbols represent the mass of anions in the diluate, the concentrate and the membrane, correspondingly. The initial concentration of perchlorate, nitrate, sulfate and bicarbonate was 1, 10, 4.3 and 9.15 mg/L in the diluate, respectively. The solid lines represent the fitted transport kinetics of anions across the membrane based on the calculated  $k_1$  and  $k_2$  values. With the MTBA membrane, within 7 h, 60% of perchlorate was separated from the solution while only less than 9% of other anions appeared in the diluate.





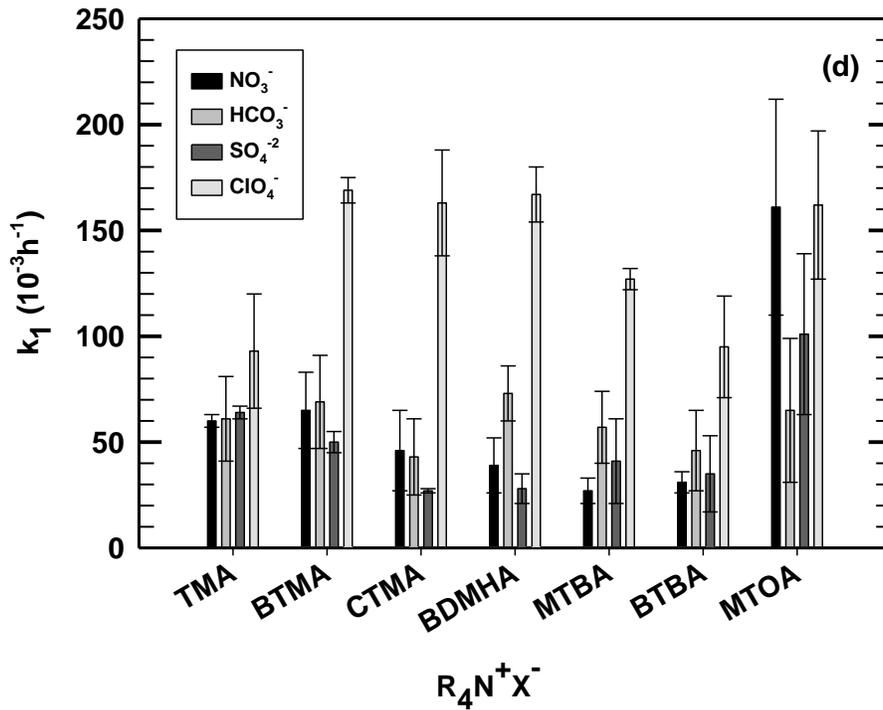
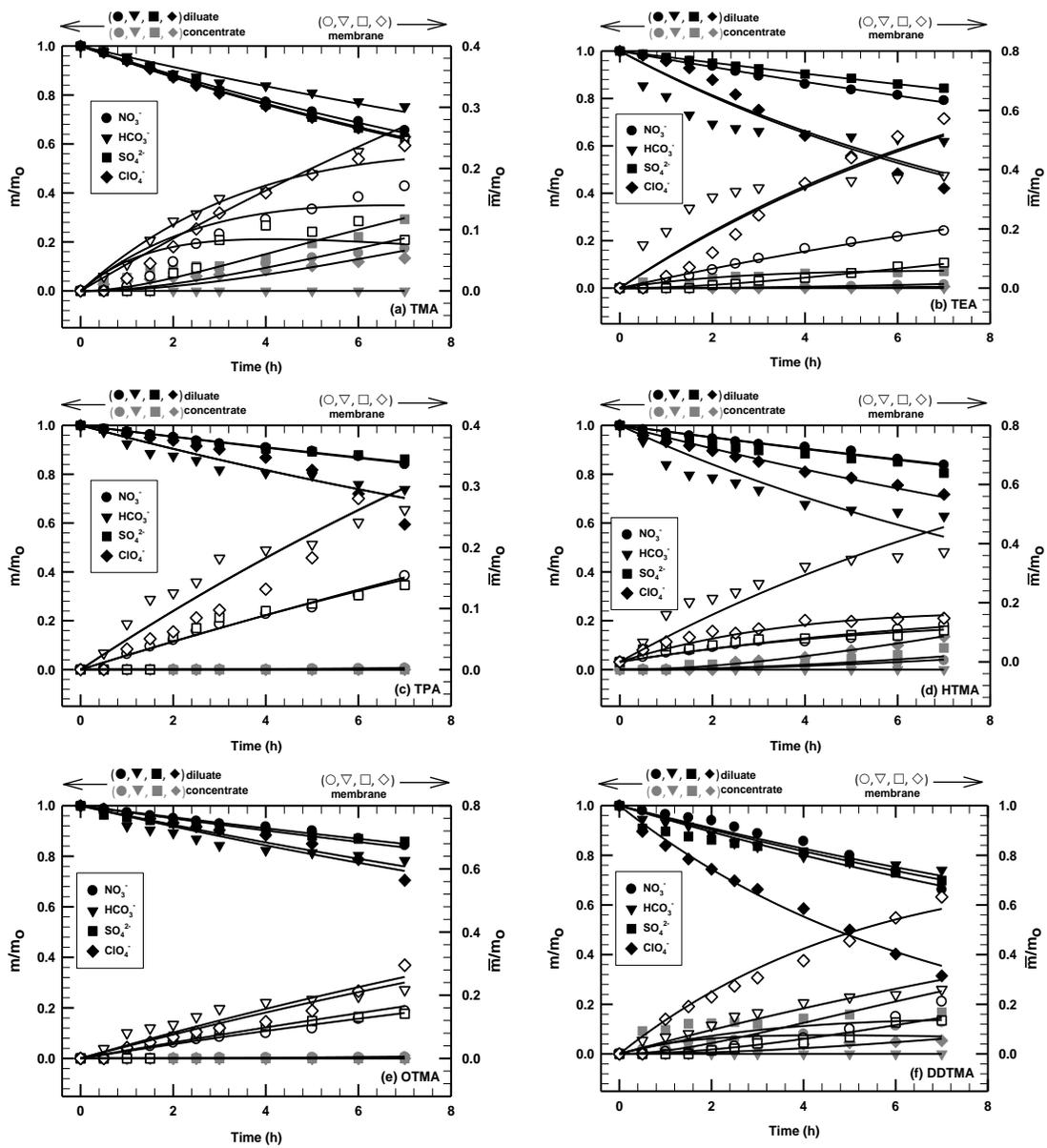


Figure 4.10. Kinetics of ion transport across different membranes. (a) Change of ion concentrations in the dilute and the concentrate streams as a function of time across the MTBA membrane. (b-d)  $k_1$ , rate constant of anions transport from the diluate to the membrane ( $n = 3$ ). Experimental conditions: [Alkalinity] = 15 mg/L as  $\text{CaCO}_3$ ;  $[\text{NO}_3^-] = 10 \text{ mg/L}$ ;  $[\text{SO}_4^{2-}] = 4.3 \text{ mg/L}$ ;  $[\text{ClO}_4^-] = 1.0 \text{ mg/L}$ . Temperature = 21 ~ 23 °C; pH = 5 ~7; ED current = 1 mA.

Results of functionalized membranes on perchlorate separation with ED are also shown in Fig. 4.11(a) to (k). Again, the results were compared by dividing into three groups based on the types of functional groups. Fig. 4.10(b) shows the  $k_1$  values of anions of TMA-, TEA- and TPA-membrane. With Turkey's test, there are no significant ( $\alpha=0.05$ ) differences of  $k_1$  values of perchlorate in the three membranes. However,  $k_1$  values of sulfate and nitrate in TMA membrane were larger than that of

TPA system with p-values <0.0001 and 0.0384, respectively. For amines with one long chain groups, no significant difference of  $k_1$  values of anion among the examined membranes was observed.

Fig. 4.10 (d) showed that the  $k_1$  values of perchlorate of BTMA membrane is significant ( $\alpha=0.05$ ) different from that of TMA membrane with p-value 0.0114. Overall, membranes modified with benzyl groups containing amines, such as BTMA, BDMHA and BTBA showed comparable  $k_1$  value of perchlorate ion with that of MTBA membrane. In addition, MTOA and CTMA also showed larger of perchlorate ion than that of MTBA membrane (Fig. 4.10(d)). However, from ED experiments results (Fig. 4.11(g)-(k)), perchlorate could not pass through the membranes only possessing large  $k_1$  values, effectively. For example, it was found that perchlorate was retained in the MTOA-membrane as mentioned above (contact angle experiments). Although the MTOA membrane (Fig. 4.11(k)) could separate about 80% of perchlorate from the diluate, no detectable concentration of perchlorate was found in the concentrate stream indicating the small  $k_2$  value of perchlorate of MTOA membrane. Moreover, it was shown that the CTMA-membrane had the smallest contact angle among all membranes studied. The highly hydrophilic characteristics of the CTMA-membrane would hinder the passage of the perchlorate ion across the membranes. Table 4.3 summarizes the calculated rate constants ( $k_1$  and  $k_2$ ) of anions across different membranes in the ED system. The  $k_2$  value of perchlorate of MTBA



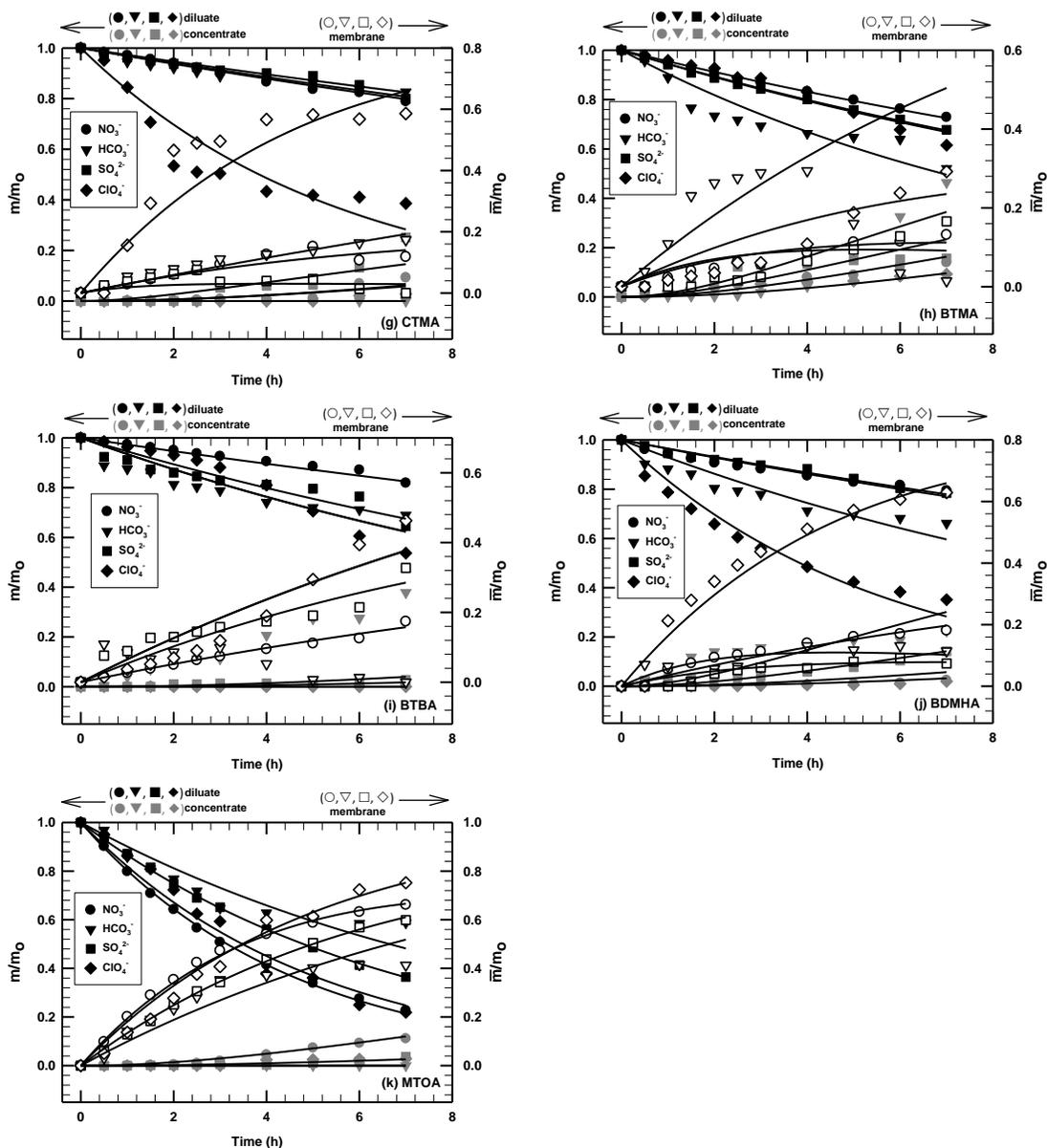


Figure 4.11. Electrodynamic separation of perchlorate from water containing major anions, namely  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$  with different membranes. (a)TMA; (b)TEA; (c)TPA; (d) HTMA; (e)OTMA, (f)DDTMA; (g)CTMA; (h)BTMA; (i)BTBA; (j) BDMHA and (k)MTOA. [Alkalinity] = 15 mg/L as  $\text{CaCO}_3$  (3 mg/L);  $[\text{NO}_3^-] = 10$  mg/L;  $[\text{SO}_4^{2-}] = 4.3$  mg/L;  $[\text{ClO}_4^-] = 1.0$  mg/L. Experimental conditions: Temperature = 21 ~ 23 °C; pH = 5 ~7; ED current = 1mA.

membrane is larger than that of BTMA, BDMHA, BTBA and MTOA membrane. Therefore, both  $k_1$  and  $k_2$  values would influence on the preferential separation of perchlorate over the other anions. The MTBA functionalized PVC membrane was capable of separating perchlorate from other major anions in water effectively.

Table 4.3. Rate constants of anions passed through various membranes in electro dialysis separation (n = 3).

	$k_1 (10^{-3}h^{-1})$				$k_2 (10^{-3}h^{-1})$			
	$NO_3^-$	$HCO_3^-$	$SO_4^{2-}$	$ClO_4^-$	$NO_3^-$	$HCO_3^-$	$SO_4^{2-}$	$ClO_4^-$
TMA	60±3	61±20	64±3	93±27	350±78	0±0	711±155	193±61
TEA	39±2	96±7	26±2	146±34	31±15	1307±777	0±0	2±1
TPA	32±7	38±4	25±3	97±40	64±44	0±0	0±0	5±4
MTBA	27±6	57±17	41±20	127±5	145±32	0±0	403±82	128±15
BTBA	31±5	46±19	35±18	95±24	101±67	0±0	213±80	0±0
BDMHA	39±13	73±13	28±7	167±13	24±22	0±0	0±0	10±8
MTOA	161±51	65±34	101±38	162±35	123±83	0±0	748±56	20±5
BTMA	65±18	69±22	50±5	169±6	484±68	0±0	1971±673	58±3
HTMA	40±16	86±2	42±17	80±31	109±51	0±0	945±343	227±35
OTMA	53±27	41±9	28±2	127±32	0±0	0±0	0±0	0±0
DDTMA	68±26	139±7	37±17	154±30	53±8	1135±230	295±9	13±1
CTMA	48±14	43±18	27±1	163±25	0±0	0±0	0±0	0±0

#### 4.4.7 Perchlorate Permselective Membrane

From above results, it was observed that different  $R_4N^+X^-$  of membrane would show varied physical and chemical properties of the membrane. In general, the membrane with larger  $K_{ClO_4^-,X^-}$  must be able to attract perchlorate ion from solution phase to the one side of membrane surface and then release perchlorate to the other side of the membrane.

The performance of preferential permeation of specific ions by membrane separation can be evaluated by permselectivity factor. The permselectivity ( $K_{A,B}$ ) between two ions (A and B) is defined as (Toshikatsu 2000):

$$K_{A,B} = \frac{\mu_A \bar{C}_A C_B}{\mu_B \bar{C}_B C_A} \quad (4.13)$$

where  $\mu_A$ ,  $\mu_B$  are mobility of ion A and B in the membrane phase ( $cm^2/(V s)$ );  $\bar{C}_A$ ,  $\bar{C}_B$  and  $C_A$ ,  $C_B$  are the concentration of ion A and B in the membrane phase ( $equiv/cm^3$ ) and in the solution phase of the desalting side ( $equiv./cm^3$ ). The perchlorate permselectivity of the membrane was calculated from the results of electro dialysis separation experiments.

It is then hypothesized that strong binding between anion and membrane would not favor transport of anions across the membrane in electrostatic field. Fig. 4.12(a) shows the relationship between  $K_{ClO_4^-,X^-}$  and Ks (adsorption constant). As Ks values increased (Ks: MTOA > TEA > CTMA > DDTMA > TMA > BDMHA > OTMA > BTBA > HTMA > BTMA > TPA > MTBA)  $K_{ClO_4^-,X^-}$  decreased. In contrast, the  $\Gamma_m$  (maximum adsorption capacity) value increased when the  $K_{ClO_4^-,X^-}$  increased as shown in Fig. 4.12 b).

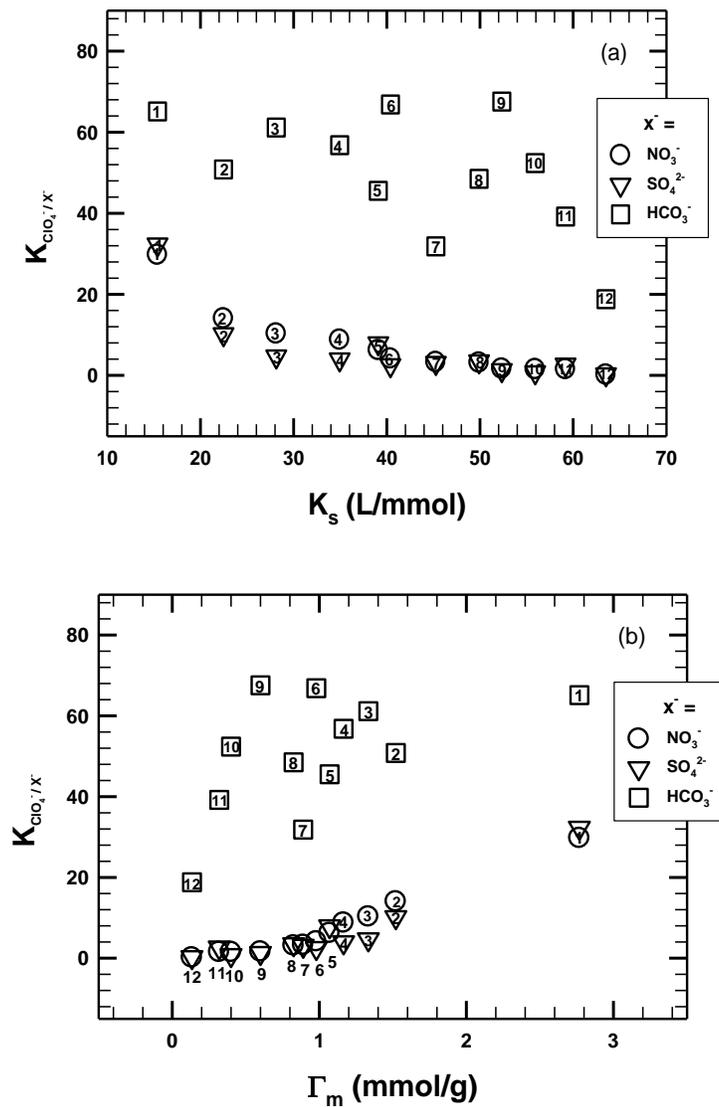
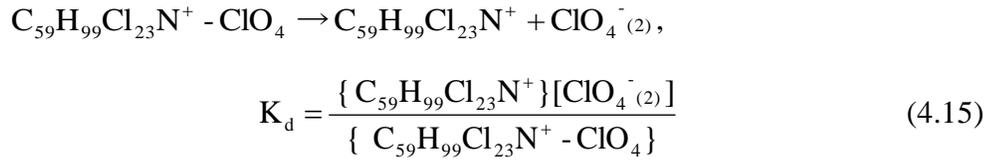
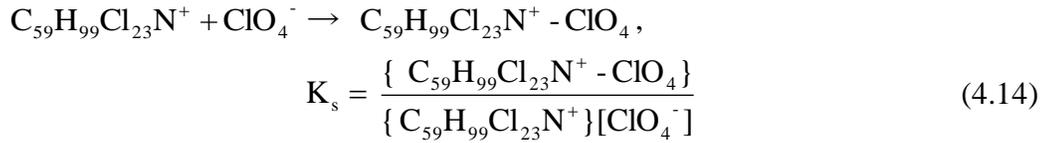


Figure 4.12. Relationship between permselective constant of major anions with respect to perchlorate and (a) maximum adsorption constant and (b) monolayer adsorption capacity corresponding major anions of various [PVC- $R_4N^+X^-$ ] membranes. Experimental Conditions: [PVC] = 34.5%; [ $R_4N^+X^-$ ] = 5.7%; [TBOAC] = 59.8%; THF = 10 mL; ED Current = 1 mA; pH = 6.8; temperature =  $22 \pm 1^\circ C$ ; I = 0.13 mM (NaCl). The numbers in the plot represents different quaternary ammonium salts [ $R_4N^+X^-$ ]: (1)=MTBA; (2)=TPA; (3)=BTMA; (4)=HTMA; (5)=BTBA; (6)=OTMA; (7)=BDMHA; (8)=TMA; (9)=DDTMA; (10)=CTMA; (11)=TEA; (12)=MTOA.

Therefore, the quaternary ammonium salts with high adsorption constant would have low permselectivity. It implies that quaternary ammonium salts of larger  $K_s$ , would bind perchlorate ion firmly on the membrane surfaces instead of allowing the adsorbed perchlorate ion pass through. In addition, for the membrane that exhibits larger perchlorate adsorption density,  $\Gamma_m$ , it means that the perchlorate adsorption has the higher tendency to take place on the surface of membrane. If more perchlorate ions could be hold (but not tightly) on the surface of membrane, then more perchlorate would be able to transport across the membrane in the presence of the electric field. The adsorption and desorption process can be expressed as the following equations,



Where  $\{ C_{59}H_{99}Cl_{23}N^+ \}$  is the concentration of free surface site of the membrane;  $\{ C_{59}H_{99}Cl_{23}N^+ - ClO_4 \}$  is the amount of perchlorate adsorbed on the surface sites of membrane;  $[ClO_4^-]$  and  $[ClO_4^{-(2)}]$  are the equilibrium concentration of perchlorate in the diluted and concentrated phase, respectively. The total concentration of surface site of the membrane can be expressed by following mass balance equation,

$$\Gamma_m = \{ C_{59}H_{99}Cl_{23}N^+ \} + \{ C_{59}H_{99}Cl_{23}N^+ - ClO_4 \} \quad (4.16)$$

By define  $\Gamma = \{ C_{59}H_{99}Cl_{23}N^+ - ClO_4 \}$ , the Eq 4.16 can be rewritten as,

$$\Gamma = \frac{\Gamma_m K_s [ClO_4^-]}{1 + K_s [ClO_4^-]} \quad (4.17)$$

With Eq 4.13 and 4.17, Perchlorate permselectivity of membrane can be expressed as,

$$K_{\text{ClO}_4^-, \text{B}} = \frac{U_{\text{ClO}_4^-} \Gamma_m K_s}{1 + K_s [\text{ClO}_4^-]} \times \frac{C_B}{U_B (C_{\text{RB}})} \quad (4.18)$$

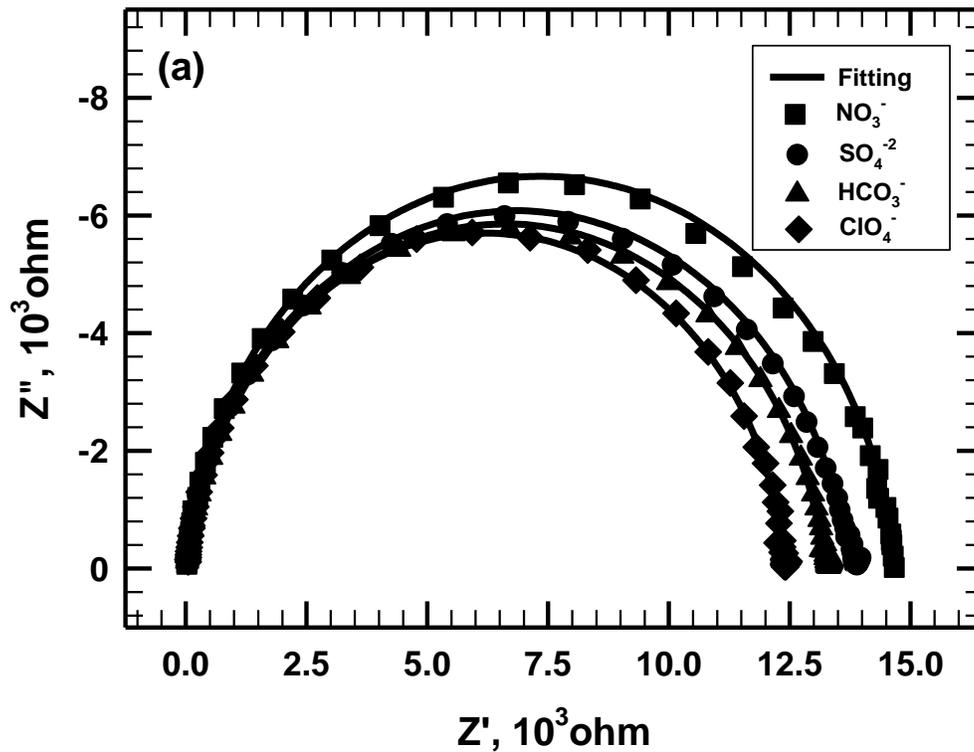
From equation (4.18), it can be found that  $K_{\text{B}}^{\text{ClO}_4^-}$  is in proportional to the value of  $\Gamma_m$ ; and when  $K_s$  is increasing,  $K_{\text{ClO}_4^-, \text{B}}$  would approach to constant. From Fig. 4.12 (a) and (b), it can be seen that as the value of  $K_s$  is increasing, the value of  $K_{\text{ClO}_4^-, \text{B}}$  is decreasing and reaching to a plateau; and  $K_{\text{ClO}_4^-, \text{B}}$  shows linear proportion to the value of  $\Gamma_m$ .

In addition, electro impedance spectroscopy (EIS) would explain the charge transport of ion across membrane in more details (Sistat, Kozmai et al. 2008). Fig. 4.13(a) shows the Nyquist plots of the impedance spectrums for MTBA membrane in 0.1 M  $\text{NaNO}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{NaHCO}_3$  and  $\text{NaClO}_4$ , respectively. The imaginary component of impedance ( $Z''$ ) is plotted against the real component ( $Z'$ ) of impedance as a function of frequency. The semi-circle represents the response of an equivalent electrical circuit including a resistor-capacitor parallel combination. The overall charge transport processes can be modeled by an equivalent circuit that consists of two resistors and one constant phase element (CPE) as shown in Fig. 4.13(b). The impedance of the equivalent circuit can be expressed by the following equation:

$$Z = R_1 + \frac{R_2}{1 + R_2 T (j\omega)^P} \quad (4.19)$$

where  $Z$  is impedance,  $R_1$  represents the resistance of bulk solution,  $R_2$  is the resistance of membrane-solution interface,  $\omega$  is angular frequency ( $= 2\pi f$ ),  $T$  is admittance ( $1/Z$ ),  $P$  is capacitance dispersion index of the constant phase element. The value of  $P$  is between -1 and 1. When  $P$  equals to 1, 0 or -1, CPE behaves as a capacitance, resistance or conductance, respectively. From the equivalent circuit, the existence of CPE indicates the non-homogeneity in the system. In Table 4.4, the  $P$

value ranges from 0.9237 to 0.9489. It is known that a rough or porous surface can cause a double-layer capacitance to appear as a constant phase element with a P value between 0.9 and 1 (Park, Choi et al. 2006; Moya 2012). Therefore, the fitting P values are in accordance to the results from SEM image, BET and AFM surface analysis of MTBA membrane that the surface of membrane is non-homogenous. Furthermore, the resistance of perchlorate solution ( $R_1$ ) is the largest among the other anions solution; however, the resistance of membrane-solution interface ( $R_2$ ) in perchlorate solution was the smallest among the other anions. It implied that although the mobility of perchlorate is slowest in the bulk solution, once perchlorate ion was closed the surface of membrane with the existence of electric field and MTBA, perchlorate ion can be transported through the membrane more feasible than the other anions.



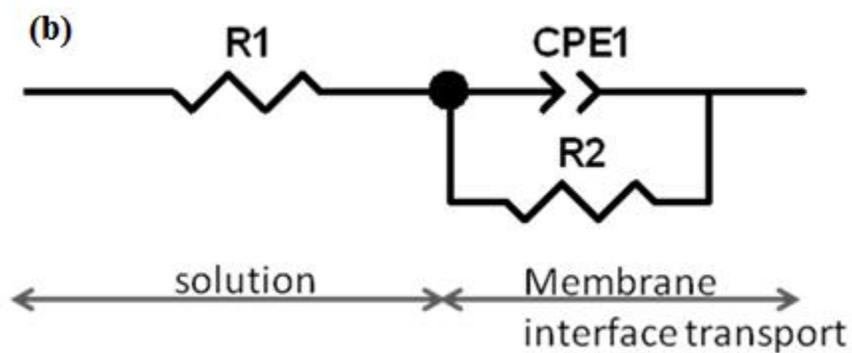


Figure 4.13. (a) Nyquist plots of the impedance spectrums for PVC-MTBA membrane in 0.1 M of  $\text{NaNO}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{NaHCO}_3$  and  $\text{NaClO}_4$  electrolyte, respectively. (b) The equivalent circuit of PVC-MTBA membrane based on EIS data. Experimental Conditions: Scan frequency = 0.1 to  $5 \times 10^5$  Hz; membrane area =  $38.48 \text{ cm}^2$ .

Table 4.4. Values of electrochemical parameters obtained by fitting the experimental impedance data.

Parameters	$\text{ClO}_4^-$	$\text{NO}_3^-$	$\text{HCO}_3^-$	$\text{SO}_4^{2-}$
R1	35.54	14.60	12.86	10.48
R2	$1.23 \times 10^4$	$1.47 \times 10^4$	$1.32 \times 10^4$	$1.38 \times 10^4$
T	$5.64 \times 10^{-9}$	$1.06 \times 10^{-8}$	$7.90 \times 10^{-9}$	$7.97 \times 10^{-9}$
P	0.949	0.940	0.924	0.925
C	$8.76 \times 10^{-11}$	$1.58 \times 10^{-10}$	$9.64 \times 10^{-11}$	$9.88 \times 10^{-11}$

R: resistor (ohm);  
T: admittance (mho);  
P: capacitance dispersion index of the constant phase element (P value is between -1 and 1)  
C: capacitance (F)

## 4.5 Summary

In this study, novel perchlorate-permselective membranes were synthesized via functionalizing PVC polymer with quaternary ammonium salts. The perchlorate permselectivity of the membrane was governed by both the physical and the chemical characteristics of the polymer and its endowed functional groups. Based on the physical structure, the results showed that the perchlorate permselectivity of the membrane could be enhanced as the thickness and the polymer content were increased. However, the electric resistance of the membrane could also be increased as membrane became structurally denser and thicker. With 34.5 wt% of PVC polymer and thickness control at c.a. 300  $\mu\text{m}$ , the membrane demonstrated homogeneous structure, which enabled effective transport of ions.

In addition, the physical and chemical properties derived from the endowed functional groups in the membrane would determine the permselectivity of membrane. Regardless of the large hydration size of perchlorate, larger than that of nitrate, sulfate and bicarbonate ion, the physical and chemical affinity contributed from the quaternary ammonium salts in the membrane structure could selectively separate perchlorate from the other anions under electrostatic field. FTIR and SEM results showed the changes of PVC polymer in terms of wavenumber shift and surface feature through the incorporation of quaternary ammonium salts into the polymer structure. MTBA compound with moderate chain length offered steric effect for perchlorate separation and balanced both the selectivity and the kinetic rate on adsorption and desorption of the perchlorate. The surface hydrophobicity of MTBA membrane increased slightly after electrodialysis which means most of perchlorate molecule

could be transported through the membrane feasibly while very small amount of perchlorate ion was retained on the membrane surface.

A mathematical model for transport kinetics of anions across the membrane was developed and successfully used to calculate the rate constants of anions passing through the membranes. Thus, it has been shown that 60% of perchlorate while 9% of other anions could be separated by MTBA membrane in electro dialysis process. The findings of this study could lead to a better, sustainable method for separation of perchlorate from drinking water source using electro dialysis without adding additional chemicals. The concentrated perchlorate solution could be collected for the purpose of further treatment or reuse.

## REFERENCES

- Barrett, E. P., L. G. Joyner, et al. (1951). "The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms." *Journal of the American Chemical Society* 73(1): 373-380.
- Gu, B. H., G. M. Brown, et al. (2007). "Treatment of perchlorate-contaminated groundwater using highly selective, regenerable ion-exchange technologies." *Environmental Science & Technology* 41(17): 6277-6282.
- Hwang, G. J. and H. H. Ohya (1998). "Preparation of anion-exchange membrane based on block copolymers Part 1. Amination of the chloromethylated copolymers." *Journal of Membrane Science* 140(2): 195-203.
- Kesore, K., F. Janowski, et al. (1997). "Highly effective electro dialysis for selective elimination of nitrates from drinking water." *Journal of Membrane Science* 127(1): 17-24.
- Klaysom, C., S. H. Moon, et al. (2011). "Preparation of porous ion-exchange membranes (IEMs) and their characterizations." *Journal of Membrane Science* 371(1-2): 37-44.
- Mahmudov, R. and C. P. Huang (2010). "Perchlorate removal by activated carbon adsorption." *Separation and Purification Technology* 70(3): 329-337.
- Moya, A. A. (2012). "Electric circuits modelling the low-frequency impedance of ideal ion-exchange membrane systems." *Electrochimica Acta* 62: 296-304.
- Moyer, B. A. and P. V. Bonnesen (1997). *Physical Factors in Anion Separations. Supramolecular Chemistry of Anions*. A. Bianchi, K. Bowman-James and E. Garcia-Espana. New York, Wiley-VCH: 1-44.
- Nagarale, R. K., G. S. Gohil, et al. (2006). "Recent developments on ion-exchange membranes and electro-membrane processes." *Advances in Colloid and Interface Science* 119(2-3): 97-130.
- Park, J.-S., J.-H. Choi, et al. (2006). "An electrical impedance spectroscopic (EIS) study on transport characteristics of ion-exchange membrane systems." *Journal of Colloid and Interface Science* 300(2): 655-662.

- Rajendran, S., M. R. Prabhu, et al. (2008). "Characterization of PVC/PEMA based polymer blend electrolytes." *International Journal of Electrochemical Science* 3(3): 282-290.
- Ramesh, S., K. H. Leen, et al. (2007). "FTIR studies of PVC/PMMA blend based polymer electrolytes." *Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy* 66(4-5): 1237-1242.
- Roach, J. D., R. F. Lane, et al. (2011). "Comparative study of the uses of poly(4-vinylpyridine) and poly(diallyldimethylammonium) chloride for the removal of perchlorate from aqueous solution by polyelectrolyte-enhanced ultrafiltration." *Water Research* 45(3): 1387-1393.
- Roach, J. D. and D. Tush (2008). "Equilibrium dialysis and ultrafiltration investigations of perchlorate removal from aqueous solution using poly(diallyldimethylammonium) chloride." *Water Research* 42(4-5): 1204-1210.
- Roquebert, V., S. Booth, et al. (2000). "Electrodialysis reversal (EDR) and ion exchange as polishing treatment for perchlorate treatment." *Desalination* 131(1-3): 285-291.
- Sata, T. (2000). "Studies on anion exchange membranes having permselectivity for specific anions in electrodialysis - effect of hydrophilicity of anion exchange membranes on permselectivity of anions." *Journal of Membrane Science* 167(1): 1-31.
- Sata, T., K. Mine, et al. (1998). "Changing permselectivity between halogen ions through anion exchange membranes in electrodialysis by controlling hydrophilicity of the membranes." *Journal of the Chemical Society, Faraday Transactions* 94(1): 147-153.
- Sata, T., T. Sata, et al. (2002). "Studies on cation-exchange membranes having permselectivity between cations in electrodialysis." *Journal of Membrane Science* 206(1-2): 31-60.

- Sata, T., K. Teshima, et al. (1996). "Permeability between two anions in anion exchange membranes crosslinked with various diamines in electrodialysis." *Journal of Polymer Science, Part A: Polymer Chemistry* 34(8): 1475-1482.
- Sata, T., T. Yamaguchi, et al. (1995). "Anion exchange membranes for nitrate ion removal from groundwater by electrodialysis." *Journal of the Chemical Society, Chemical Communications*(11): 1153-1154.
- Sistat, P., A. Kozmai, et al. (2008). "Low-frequency impedance of an ion-exchange membrane system." *Electrochimica Acta* 53(22): 6380-6390.
- Sobolev, V. D., V. M. Starov, et al. (2003). "On the accuracy of measuring small contact angles by the sessile drop method." *Colloid Journal* 65(5): 611-614.
- Soman, V. V. and D. S. Kelkar (2009). "FTIR Studies of Doped PMMA - PVC Blend System." *Macromolecular Symposia* 277(1): 152-161.
- Strathmann, H. (2010). "Electrodialysis, a mature technology with a multitude of new applications." *Desalination* 264(3): 268-288.
- Toshikatsu, S. (2000). "Studies on anion exchange membranes having permeability for specific anions in electrodialysis ??effect of hydrophilicity of anion exchange membranes on permeability of anions." *Journal of Membrane Science* 167(1): 1-31.
- Vanýsek, P. (2002). *Ionic conductivity and diffusion at infinite dilution*. Boca Raton, CRC Press.
- Wang, P.-Y., S. I. Shah, et al. (2013). "A polymeric membrane electrode for the detection of perchlorate in water at the sub-micro-molar level." *Analytical Methods* 5(14): 3530-3537.
- Xie, Y., S. Li, et al. (2011). "A hybrid adsorption/ultrafiltration process for perchlorate removal." *Journal of Membrane Science* 366: 237-244.
- Yoon, J., Y. Yoon, et al. (2003). "Use of surfactant modified ultrafiltration for perchlorate (ClO<sub>4</sub><sup>-</sup>) removal." *Water Research* 37(9): 2001-2012.
- Yoon, Y., G. Amy, et al. (2002). "Transport of perchlorate (ClO<sub>4</sub><sup>-</sup>) through NF and UF membranes." *Desalination* 147(1??): 11-17.

Yoon, Y., G. Amy, et al. (2005). "Effect of pH and conductivity on hindered diffusion of perchlorate ions during transport through negatively charged nanofiltration and ultrafiltration membranes." *Desalination* 177(1??): 217-227.

## CATALYTIC ELECTROCHEMICAL REDUCTION OF PERCHLORATE WITH METALLIC DOPED ELECTRODE

### 5.1 Abstract

Mono metallic (Mo, Ru, Rh, Cu, Pd), bimetallic (Rh\_Cu, Rh\_Ru) catalysts were prepared for perchlorate reduction in the study. The electrodes were characterized for surface structure and chemical composition using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The results showed that with applying the same current and pH in the system, perchlorate reduction efficiency of mono metallic doped electrodes were in the order of Rh>Cu>Ru>Mo>Pd. For bi-metallic elements doped electrodes, Rh\_Cu (75% reduction) is greater than Rh\_Ru (60% reduction) doped electrode. The mass balance of chlorine species (chloride and perchlorate) in the system can be up to 95%. The imbalance part of chlorine species mass would be due to the adsorption of perchlorate by the electrode. The testing results of the catalytic electrochemical technique showed its suitability for reduction of perchlorate. X-ray photoelectron spectroscopy (XPS) analysis of the bimetallic catalyst indicated the presence of metal oxide and elemental metals. X-ray diffraction (XRD) spectra showed the presence of both crystalline and amorphous metallic catalysts.

## 5.2 Introduction

Electrochemical reduction is an easy process and has high public recognition. Electrochemical reduction of perchlorate is practically attractive. The reduction potential of perchlorate is 1.38 V (Eq.5.1) which indicates the reaction is thermodynamically favorable.



However, perchlorate reduction to chloride by this reaction does not occur spontaneously at ambient temperatures due to the chemical inertness of perchlorate makes the reaction rate extremely slow. The aim of this work was to explore the reduction of perchlorate in electrochemical system using both mono-metallic and bimetallic catalysts. The electrode materials were characterized via X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and scanning electron microscope (SEM) as to compare the effect of electrode material on perchlorate reduction. The cyclic voltammetric experiments were performed to establish the potential corresponding to the reduction reaction. Reduction products of perchlorate were analyzed by using ion chromatography.

## 5.3 Materials and Methods

### 5.3.1 Chemicals and Reagents

All chemicals were either of analytical or reagent grade, or the highest purity available from suppliers. All aqueous solutions were prepared with de-ionized, distilled water. The certified standard perchlorate ( $\text{ClO}_4^-$ ) solution was purchased from SPEX CertiPrep (Metuchen, NJ, USA). Sodium perchlorate (ACS reagent, >98 %, Sigma-Aldrich, St. Louis, MO, USA), sodium bicarbonate (analytical grade ACS, 99.7 %), sodium chloride (reagent grade ACS, >99 %), sodium nitrate (analytical

grade ACS, >99 %) from Acros Organics, sodium carbonate (HPLC grade), sodium sulfate (certified ACS) from Fisher Scientific were individually dissolved into deionized water to prepare stock solutions. NaOH (50% w/w, Fisher Scientific, Fair Lawn, NJ, USA) was used as mobile phase solution in ion chromatography analysis.

### **5.3.2 Preparation of Metallic Catalysts**

The stainless steel (SS) mesh (30.6% opening) was immersed in the 0.01 M sulfuric solution for cleaning. After cleaning, the meshes were rinsed with deionized water. Each mesh was dried in the dryer for 1 h and weighted before coating of the catalyst. The metal ion solutions were prepared by dissolving the metal salts in deionized water at concentration range from 0.01 mM to 0.4 M depending on the solubility of the metal salts (Mo, Ru, Rh, Cu, Pd). The washed SS mesh was then immersed in the metal solution as the cathode and graphite as the anode in a two-electrode potentiostat system (Model WP705B, Vector-VID). A direct current potential was applied at a constant current of 30 to 60 mA. After electroplating, the catalyst coated SS mesh was washed with deionized water again and dried in an oven (300K). In this study, mono metallic, bimetallic catalysts were prepared in the similar way as stated above.

### **5.3.3 Cyclic Voltammetry Experiments**

The three electrodes were connected to a potentiostat (model AFRDE 4, Pine Instrument Inc., USA), which controlled the applied voltage and recorded corresponding current. The stainless steel supported mono metallic or bimetallic electrode was used as working electrode (area = 1.2 cm<sup>2</sup>). A platinum wire and a saturated calomel electrode (SCE) were used as the counter electrode and reference

electrode, respectively. The reaction vessel was a 250-mL beaker. The concentration of NaClO<sub>4</sub> or HClO<sub>4</sub> solution was in the range of 5 to 29 mM. Voltammetry experiments were operated at sweep rate of 0.05 V/s between 1.0 V to -1.0 V (vs. SCE) to evaluate the activity of the electrode in terms of perchlorate reduction. In all cases, the voltammetric experiments were scanned at least 3 times in this potential range to achieve a stable potential-current curve.

#### **5.3.4 Surface Characterization**

The microstructure and surface property of catalysts was examined by SEM/EDS, XRD and XPS analyses. The SEM/EDS analysis was performed by a JSM-7400F scanning electron microscope with a resolution of 1 nm at 15 kV. An XEDS detector was used to detect the elements of the solid product. The crystal structures of the catalysts were characterized by X-ray diffraction (Rigaku D-Max B) with Cu K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) operating at a voltage of 30 kV and a current of 30 mA. Samples were also analyzed by Bragg Brentano geometry and are scanned with 0.05-step size between 20° and 80°. The chemical composition of the solid byproduct was studied by X-ray photoelectron spectra with Omicron surface science instruments (Omicron EA125). The system pressure was maintained at  $1-3 \times 10^{-8}$  Torr during the acquisition of the spectra. M-monochromatic Al X-rays (1486.5 eV) were employed and C 1s peak related to the C-C bond located at 284.6 eV was used as a reference peak for calibration. The resulting spectra were fitted by XPSPEAK with Shirley background.

### 5.3.5 Electrochemical Reduction System

A two chambers reactor was used in perchlorate electrochemical reduction study (see Fig. 5.1). Anode and cathode chambers were separated by a Nafion N117 membrane (Ion Power, Inc., New Castle, DE) in order to isolate anodic and cathodic reactions. The prepared mono-metallic or bimetallic electrode was placed in one chamber with perchlorate solution as the cathode and a graphite electrode was placed in the other chamber with 1 mM  $\text{H}_3\text{PO}_4$  solution as the cathode. A direct current potential was applied at a constant current of 20 mA (Model WP705B, Vector-VID). Perchlorate solution in cathodic chamber was sampled for analysis. The pH of cathodic chamber was controlled by adding acids or bases for reduction reaction. The temperature of the reactor during reaction was regulated by the water jacket.

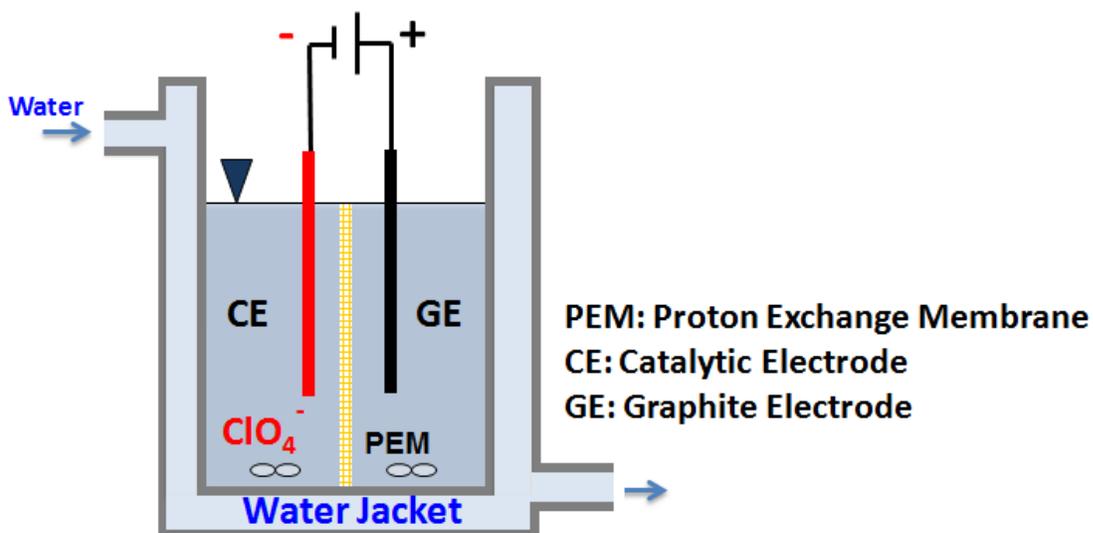


Figure 5.1. Electrocatalytic reactor for reduction of perchlorate.

### **5.3.6 Analytical Method**

A Dionex DX500 (CA, USA) ion chromatography system equipped with Dionex AS40 auto-sampler and the guard column (IonPac AG16, 50mm×4mm) and analytical column (IonPac AS16, 250mm×4mm) was used to analyze the chloride, chlorite, chlorate and perchlorate in this study. The Anion Self Regenerating Suppressor (ASRS300, Dionex, CA, USA) was operated in the external water mode with 300mA current. An oven module was incorporated to keep the analytical columns and suppressor at 30°C and the temperature of conductivity detector cell is fixed at 35°C. A computer with PeakNet software (version 5.1) was utilized to control the instrument and to process data. Dionex auto-sampler vials (5ml volume with 20µm filter caps) were used to filter all samples and standards before analysis. The effluent mobile phase was a mixture of deionized water and 50 mM NaOH and the flow rate is set at 1 mL/min. The injection volume is 25 µL and the total analysis time for each sample is 30 minutes.

## **5.4 Results and Discussion**

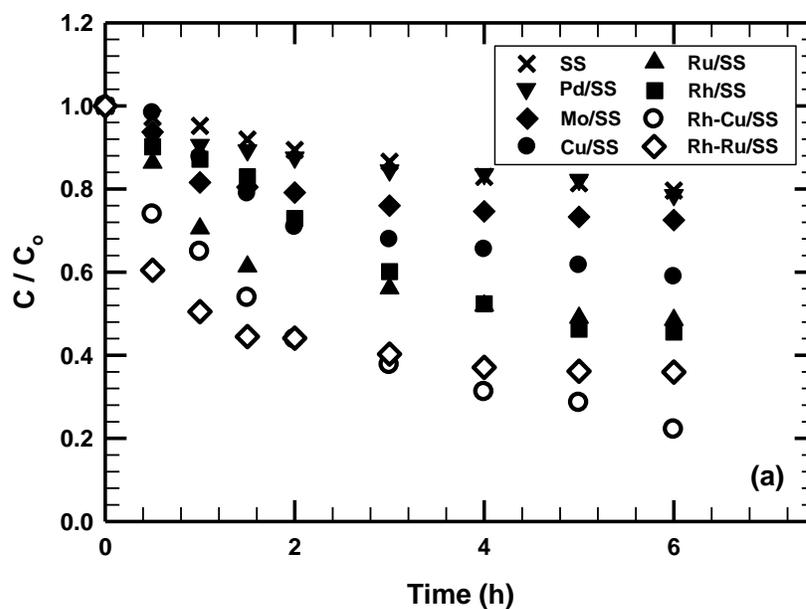
### **5.4.1 Reduction of Perchlorate**

To improve the reduction efficiency of the electrodes, various catalysts with different combinations were examined in this study. Two types of electrodes were investigated, (1) mono-metallic element electrode, namely Mo, Ru, Rh, Cu, Pd doped electrode and (2) bimetallic elements doped electrodes, namely Rh\_Ru, Rh\_Cu doped electrode. Fig. 5.2(a) shows the reduction of perchlorate with different catalysts. Fig. 5.2(b) shows the concentration of chloride in reduction reactor with different catalysts. pH of solution was controlled at 3.4 with phosphoric acids in the reactor. Also, a blank stainless steel mesh electrode without catalyst was used as the control group. With the

lowest oxidation number -1, chloride ion is the final reduction product of perchlorate. It is noted that chloride ion was the only reduction product observing in this study. No other oxyanions of chlorine, such as  $\text{ClO}_3^-$ ,  $\text{ClO}_2^-$  or  $\text{ClO}^-$  was detected as the intermediates during the reduction process. This implies that those intermediates are kinetically much less stable than perchlorate and they are reduced to chloride ion completely and immediately. Similar observation was also reported in the Pd/IX-E heterogeneous catalytic reduction of perchlorate (Kim and Choi 2014). In this study, under the same current and pH condition in the system, within six hours, perchlorate reduction efficiency of mono metallic doped electrodes were in the order of Rh(56%)> Ru(45%)>Cu(37%)> Mo~Pd(21%)>SS(17%). The control group (SS blank electrode) also showed the ability of perchlorate reduction. It was found later by element analysis that SS contained 1.20% of Al as one of the compositions (Table 5.1). And Al was shown (Painot and Augustynski 1975) to have the occurrence of the perchlorate reduction process. Among the five examined metallic catalysts, Rh had the highest perchlorate reduction efficiencies; lots of literatures (Rhee, Wasberg et al. 1991; Zelenay, Horanyi et al. 1991; Wasberg and Horányi 1995; Láng and Horányi 2003; Láng, Sas et al. 2008) have shown that rhodium has promising perchlorate reduction rate due to its crystalline structures. It was reported that the catalytic rate order is Rh(100) ~Rh(polycrystalline) > Rh(111)(Rhee, Wasberg et al. 1991). The physical characterization of the electrode will be discussed later. In addition, Ru has been reported to have perchlorate reduction and the process can be enhanced by increasing temperature and perchlorate concentration (Colom and González-Tejera 1985).

From the above results, three metallic catalysts, rhodium, ruthenium and copper which showed high perchlorate reduction efficiencies were chosen for

fabrication of bimetallic elements doped electrodes. As shown in Fig. 5.2(b), the reduction efficiency of  $Rh_{0.11}-Cu_{0.89}$  (78% reduction) is greater than that of Rh-Ru (60% reduction) doped electrode. Rh-Cu alloys were tested for the reduction of nitrates (Witonska, Karski et al. 2007) and found to have significant catalytic activity for oxyanion reduction than Pd-Cu, Pt-Cu, and Ir-Cu. It was found that combination of noble metals such as Rh, Ru, Pd or Pt with the transition metals (Cu, Fe, Sn or Ni) can greatly enhance catalytic efficiency than the monometallic catalysts. The role of the transition metal serves as promoter to increase the hydrogenation process. (Olívia Salomé G. P. Soares, José J. M. Órfão et al. 2008; Olívia Salomé G.P. Soares, José J.M. Órfão et al. 2009; Comisso, Cattarin et al. 2012). Therefore, Rh would be served as an oxygen atom transfer center for perchlorate to form a perchlorato-complex and Cu would be served as hydrogenation promoter to process hydrogenation reaction.



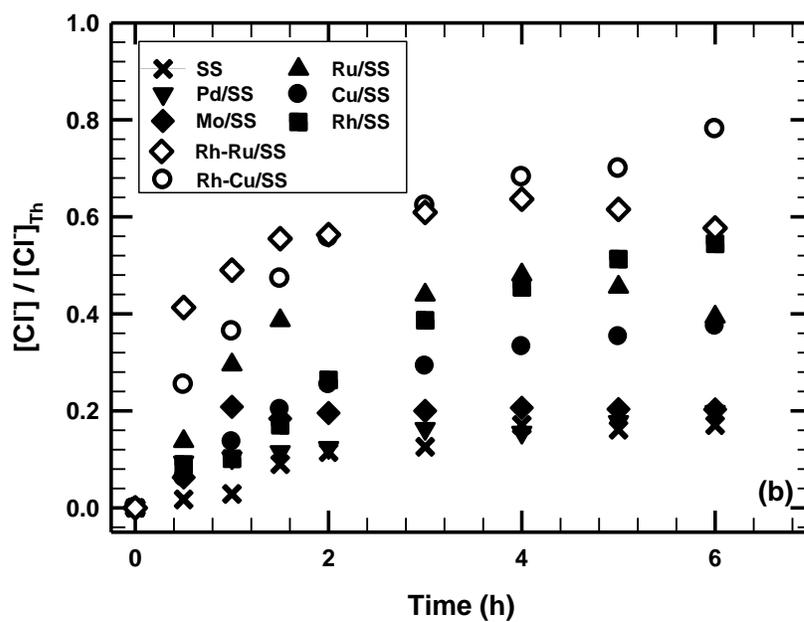


Figure 5.2. (a) Electrochemical reduction of perchlorate and (b) formation of chloride with various catalytic electrodes. Experimental conditions:  $[\text{ClO}_4^-] = 10$  mM; catalytic cathode = various metals, anode = graphite; current = 20 mA;  $T = 298\text{K}$ ;  $\text{pH} = 3.4$ .

Table 5.1. Elements composition of various electrodes.

Elements	Atomic% of Electrode							
	Blank (SS)	Cu/SS	Rh/SS	Pd/SS	Ru/SS	Mo/SS	Rh-Ru/SS	Rh <sub>0.11</sub> - Cu <sub>0.89</sub> /SS
Al	1.23	--	--	--	--	--	--	0.71
Cl	1.45	--	--	--	--	1.37	4.51	2.43
Cr	18.56	--	31.26	4.11	9.53	16.96	11.93	12.20
Mn	2.17	--	--	--	0.71	1.21	--	1.35
Fe	41.64	--	19.77	5.78	15.00	29.00	17.65	19.37
Ni	8.20	--	6.57	1.65	3.97	8.66	4.66	3.79
Cu	--	68.96	--	--	--	--	--	45.17
Rh	--	--	42.41	--	--	--	9.14	5.77
Pd	--	--	--	88.46	--	--	--	--
Ru	--	--	--	--	70.79	--	7.72	--
Mo	--	--	--	--	--	17.52	--	--
C	26.74	31.04	--	--	--	25.27	44.39	9.21

## 5.4.2 Electrode Characterizations

The images of the catalytic electrodes were observed using SEM to reveal the morphology and the degree of surface coverage of the metallic catalysts on surface. Here, five mono-metallic element doped electrodes (Mo, Ru, Rh, Cu, Pd) and two bimetallic element doped electrode (Rh-Ru, Rh-Cu) were present in the Fig. 5.3. Without any metallic-elements, the surface of the electrode is relative smooth as shown in Fig. 5.3(a). After electrodeposition with different metallic particles, the surface of electrode posses different extent of roughness and distinct features as shown in Fig. 5.3(b) – (h). For example, Rh shows the nano crystal clusters on the surface of the support; Cu shows cubic crystalline structure; Pd shows nano-flowers like feature. And Rh-Cu shows the combination of cubic structures and crystal clusters. In addition, the sizes of the catalysts were in the range from 50 nm to several hundred nm.

(a) SS



(b) Rh/SS



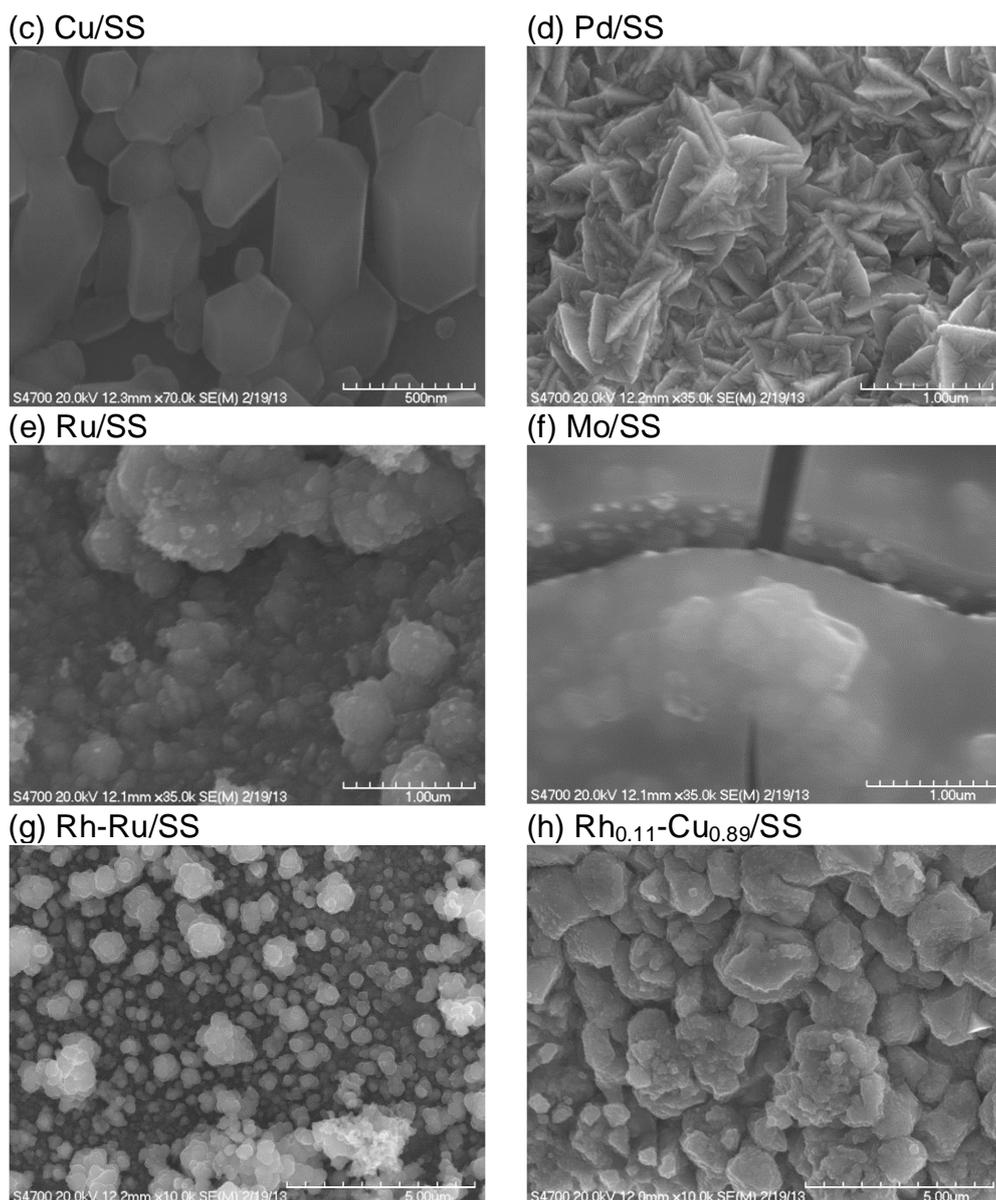


Figure 5.3. SEM images on the surface of various metals doped electrodes. (a) stainless steel; (b) Rh/SS; (c) Cu/SS; (d) Pd/SS; (e) Ru/SS; (f) Mo/SS; (g) Rh-Ru/SS and (h) Rh<sub>0.11</sub>-Cu<sub>0.89</sub>/SS.

The presence of the metallic catalysts on the SS surface was shown in Table 5.1, which gives the atomic distribution of various metals on the catalytic electrode surface using X-ray dispersive energy spectroscopy (EDS) technique.

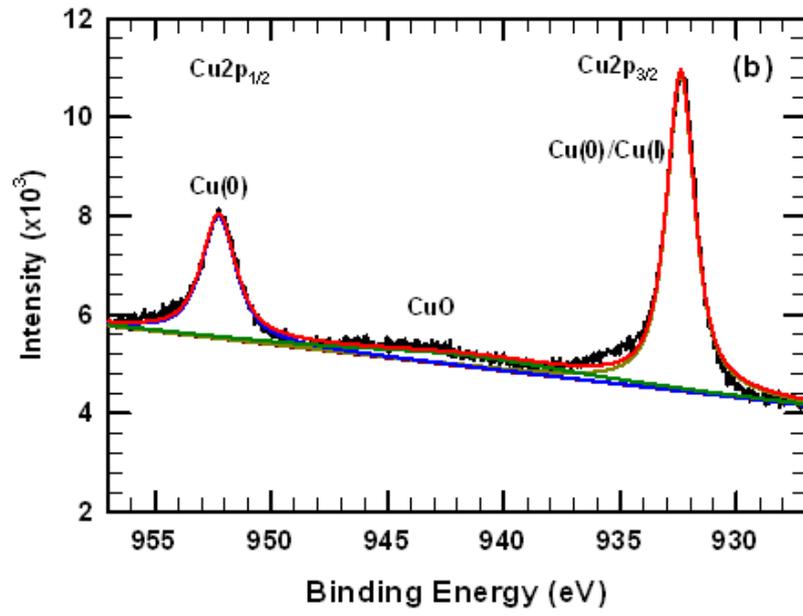
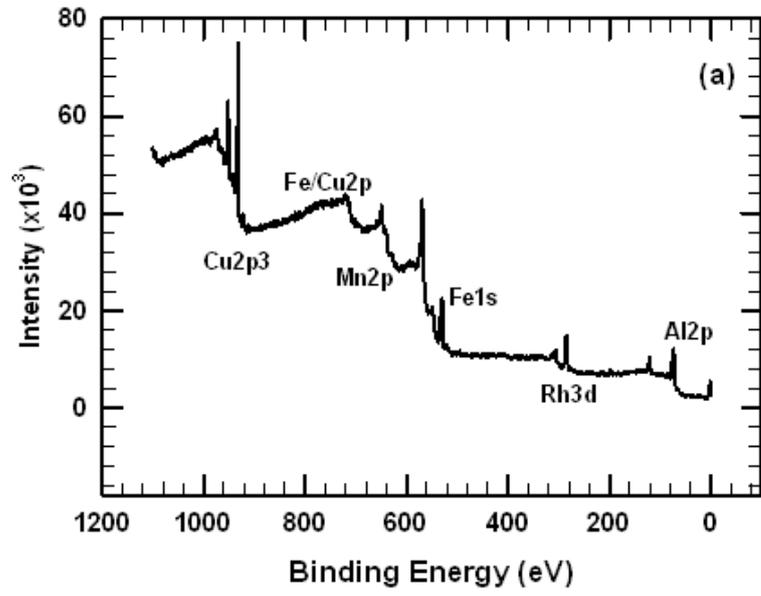
The atomic percentage of Rh, Cu, Pd, Ru and Mo on the SS mesh is 42.41%, 68.96%, 88.46%, 70.79% and 17.52%, respectively. All the electrodeposited materials covered the stainless steel substrate. The atomic ratio of Rh/Ru on Ru-Rh/SS electrode and Cu/Rh on Rh-Cu/SS electrode is 1.2 and 7.8, respectively.

In order to analyze the states of the chemical bonding, XPS spectra were also analyzed. Fig. 5.4 (a) shows the full spectra of the Rh\_Cu electrode, again, Rh and Cu were found on the surface of the SS electrode while Al, Fe and Mn elements are the composition materials of the stainless steel. It could be seen that Cu 2p spectra consists of two peaks (Fig. 5.4b) at around 932.36 eV (Cu 2p<sub>3/2</sub>) and 952.27 eV (Cu 2p<sub>1/2</sub>). The Cu 2p region showed that Cu was mainly in +1 state or element state. There is a weak satellite around 945eV which support no (or barely) presence of CuO. The binding energies data measured for the Rh (Fig. 5.3c) showed to major peaks at 306.3 eV (Rh 3d<sub>5/2</sub>) and 311.3 eV (Rh 3d<sub>3/2</sub>) indicating the existence of Rh metallic state. The other two broad and weak peaks at 308.9 eV and 314.2 eV indicating the presence of Rh oxides. The metallic Rh and the oxides surface were beneficial for adsorption of perchlorate ion. Therefore, the major Cu(I) and Cu species and Rh would contribute to the major reduction of perchlorate. From above EDS results, the atomic ratio of Cu/Rh is around 8, it is suggested that 8 Cu(I) contributed 8 electron while Rh provide a surface for forming perchlorate-complex for hydrogenation and oxygen atom transfer (OAT) reaction.

Figure 5.4(d) shows results of the XRD characterization of the Rh-Cu/SS electrodes. From the XRD spectrums, Rh-Cu/SS showed peaks at 43.4°, 50.5° and 74.2° even without sintered the catalysts after electrodeposition. The crystal structure matched with copper nano-particles (Theivasanthi and Alagar 2011). The corresponding Miller Indices (h k l) to all peaks is assigned as shown in Table 5. 2. The size of the crystal metal can be calculated using the Braggs' law,

$$B(2\theta) = \frac{0.94\lambda}{d \cos \theta} \quad (5.2)$$

where B is FWHM (full width at half maximum) ;  $\lambda$  is wavelength of X-ray; d is diameter of crystalline particles. From the Eq. 5.2, the calculated copper crystal sizes are ranging from 48.6 nm to 90.3 nm. The values were closed to the observed crystal sized in Fig. 5.3(c) and (h).



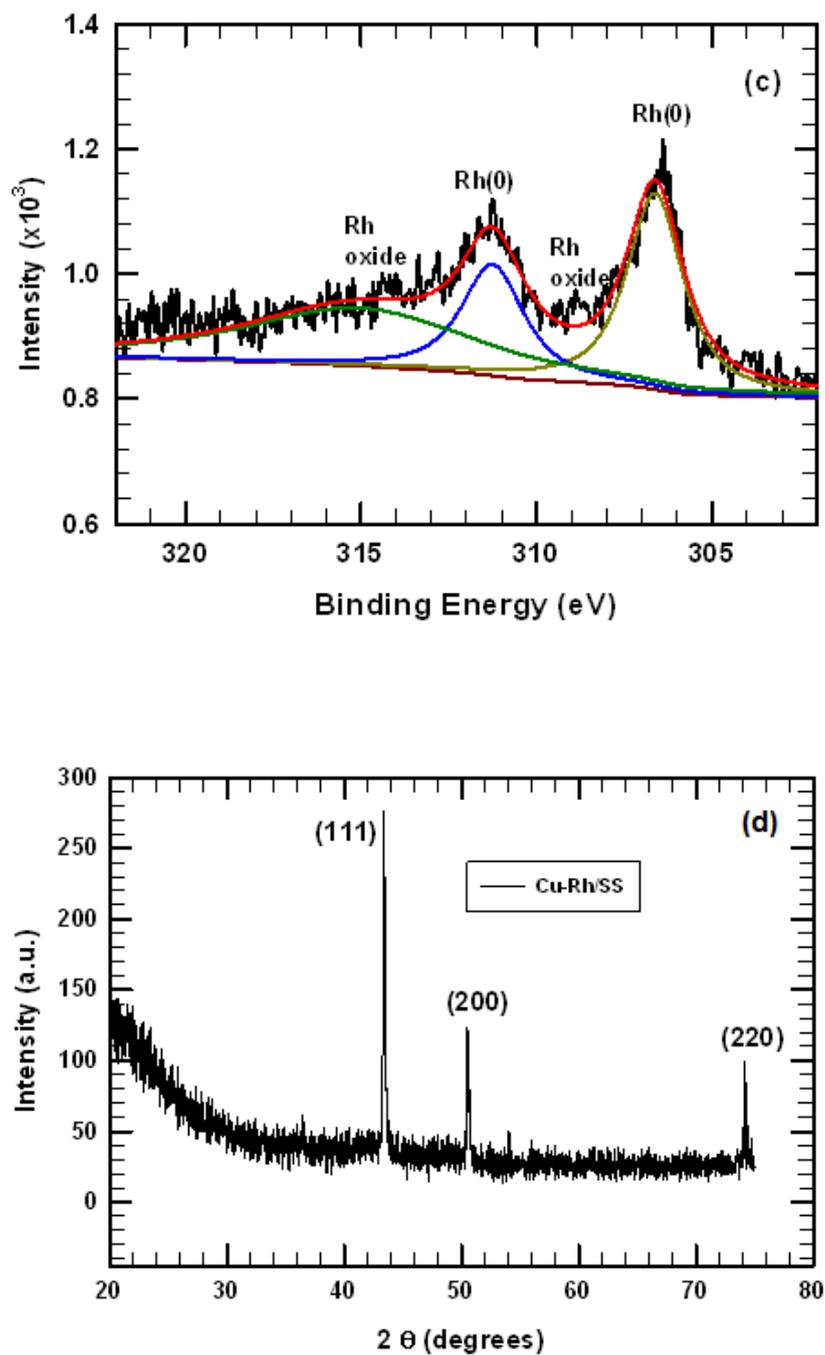


Figure 5.4. XPS patterns of  $\text{Rh}_{0.11}\text{-Cu}_{0.89}/\text{SS}$  catalysts (a) full; (b)Cu; (c) Rh spectra and (d) XRD patterns of  $\text{Rh}_{0.11}\text{-Cu}_{0.89}/\text{SS}$  catalysts.

Table 5.2. Rh<sub>0.11</sub>-Cu<sub>0.89</sub>/SS XRD analysis.

Crystalline	2 $\theta$	FWHM	d (nm)
(111)	43.40	0.158	54.2
(200)	50.50	0.181	48.6
(220)	74.20	0.110	90.3

### 5.4.3 CV Scan Rate Selection

Fig. 5. 5(a) shows the cyclic voltammograms of the solution containing 20 mM NaClO<sub>4</sub> over the Rh<sub>0.11</sub>-Cu<sub>0.89</sub>/SS electrode as a function of scan rate. The voltammetric curves were measured in the potential range from -2.0 V to 2.0 V (vs. SCE). Only one reduction peak was observed sweep under negative-direction at all scan rates and there was no corresponding oxidation peak under the positive-direction of scan, indicating the presence of an irreversible redox process. In addition, it was noted that the reduction peak was shifted to more negative potential as the scan rate was increased from 0.05 V/s to 0.20 V/s which indicating an irreversible system. For an irreversible reaction, the peak potential is a function of the scan rate, shifting (for a reduction) in a negative direction with increasing scan rate as described in Eq.5. 3 (Bard and Faulkner 2000).

$$E_p = E^0 - \frac{RT}{\alpha F} \left[ 0.78 + \ln \left( \frac{D^{0.5}}{k^0} \right) + \ln \left( \frac{\alpha F v}{RT} \right)^{0.5} \right] \quad (5.3)$$

where  $E_p$  is the peak potential (V),  $E^0$  is the formal potential of an electrode (V),  $R$  is the gas law constant ( $8.314 \times 10^3 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $T$  is the temperature (K),  $F$  is the Faraday constant ( $96485 \text{ C eq}^{-1}$ ),  $\alpha$  is the transfer coefficient,  $D$  is the perchlorate diffusion coefficient ( $1.47 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  at 293K (Hiqaily and Clifton 1984)),  $k^0$  is the standard rate constant ( $\text{cm s}^{-1}$ ), and  $v$  is the potential scan rate ( $\text{V s}^{-1}$ ).

The magnitude of the peak current in the CV curve can be expressed by the Nicholson and Shain equation. (Nicholson and Shain 1964) as shown below.

$$I_p = -(2.99 \times 10^5) nAC^* \alpha^{0.5} D^{0.5} \nu^{0.5} \quad (5.4)$$

where  $I_p$  is the cathodic peak current (A),  $n$  is the number of electron involved in the charge transfer step,  $\alpha$  is the transfer coefficient,  $A$  is the electrode surface area ( $\text{cm}^2$ ),  $D$  is the perchlorate diffusion coefficient ( $\text{cm}^2 \text{ s}^{-1}$ ),  $\nu$  is the potential scan rate ( $\text{V s}^{-1}$ ), and  $C^*$  is the bulk perchlorate concentration ( $\text{mol cm}^{-3}$ ). The term  $\alpha$  in Eq. 5.4 was obtained from the following relationship:

$$|E_p - E_{p/2}| = \frac{1.857RT}{\alpha F} = \frac{47.7}{\alpha} \text{ (mV at 298K)} \quad (5.5)$$

where  $E_p$  is the peak potential (mV) and  $E_{p/2}$  is the potential where the current is at the half the peak value.

Fig. 5.5(b) shows plot between the reduction peak current,  $I_p$ , and the square root of scan rate,  $\nu^{1/2}$ , where the Rh-Cu/SS electrode surface area,  $A$ , was  $1.2 \text{ cm}^2$ . There was one slope of the plot and it exhibited a linear relationship ( $R^2 = 0.984$ ) between the cathodic  $I_p$  and  $\nu^{1/2}$ , meaning the result obeys the Nicholson and Shain equation (Eq. 5.4). In Fig. 5.5(a), it can be noted that the signal of reduction peak is more distinct at lower scan rate. It is due to the kinetics of the irreversible reaction were 'slow' and thus the equilibrium was not established rapidly (in comparison to the "higher" scan rate) and the current took more time to respond to the applied voltage (Bard and Faulkner 2000). Therefore,  $0.05 \text{ V/s}$  was used for the following CV experiments in this study.

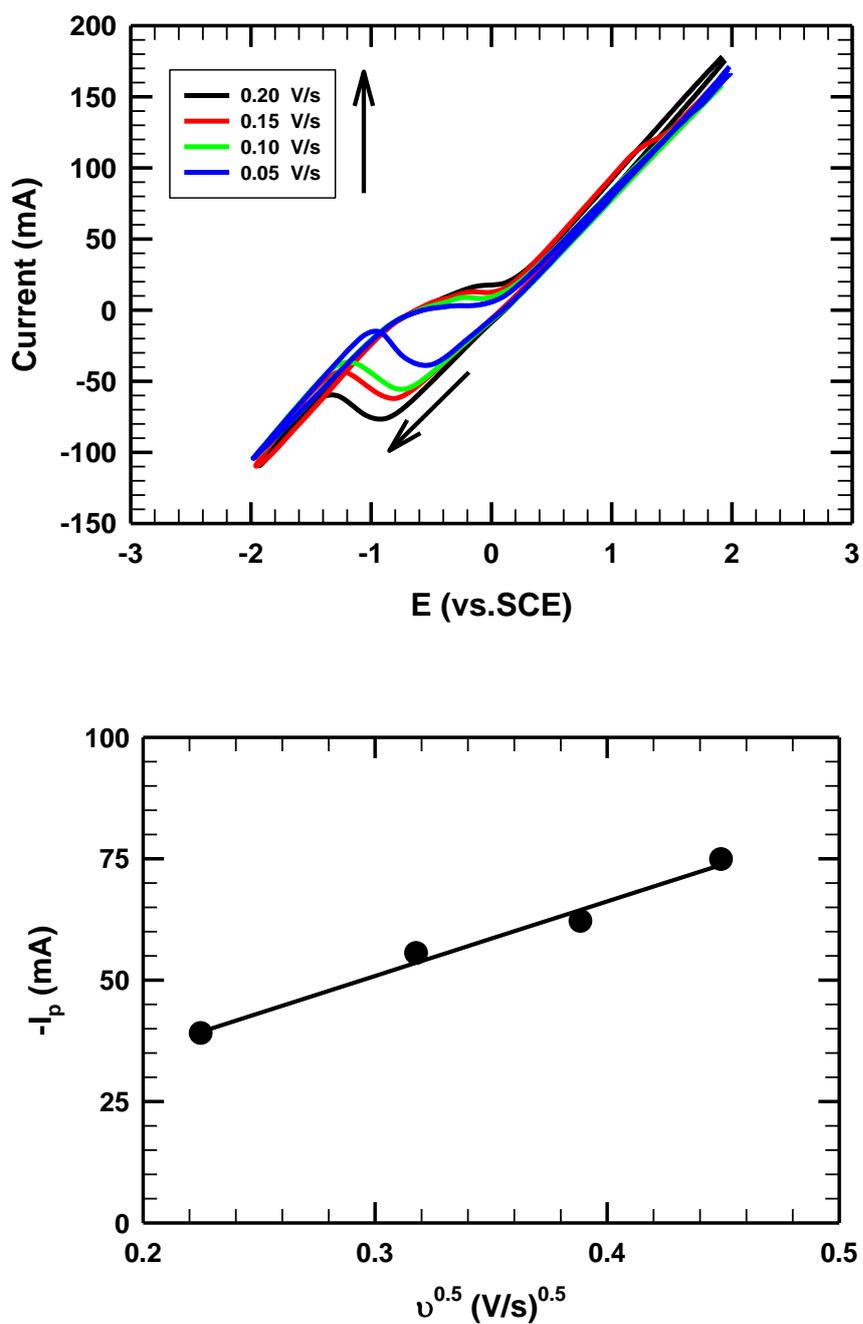
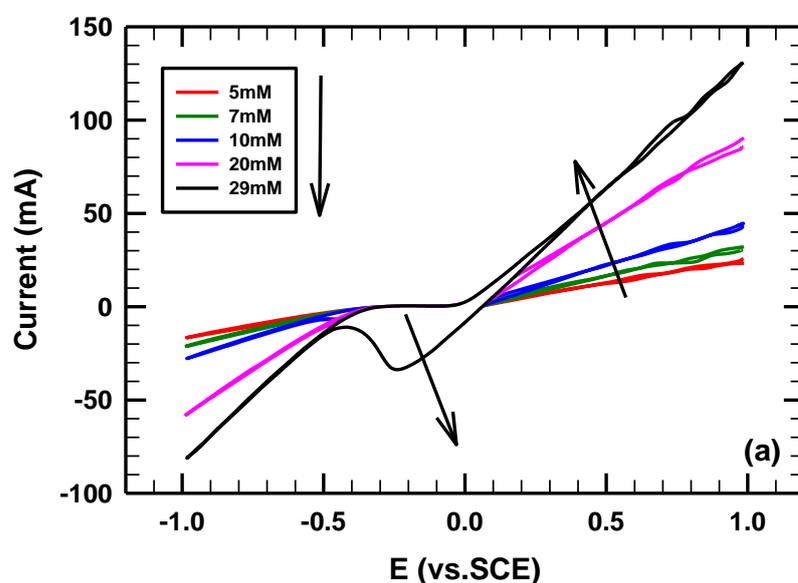


Figure 5.5. Cyclic voltammograms on  $\text{Rh}_{0.11}\text{-Cu}_{0.89}/\text{SS}$  electrode recorded at different scan rate (from 0.05 to 0.20 V/s) in 20 mM  $\text{NaClO}_4$  solution; (b) The peak currents versus the square root of the scan rate ( $v^{0.5}$ ) extracted from Fig. 5.5(a). Experimental condition: counter electrode = Pt; reference electrode = SCE;  $T = 298\text{K}$ ;  $\text{pH} = 5.0$ .

#### 5.4.4 CV Study on Perchlorate Reduction with Rh-Cu/SS Electrode

Fig. 5.6(a) shows the cyclic voltammograms at a Rh-Cu/SS electrode starting from 1.0 V to -1.0 V (vs. SCE) at the scan rate of 0.05 V/s in perchlorate solution at various concentration. The cyclic voltammograms indicate that current for the reduction of perchlorate is observed at positive potentials following a negative potential process involving hydrogen evolution. The reaction requires prior adsorption of perchlorate anion at the electrode surface. In addition, the  $\text{ClO}_4^-$  concentration was increased; larger cathodic peaks appeared as shown in Fig. 5.6(a). The formation of cathodic peaks was resulted from the reduction of perchlorate and the intermediates during the negative-wide scan. To resolve multiple peaks in the reduction curve, Origin 8.0 Pro software was applied to fit the data. Fig. 5.6(b) shows the fitting result of 29 mM perchlorate solution. Three reduction peaks (vs. SCE) were identified at -0.064 V ( $R_1$ ), -0.158 V ( $R_2$ ), and -0.252 V ( $R_3$ ). To determine the corresponding redox couple for every peak, the number of electron transfer at each peak was calculated via Eq. 5.4 and Eq. 5.5.



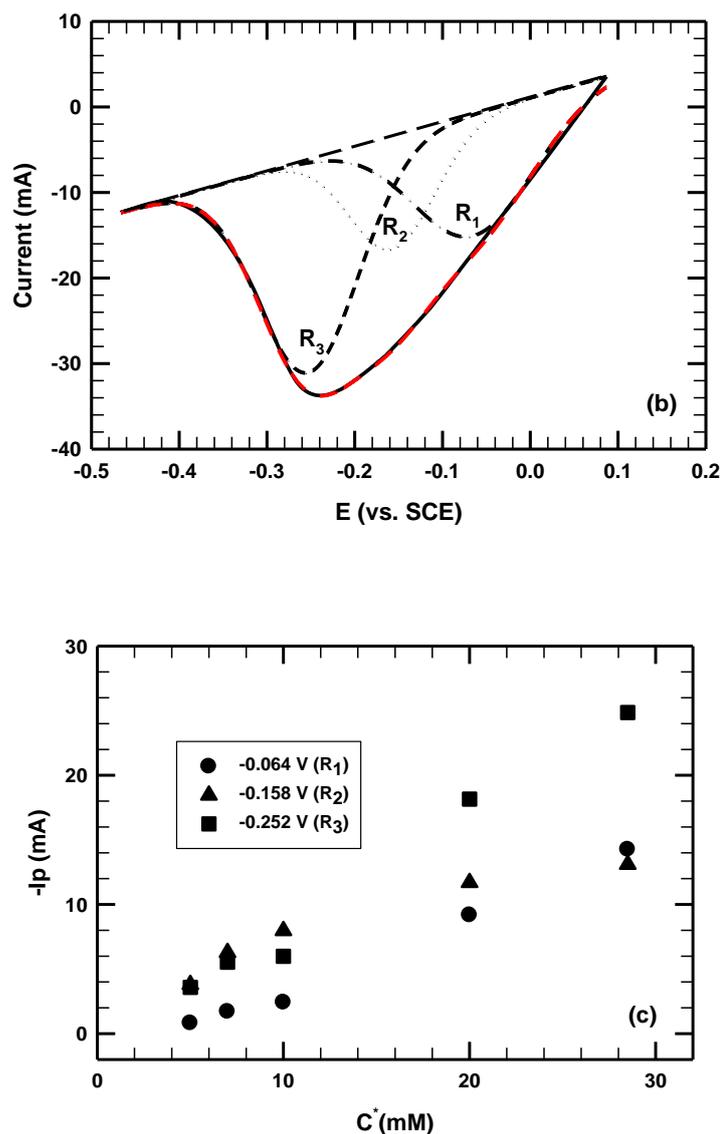


Figure 5.6. (a) Cyclic voltammograms on Rh<sub>0.11</sub>-Cu<sub>0.89</sub>/SS electrode recorded at different concentration (from 5 mM to 29 mM ) of NaClO<sub>4</sub> solution; (b) The fitting results from cycle voltammetric curve in 29 mM NaClO<sub>4</sub> solution (Fig. 5.6(a)) on Rh<sub>0.11</sub>-Cu<sub>0.89</sub>/SS electrode; and (c) The corresponding Nicholson and Shain plot at R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub> peaks. Experimental condition: scan rate = 0.05 V/s; counter electrode = Pt; reference electrode = SCE; T = 298K; pH =5.0.

Therefore, the current of cathodic peaks  $I_p$  can be plotted as a function of bulk perchlorate concentration,  $C^*$ , as shown in Fig. 5.6(c). The peak current and

the bulk perchlorate concentration exhibited a linear relationship in all three reactions ( $R_1, R_2, R_3$ ), and the slope can be used to calculate the number of electrons transferred during the reaction. From the results ( $C^* = 5, 7, 10, 20,$  and  $29$  mM),  $n$  for  $R_1$  peak was equal to 2, meaning the  $R_1$  peak was corresponding to a two-electrons transfer redox reaction. The number of electron transfer for  $R_2$ , and  $R_3$  peaks were calculated in the same fashion. The value of  $n$  for  $R_2$  and  $R_3$  peak was equal to 2 and 4, respectively. Table 5.3 lists the slope,  $\alpha$ , and  $n$  for all peaks.

Generally,  $\alpha$  is a potential-dependent factor and can be used to estimate the symmetry of the energy barrier. If the redox reaction is in equilibrium,  $\alpha$  would be equal to 0.5. When  $0 < \alpha < 0.5$  and  $0.5 < \alpha < 1$ , the reduction (cathodic) and the oxidation (anodic), respectively, was favored (Bard and Faulkner 2000), which was in agreement with our results. The perchlorate reduction potential on Rh-Cu/SS electrode can be summarized as the following:

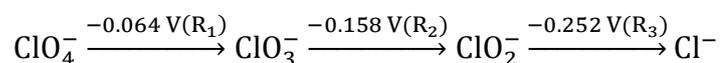


Table 5.3. Electrochemical parameters (slope,  $\alpha$ , and  $n$ ) of perchlorate reduction on  $\text{Rh}_{0.11}\text{-Cu}_{0.89}/\text{SS}$  electrode.

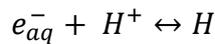
Peak ID	-0.064 V ( $R_1$ )	-0.158 V ( $R_2$ )	-0.252V ( $R_3$ )
slope	$5.86 \times 10^{-4}$	$3.72 \times 10^{-4}$	$9.40 \times 10^{-4}$
$n\alpha^{0.5}$	1.90	1.21	3.06
$\alpha$	0.64	0.28	0.62
$n$	2	2	4

#### 5.4.5 Perchlorate Reduction with Rh-Cu/SS Electrode at Different pH

As shown in Eq. 5.1, the reduction of perchlorate process required the involving of proton. Many literatures have reported that low pH condition would favor the reduction of perchlorate with metallic catalysts (Cao, Elliott et al. 2005; Hurley and Shapley 2007; Wang, Huang et al. 2007; Wang and Huang 2008; Choe, Shapley et al. 2010; Zhang, Hurley et al. 2011). Here, four different pH perchlorate solutions, namely, 3.4, 5.0, 7.2 and 10.0 were examined as shown in Fig. 5.7(a). The Rh-Cu/SS electrode was used to do the reduction reaction in a two chambers reactor. The results showed that low pH condition still had higher perchlorate reduction than high pH solution. At pH 10 environments merely 20% of perchlorate was reduced while ~80% of perchlorate was reduced at pH 3.4 solution. Here we assume the observed reaction rate is a function of  $[H^+]$  as shown in Eq. 6.6

$$k_{obs} = k'[H^+]^a \quad (5.6)$$

Therefore, the  $\log(k_{obs})$  can be plotted as a function of pH as shown in Fig. 5.7(b). There was one slope of the plot and it exhibited a linear relationship ( $R^2 = 0.996$ ). The slope,  $a$ , shows value of 0.121 indicating the concentration  $[H^+]$  is not directly influence the reduction rate. It was reported that hydrogen atom would be the major reducing species in the reaction. The hydrogen atom is the conjugate acid of  $e_{aq}^-$ , and it is the major reducing species in acidic solution,



It is suggested that the hydrogen atom from water on the cathode surface would involve in the reduction process. Therefore, the electrode can reduce perchlorate at  $pH > 7$ .

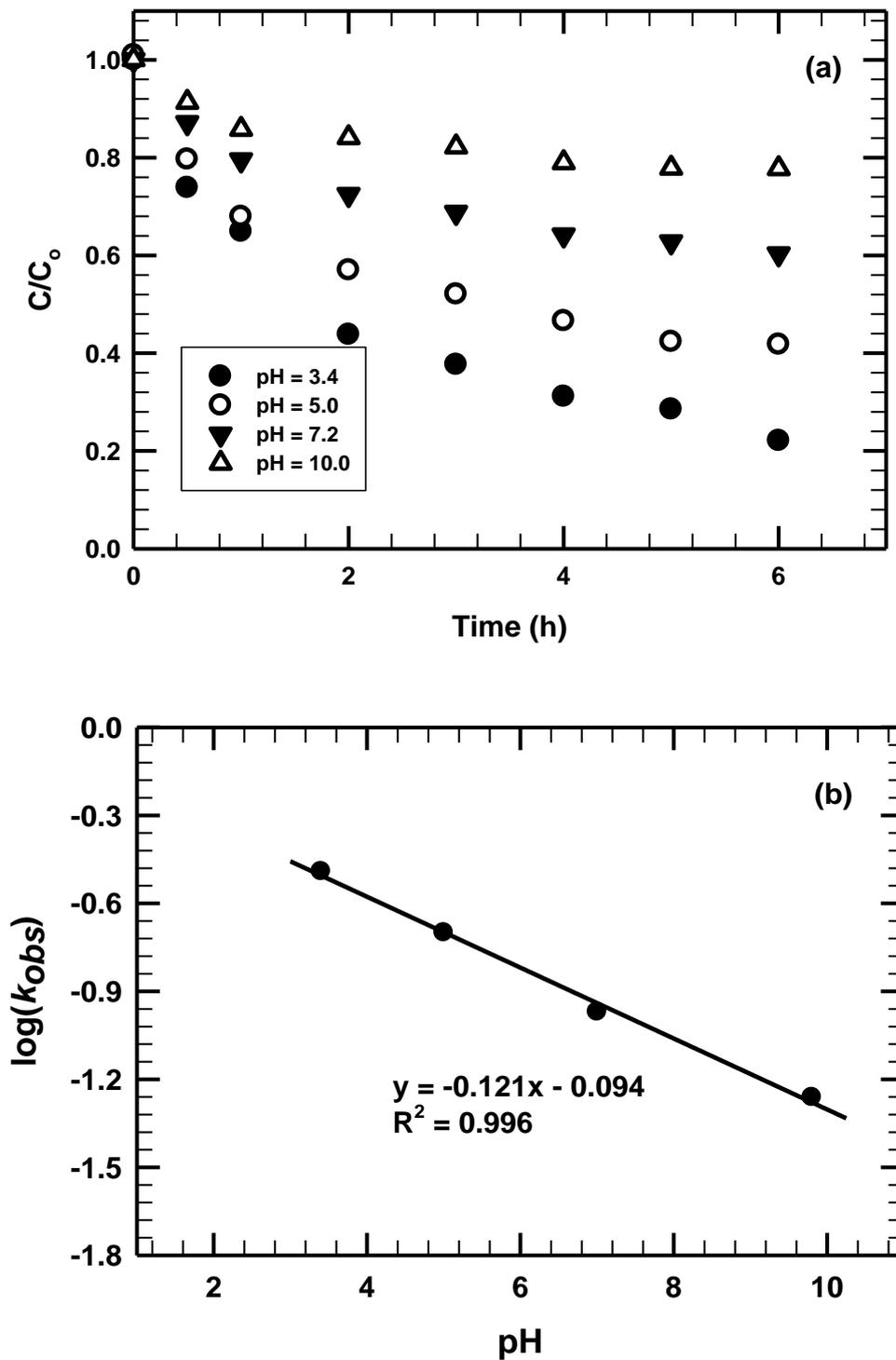


Figure 5.7. Reduction of perchlorate (a) at different pH and (b) reaction kinetic. Experimental conditions:  $[\text{ClO}_4^-] = 1 \text{ mM}$ ; catalytical cathode =  $\text{Rh}_{0.11}\text{-Cu}_{0.89}/\text{SS}$  metals, anode = graphite; current = 20.0 mA,  $T = 298\text{K}$ .

#### 5.4.6 Perchlorate Reduction with Rh-Cu/SS Electrode at Different Concentration and Temperature

Fig. 5.8(a) shows the change in perchlorate concentration with time at various initial perchlorate concentrations using Rh-Cu/SS electrode. The higher the initial concentration, the greater was the perchlorate reduction efficiency. The initial reaction rate constant was 0.86, 6.52, 9.84, 12.69, 13.16, and 322.11  $\mu\text{M}/\text{h}$  for the initial perchlorate concentration of 0.01, 0.05, 0.10, 0.25, 0.50, and 1.00 mM, respectively. Further analysis of the rate constants revealed that the perchlorate reduction could be described by the Langmuir–Hinshelwood equation, i.e.,

$$r = -\frac{dC}{dt} = \frac{k_r KC}{1+KC} \quad (5.7)$$

where  $r$  is the rate of reaction that changes with time,  $k_r$  is the limiting rate constant of reaction at the maximum coverage of the reaction site,  $K$  is the adsorption constant of reactant on the catalysts surface, and  $C$  is the concentration of the reactant.

A linearized plot of the Langmuir–Hinshelwood equation (Fig. 5.8b) yields slope and intercept from which the value of  $k_r$  and  $K$  were obtained ( $2.11 \times 10^{-3}$  M/h and  $4.11 \times 10^{-5}$  M, respectively). From the adsorption constant, the free energy of perchlorate adsorption on the catalytic medium was calculated to be ca. 25 kJ/mol. The value is in the adsorption energy range of physical process. It also implies that the perchlorate adsorption onto the surface of catalysts was mainly from van der Waals attraction. The excellent fit of the rate constant with the Langmuir–Hinshelwood equation clearly indicated that the reduction reaction rate was limited by the surface concentration of perchlorate.

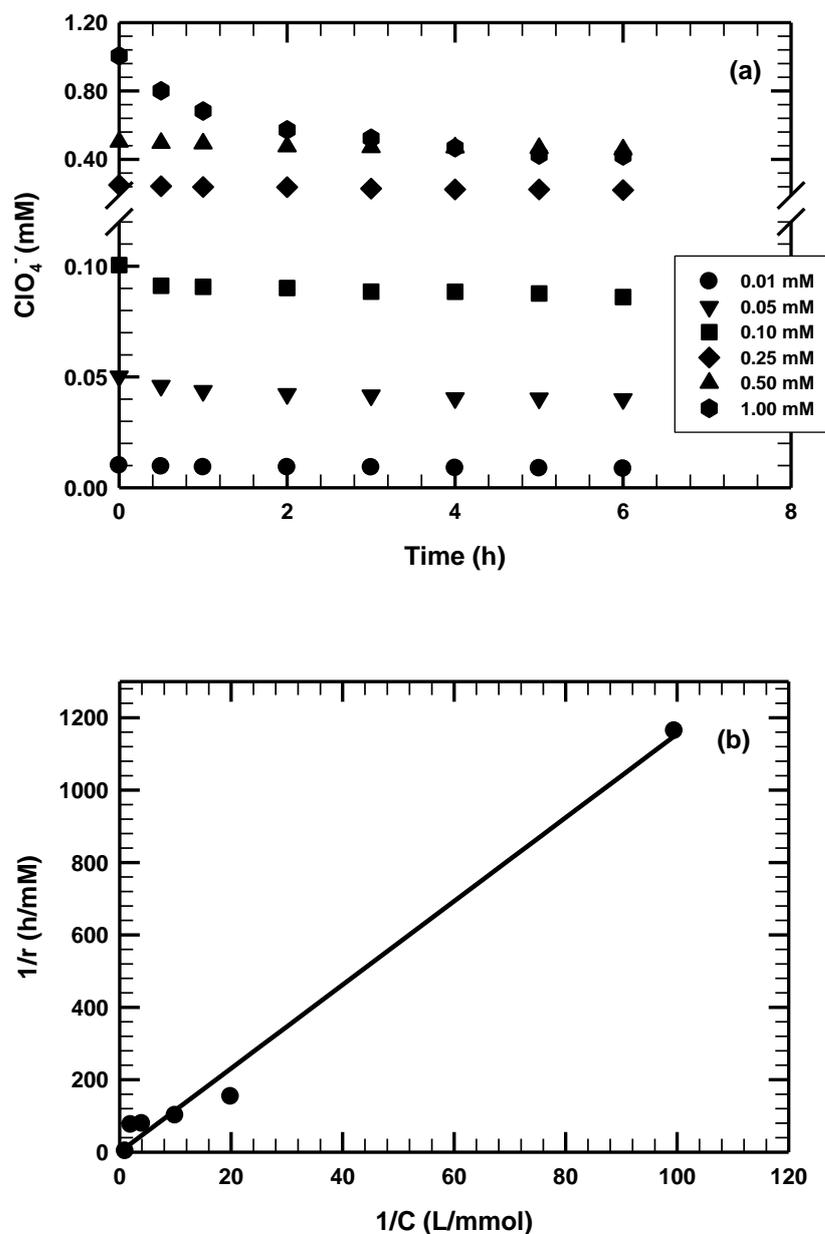
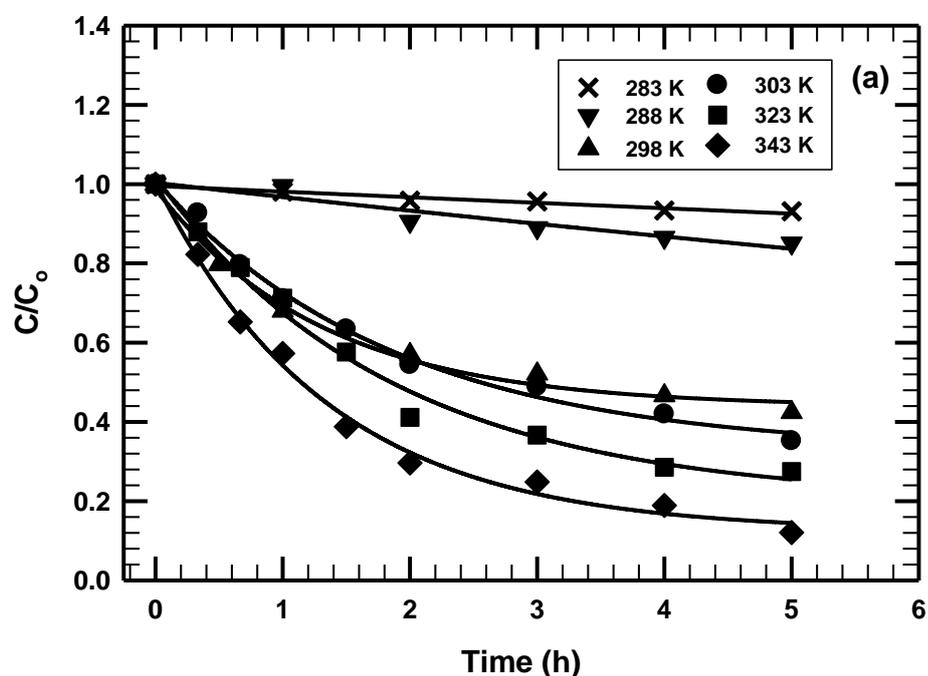


Figure 5.8. Reduction of perchlorate (a) at different concentration of perchlorate and (b) the Langmuir-Hinshelwood plot. Experimental conditions:  $[\text{ClO}_4^-] = 1 \text{ mM}$ ; catalytical cathode =  $\text{Rh}_{0.11}\text{-Cu}_{0.89}/\text{SS}$  metals, anode = graphite; current = 20 mA,  $T = 298\text{K}$ ;  $\text{pH} = 5.0$ .

Fig. 5.9(a) shows the effect of temperature on the reduction of perchlorate using Rh-Cu/SS electrode. Results indicated that generally the rate increased with

increase in temperature. Fig. 5.9(b) shows a concave Arrhenius plot which yields two slopes. It implies to at least two different types of reaction steps are involved. The activation energy ( $E_a$ ) is  $19.5 \pm 1.3$  and  $110.9 \pm 0.8$   $\text{kJ mol}^{-1}$  at 303 to 343 K and 283 to 298 K, respectively. In general, the activation energy greater than  $80 \text{ kJ mol}^{-1}$  are considered as chemical-controlled reaction steps. If the activation energy is less than  $20 \text{ kJ mol}^{-1}$ , it is indicative of diffusion controlled reactions (Lasaga and Kirkpatrick 1981). At high temperature region (303 to 343 K), the mass transport or diffusion rate of perchlorate from solution to electrode surface is fast so more perchlorate can be adsorbed on the surface of the electrode for proceeding reduction reaction. At low temperature range (283 to 298K), the large activation energy is indicative of chemical-controlled reaction of perchlorate reduction. This is expected as perchlorate has a low-lying electron configuration. The sharing of electrons in the unoccupied oxygen atom orbital is difficult at low temperature.



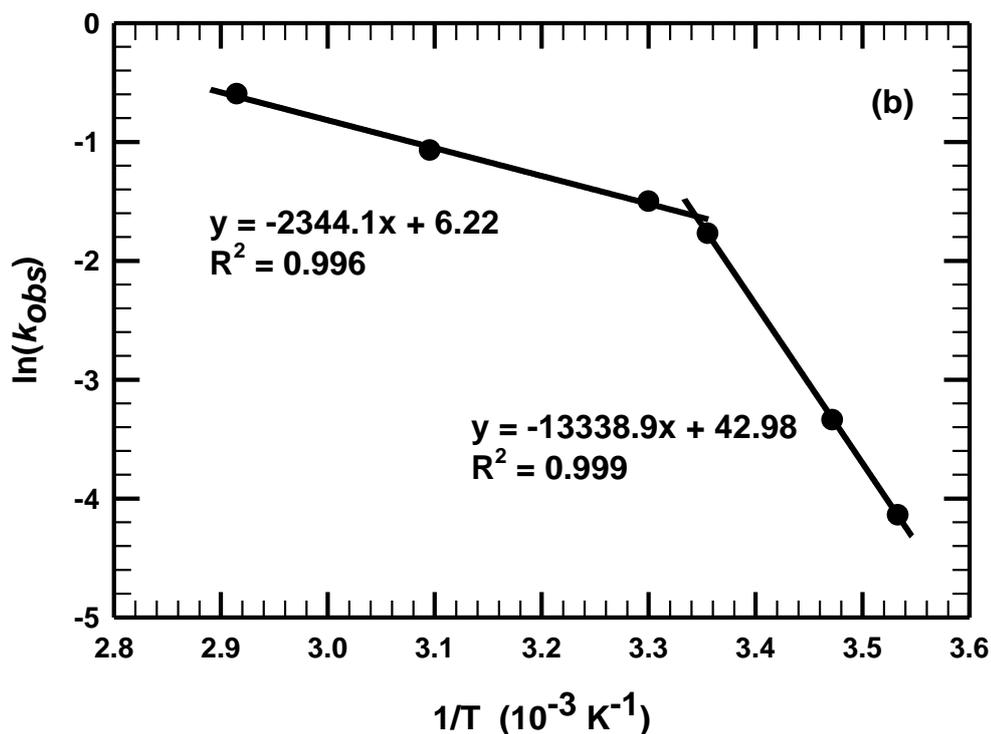
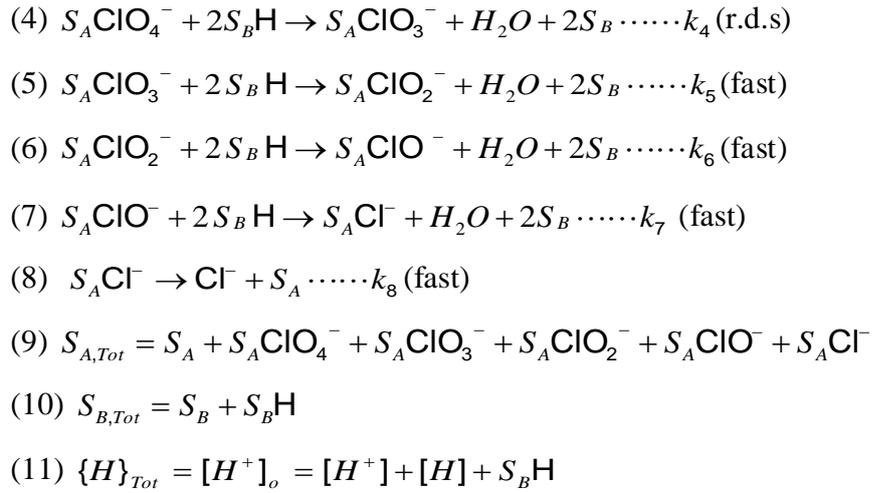


Figure 5.9. Reduction of perchlorate (a) at different temperature and (b) Arrhenius plot of the observed first-order rate constant as a function of  $1/T$ . Experimental conditions:  $[\text{ClO}_4^-] = 1 \text{ mM}$ ; catalytic cathode =  $\text{Rh}_{0.11}\text{-Cu}_{0.89}/\text{SS}$  metals, anode = graphite; current = 20.0 mA,  $T = 283$  to  $343\text{K}$ ;  $\text{pH} = 5.0$ .

#### 5.4.7 Proposed Perchlorate Reduction Mechanism

According to the experimental results of the present study, a reduction mechanism of perchlorate on the electrode surface was proposed here. It is speculated that the reaction began with the adsorption of perchlorate ions on one of the metallic catalyst surface. Also, it is assumed that hydrogen atom is the major species being present on the other metallic catalyst surface. That is:

- (1)  $\text{ClO}_4^- + S_A \rightleftharpoons S_A\text{ClO}_4^- \cdots \cdots K_1$
- (2)  $H^+ + e^- \rightarrow H \cdots \cdots k_2$  (fast)
- (3)  $H + S_B \rightleftharpoons S_B\text{H} \cdots \cdots K_3$



where  $S_A$  denotes a vacant surface Rh site and  $S_B$  represents a vacant surface Cu site on the Rh-Cu/SS electrode. The key features of the above reaction scheme are, (1) adsorption of  $\text{ClO}_4^-$  onto Rh site; (2) the formation of hydrogen atom on the Cu site; (3) a series of surface reaction involved the surface hydrogen atom (on the Cu site) with various surface oxy-chlorine species eventually lead to the production of chloride ion. Based on the above reaction steps, the transient concentration of major reaction products and perchlorate can be derived.

It has been reported the rate constant for chlorate reduction is at least  $10^5$  times greater than that for perchlorate reduction (Brown 1986). Therefore, we assume reaction (4) is rate determined step (r.d.s.) and all other reactions are at equilibrium, from reaction (1) to (11), the rate of each species can be expressed as,

$$\begin{aligned}
(12) \quad & \frac{d(\text{ClO}_4^-)}{dt} = -k_1(\text{ClO}_4^-)(S_A) + k_{-1}(S_A \text{ClO}_4^-) \\
(13) \quad & \frac{d(S_A \text{ClO}_4^-)}{dt} = k_1(\text{ClO}_4^-)(S_A) - k_{-1}(S_A \text{ClO}_4^-) - k_4(S_A \text{ClO}_4^-)(S_B \text{H})^2 \\
(14) \quad & \frac{d(S_A \text{ClO}_3^-)}{dt} = k_4(S_A \text{ClO}_4^-)(S_B \text{H})^2 - k_5(S_A \text{ClO}_3^-)(S_B \text{H})^2 \\
(15) \quad & \frac{d(S_A \text{ClO}_2^-)}{dt} = k_5(S_A \text{ClO}_3^-)(S_B \text{H})^2 - k_6(S_A \text{ClO}_2^-)(S_B \text{H})^2
\end{aligned}$$

$$(16) \frac{d(S_A \text{ClO}^-)}{dt} = k_6(S_A \text{ClO}_2^-)(S_B H)^2 - k_7(S_A \text{ClO}^-)(S_B H)^2$$

$$(17) \frac{d(S_A \text{Cl}^-)}{dt} = k_7(S_A \text{ClO}^-)(S_B H)^2 - k_8(S_A \text{Cl})$$

$$(18) \frac{d(\text{Cl}^-)}{dt} = k_8(S_A \text{Cl})$$

$$(19)$$

$$\frac{d(S_B H)}{dt} = k_3(H)(S_B) - k_{-3}(S_B H) - 2k_4(S_A \text{ClO}_4^-)(S_B H)^2 - 2k_5(S_A \text{ClO}_3^-)(S_B H)^2 - 2k_6(S_A \text{ClO}_2^-)(S_B H)^2 - 2k_7(S_A \text{ClO}^-)(S_B H)^2$$

$$(20) \frac{d(H)}{dt} = k_2(H^+)(e^-) - k_3(H)(S_B) + k_{-3}(S_B H)$$

$$(21) \frac{d(H^+)}{dt} = k_2(H^+)(e^-)$$

$$(22) K_1 = \frac{(S_A \text{ClO}_4^-)}{(\text{ClO}_4^-)(S_A)} = \frac{k_1}{k_{-1}}$$

$$(23) K_3 = \frac{(S_B H)}{(H)(S_B)} = \frac{k_3}{k_{-3}}$$

At steady state, Eq. (13) to (17), Eq. (19) and Eq. (20) equal to zero, then from Eq. (13)

$$-k_1(\text{ClO}_4^-)(S_A) + k_{-1}(S_A \text{ClO}_4^-) = -k_4(S_A \text{ClO}_4^-)(S_B H)^2$$

Therefore, Eq. (12) can be rewritten as

$$\frac{d(\text{ClO}_4^-)}{dt} = -k_1(\text{ClO}_4^-)(S_A) + k_{-1}(S_A \text{ClO}_4^-) = -k_4(S_A \text{ClO}_4^-)(S_B H)^2 \quad (\text{Eq. 24})$$

Also,

$$S_A \text{ClO}_3^- = \frac{k_4}{k_5}(S_A \text{ClO}_4^-)$$

$$S_A \text{ClO}_2^- = \frac{k_5}{k_6}(S_A \text{ClO}_3^-) = \frac{k_4}{k_6}(S_A \text{ClO}_4^-)$$

$$S_A \text{ClO}^- = \frac{k_6}{k_7} (S_A \text{ClO}_2^-) = \frac{k_4}{k_7} (S_A \text{ClO}_4^-)$$

$$S_A \text{Cl}^- = \frac{k_4}{k_8} (S_A \text{ClO}_4^-) (S_B H)^2$$

$$S_A \text{Cl}^- = \frac{k_4}{k_8} (S_A \text{ClO}_4^-) (S_B H)^2$$

From Eq. (20)

$$\frac{d(\mathbf{H})}{dt} = 0 = k_2 (H^+) (e^-) - k_3 (H) (S_B) + k_{-3} (S_B H)$$

$$\text{Therefore, } k_2 (H^+) (e^-) = k_3 (H) (S_B) - k_{-3} (S_B H)$$

And Eq. (19) can be rewritten as,

$$\frac{d(S_B H)}{dt} = k_2 (H^+) (e^-) - 8k_4 (S_A \text{ClO}_4^-) (S_B H)^2 = 0$$

From Eq. (9)

$$\begin{aligned} S_{A,Tot} &= S_A + S_A \text{ClO}_4^- + S_A \text{ClO}_3^- + S_A \text{ClO}_2^- + S_A \text{ClO}^- + S_A \text{Cl}^- \\ &= S_A \times \left[ 1 + K_1 (\text{ClO}_4^-) + K_1 (\text{ClO}_4^-) \times \left( \frac{k_4}{k_5} + \frac{k_4}{k_6} + \frac{k_4}{k_7} + \frac{k_4}{k_8} (S_B H)^2 \right) \right] \end{aligned}$$

$$S_A = \frac{S_{A,Tot}}{\left[ 1 + K_1 (\text{ClO}_4^-) + K_1 (\text{ClO}_4^-) \times \left( \frac{k_4}{k_5} + \frac{k_4}{k_6} + \frac{k_4}{k_7} + \frac{k_4}{k_8} (S_B H)^2 \right) \right]}$$

(Eq. 25)

From (Eq.10 and Eq. 23)

$$S_{B,Tot} = S_B + S_B H = \frac{S_B H}{K_3 [H]} + S_B H$$

Then,

$$S_B H = \frac{S_{B,Tot} K_3 [H]}{(1 + K_3 [H])} \quad (\text{Eq. 26})$$

With Eq. (22), Eq. (25) and Eq. (26), Eq. (24) can be expressed as,

$$\begin{aligned}
\frac{d(\text{ClO}_4^-)}{dt} &= -k_4 (S_A \text{ClO}_4^-) (S_B H)^2 = -k_4 K_1 (\text{ClO}_4^-) (S_A) (S_B H)^2 \\
&= -k_4 K_1 (\text{ClO}_4^-) \times \frac{(S_{B,Tot} K_3 [H])^2}{(1 + K_3 [H])^2} \\
&\quad \times \left[ \frac{S_{A,Tot}}{1 + K_1 (\text{ClO}_4^-) + K_1 (\text{ClO}_4^-) \times \left( \frac{k_4}{k_5} + \frac{k_4}{k_6} + \frac{k_4}{k_7} + \frac{k_4}{k_8} \frac{(S_{B,Tot} K_3 [H])^2}{(1 + K_3 [H])^2} \right)} \right]
\end{aligned}$$

$k_4$  is r.d.s, therefore is less than  $k_5, k_6, k_7$  and  $k_8$ ,

$$\frac{d(\text{ClO}_4^-)}{dt} = -\frac{k_4 K_1 S_{A,Tot} (\text{ClO}_4^-) (S_{B,Tot} K_3 [H])^2}{1 + K_1 (\text{ClO}_4^-) (1 + K_3 [H])^2}$$

We assume that  $1 > K_1 (\text{ClO}_4^-)$  and  $1 > K_3 [H]$ , then

$$\frac{d(\text{ClO}_4^-)}{dt} = -k_4 K_1 S_{A,Tot} (\text{ClO}_4^-) (S_{B,Tot} K_3 [H])^2 \quad (\text{Eq. 27})$$

To solve  $[H]$ , from Eq. 21,

$$[H^+] = [H^+]_o e^{(-k_2 [e^-] t)} \quad (\text{Eq. 28})$$

Using Eq. (11), Eq. (26) and Eq. (28)

$$\begin{aligned}
[H^+]_o &= [H^+] + [H] + S_B H \\
&= [H^+]_o e^{(-k_2 [e^-] t)} + [H] \left( 1 + \frac{S_{B,Tot} K_3}{(1 + K_3 [H])} \right)
\end{aligned}$$

With the same assumption  $1 > K_3 [H]$ ,

$$[H] = \frac{[H^+]_o (1 - e^{(-k_2 [e^-] t)})}{1 + S_{B,Tot} K_3}$$

Where  $k_{obs} = k_4 K_1 S_{A,Tot} (S_{B,Tot} K_3 [H])^2$

$$\text{Then, } [\text{ClO}_4^-] = [\text{ClO}_4^-]_o e^{-k_{obs}t} \quad (\text{Eq. 29})$$

Since the intermediates was not observed, it is assume that chloride and perchlorate are the two chlorine species in the systems, that is,

$$[\text{ClO}_4^-]_o = [\text{ClO}_4^-] + [\text{Cl}^-]$$

Then

$$[\text{Cl}^-] = [\text{ClO}_4^-]_o \times (1 - e^{-k_{obs}t}) \quad (\text{Eq. 30})$$

With Eq. 29 and 30, the fitted perchlorate and chloride concentration was shown in Fig. 5.10.

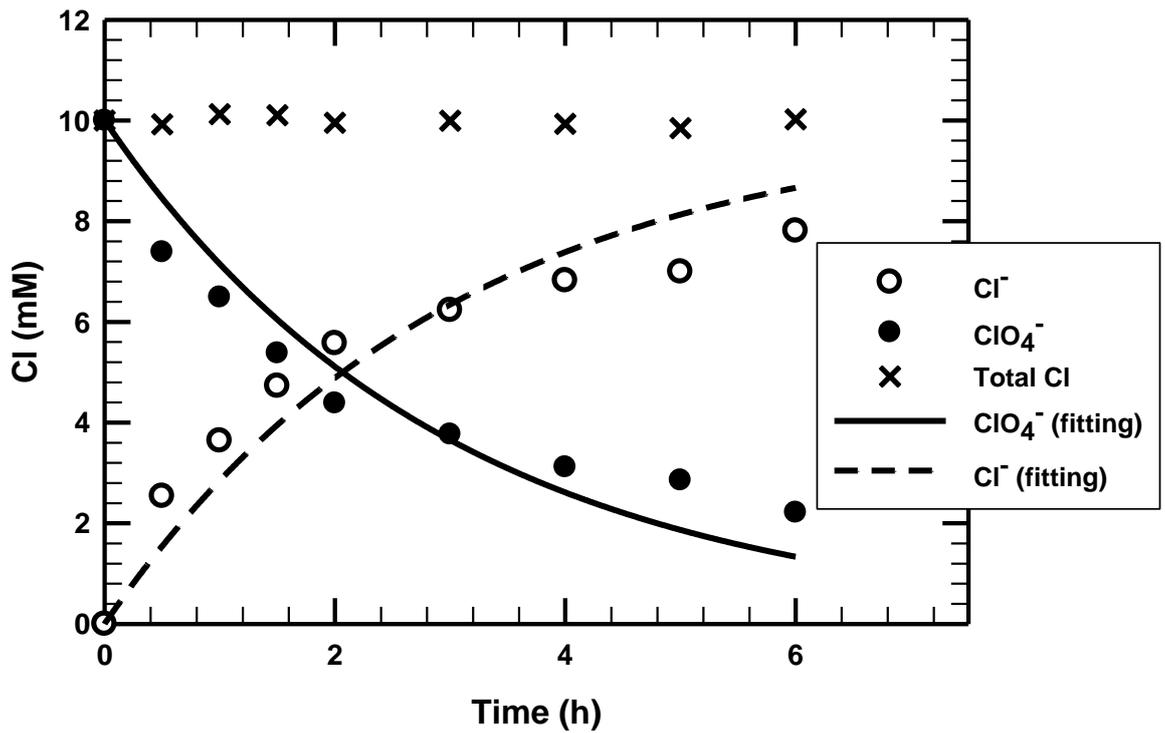


Figure 5.10. The mechanistic model fit to Figure 5.2 (a) and (b) obtained over the Rh<sub>0.11</sub>-Cu<sub>0.89</sub>/SS electrode. . Experimental conditions: [ClO<sub>4</sub><sup>-</sup>] = 10 mM; catalytical cathode = various metals, anode = graphite; current = 20 mA; T = 298K; pH = 3.4.

## 5.5 Summary

In this study, several perchlorate reduction monometallic and bimetallic catalysts were prepared on stainless steel support via electro-deposition process. The perchlorate electrochemical reduction efficiencies were governed by both solution pH conditions and types of catalysts. The reduction rate of perchlorate showed faster at low pH condition than that at high pH condition. The reduction efficiencies of monometallic catalysts were in the order of Rh(56%) > Cu(50%) > Ru(45%) > Mo~Pd(21%) > SS(17%). The bimetallic catalysts (Rh-Cu/SS:78% reduction and Rh-Ru/SS:60% reduction) have superior reduction efficiencies than that of monometallic catalysts.

In addition, the physical characterization of the catalysts show the sizes of the catalyst crystal are in the range of 50 nm to several hundred nm. For Rh-Cu/SS bimetallic catalysts, the major Cu(I) and Cu species and Rh would contribute to the major reduction of perchlorate. From EDS results, the atomic ratio of Cu/Rh is around 8, it is suggested that the reduction reaction need 8 Cu(I) for providing electrons while one Rh surface for providing adsorption site to proceed hydrogenation and oxygen atom transfer (OAT) reaction. According to the experimental results of the present study, a reduction mechanism of perchlorate on the electrode surface was proposed.

## REFERENCES

- Bard, A. J. and L. R. Faulkner (2000). Electrochemical methods: fundamentals and applications. Hoboken, NJ, John Wiley & Sons, Inc.
- Brown, G. M. (1986). "The reduction of chlorate and perchlorate ions at an active titanium electrode." Journal of Electroanalytical Chemistry and Interfacial Electrochemistry **198**(2): 319-330.
- Cao, J., D. Elliott, et al. (2005). "Perchlorate Reduction by Nanoscale Iron Particles." Journal of Nanoparticle Research **7**(4-5): 499-506.
- Choe, J. K., J. R. Shapley, et al. (2010). "Influence of Rhenium Speciation on the Stability and Activity of Re/Pd Bimetal Catalysts used for Perchlorate Reduction." Environmental Science & Technology **44**(12): 4716-4721.
- Colom, F. and M. J. González-Tejera (1985). "Reduction of perchlorate ion on ruthenium electrodes in aqueous solutions." Journal of Electroanalytical Chemistry and Interfacial Electrochemistry **190**(1-2): 243-255.
- Comisso, N., S. Cattarin, et al. (2012). "Electrodeposition of Cu-Rh alloys and their use as cathodes for nitrate reduction." Electrochemistry Communications **25**: 91-93.
- Hiquily, N. and M. J. Clifton (1984). "Diffusion coefficient of ammonium perchlorate in concentrated aqueous solutions between 20 and 30.degree.C." Journal of Chemical & Engineering Data **29**(4): 371-373.
- Hurley, K. D. and J. R. Shapley (2007). "Efficient heterogeneous catalytic reduction of perchlorate in water." Environmental Science & Technology **41**(6): 2044-2049.
- Kim, Y.-N. and M. Choi (2014). "Synergistic Integration of Ion-Exchange and Catalytic Reduction for Complete Decomposition of Perchlorate in Waste Water." Environmental Science & Technology **48**(13): 7503-7510.
- Láng, G. G. and G. Horányi (2003). "Some interesting aspects of the catalytic and electrocatalytic reduction of perchlorate ions." Journal of Electroanalytical Chemistry **552**: 197-211.
- Láng, G. G., N. S. Sas, et al. (2008). "The kinetics of the electrochemical reduction of perchlorate ions on rhodium." Electrochimica Acta **53**(25): 7436-7444.
- Lasaga, A. C. and R. J. Kirkpatrick, Eds. (1981). Kinetics of geochemical processes. Reviews in Mineralogy and Geochemistry.
- Nicholson, R. S. and I. Shain (1964). "Theory of Stationary Electrode Polarography. Single Scan and Cyclic Methods Applied to Reversible, Irreversible, and Kinetic Systems." Analytical Chemistry **36**(4): 706-723.
- Olívia Salomé G. P. Soares, José J. M. Órfão, et al. (2008). "Activated Carbon Supported Metal Catalysts for Nitrate and Nitrite Reduction in Water." Catalysis Letters **126**(3-4): 253-260.
- Olívia Salomé G.P. Soares , José J.M. Órfão , et al. (2009). "Bimetallic catalysts supported on activated carbon for the nitrate reduction in water: Optimization of catalysts composition." Applied Catalysis B: Environmental **91**(1-2): 441-448.

- Paoinot, J. and J. Augustynski (1975). "Etude potentiostatique et spectroscopique de l'aluminium recouvert par une couche d'oxyde: effet de differents anions." Electrochimica Acta **20**(10): 747-752.
- Rhee, C. K., M. Wasberg, et al. (1991). "Reduction of perchlorate on rhodium and its specificity to surface crystallographic orientation." Catalysis Letters **10**(3-4): 149-164.
- Theivasanthi, T. and M. Alagar (2011). "Nano sized copper particles by electrolytic synthesis and characterizations." International Journal of Physical Sciences **6**(15): 3662-3671.
- Wang, D. M. and C. P. Huang (2008). "Electrodialytically assisted catalytic reduction (EDACR) of perchlorate in dilute aqueous solutions." Separation and Purification Technology **59**(3): 333-341.
- Wang, D. M., C. P. Huang, et al. (2007). "Reduction of perchlorate in dilute aqueous solutions over monometallic nano-catalysts: Exemplified by tin." Separation and Purification Technology **58**(1): 129-137.
- Wasberg, M. and G. Horányi (1995). "The reduction of  $\text{ClO}_4^-$  ions on Rh electrodes." Journal of Electroanalytical Chemistry **385**(1): 63-70.
- Witonska, I., S. Karski, et al. (2007). "Kinetic studies on the hydrogenation of nitrate in water using Rh/Al(2)O(3) and Rh-Cu/Al(2)O(3) catalysts." Kinetics and Catalysis **48**(6): 823-828.
- Zelenay, P., G. Horanyi, et al. (1991). "VOLTAMMETRIC AND RADIOACTIVE LABELING STUDIES OF SINGLE-CRYSTAL AND POLYCRYSTALLINE RHODIUM ELECTRODES IN SULFATE-CONTAINING ELECTROLYTES." Journal of Electroanalytical Chemistry **300**(1-2): 499-519.
- Zhang, Y. X., K. D. Hurley, et al. (2011). "Heterogeneous Catalytic Reduction of Perchlorate in Water with Re-Pd/C Catalysts Derived from an Oxorhenium(V) Molecular Precursor." Inorganic Chemistry **50**(4): 1534-1543.

**INTEGRATED ELECTRODIALYSIS AND CATALYTIC  
ELECTROCHEMICAL REDUCTION (CECR) PROCESS FOR THE  
REMOVAL OF PERCHLORATE**

**6.1 Abstract**

The ED-CECR system provides an integrated process for separation and reduction of perchlorate from water. With perchlorate permselective membrane, perchlorate can exclusively separate and concentrate from water in presence of other anions. Followed by using perchlorate reduction electrodes, perchlorate can be reduced to chloride. Several factors such as concentration of initial anions, ED current and were examined and showed that low ED current (1 mA) would be favored for entire separation and reduction process.

A proposed model for perchlorate reduction was developed and successfully used to calculate the rate constants of anions passing through the membranes. Thus, it has been shown that 80% of perchlorate could be separated by MTBA membrane in electrodialysis process and up to 95% of separated perchlorate can be readily reduced to chloride within 6 hours. No other oxyanions of chlorine, such as  $\text{ClO}_3^-$ ,  $\text{ClO}_2^-$  or  $\text{ClO}^-$  was detected as the intermediates during the reduction process. This integrated ED-CECR process can be applied for the removal of low concentration of perchlorate from drinking water sources.

**6.2 Introduction**

Wang et al.(Wang and Huang 2008) developed an electrodiallytically assisted catalytic reduction (EDACR) system, where electrodialysis facilitated the movement of perchlorate towards a stainless steel cathode coated with

nanometallic catalysts that eventually reduces perchlorate. However, in the presence of other anions such as nitrate, sulfate or bicarbonate, the reduction efficiency would be decreased due to the competition reduction between the other anions and perchlorate. To improve perchlorate permselectivity of the anion exchange membrane in the electro dialysis would increase the flux of the perchlorate transport across the membrane from the dilute stream to concentrate stream at the mean time maintain low flux of other anions. In the Chapter 4 we have shown a PVC based polymer with quaternary ammonium functional group modification would enhance perchlorate permselectivity of the membrane. In Chapter 5, we have developed bimetallic electrode for reduction of perchlorate. Therefore, the objectives of this work are to use integrated electro dialysis and catalytic electrochemical system to separate perchlorate from other anions and reduce perchlorate to chloride. Several factors, such as concentration of anions, current of electro dialysis were also discussed.

### **6.3 Materials and Methods**

#### **6.3.1 Chemicals and Reagents**

All chemicals were either of analytical or reagent grade, or the highest purity available from suppliers. All aqueous solutions were prepared with de-ionized, distilled water. The certified standard perchlorate ( $\text{ClO}_4^-$ ) solution was purchased from SPEX CertiPrep (Metuchen, NJ, USA). Sodium perchlorate (ACS reagent, >98 %, Sigma-Aldrich, St. Louis, MO, USA), sodium bicarbonate (analytical grade ACS, 99.7 %), sodium chloride (reagent grade ACS, >99 %), sodium nitrate (analytical grade ACS, >99 %) from Acros Organics, sodium carbonate (HPLC grade), sodium sulfate (certified ACS) from Fisher Scientific were individually dissolved into deionized water to prepare stock solutions. NaOH

(50% w/w, Fisher Scientific, Fair Lawn, NJ, USA) was used as mobile phase solution in ion chromatography analysis.

### **6.3.2 Preparation of Metallic Catalysts**

The stainless steel (SS) mesh (30.6% opening) was immersed in the 0.01 M sulfuric solution for cleaning. After cleaning, the meshes were rinsed with deionized water. Each mesh was dried in the dryer for 1 h and weighted before coating of the catalyst. The metal ion solutions were prepared by dissolving the metal salts in deionized water at concentration range from 0.01 mM to 0.4 M depending on the solubility of the metal salts. The washed SS mesh was then immersed in the metal solution as the cathode and graphite as the anode. A direct current potential was applied at a constant current of 30 to 60 mA. After electroplating, the catalyst coated SS mesh was washed with deionized water again and dried in an oven (300K).

### **6.3.3 Perchlorate Separation and Reduction system**

Integrated electro dialysis and catalytic electrochemical system is set up as shown in Fig. 6.1. Perchlorate permselective membrane (MTBA/PVC) was placed between cathode (diluted stream) and anode (concentrated stream) chambers. The detailed preparation procedures for preparation of the perchlorate permselective membrane are described in the previous report (Wang, Shah et al. 2015). Graphite was used as cathode and anode electrodes in ED system with cation exchange membrane. A constant direct current was applied through graphite electrodes. The catalytic electrode and another graphite electrode were placed in the concentrated chamber and electrolyte chamber, respectively. Perchlorate and other major anions mixed solution was placed in the ED cathode chamber. pH of concentrated chamber was controlled by adding acids or bases for reduction reaction. Two

separate power supplies were used to provide current for ED separation and for electrochemical reduction. A pump was used to circulate the electrolyte solution in cathode and anode of ED system.

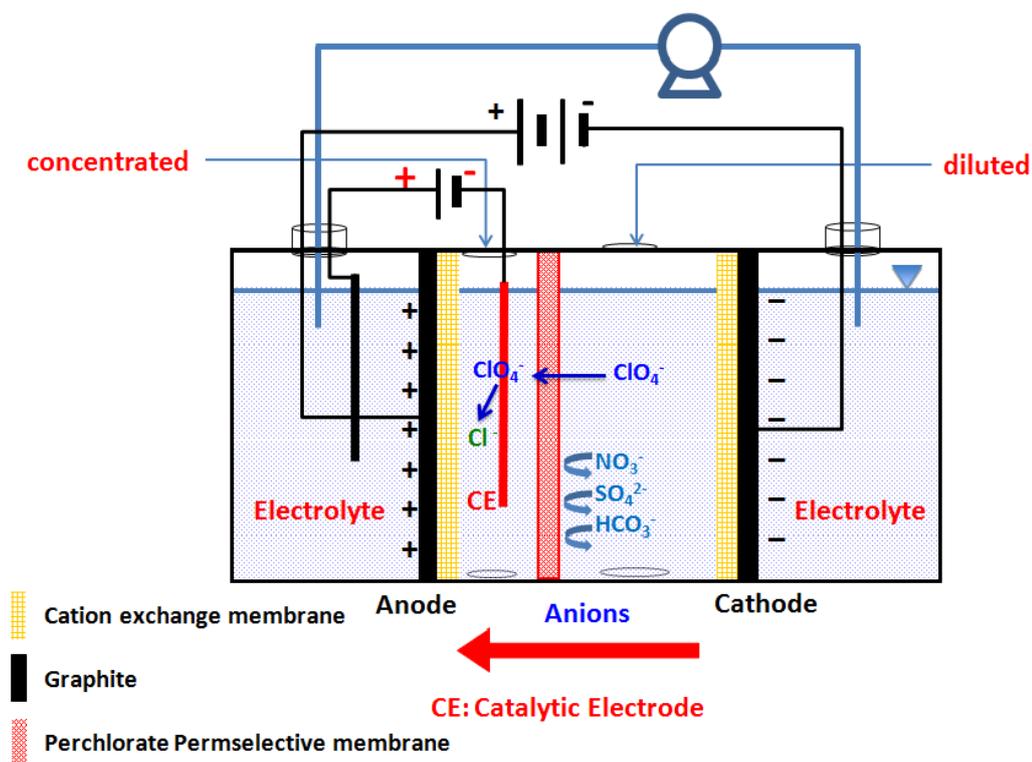


Figure 6.1. Integrated electrodiolytic separation and catalytic electrochemical reduction system (ES-CERs) for perchlorate.

## 6.4 Results and Discussion

### 6.4.1 Effect of Anion Concentration

Fig. 6.2 shows the separation rate of anions, namely, perchlorate, nitrate, sulfate and bicarbonate in the electrodiolysis with perchlorate permselective membrane at different initial concentration. When changing different initial concentration of perchlorate, nitrate, sulfate and bicarbonate, the removal rate

constant ( $k_i$ ) of the anions kept the same order:  $k_{\text{ClO}_4^-} > k_{\text{NO}_3^-} > k_{\text{SO}_4^{2-}} > k_{\text{HCO}_3^-}$ . It means that perchlorate permselective membrane could separate perchlorate from other anions effectively at concentration ranging from 0.01 to 2.0 mM.

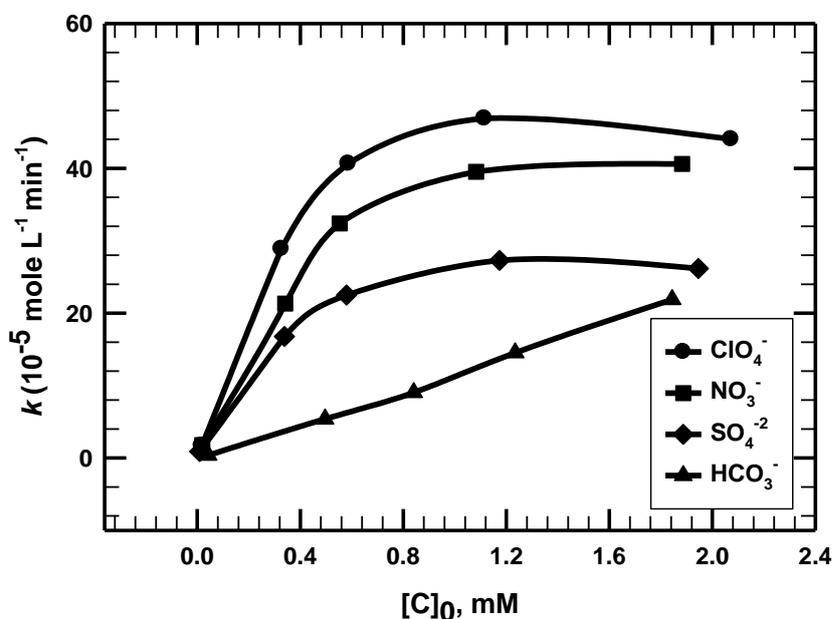


Figure 6.2. Separation rate constant of perchlorate and other anions (nitrate, sulfate and bicarbonate) with MTBA membrane at different initial concentration. Experimental conditions: each anion =  $10^{-5}$  M to  $2 \times 10^{-3}$  M; ED cathode and anode = graphite, current = 1 mA; temperature = 295K.

#### 6.4.2 Effect of ED Current

Fig. 6.3 shows the separation rate of anions, namely, perchlorate, nitrate, sulfate and bicarbonate in the electro dialysis with perchlorate permselective membrane at different ED current. The initial concentration of each anion was at 0.1 mM. The removal rate constant ( $k_i$ ) of the anions kept the order:  $k_{\text{ClO}_4^-} > k_{\text{NO}_3^-} > k_{\text{SO}_4^{2-}} > k_{\text{HCO}_3^-}$ . But the difference between  $k_{\text{ClO}_4^-}$  and the rate constant of other anions were decreasing after 30 mA of ED current. It means that with large current, the large driving force from the electric field would force all the ions

passing through the membrane. Therefore, the permselectivity property of membrane would be inactive under high electric field condition

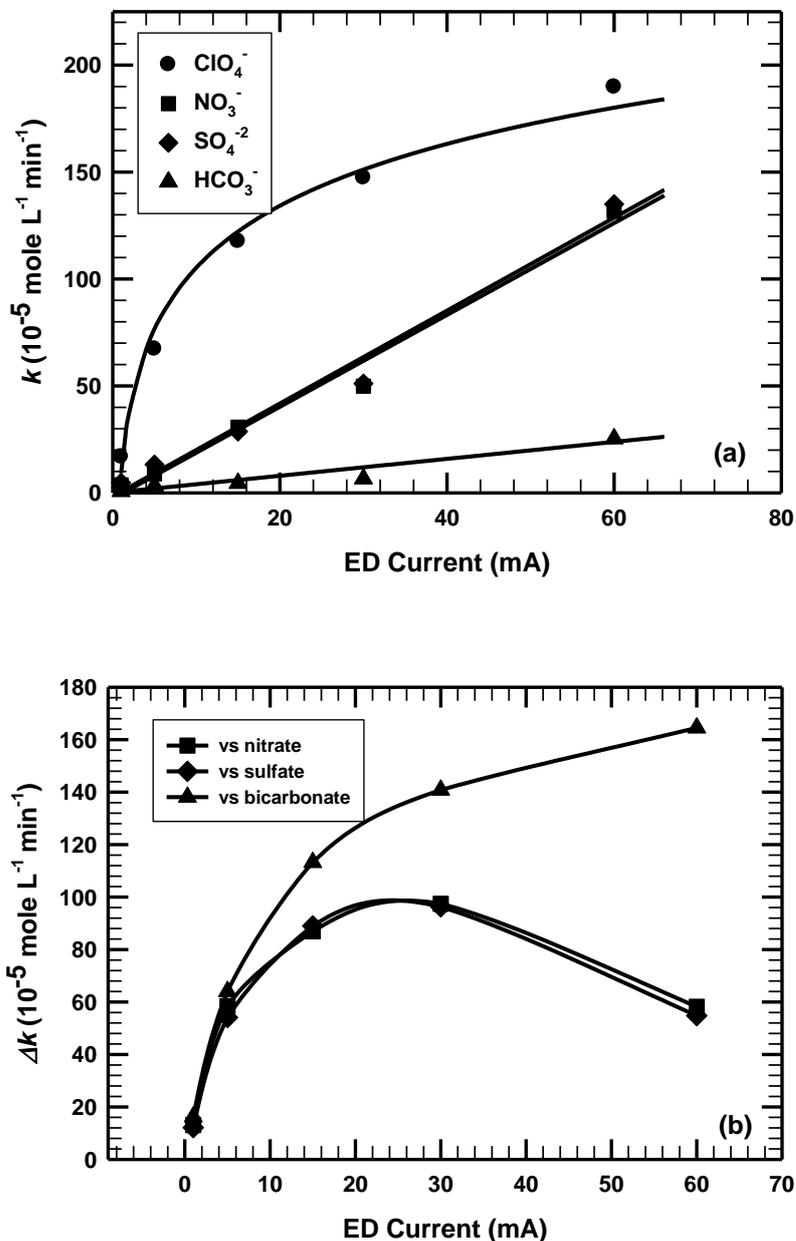


Figure 6.3. Separation rate constant of perchlorate and other anions (nitrate, sulfate and bicarbonate) with MTBA membrane at different ED current. Experimental conditions: each anion =  $10^{-4}$ M; ED cathode and anode = graphite, current = 1 to 60 mA; temperature = 295K.

. From Fig. 6.4, it indicates that 75% of perchlorate (initial concentration is 0.1 mM) could be separated from dilute stream to concentrate stream within 7 hours using electro dialysis current at 1 mA. Also, from the energy saving point of view, it is also more cost effective to operate ED at low current condition. Hence, in the ED-CECR system, low ED current would be applied for separation of perchlorate.

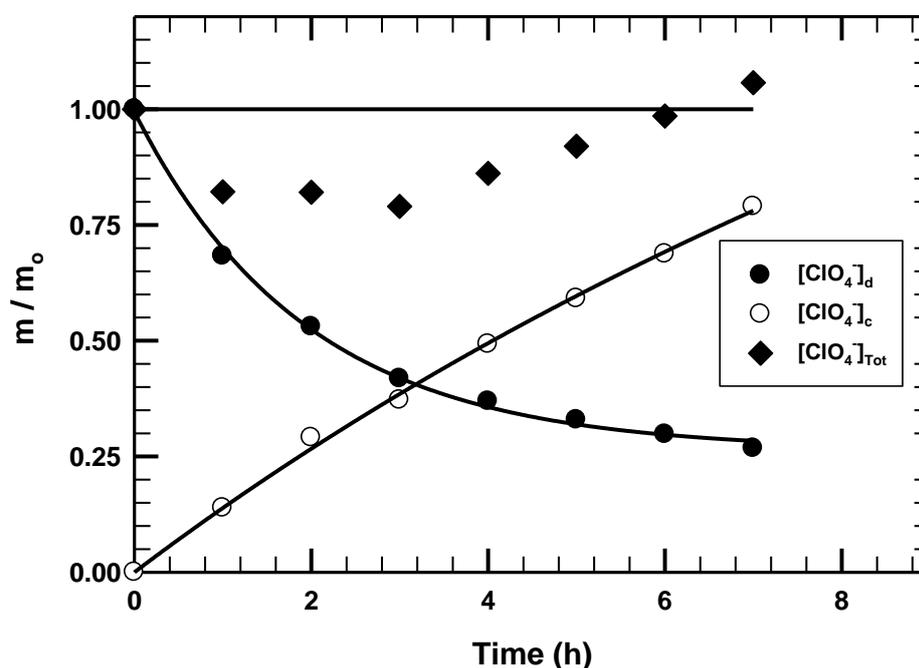
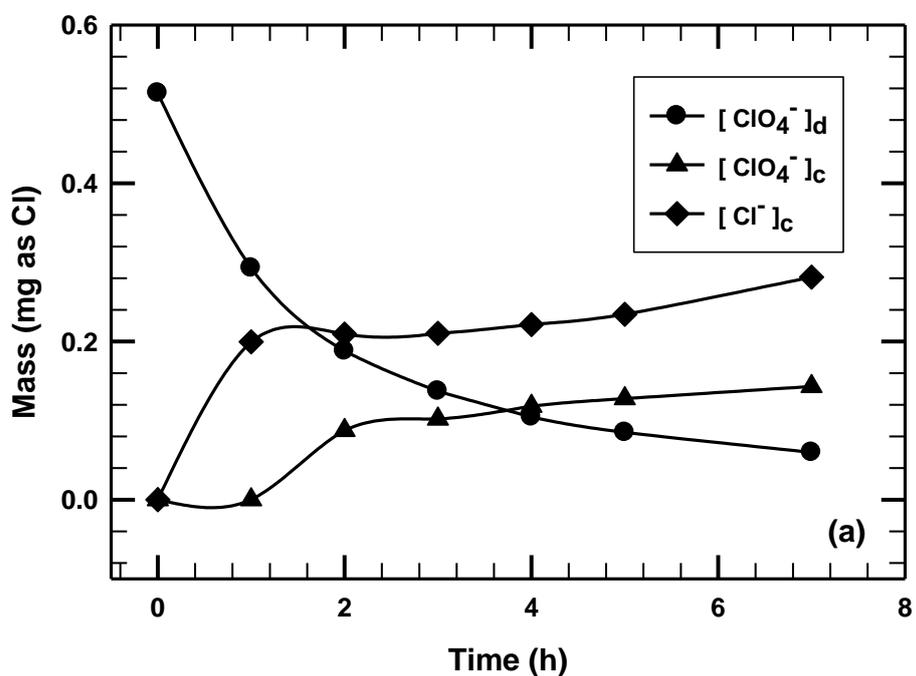


Figure 6.4. Separation of perchlorate with MTBA membrane. Experimental conditions:  $[\text{ClO}_4^-] = 10^{-4}$  M; ED cathode and anode = graphite, current = 1 mA; temperature = 295K; pH = 5.5 in dilute stream; pH = 4.5 in concentrate stream.

### 6.4.3 Effect of ED Current on Perchlorate Reduction

The effect of ED current on perchlorate reduction was also investigated in this study. Fig. 6.5 shows mass balance of  $[\text{ClO}_4^-]$  and  $[\text{Cl}^-]$  in ED-CECR system with different ED current. With higher current (2 mA) as shown in Fig. 6.5(b),

chlorate ion was detected in concentrated side of the membrane. With smaller current (1 mA) as show in Fig. 6.5(a), chlorate ion was not observed. High ED current pushed perchlorate ion passed through the reduction electrode so the uncompleted reduction of perchlorate was occurred. The intermediate product chlorate was observed in high ED current system not in low ED current system. Therefore, low ED current (1 mA) was applied for reduction of the perchlorate to chloride.



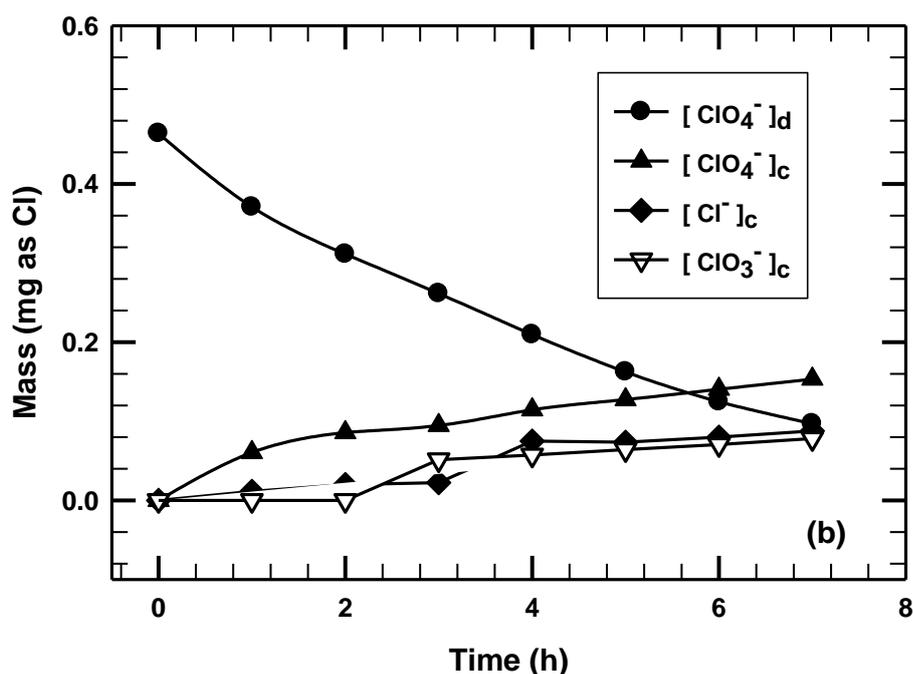


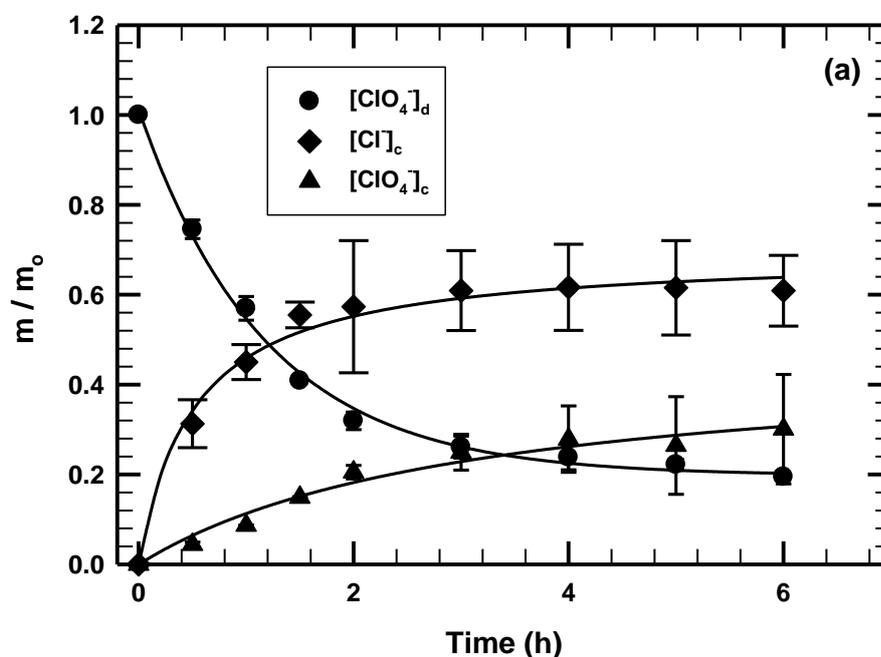
Figure 6.5. Mass balance of  $[\text{ClO}_4^-]$  and  $[\text{Cl}^-]$  in integrated separation and reduction of the perchlorate by Rh-Cu/SS bimetallic catalysts under (a) 1 mA and (b) 2 mA ED current. Experimental conditions:  $[\text{ClO}_4^-] = 10^{-5} \text{ M}$ ; catalytical cathode = Rh-Cu/SS, anode = graphite; reduction current = 20 mA; ED cathode and anode = graphite, ED current = 1 and 2 mA; temperature = 295K; pH = 5.5 in dilute stream; pH = 4.5 in concentrate stream.

#### 6.4.4 Separation and Reduction of Perchlorate in ED-CECR System

Fig. 6.6 shows the separation of perchlorate in the integrated electro dialysis and catalytic electrochemical system. Two types of electrodes were tested in the system: (a) Rh-Ru/SS and (b) Rh-Cu/SS elements doped electrodes. Within 6 hours, about 80% of perchlorate was able to be separated from feeding side of membrane and concentrated at the other side of membrane for both type of electrodes. It is reasoned that the efficiency on separation was mainly controlled by the ED current and the perchlorate permselective membrane. However, the perchlorate reduction efficiencies are around 55%, 80% with Rh-Ru/SS and Rh-Cu/SS electrode, respectively. It is noted that the pH value was controlled at 4.5 at concentrate stream; however perchlorate reduction efficiencies still remain promising. Due to ED electric field carried perchlorate ion across membrane and

pushed perchlorate ion to the surface of electrode, the probabilities for perchlorate ion contacting the electrode surface would increase. Therefore, the overall reduction efficiency was better in the presence of ED electric field. The concentration of chloride in reduction system showed the trend of incensement. It means that the chlorine atom of perchlorate was reduced to its lowest oxidation state through the catalytic electrochemical reaction. Again, no other oxyanions of chlorine, such as  $\text{ClO}_3^-$ ,  $\text{ClO}_2^-$  or  $\text{ClO}^-$  was detected as the intermediates during the reduction process.

Fig. 6.6 also shows the concentration of residual perchlorate in integrated electro dialysis and catalytic electrochemical system. The results indicated that less than 20% of perchlorate was left after reduced by Rh-Cu/SS electrode. In Rh-Ru/SS electrode system, residual perchlorate concentration was in the range of 20 to 30% of the initial perchlorate concentration. In the Fig. 6.6 (a) and (b), the mass balance of chlorine species (chloride and perchlorate in concentrate stream) in the system can be 90 to 98%. The imbalance part of chlorine species mass would be due to the adsorption of perchlorate by either the membrane or electrode.



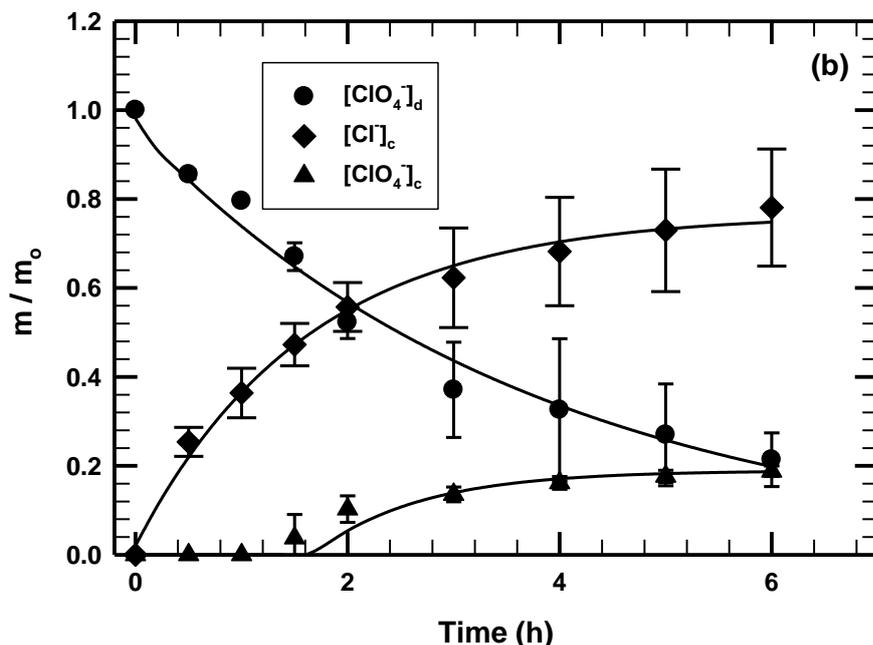
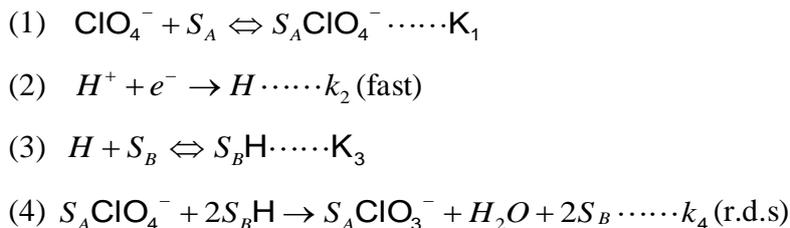
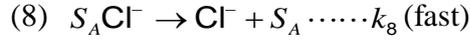


Figure 6.6. Integrated separation and reduction of the perchlorate by different bimetallic catalysts. (a) Rh-Ru/SS and (b) Rh-Cu/SS. Experimental conditions:  $[\text{ClO}_4^-] = 10^{-4}$  M; catalytical cathode = various metals, anode = graphite; current = 20 mA; ED cathode and anode = graphite, current = 1 mA; temperature = 295K; pH = 5.5 in dilute stream; pH = 4.5 in concentrate stream.

#### 6.4.5 Proposed Model for Perchlorate Reduction with Bimetallic Catalysts

Based on the above observation, it is speculated that the reaction began with the adsorption of perchlorate ions on one of the metallic catalyst surface. Also, it is assumed that hydrogen atom are the major species being present on the other metallic catalyst surface. In the chapter 5, a reduction mechanism was proposed,





Assume Eq. (4) is rate determined step (r.d.s.) and all other reactions are at equilibrium, the perchlorate reaction rate can expressed as,

$$\begin{aligned} \frac{d(\text{ClO}_4^-)}{dt} &= -k_4 (S_A \text{ClO}_4^-) (S_B \text{H})^2 = -k_4 K_1 (\text{ClO}_4^-) (S_A) (S_B \text{H})^2 \\ &= -k_4 K_1 (\text{ClO}_4^-) \times \frac{(S_{B,Tot} K_3 [H])^2}{(1 + K_3 [H])^2} \\ &\quad \times \left[ \frac{S_{A,Tot}}{1 + K_1 (\text{ClO}_4^-) + K_1 (\text{ClO}_4^-) \times \left( \frac{k_4}{k_5} + \frac{k_4}{k_6} + \frac{k_4}{k_7} + \frac{k_4}{k_8} \frac{(S_{B,Tot} K_3 [H])^2}{(1 + K_3 [H])^2} \right)} \right] \end{aligned}$$

Then, it can be further simplified as

$$[\text{ClO}_4^-] = [\text{ClO}_4^-]_o e^{-k_{obs}t} \quad (6.9)$$

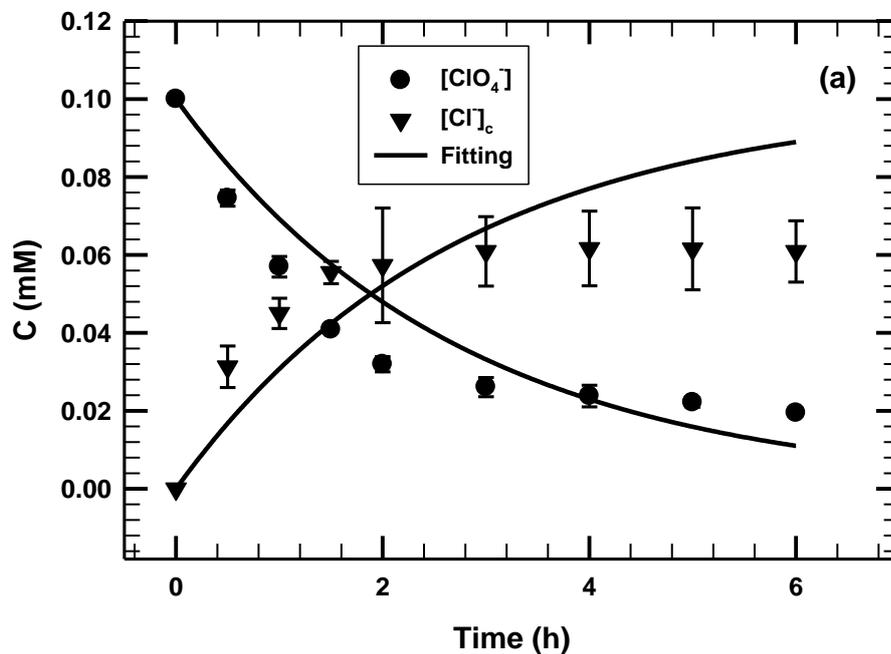
$$\text{where } k_{obs} = k_4 K_1 S_{A,Tot} (S_{B,Tot} K_3 [H])^2$$

In the ED-CECR system, we assume the transported perchlorate will be reduced immediately by the catalyst and since there is no other intermediates accumulate in the reduction process,

$$\begin{aligned} [\text{ClO}_4^-]_o &= [\text{Cl}^-] + [\text{ClO}_4^-] \\ [\text{Cl}^-] &= [\text{ClO}_4^-]_o - \exp(k_{obs}t + \ln([\text{ClO}_4^-]_o)) \end{aligned} \quad (6.10)$$

with Eq. (6.9) and (6.10), chloride ion can be predicted based on the observed perchlorate reduction rate.

Figure 6.7(a) and 6.7(b) show the fitted model and measured perchlorate and chloride concentration with Rh-Ru/SS and Rh-Cu/SS catalytic electrode, respectively. In Fig. 6.7 (a) system, model predicted continuing incensement of chloride concentration after 3 hours, however, the measured chloride concentration remaining stable after 3 hours. It is suggested that the catalytic activity of Rh-Ru was poisoned. It has been reported(Hurley and Shapley 2007; Wang, Huang et al. 2007) that in the presence of chloride or sulfate, perchlorate reduction catalysts such as Rh or  $\text{ReO}_4^-$  would be inactive. And it is also the reason why the residual concentration of perchlorate was found in the concentrate stream as shown is Fig. 6.7(a). However, in Rh\_Cu system, the fitted values for both perchlorate and chloride are closed to the measured values. The catalytic activities still remained at 80% after 6 hours and the concentration of perchlorate in concentrated stream was relative low.



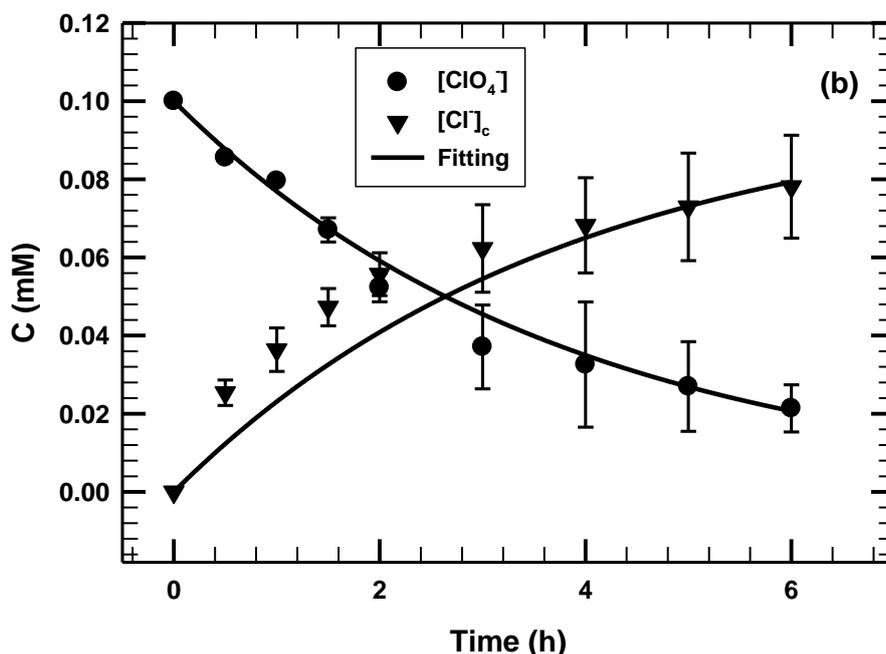


Figure 6.7. Model fitted separation and reduction of perchlorate by different bimetallic catalysts. (a) Rh-Ru/SS and (b) Rh-Cu/SS. Experimental conditions:  $[\text{ClO}_4^-] = 10 \text{ mg/L}$ ; catalytical cathode = various metals, anode = graphite; current = 20 mA; ED cathode and anode = graphite, current = 1 mA; temperature = 295K; pH = 5.5 in dilute stream; pH = 4.5 in concentrate stream.

## 6.5 Summary

In this study, an integrated separation and reduction process for perchlorate containing water remediation was successfully developed. The ED-CECR system provides an integrated process for separation and reduction of perchlorate from water. With perchlorate permselective membrane (PVC/MTBA), perchlorate can exclusively separate and concentrate from water in presence of other anions. Followed by using Rh-Cu/SS reduction electrodes, perchlorate can be reduced to chloride. Several factors such as concentration of initial anions, ED current and were examined and showed that low ED current (1 mA) would be favored for entire separation and reduction process.

A proposed model for perchlorate reduction was developed and successfully used to calculate the rate constants of anions passing through the membranes. Thus, it has been shown that 80% of perchlorate could be separated by MTBA membrane in electro dialysis process and up to 95% of separated perchlorate can be readily reduced to chloride within 6 hours. No other oxyanions of chlorine, such as  $\text{ClO}_3^-$ ,  $\text{ClO}_2^-$  or  $\text{ClO}^-$  was detected as the intermediates during the reduction process. This integrated ED-CECR process can be applied for the removal of low concentration of perchlorate from drinking water sources.

## REFERENCES

- Amemiya, S., P. Bühlmann, et al. (2003). "A Generalized Model for Apparently "Non-Nernstian" Equilibrium Responses of Ionophore-Based Ion-Selective Electrodes. 1. Independent Complexation of the Ionophore with Primary and Secondary Ions." Analytical Chemistry **75**(14): 3329-3339.
- ASTSWMO (2011). Perchlorate policy update, Federal Facilities Research Center - Emerging Issues Focus Group.
- Backus, S. M., P. Klawuun, et al. (2005). "Determination of perchlorate in selected surface waters in the Great Lakes Basin by HPLC/MS/MS." Chemosphere **61**(6): 834-843.
- Bakker, E., P. Bühlmann, et al. (1997). "Carrier-Based Ion-Selective Electrodes and Bulk Optodes. 1. General Characteristics." Chem. Rev. **97**(8): 3083-3132.
- Bakker, E. and E. Pretsch (2007). "Modern Potentiometry." Angew. Chem. Int. Ed. **46**(30): 5660-5668.
- Bakker, E., E. Pretsch, et al. (2000). "Selectivity of potentiometric ion sensors." Analytical Chemistry **72**(6): 1127-1133.
- Bard, A. J. and L. R. Faulkner (2000). Electrochemical methods: fundamentals and applications. Hoboken, NJ, John Wiley & Sons, Inc.
- Barrett, E. P., L. G. Joyner, et al. (1951). "The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms." Journal of the American Chemical Society **73**(1): 373-380.
- Barron, L., P. N. Nesterenko, et al. (2006). "Rapid on-line preconcentration and suppressed micro-bore ion chromatography of part per trillion levels of perchlorate in rainwater samples." Analytica Chimica Acta **567**(1): 127-134.
- Bobacka, J., A. Ivaska, et al. (2008). "Potentiometric Ion Sensors." Chem. Rev. **108**(2): 329-351.
- Bonnesen, P. V., G. M. Brown, et al. (2000). "Development of Bifunctional Anion-Exchange Resins with Improved Selectivity and Sorptive Kinetics for Perchlorate: Batch-Equilibrium Experiments." Environmental Science & Technology **34**(17): 3761-3766.
- Brandhuber, P. and S. Clark (2005). "Perchlorate Occurrence Mapping " American Water Works Association.
- Brown, G. M. (1986). "The reduction of chlorate and perchlorate ions at an active titanium electrode." Journal of Electroanalytical Chemistry and Interfacial Electrochemistry **198**(2): 319-330.
- Cao, J., D. Elliott, et al. (2005). "Perchlorate Reduction by Nanoscale Iron Particles." Journal of Nanoparticle Research **7**(4-5): 499-506.
- CDPH. (2015). "Perchlorate in Drinking Water." Retrieved July 3rd, 2015, from [http://www.waterboards.ca.gov/drinking\\_water/certlic/drinkingwater/Perchlorate.shtml](http://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/Perchlorate.shtml).
- Ceresa, A., T. Sokalski, et al. (2001). "Influence of key parameters on the lower detection limit and response function of solvent polymeric membrane ion-

- selective electrodes." Journal of Electroanalytical Chemistry **501**(1-2): 70-76.
- Chen, W., F. S. Cannon, et al. (2005). "Ammonia-tailoring of GAC to enhance perchlorate removal. I: Characterization of NH<sub>3</sub> thermally tailored GACs." Carbon **43**(3): 573-580.
- Chen, W., F. S. Cannon, et al. (2005). "Ammonia-tailoring of GAC to enhance perchlorate removal. II: Perchlorate adsorption." Carbon **43**(3): 581-590.
- Choe, J. K., J. R. Shapley, et al. (2010). "Influence of Rhenium Speciation on the Stability and Activity of Re/Pd Bimetal Catalysts used for Perchlorate Reduction." Environmental Science & Technology **44**(12): 4716-4721.
- Colom, F. and M. J. González-Tejera (1985). "Reduction of perchlorate ion on ruthenium electrodes in aqueous solutions." Journal of Electroanalytical Chemistry and Interfacial Electrochemistry **190**(1-2): 243-255.
- Comisso, N., S. Cattarin, et al. (2012). "Electrodeposition of Cu-Rh alloys and their use as cathodes for nitrate reduction." Electrochemistry Communications **25**: 91-93.
- Craggs, A., G. J. Moody, et al. (1974). "PVC matrix membrane ion-selective electrodes. Construction and laboratory experiments." J. Chem. Educ. **51**(8): 541.
- Dasgupta, P. K., P. K. Martinelango, et al. (2005). "The origin of naturally occurring perchlorate: The role of atmospheric processes." Environmental Science & Technology **39**(6): 1569-1575.
- Egorov, V., E. Rakhman'ko, et al. (2004). "Novel Anion Exchangers for Electrodes with Improved Selectivity to Divalent Anions." Electroanalysis **16**(17): 1459-1462.
- El Aribi, H., Y. J. C. Le Blanc, et al. (2006). "Analysis of perchlorate in foods and beverages by ion chromatography coupled with tandem mass spectrometry (IC-ESI-MS/MS)." Analytica Chimica Acta **567**(1): 39-47.
- Fang, Q. and B. Chen (2012). "Adsorption of perchlorate onto raw and oxidized carbon nanotubes in aqueous solution." Carbon **50**(6): 2209-2219.
- Fisher, H., E. G. Brown, et al. (1964). Folsom-East Sacramento ground water quality investigation, California Department of Water Resources. **Bulletin no. 133**.
- Ganjali, M. R., P. Norouzi, et al. (2007). "Perchlorate-selective membrane sensors based on two nickel-hexaazamacrocyclic complexes." Sensors and Actuators B: Chemical **120**(2): 494-499.
- GAO (2010). Perchlorate: Occurrence Is Widespread But At Varying Levels; Federal Agencies have Taken Some Actions to Respond to and Lessen Releases, Government Accounting Office. **GAO-10-769**.
- Greenhaw, K. (2014). "Rules to Watch (and Wait) for in 2014." Retrieved March 3rd, 2014, from <http://www.foreffectivegov.org/rules-watch-and-wait-2014>.
- Gu, B., Y.-K. Ku, et al. (2005). "Sorption and Desorption of Perchlorate and U(VI) by Strong-Base Anion-Exchange Resins." Environmental Science & Technology **39**(3): 901-907.

- Gu, B. H., G. M. Brown, et al. (2007). "Treatment of perchlorate-contaminated groundwater using highly selective, regenerable ion-exchange technologies." Environmental Science & Technology **41**(17): 6277-6282.
- Hara, H., H. Ohkubo, et al. (1993). "Nitrate ion-selective coated-wire electrode based on tetraoctadecylammonium nitrate in solid solvents and the effect of additives on its selectivity." Analyst **118**(5): 549-552.
- Hecht, M. H., S. P. Kounaves, et al. (2009). "Detection of Perchlorate and the Soluble Chemistry of Martian Soil at the Phoenix Lander Site." Science **325**(5936): 64-67.
- Hiquily, N. and M. J. Clifton (1984). "Diffusion coefficient of ammonium perchlorate in concentrated aqueous solutions between 20 and 30.degree.C." Journal of Chemical & Engineering Data **29**(4): 371-373.
- Horányi, G. and I. Bakos (1994). "Investigation of the electrodeposition and behaviour of Re layers by coupled radiochemical and electrochemical methods." Journal of Electroanalytical Chemistry **378**(1-2): 143-148.
- Horányi, G. and G. Vértes (1975). "Catalytic and electrochemical reduction of perchlorate ions on platinum in aqueous solution." Journal of Electroanalytical Chemistry and Interfacial Electrochemistry **64**(2-3): 252-254.
- Hurley, K. D. and J. R. Shapley (2007). "Efficient heterogeneous catalytic reduction of perchlorate in water." Environmental Science & Technology **41**(6): 2044-2049.
- Hurley, K. D., Y. X. Zhang, et al. (2009). "Ligand-Enhanced Reduction of Perchlorate in Water with Heterogeneous Re-Pd/C Catalysts." Journal of the American Chemical Society **131**(40): 14172-3.
- Hwang, G. J. and H. H. Ohya (1998). "Preparation of anion-exchange membrane based on block copolymers Part 1. Amination of the chloromethylated copolymers." Journal of Membrane Science **140**(2): 195-203.
- IUPAC (1976). "Recommendations for Nomenclature of Ion-Selective Electrodes." Pure and Applied Chemistry **48**(1): 127-132.
- Kesore, K., F. Janowski, et al. (1997). "Highly effective electrodialysis for selective elimination of nitrates from drinking water." Journal of Membrane Science **127**(1): 17-24.
- Kim, T.-H., M. Jang, et al. (2008). "Bifunctionalized mesoporous molecular sieve for perchlorate removal." Microporous and Mesoporous Materials **108**(1-3): 22-28.
- Kim, Y.-N. and M. Choi (2014). "Synergistic Integration of Ion-Exchange and Catalytic Reduction for Complete Decomposition of Perchlorate in Waste Water." Environmental Science & Technology **48**(13): 7503-7510.
- Kirk, A. B. (2006). "Environmental perchlorate: Why it matters." Analytica Chimica Acta **567**(1): 4-12.
- Kirk, A. B., J. V. Dyke, et al. (2007). "Temporal patterns in perchlorate, thiocyanate, and iodide excretion in human milk." Environmental Health Perspectives **115**(2): 182-186.
- Kirk, A. B., P. K. Martinelango, et al. (2005). "Perchlorate and Iodide in Dairy and Breast Milk." Environmental Science & Technology **39**(7): 2011-2017.

- Klaysom, C., S. H. Moon, et al. (2011). "Preparation of porous ion-exchange membranes (IEMs) and their characterizations." Journal of Membrane Science **371**(1-2): 37-44.
- Kosaka, K., M. Asami, et al. (2007). "Occurrence of perchlorate in drinking water sources of metropolitan area in Japan." Water Research **41**(15): 3474-3482.
- Kumar, E., A. Bhatnagar, et al. (2010). "Perchlorate removal from aqueous solutions by granular ferric hydroxide (GFH)." Chemical Engineering Journal **159**(1-3): 84-90.
- Kumar, M., S. Singh, et al. (2010). "Cross-Linked Poly(vinyl alcohol)-Poly(acrylonitrile-co-2-dimethylamino ethylmethacrylate) Based Anion-Exchange Membranes in Aqueous Media." J. Phys. Chem. B **114**(1): 198-206.
- Lakshmi, J. and S. Vasudevan (2013). "Graphene - a promising material for removal of perchlorate ( $\text{ClO}_4^-$ ) from water." Environmental Science and Pollution Research **20**(8): 5114-5124.
- Lamb, J. D., D. Simpson, et al. (2006). "Determination of perchlorate in drinking water by ion chromatography using macrocycle-based concentration and separation methods." Journal of Chromatography A **1118**(1): 100-105.
- Láng, G. G. and G. Horányi (2003). "Some interesting aspects of the catalytic and electrocatalytic reduction of perchlorate ions." Journal of Electroanalytical Chemistry **552**: 197-211.
- Láng, G. G., N. S. Sas, et al. (2008). "The kinetics of the electrochemical reduction of perchlorate ions on rhodium." Electrochimica Acta **53**(25): 7436-7444.
- Lasaga, A. C. and R. J. Kirkpatrick, Eds. (1981). Kinetics of geochemical processes. Reviews in Mineralogy and Geochemistry.
- Levitskaia, T. G., S. I. Sinkov, et al. (2007). "In situ perchlorate determination on Purolite A850 ion exchange resin via Raman spectroscopy." Vibrational Spectroscopy **44**(2): 316-323.
- Maccà, C. (2004). "Response time of ion-selective electrodes: Current usage versus IUPAC recommendations." Analytica Chimica Acta **512**(2): 183-190.
- Mahmudov, R. and C. P. Huang (2010). "Perchlorate removal by activated carbon adsorption." Separation and Purification Technology **70**(3): 329-337.
- Mahmudov, R. and C. P. Huang (2011). "Selective adsorption of oxyanions on activated carbon exemplified by Filtrasorb 400 (F400)." Separation and Purification Technology **77**(3): 294-300.
- Martinelango, P. K. and P. K. Dasgupta (2007). "Dicationic ion-pairing agents for the mass spectrometric determination of perchlorate." Analytical Chemistry **79**(18): 7198-7200.
- Martinelango, P. K., G. Gumus, et al. (2006). "Matrix interference free determination of perchlorate in urine by ion association-ion chromatography-mass spectrometry." Analytica Chimica Acta **567**(1): 79-86.
- MDEP. (2006). "Drinking Water Standard for Perchlorate." Retrieved March 3rd, 2014, from <http://www.mass.gov/eea/docs/dep/water/laws/i-thru-z/perchlorate-310cmr22-07282006.pdf>.

- Moody, G. J., R. B. Oke, et al. (1970). "A calcium-sensitive electrode based on a liquid ion exchanger in a poly(vinyl chloride) matrix." *Analyst* **95**(1136): 910-918.
- Moya, A. A. (2012). "Electric circuits modelling the low-frequency impedance of ideal ion-exchange membrane systems." *Electrochimica Acta* **62**: 296-304.
- Moyer, B. A. and P. V. Bonnesen (1997). Physical Factors in Anion Separations. *Supramolecular Chemistry of Anions*. A. Bianchi, K. Bowman-James and E. Garcia-Espana. New York, Wiley-VCH: 1-44.
- Nagarale, R. K., G. S. Gohil, et al. (2006). "Recent developments on ion-exchange membranes and electro-membrane processes." *Advances in Colloid and Interface Science* **119**(2-3): 97-130.
- Nicholson, R. S. and I. Shain (1964). "Theory of Stationary Electrode Polarography. Single Scan and Cyclic Methods Applied to Reversible, Irreversible, and Kinetic Systems." *Analytical Chemistry* **36**(4): 706-723.
- NRC (2005). *Health Implications of Perchlorate Ingestion*. Washington, D. C., National Academies Press.
- Okeke, B. C., G. Y. Ma, et al. (2007). "Development of a perchlorate reductase-based biosensor for real time analysis of perchlorate in water." *Journal of Microbiological Methods* **68**(1): 69-75.
- Olívia Salomé G. P. Soares, José J. M. Órfão, et al. (2008). "Activated Carbon Supported Metal Catalysts for Nitrate and Nitrite Reduction in Water." *Catalysis Letters* **126**(3-4): 253-260.
- Olívia Salomé G.P. Soares , José J.M. Órfão , et al. (2009). "Bimetallic catalysts supported on activated carbon for the nitrate reduction in water: Optimization of catalysts composition." *Applied Catalysis B: Environmental* **91**(1-2): 441-448.
- Ozawa, S., H. Miyagi, et al. (1996). "Anion-Selective Electrodes Based on Long-Chain Methyltrialkylammonium Salts." *Analytical Chemistry* **68**(23): 4149-4152.
- Paoinot, J. and J. Augustynski (1975). "Etude potentiostatique et spectroscopique de l'aluminium recouvert par une couche d'oxyde: effet de differents anions." *Electrochimica Acta* **20**(10): 747-752.
- Parette, R. and F. S. Cannon (2005). "The removal of perchlorate from groundwater by activated carbon tailored with cationic surfactants." *Water Research* **39**(16): 4020-4028.
- Park, J.-S., J.-H. Choi, et al. (2006). "An electrical impedance spectroscopic (EIS) study on transport characteristics of ion-exchange membrane systems." *Journal of Colloid and Interface Science* **300**(2): 655-662.
- Parker, D. R. (2009). "Perchlorate in the environment: the emerging emphasis on natural occurrence." *Environ. Chem.* **6**: 10-27.
- Quiñones, O., J.-E. Oh, et al. (2007). "Perchlorate assessment of the Nakdong and Yeongsan watersheds, Republic of Korea." *Environmental Toxicology and Chemistry* **26**(7): 1349-1354.
- Rajagopalan, S., T. Anderson, et al. (2009). "Perchlorate in Wet Deposition Across North America." *Environmental Science & Technology* **43**(3): 616-622.

- Rajendran, S., M. R. Prabhu, et al. (2008). "Characterization of PVC/PEMA based polymer blend electrolytes." International Journal of Electrochemical Science **3**(3): 282-290.
- Ramesh, S., K. H. Leen, et al. (2007). "FTIR studies of PVC/PMMA blend based polymer electrolytes." Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy **66**(4-5): 1237-1242.
- Rezaei, B., S. Meghdadi, et al. (2009). "Perchlorate-selective polymeric membrane electrode based on bis(dibenzoylmethanato)cobalt(II) complex as a neutral carrier." Journal of Hazardous Materials **161**(2-3): 641-648.
- Rezaei, B., S. Meghdadi, et al. (2007). "Fast response and selective perchlorate polymeric membrane electrode based on bis(dibenzoylmethanato) nickel(II) complex as a neutral carrier." Sensors and Actuators B: Chemical **121**(2): 600-605.
- Rhee, C. K., M. Wasberg, et al. (1991). "Reduction of perchlorate on rhodium and its specificity to surface crystallographic orientation." Catalysis Letters **10**(3-4): 149-164.
- Roach, J. D., R. F. Lane, et al. (2011). "Comparative study of the uses of poly(4-vinylpyridine) and poly(diallyldimethylammonium) chloride for the removal of perchlorate from aqueous solution by polyelectrolyte-enhanced ultrafiltration." Water Research **45**(3): 1387-1393.
- Roach, J. D. and D. Tush (2008). "Equilibrium dialysis and ultrafiltration investigations of perchlorate removal from aqueous solution using poly(diallyldimethylammonium) chloride." Water Research **42**(4): 1204-1210.
- Roquebert, V., S. Booth, et al. (2000). "Electrodialysis reversal (EDR) and ion exchange as polishing treatment for perchlorate treatment." Desalination **131**(3): 285-291.
- Sanchez, C. A., R. I. Krieger, et al. (2005). "Accumulation and perchlorate exposure potential of lettuce produced in the Lower Colorado River region." Journal of Agricultural and Food Chemistry **53**(13): 5479-5486.
- Sata, T. (2000). "Studies on anion exchange membranes having permselectivity for specific anions in electrodialysis - effect of hydrophilicity of anion exchange membranes on permselectivity of anions." Journal of Membrane Science **167**(1): 1-31.
- Sata, T., K. Mine, et al. (1998). "Changing permselectivity between halogen ions through anion exchange membranes in electrodialysis by controlling hydrophilicity of the membranes." Journal of the Chemical Society, Faraday Transactions **94**(1): 147-153.
- Sata, T., T. Sata, et al. (2002). "Studies on cation-exchange membranes having permselectivity between cations in electrodialysis." Journal of Membrane Science **206**(2): 31-60.
- Sata, T., K. Teshima, et al. (1996). "Permselectivity between two anions in anion exchange membranes crosslinked with various diamines in electrodialysis." Journal of Polymer Science, Part A: Polymer Chemistry **34**(8): 1475-1482.

- Sata, T., T. Yamaguchi, et al. (1995). "Anion exchange membranes for nitrate ion removal from groundwater by electrodialysis." Journal of the Chemical Society, Chemical Communications(11): 1153-1154.
- Shi, Y. L., P. Zhang, et al. (2007). "Perchlorate in sewage sludge, rice, bottled water and milk collected from different areas in China." Environment International **33**(7): 955-962.
- Sistat, P., A. Kozmai, et al. (2008). "Low-frequency impedance of an ion-exchange membrane system." Electrochimica Acta **53**(22): 6380-6390.
- Smirnova, A. L., V. N. Tarasevitch, et al. (1994). "Some properties of sulfate ion-selective PVC membranes based on a neutral carrier and ion-exchanger." Sensors and Actuators B: Chemical **19**: 392-395.
- Sobolev, V. D., V. M. Starov, et al. (2003). "On the accuracy of measuring small contact angles by the sessile drop method." Colloid Journal **65**(5): 611-614.
- Soldatov, D. V. and J. A. Ripmeester (2001). "Modified metal dibenzoylmethanates and their clathrates part III - Novel 4-vinylpyridine-extended metal-dibenzoylmethanate host frameworks: Structure, polymorphism, and inclusion properties." Chemistry A European Journal **7**(14): 2979-2994.
- Soleymanpour, A., E. H. Asl, et al. (2007). "Perchlorate selective membrane electrodes based on synthesized platinum(II) complexes for low-level concentration measurements." Sensors and Actuators B: Chemical **120**(2): 447-454.
- Soleymanpour, A., B. Garaili, et al. (2008). "Perchlorate selective membrane electrodes based on a platinum complex." Monatshefte Fur Chemie **139**(12): 1439-1445.
- Soman, V. V. and D. S. Kelkar (2009). "FTIR Studies of Doped PMMA - PVC Blend System." Macromolecular Symposia **277**(1): 152-161.
- Strathmann, H. (2010). "Electrodialysis, a mature technology with a multitude of new applications." Desalination **264**(3): 268-288.
- Theivasanthi, T. and M. Alagar (2011). "Nano sized copper particles by electrolytic synthesis and characterizations." International Journal of Physical Sciences **6**(15): 3662-3671.
- Thrash, J. C., J. I. Van Trump, et al. (2007). "Electrochemical stimulation of microbial perchlorate reduction." Environmental Science & Technology **41**(5): 1740-1746.
- Toshikatsu, S. (2000). "Studies on anion exchange membranes having permselectivity for specific anions in electrodialysis ??effect of hydrophilicity of anion exchange membranes on permselectivity of anions." Journal of Membrane Science **167**(1): 1-31.
- Urbansky, E. T. (1998). "Perchlorate Chemistry: Implications for Analysis and Remediation." Bioremediation Journal **2**(2): 81 - 95.
- Urbansky, E. T. and S. K. Brown (2003). "Perchlorate retention and mobility in soils." Journal of Environmental Monitoring **5**(3): 455-462.
- USEPA (1998). "Announcement of the Drinking Water Contaminant Candidate List; Notice." Federal Register **63**(40): 10273.

- USEPA (1998). Perchlorate Environmental Contamination: Toxicological review and risk characterization based on emerging information, Environmental Protection Agency.
- USEPA. (2011). "Drinking Water: Regulatory Determination on Perchlorate." Retrieved March 3rd, 2014, from <http://www.gpo.gov/fdsys/pkg/FR-2011-02-11/pdf/2011-2603.pdf>.
- USEPA. (2015). "National Primary Drinking Water Regulations: Regulation of Perchlorate." Retrieved June, 2015, from <http://yosemite.epa.gov/opei/rulegate.nsf/byRIN/2040-AF28#1>.
- Vanýsek, P. (2002). Ionic conductivity and diffusion at infinite dilution. Boca Raton, CRC Press.
- Wang, D. M. and C. P. Huang (2008). "Electrodialytically assisted catalytic reduction (EDACR) of perchlorate in dilute aqueous solutions." Separation and Purification Technology **59**(3): 333-341.
- Wang, D. M., C. P. Huang, et al. (2007). "Reduction of perchlorate in dilute aqueous solutions over monometallic nano-catalysts: Exemplified by tin." Separation and Purification Technology **58**(1): 129-137.
- Wang, D. M., H. Y. Lin, et al. (2009). "Indirect electrochemical reduction of perchlorate and nitrate in dilute aqueous solutions at the Ti-water interface." Separation and Purification Technology **67**(2): 127-134.
- Wang, D. M., S. I. Shah, et al. (2008). "Catalytic reduction of perchlorate by H<sub>2</sub> gas in dilute aqueous solutions." Separation and Purification Technology **60**(1): 14-21.
- Wang, P.-Y., I. Shah, et al. (2015). "Preparation and characterization of functionalized poly(vinyl chloride) membranes for selective separation of perchlorate from water." Journal of Membrane Science **476**: 561-570.
- Wang, P.-Y., S. I. Shah, et al. (2013). "A polymeric membrane electrode for the detection of perchlorate in water at the sub-micro-molar level." Analytical Methods **5**(14): 3530-3537.
- Wasberg, M. and G. Horányi (1995). "The reduction of ClO<sub>4</sub><sup>-</sup> ions on Rh electrodes." Journal of Electroanalytical Chemistry **385**(1): 63-70.
- Witonska, I., S. Karski, et al. (2007). "Kinetic studies on the hydrogenation of nitrate in water using Rh/Al(2)O(3) and Rh-Cu/Al(2)O(3) catalysts." Kinetics and Catalysis **48**(6): 823-828.
- Wolff, J. (1998). "Perchlorate and the thyroid gland." Pharmacological Reviews **50**(1): 89-105.
- Xie, Y., S. Li, et al. (2011). "A hybrid adsorption/ultrafiltration process for perchlorate removal." Journal of Membrane Science **366**: 237-244.
- Xiong, Z., D. Zhao, et al. (2007). "Sorption and Desorption of Perchlorate with Various Classes of Ion Exchangers: A Comparative Study." Industrial & Engineering Chemistry Research **46**(26): 9213-9222.
- Yoon, J., Y. Yoon, et al. (2003). "Use of surfactant modified ultrafiltration for perchlorate (ClO<sub>4</sub><sup>-</sup>) removal." Water Research **37**(9): 2001-2012.
- Yoon, Y., G. Amy, et al. (2002). "Transport of perchlorate (ClO<sub>4</sub><sup>-</sup>) through NF and UF membranes." Desalination **147**(1??): 11-17.

- Yoon, Y., G. Amy, et al. (2005). "Effect of pH and conductivity on hindered diffusion of perchlorate ions during transport through negatively charged nanofiltration and ultrafiltration membranes." Desalination **177**(1??): 217-227.
- Zanjanchi, M. A., M. Arvand, et al. (2006). "Perchlorate-selective polymeric membrane electrode based on a cobaloxime as a suitable carrier." Sensors and Actuators B: Chemical **113**(1): 304-309.
- Zelenay, P., G. Horanyi, et al. (1991). "VOLTAMMETRIC AND RADIOACTIVE LABELING STUDIES OF SINGLE-CRYSTAL AND POLYCRYSTALLINE RHODIUM ELECTRODES IN SULFATE-CONTAINING ELECTROLYTES." Journal of Electroanalytical Chemistry **300**(1-2): 499-519.
- Zhang, Y. X., K. D. Hurley, et al. (2011). "Heterogeneous Catalytic Reduction of Perchlorate in Water with Re-Pd/C Catalysts Derived from an Oxorhenium(V) Molecular Precursor." Inorganic Chemistry **50**(4): 1534-1543.

## CONCLUSION AND SUGGESTIONS

### 7.1 Conclusion

In this study, two types of polymeric membrane, MTOA, MTBA functionalized membrane, were developed for analysis and separation of perchlorate, respectively. To reduce perchlorate, bimetallic catalysts were also doped on a stainless steel surface as a cathodic electrode. First, the perchlorate selective membrane was used to construct an electrode for detection at the sub-micro-molar level. The perchlorate selective electrode functioned well in the presence of common interfering anions such as chloride, sulfate, nitrate, bicarbonate. The membrane electrode had a wide application pH range (3.0 to 11.0), low detection limit ( $7.0 \times 10^{-7}$  M), and favorable potentiometric selectivity coefficients over other interfering anions in natural water thereby making it a great convenience for field perchlorate analysis.

Also, a novel perchlorate permselective membrane were synthesized via functionalizing PVC polymer with quaternary ammonium salts. Both the physical and the chemical characteristics of the polymer and its endowed functional groups determine the permselectivity of the membranes. Based on the physical structure, the results showed that the perchlorate permselectivity of the membrane could be enhanced as the thickness and the polymer content were increased. Regardless of the large hydration size of perchlorate, larger than that of nitrate, sulfate and bicarbonate ion, the physical and chemical affinity contributed from the quaternary ammonium salts in the membrane structure could selectively separate perchlorate from the other anions under an electrostatic field. FTIR and SEM results showed

the changes of PVC polymer in terms of wavenumber shift and surface feature through the incorporation of quaternary ammonium salts into the polymer structure. MTBA compound with moderate chain length offered steric effect for perchlorate separation and balanced both the selectivity and the kinetic rate on adsorption and desorption of the perchlorate. The surface hydrophobicity of MTBA membrane increased slightly after electro dialysis which means most of perchlorate molecule could be transported through the membrane feasibly while a very small amount of perchlorate ion was retained on the membrane surface.

A mathematical model for transport kinetics of anions across the membrane was developed and successfully used to calculate the rate constants of anions passing through the membranes. The calculations demonstrate that the MTBA membrane with electro dialysis separated 60% of perchlorate versus 9% of other anions. The findings of this study could lead to a better, sustainable method for separation of perchlorate from drinking water source using electro dialysis without adding additional chemicals. The concentrated perchlorate solution could be collected for the purpose of further treatment or reuse.

Moreover, monometallic (Mo, Ru, Rh, Cu, Pd) and bimetallic (Rh-Cu, Rh-Ru) catalysts were prepared for perchlorate reduction in the study. The results showed that with applying the same current and pH in the system, perchlorate reduction efficiency of monometallic doped electrodes were in the order of Rh>Cu>Ru>Mo>Pd. For bi-metallic doped electrodes, Rh-Cu (75% reduction) is greater than Rh-Ru (60% reduction). The mass balance of chlorine species (chloride and perchlorate) in the system can be up to 95%. The testing results of the catalytic electrochemical technique demonstrate its suitability for the reduction of perchlorate.

Finally, the ED-CECR system provides an integrated process for the separation and reduction of perchlorate from water. With the perchlorate

permselective membrane (PVC/MTBA), perchlorate can exclusively separate and concentrate from water in the presence of other anions. When paired with using Rh-Cu/SS reduction electrodes, perchlorate can be reduced to chloride.

A proposed model for perchlorate reduction was developed and successfully used to calculate the rate constants of anions passing through the membranes. The calculations show that 80% of perchlorate could be separated by MTBA membrane in electrodialysis process and up to 95% of separated perchlorate can be readily reduced to chloride within 6 hours. No other oxyanions of chlorine, such as  $\text{ClO}_3^-$ ,  $\text{ClO}_2^-$  or  $\text{ClO}^-$  were detected as intermediates during the reduction process. This integrated ED-CECR process can be applied for the removal of low concentration of perchlorate from drinking water sources.

## **7.2 Suggestions for Future Works**

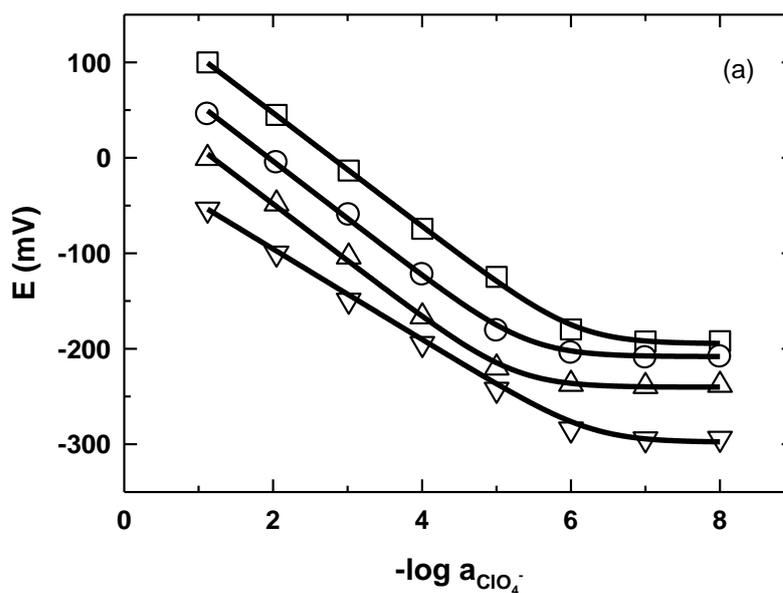
Results of the present study revealed a process to detect, remove, and reduce perchlorate under ambient conditions. However, several issues need to be addressed for future research. The first issue is to “fine-tune” the bimetallic catalyst. The characterization of the reactive surface of the catalyst can benefit its performance. While preliminary results indicate that Rh-Cu/SS is promising for perchlorate reduction, further research can explore the crystal structure, optimize the ratio of the bimetals, and adjust the size of the catalysts to improve upon efficiency and durability. The second issue is to develop a continue-flow system with a flow reactor. The removal efficiency is high under the batch system in this study. The performance and durability can be further examined by using the continue-flow system. The third issue is the long term operation for (1) perchlorate ion selective electrode for the detection of perchlorate; (2) perchlorate permselective membrane for the separation of perchlorate and (3) Rh-Cu/SS electrode for the reduction of perchlorate under near-pilot scale with real water samples.

## Appendix A

### POLYMERIC MEMBRANE ELECTRODE FOR THE DETECTION OF PERCHLORATE IN WATER AT THE SUB-MICRO-MOLAR LEVEL

#### A.1 Internal Solution

Two types of internal solutions were tested, (1) perchlorate solution and (2) Ni(DBM)<sub>2</sub> + perchlorate, to optimize the sensitivity of perchlorate-ISE. Results (Fig A1 and Table A1 showed that 10<sup>-4</sup> M of internal solution without addition of Ni(II) complexes was adequate in attaining Nernstian slope response and sensitivity.



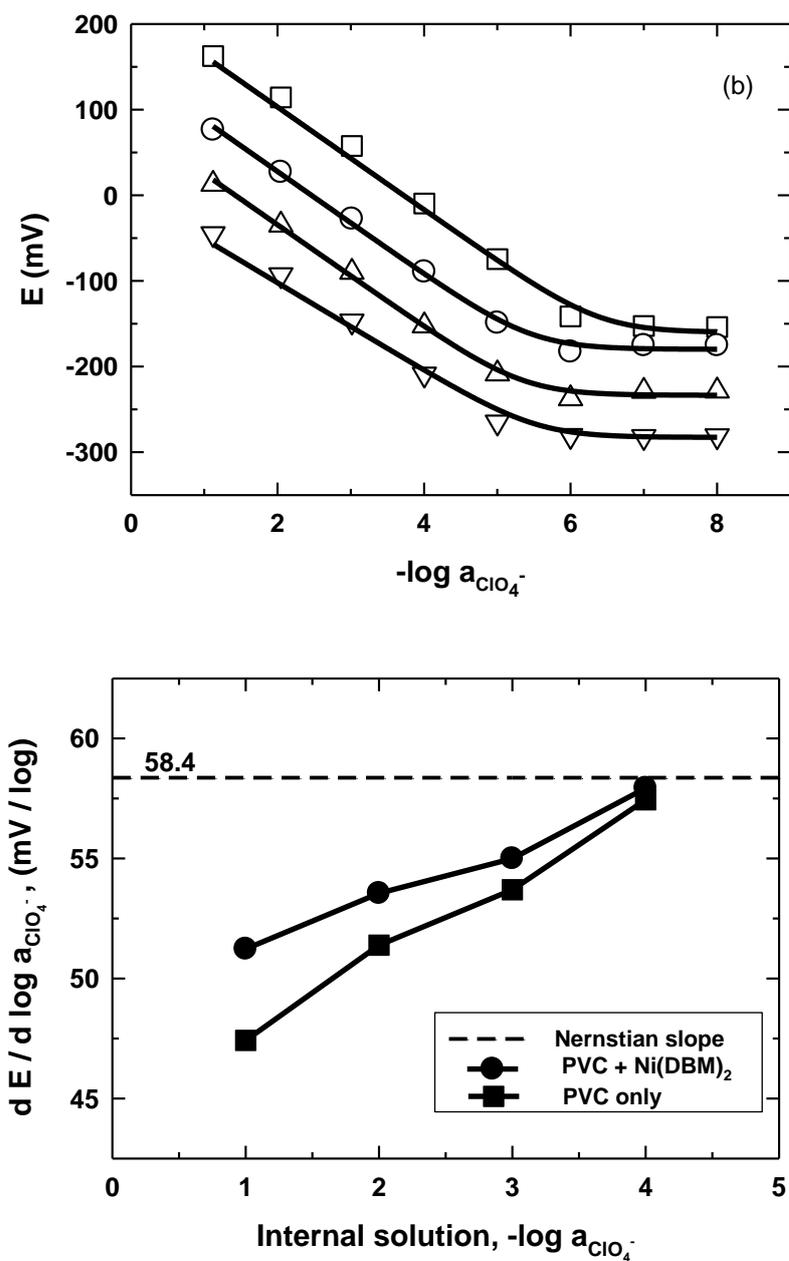


Figure A1. Effect of internal perchlorate concentration on the potentiometric response of (a) PVC, (b) PVC+Ni(DBM)<sub>2</sub> electrode and (c) changes of Nernstian slope. Experimental conditions: temperature = 21 ~ 23 °C; pH = 5 ~7. Symbols: (□) 0.1 mM, (○) 1.0 mM, (△) 10 mM, (▽) 100 mM. The dashed line represents the theoretical Nernstian slope of 58.4 mV/log.

## A.2 Thickness of ISE Membrane

The electrode potential decreased with perchlorate activity (log) in the perchlorate activity range of  $10^{-6}$  to  $10^{-1}$  M (Fig. A2). The membrane resistance will increase with thickness which consequently will decrease the ion flux across the membrane.

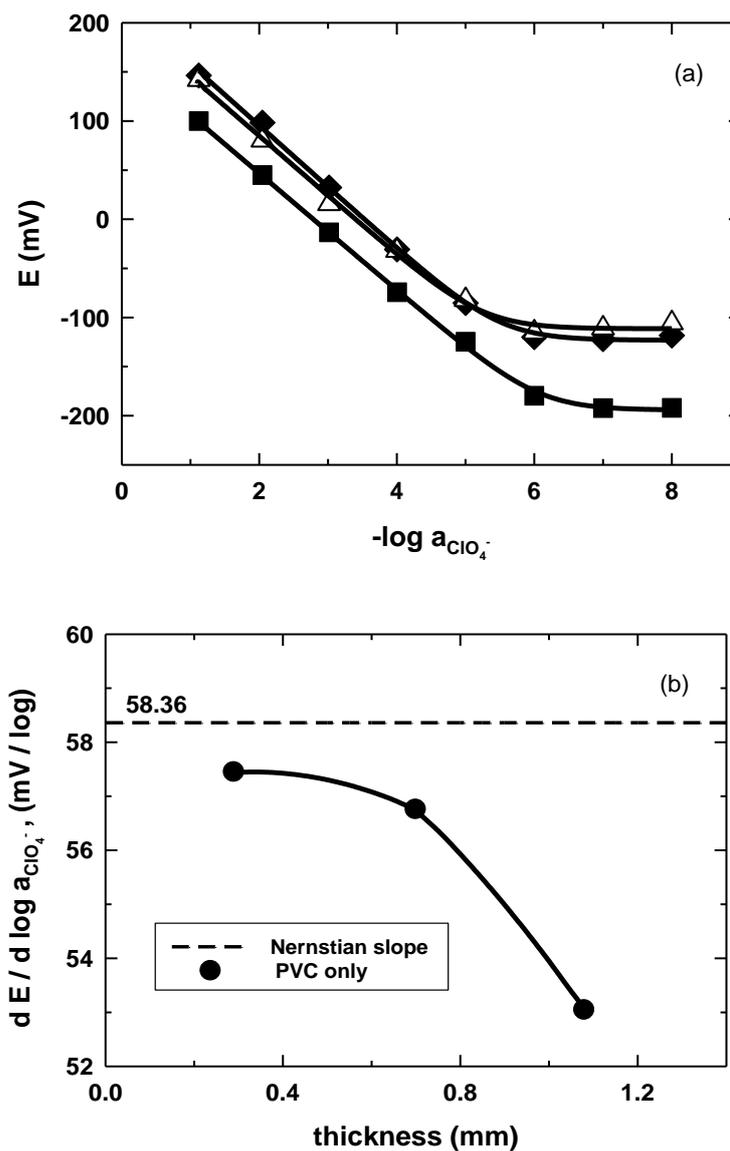


Figure A2. Effect membrane thickness on the (a) potentiometric response and (b) Nernstian slope of PVC-only electrodes. Experimental conditions: temperature = 21~23 oC; pH = 6 ~7. Thickness: (■) 0.29 mm; (◆) 0.70 mm and (△) 1.08 (mm).

Table A1. Effect of ionophore and presence of perchlorate in the internal solution on the performance of the PVC-only and the PVC+ionophore electrodes. Experimental conditions: Perchlorate concentration =  $10^{-8}$  to 0.1 M; Temperature = 21 ~ 23 °C; pH = 5 ~7; Reference electrode = SCE.

Membrane	Internal solution	Nernstian slope (mV/log)	Linear range (M)	R <sup>2</sup>
PVC <sup>a</sup>	DIW	60.6 ± 0.1	1.0 x 10 <sup>-6</sup> to 1.0 x 10 <sup>-1</sup>	0.9971
PVC <sup>a</sup>	ClO <sub>4</sub> <sup>-</sup> (10 <sup>-4</sup> M)	58.5 ± 0.3	1.0 x 10 <sup>-6</sup> to 1.0 x 10 <sup>-1</sup>	0.9964
PVC <sup>a</sup>	ClO <sub>4</sub> <sup>-</sup> (10 <sup>-4</sup> M) + ionophore (10 <sup>-5</sup> M)	55.8 ± 0.4	1.0 x 10 <sup>-6</sup> to 1.0 x 10 <sup>-1</sup>	0.9984
PVC + ionophore <sup>b</sup>	ClO <sub>4</sub> <sup>-</sup> (10 <sup>-4</sup> M)	56.7 ± 0.2	1.0 x 10 <sup>-6</sup> to 1.0 x 10 <sup>-1</sup>	0.9955
PVC + ionophore <sup>b</sup>	ClO <sub>4</sub> <sup>-</sup> (10 <sup>-4</sup> M) + ionophore (10 <sup>-5</sup> M)	52.2 ± 0.2	1.0 x 10 <sup>-6</sup> to 1.0 x 10 <sup>-1</sup>	0.9949
<p>a: PVC (wt%):51.55; DBP (wt%):44.67; MTOAC (wt%):3.78.</p> <p>b: PVC (wt%):49.36; DBP (wt%):42.90; MTOAC (wt%):3.62 ; Ionophore (wt%):4.12, Ni(DBM)<sub>2</sub>.</p>				

Table A2. Chemical composition of water samples studied.

Samples	Cations (meq/L)								Anions (meq/L)				
	pH	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Cu <sup>2+</sup>	Fe <sup>2+</sup>	Σ	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	Σ
Creek Water	6.60	2.74	1.05	4.11	0.06	-	-	7.96	2.92	0.53	4.50	0.07	8.02
Rain Water	5.88	0.03	-	0.02	-	-	-	0.05	0.09	0.07	0.08	0.05	0.29
Tap Water	6.27	2.28	1.16	0.78	0.07	0.03	-	4.32	1.75	0.84	1.27	0.34	4.20

## Appendix B

### COPYRIGHT PERMISSIONS

#### B.1 Permission for Chapter 3

##### Analytical Methods- Royal Society of Chemistry

### Deposition and sharing rights

The following details apply only to authors accepting the standard licence to publish. Authors who have accepted one of the open access licences to publish, or are thinking of doing so, should refer to the [details for open access deposition rights](#). Deposition of any form of the article is allowed in non-commercial repositories only.

### Deposition by the Royal Society of Chemistry

The Royal Society of Chemistry shall deposit the accepted version of the submitted article in non-commercial repository(ies) as deemed appropriate, including but not limited to the funding agency repository(ies) of the author(s). There shall be an embargo to making the above deposited material available to the public that will be 12 months from the date of acceptance.

### Deposition by the author(s)

When the author accepts the licence to publish for a journal article, he/she retains certain rights concerning the deposition of the whole article.

**Deposit the accepted version of the submitted article in their institutional repository(ies).** There shall be an embargo of 12 months from the date of acceptance, after which time the article will be made available to the public. There shall be a link from this article to the PDF of the version of record on the Royal Society of Chemistry's website, once this final version is available.

**Make available the accepted version of the submitted article** via the personal website(s) of the author(s) or via the intranet(s) of the organisation(s) where the author(s) work(s); no embargo period applies.

**Make available the PDF of the version of record** via the personal website(s) of the author(s) or via the intranet(s) of the organisation(s) where the author(s) work(s). No embargo period applies. 

**Republish the PDF of the version of record in theses of the author(s)** in printed form and may make available this PDF in the theses of author(s) via any website(s) that the university(ies) of the author(s) may have for the deposition of theses. No embargo period applies.

Source: <http://www.rsc.org/journals-books-databases/journal-authors-reviewers/licences-copyright-permissions/#deposition-sharing>

## B.2 Permission for Chapter 4

### Journal of Membrane Science – Elsevier

#### Journal author rights

In order for Elsevier to publish and disseminate research articles, we need publishing rights. This is determined by a publishing agreement between the author and Elsevier. This agreement deals with the transfer or license of the copyright to Elsevier and authors retain significant rights to use and share their own published articles. Elsevier supports the need for authors to share, disseminate and maximize the impact of their research and these rights, in Elsevier proprietary journals\* are defined below:

For subscription articles	For open access articles
<p>Authors transfer copyright to the publisher as part of a journal publishing agreement, but have the right to:</p> <ul style="list-style-type: none"><li>• Share their article for <a href="#">Personal Use</a>, <a href="#">Internal Institutional Use</a> and <a href="#">Scholarly Sharing</a> purposes, with a DOI link to the version of record on ScienceDirect (and with the Creative Commons <a href="#">CC-BY-NC-ND license</a> for author manuscript versions)</li><li>• Retain patent, trademark and other intellectual property rights (including raw research data).</li><li>• Proper attribution and credit for the published work.</li></ul>	<p>Authors sign an exclusive license agreement, where authors have copyright but license exclusive rights in their article to the publisher**. In this case authors have the right to:</p> <ul style="list-style-type: none"><li>• Share their article in the same ways permitted to third parties under the relevant user license (together with <a href="#">Personal Use</a> rights) so long as it contains a <a href="#">CrossMark logo</a>, the <a href="#">end user license</a>, and a DOI link to the version of record on ScienceDirect.</li><li>• Retain patent, trademark and other intellectual property rights (including raw research data).</li><li>• Proper attribution and credit for the published work.</li></ul>

## Personal use

Authors can use their articles, in full or in part, for a wide range of scholarly, non-commercial purposes as outlined below:

- Use by an author in the author's classroom teaching (including distribution of copies, paper or electronic)
- Distribution of copies (including through e-mail) to known research colleagues for their personal use (but not for Commercial Use)
- Inclusion in a thesis or dissertation (provided that this is not to be published commercially)
- Use in a subsequent compilation of the author's works
- Extending the Article to book-length form
- Preparation of other derivative works (but not for Commercial Use)
- Otherwise using or re-using portions or excerpts in other works

These rights apply for all Elsevier authors who publish their article as either a subscription article or an open access article. In all cases we require that all Elsevier authors always include a full acknowledgement and, if appropriate, a link to the final published version hosted on Science Direct.

Source: <https://www.elsevier.com/about/company-information/policies/copyright#Author%20rights>