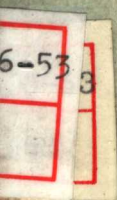


ANODES FOR ELECTROWINNING

**Edited by Douglas J. Robinson
and Stephen E. James**



ANODES FOR ELECTROWINNING

Proceedings of the sessions sponsored by The Electrolytic Processes Committee of The Metallurgical Society of AIME held at the AIME Annual Meeting in Los Angeles, California, February 28, 1984.

**Edited by
Douglas J. Robinson
Dremco
Tucson, Arizona 85710
Stephen E. James
St. Joe Minerals Corporation
Monaca, Pennsylvania 15061**

A Publication of



The Metallurgical Society of AIME

A Publication of The Metallurgical Society of AIME
420 Commonwealth Drive
Warrendale, Pennsylvania 15086
(412) 776-9000

The Metallurgical Society and American Institute of
Mining, Metallurgical, and Petroleum Engineers are
not responsible for statements or opinions in this publication.

© 1984 by American Institute of Mining, Metallurgical,
and Petroleum Engineers, Inc.
345 East 47th Street
New York, NY 10017

Printed in the United States of America.
Library of Congress Card Catalogue Number 84-60151
ISBN Number 0-89520-474-6



Foreword

Electrowinning of metals from sulfate solutions had made use of lead or lead alloy anodes almost exclusively since the inception of the process. These anodes have proven satisfactory, but some problems remain, notably corrosion to lead sulfate which forms a sludge in the cell and contaminates the cathode. Other drawbacks include their relatively low electrical conductivity and only moderate mechanical strength. Although various workers have addressed these problem areas, a truly ideal design is not yet available, and so the search for improved lead or non-lead replacement anodes continues.

Calcium lead alloys have been widely accepted for the copper FX-EW process where they have been seen to produce only limited amounts of sludge, but they are not totally satisfactory. Important among the shortcomings is the difficulty in producing homogeneous castings, which has led to premature failures in as many as 20 percent of the installed anodes. Continued research is needed to better control the properties of these cast electrodes.

The remarkable success of coated titanium anodes in the chlor-alkali industry has prompted many investigators to adapt DSA technology to metal electrolysis but cost effective substitutes for lead have not yet emerged. Still the promises of improved cathode quality, decreased energy consumption, and radically different cell design continue to stimulate work in this area.

Other studies have considered the concept of using the anodes to generate by-product chemicals such as ferric iron or sulfur trioxide to reduce energy consumption. These have not yet achieved commercial acceptance but will undoubtedly represent areas for further work in the future.

The papers in this collection address these topics and embrace a wide cross-section of the present work on metal winning anodes. This compendium continues the tradition started in 1982 to record the proceedings of the Electrolytic Processes Sessions sponsored by The Metallurgical Society of AIME at the AIME Annual Meeting. Along with the first book, *Chloride Electrometallurgy*, edited by Peter D. Parker, we hope these papers will make a useful addition to the libraries of metallurgists, engineers, and scientists involved with the electrowinning of metals from aqueous solutions.

The editors are grateful to the authors for their efforts writing the papers and meeting publication deadlines. The contributions of John Ballance and Elizabeth Luzar at TMS headquarters and of John Cigan of the TMS Publications Committee are also greatly appreciated. Finally we need to acknowledge the secretarial and typing work done by Dee Robinson of Dremco and Vivian Webster of St. Joe Minerals in order to get this book ready for publication.

Douglas J. Robinson
Dremco
Tucson, Arizona

Stephen E. James
St. Joe Minerals Corporation
Monaca, Pennsylvania

January 1984

Contents

Foreword.....	111
Chlorate Oxidation-An Alternative Anode Reaction in Electrowinning..... <i>G. R. Smith and W. R. Thompson</i>	1
Electrochemical Aspects of the Direct Electrowinning Copper from Sulphuric Acid Leach Solutions in the Presence of Iron Using Gas Sparging..... <i>K. K. Mishra and E. C. Cooper</i>	13
Cominco Zinc Electrowinning Anode Technology..... <i>C. J. Krauss, R. C. Kerby, R. D. H. Willans, and D. Ybema</i>	37
The Metallurgy of Lead Alloys for Electrowinning Anodes..... <i>R. D. Prengaman</i>	49
Wrought Lead-Calcium-Tin Anodes for Electrowinning..... <i>R. D. Prengaman</i>	59
The Oxygen Electrode in Metal Electrowinning..... <i>I. H. Warren</i>	69
Electrocatalytic Anode for Copper Electrowinning..... <i>J. K. Walker and J. I. Bishara</i>	79
The Advantages of Coated Titanium Electrodes for Electrowinning Process of Different Metals..... <i>K. R. Koziol and E. F. Wenk</i>	87
Sintered Titanium Anodes in Metal Electrowinning..... <i>G. Brewer, H. Debrodt, H. Herbst, and L. Mader</i>	101
Author Index.....	113

CHLORATE OXIDATION - AN ALTERNATIVE ANODE REACTION IN ELECTROWINNING

G. R. Smith and W. R. Thompson

U.S. Department of the Interior
Bureau of Mines
Avondale Research Center
Avondale, Maryland 20782
USA

Abstract

Electrolysis studies by the Bureau of Mines have demonstrated that zinc or copper electrowinning can be combined with the electrochemical production of sodium perchlorate to achieve a significant decrease in the use of electrolysis energy. Current efficiencies exceeding 90 pct were obtained for each half-cell reaction, using current densities and temperatures in the ranges typically employed for the respective electrowinning and electrochemical reactions. The cationic permselective membrane separating the two half-cells exhibited a high efficiency, allowing less than 4 pct of the anolyte and catholyte to interdiffuse during electrolysis.

Introduction

The need for new technology to more efficiently recover metals from complex low-grade ores by hydrometallurgical methods has generated increasing interest in sulfate electrowinning systems that employ an anode reaction other than the oxidation of water ($E_h^0 = 1.23$ V). Considerable attention has been given recently to the substitution of lower voltage reactions such as the oxidation of SO_2 to H_2SO_4 ($E_h^0 = 0.17$ V) (1-6), H_2 to H^+ ($E_h^0 = 0.0$ V) (7-9), or C to CO_2 ($E_h^0 = 0.2$ V) (10-11), but little attention has been given to anode reactions that are used in commercial electrochemical production processes. The inherent advantage of substituting these reactions in electrowinning arises as a result of a more efficient use of the total electrolysis energy rather than because of a decrease in the anodic voltage. Essentially, the wasteful water electrolysis reaction is eliminated and replaced by useful electrowinning and electrochemical reactions.

One electrochemical reaction that has been studied as an anodic substitute in electrowinning is the oxidation of Mn^{2+} to MnO_2 ($E_h^0 = 1.21$ V). Specific studies have been applied to the simultaneous recovery of zinc and γ - MnO_2 from purified sulfate leach liquors (12-13). Reported electrolysis results were promising, although careful control of parameters such as pH, current density, metal concentration, and temperature was necessary.

The previously cited studies using substitute anode reactions in sulfate electrowinning systems have generally been conducted without a membrane or diaphragm to separate the half-cell reactions. In this paper, the feasibility of combining the electrochemical half-cell reaction, sodium chlorate ($NaClO_3$) to sodium perchlorate ($NaClO_4$) ($E_h^0 = 1.19$ V), with a sulfate electrowinning half-cell by means of a cationic permselective membrane is discussed. The performance of the membrane and the effect of current density, temperature, and anolyte acidity on the operation of the cell were evaluated.

Specific references to a combination electrowinning-electrochemical cell of this type have not been found in the literature. However, practical applications can be postulated for such a cell because there is an expanding use of $NaClO_4$ as the precursor in the preparation of ammonium perchlorate for solid-fuel rocket propellants as well as a continuing use in the preparation of potassium perchlorate for pyrotechnic devices that are used extensively by the military. Furthermore, its use could be incorporated into marine mining and recovery operations where seawater would provide an immediate source of the sodium chloride starting material for production of $NaClO_3$.

An informative survey of recent advances in electrowinning technology is presented in reference (14), and pertinent discussions on the electrochemical production of $NaClO_4$ are presented in references (15-19).

Experimental

Electrolytic Cell

The rectangular experimental cell used in this study is shown schematically in figure 1. The 180-mL-capacity cell was made of polyacrylic plastic. The 0.38-mm-thick cationic permselective membrane employed to separate the cell into two equally sized anolyte and catholyte sections was a commercially available heterogeneous type consisting of a sulfonated styrene exchange resin on an inert polyolefin fabric. Resistivity of the membrane was 6 ohm-cm² in 1.0N NaCl solution. A 0.27-dm² area of the membrane was

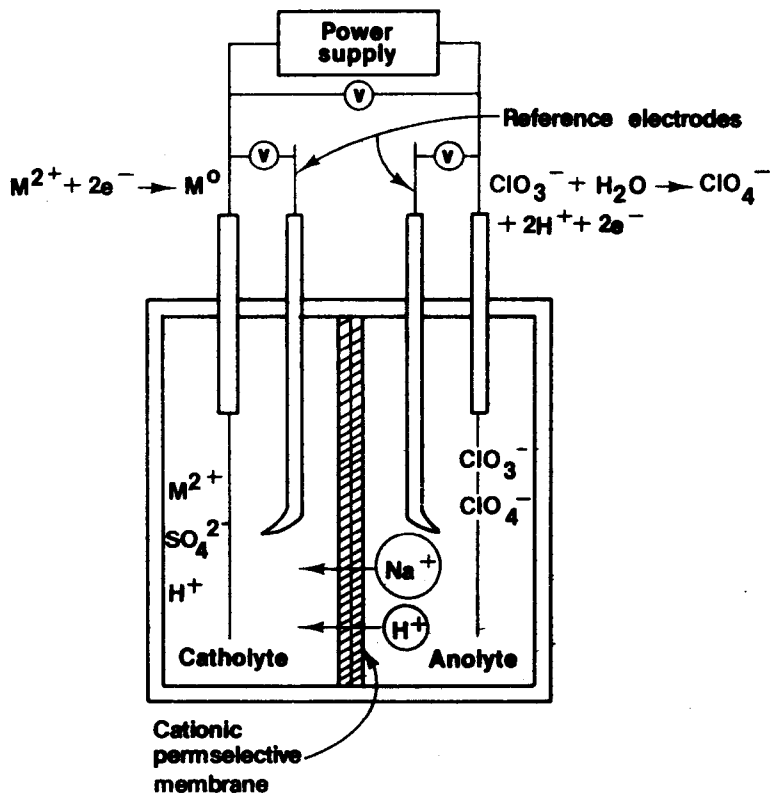


Figure 1 - Electrowinning-Electrochemical Cell
 $M^{2+} = Zn^{2+} \text{ or } Cu^{2+}$

exposed to the electrolytic current. The cathode material consisted of aluminum sheet for zinc (Zn) electrowinning and stainless steel sheet for copper (Cu) electrowinning experiments. The exposed cathode area was kept constant at 0.2 dm². The area of the smooth platinum anode was adjusted from 0.04 to 0.2 dm² to maintain the anode current density between 10 and 20 A/dm² at corresponding cathode current densities of 3 to 10 A/dm². The two electrodes were placed vertically in the center of each half-cell, spaced 50 mm apart, and positioned parallel to the membrane. Potentials in each half-cell were measured versus an Ag-AgCl (3M KCl) microelectrode fitted into a luggin capillary that was rotated between the wall of the membrane and the surface of the electrode. Potential values are reported against the standard hydrogen electrode, assuming it to be -0.210 V to the Ag-AgCl reference. A constant-current dc power supply controlled current to the cell. Individual voltages and total coulombs were recorded on a strip chart recorder and

an ampere-hour meter, respectively. Temperature of the anolyte and catholyte was controlled by partial immersion of the cell in a constant-temperature water bath.

Solutions

The catholyte for Zn electrowinning was 2.1M (137 g/L) Zn^{2+} as ZnSO_4 and 1M (98 g/L) H_2SO_4 , while that for Cu electrowinning was 1M Cu^{2+} as CuSO_4 and 1M H_2SO_4 . The anolyte solution consisted of 4.7M NaClO_3 and 1.6M NaClO_4 . In select tests the NaClO_4 was replaced by perchloric acid (HClO_4).

Analysis and Evaluation

Samples of anolyte and catholyte were taken for analysis before, during, and upon completion of the electrolysis experiments to obtain the anode current efficiencies and to evaluate the effectiveness of the membrane. Standard volumetric, gravimetric, spectrophotometric, and potentiometric analytical techniques were used to determine the concentration of Cu^{2+} , Zn^{2+} , ClO_3^- , ClO_4^- , SO_4^{2-} , and Na^+ in solution. Zn and Cu electrowinning efficiencies were calculated from the weight of the cathode deposit.

Results and Discussion

Data acquired from the operation of the electrowinning-electrochemical cell provided information on (a) the condition required for each half-cell to function simultaneously at compatible current densities and temperatures, (b) the electrolysis energy requirements, and (c) the efficiency of a cationic permselective membrane to provide physical separation and electrical connection of the anolyte and catholyte. Typical polarization curves for the reactions studied in this cell are shown in figure 2. In the anodic oxidation of NaClO_3 to NaClO_4 , the reaction kinetics increasingly favor the electrolysis of water at current densities below 10 A/dm². The maximum current density for Zn and Cu electrowinning is governed predominantly by the metal ion concentration and the extent of agitation in the electrolyte but is usually less than that of the NaClO_3 to NaClO_4 reaction. Thus, to operate each half-cell at ideal current densities, the area of the anode was reduced relative to the area of the cathode. To minimize the difference in electrode areas, the current densities were matched as closely as possible, thus preventing impractical cell geometries.

Current Density, Temperature, Current Efficiency

Zinc Electrowinning. Data in Table I confirm that the combination half-cells are compatible and can be operated efficiently using electrolyte temperatures and electrode current densities similar to those in independent commercial cells. Zn and NaClO_4 were each produced at greater than 90 pct current efficiency when the cell was operated at 50° C and the cathode and anode current densities were controlled at 4 to 10 A/dm² and 10 to 20 A/dm², respectively. Figure 3 shows photographs of the electrowon Zn produced at 4, 6.5, and 10 A/dm² using moderate mechanical agitation of the catholyte. Electrolyte additives used commercially to improve the physical quality of the Zn were not used in these experiments. The physical quality of the Zn obtained at 6.5 A/dm² was similar to that obtained when the cell was operated as an independent electrowinning cell.

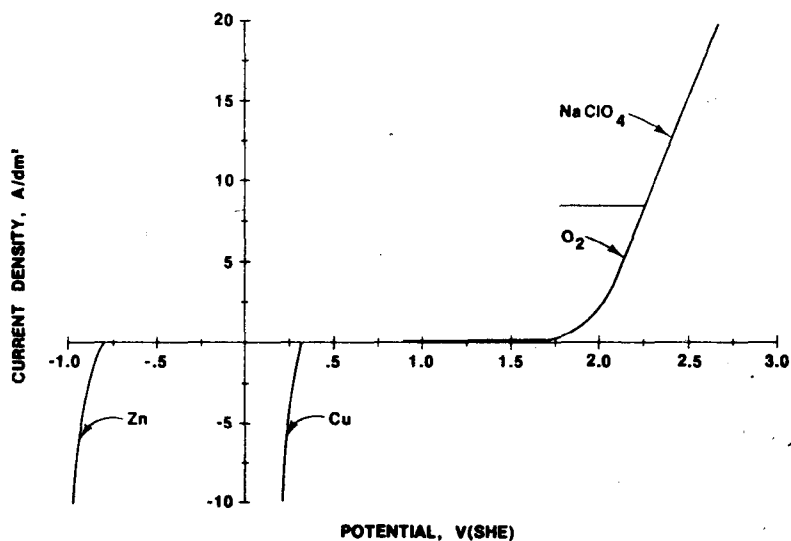


Figure 2 - Typical polarization curves for Zn and Cu electrowinning and NaClO_4 production.

Table I. Operating Parameter and Efficiency Comparisons for Zn- NaClO_4 and Commercial Cells

Electrolysis Cell	Temperature, °C	Current Density, A/dm^2		Current Efficiency, pct	
		Electrowinning	NaClO_4 Production	Electrowinning	NaClO_4 Production
Commercial Zn electrowinning*	35-40	4-10	N/A	85-93	N/A
Commercial NaClO_4 production**	30-60	N/A	15-45	N/A	80-95
Combined Zn- NaClO_4 electrolysis	50	4.5-10	10-20	92-97	90-92

*References (20), (21).

**Reference (15).

N/A Not Applicable.

Satisfactory deposits were obtained at the highest current density, indicating the possibility of combining the Zn and NaClO_4 half-cells at equal current densities of 10 A/dm^2 . To electrowin Zn most efficiently at 10 A/dm^2 in commercial cells, the Zn^{2+} and H_2SO_4 concentrations must be increased to ≈ 200 and 300 g/L , respectively. Production of NaClO_4 at 10 A/dm^2 requires careful control of the anolyte composition to avoid excessive efficiency loss through the oxidation of water. Operation of the combination cell at cathode and anode current densities of 6.5 and 15 A/dm^2 repeatedly yielded favorable results and appeared to be the most practical current density combination.

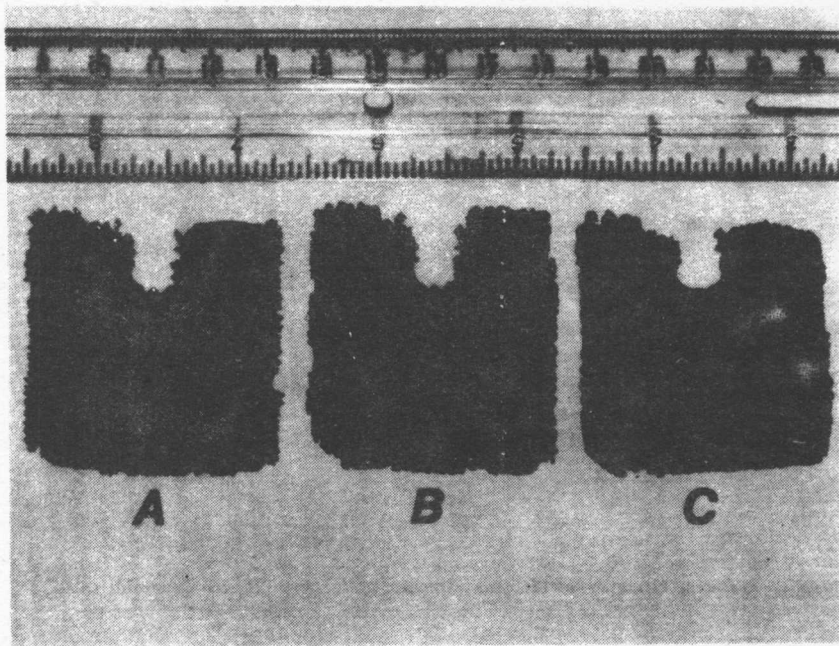


Figure 3 - Electrowin Zn at (A) 4, (B) 6.5, and (C) 10 A/dm^2 .

Copper Electrowinning. Current efficiencies exceeding 90 pct were also obtained for both the anode and cathode reaction when Cu electrowinning was combined with NaClO_4 production at 50° C (Table II). Current densities for this combination were somewhat less compatible than for Zn electrowinning because the practical current density for Cu electrowinning under normal mass transport conditions does not exceed $\approx 3 \text{ A/dm}^2$. Figure 4 shows the deterioration in quality with increasing current density of the Cu obtained at 3, 4.5, and 6.5 A/dm^2 in the combination electrowinning-electrochemical cell. No studies were conducted to improve the quality of the electrodeposits at current densities above 3 A/dm^2 . However, the feasibility of efficiently increasing the current density by as much as a factor of 10 using forced convection methods to decrease the diffusion layer thickness has been cited in the literature (23-26).

Table II. Operating Parameter and Efficiency Comparisons for Cu-NaClO₄ and Commercial Cells

Electrolysis Cell	Temperature, °C	Current Density, A/dm ²		Current Efficiency, pct	
		Electrowinning	NaClO ₄ Production	Electrowinning	NaClO ₄ Production
Commercial Cu electrowinning*	35-55	1.5-3.2	Nap	98-99	Nap
Commercial NaClO ₄ production**	30-60	Nap	15-45	Nap	80-95
Combined Cu-NaClO ₄ electrolysis	50	3.0-6.5	10-15	94-98	90-93

*References (21), (22).

**Reference (15).

Nap Not Applicable.

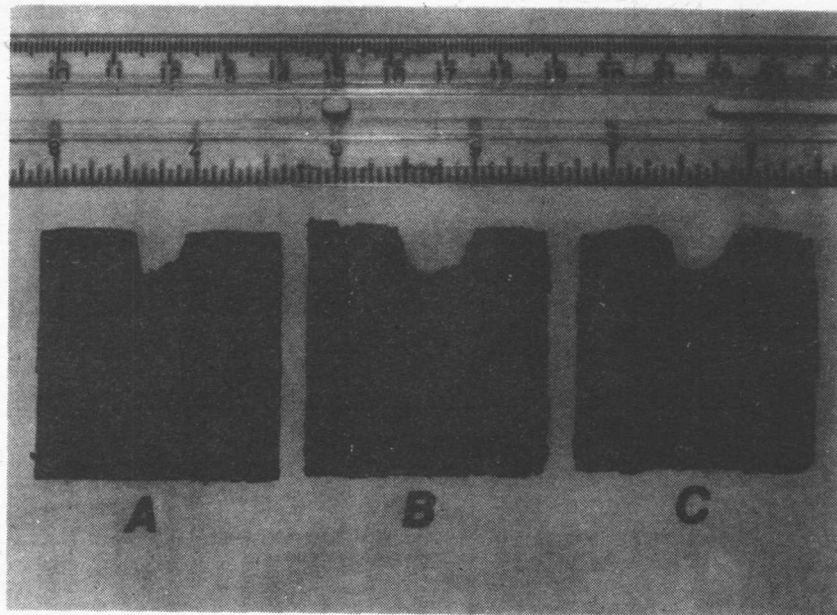


Figure 4 - Electrowon Cu at (A) 3, (B) 4.5, and (C) 6.5 A/dm².

Electrolysis Energy

Zinc Electrowinning. Figure 5 shows that a 55-pct decrease in cell voltage can be achieved when Zn electrowinning is combined with electrochemical production of NaClO₄. Using cathode and anode current densities of 6.5 and 15 A/dm², respectively, the cell voltage for the combination cell was 4.50 V compared to 9.90 V for the sum of the cell voltages of the two cells

when operated in a commercial configuration, that is, with water electrolysis as one of the cell reactions. The voltages (fig. 5) for independent Zn electrowinning and NaClO_4 production were obtained in the laboratory cell at current densities of 6.5 and 15 A/dm^2 , respectively. The cationic membrane contributed only 0.18 V to the cell voltage of the combination cell. Electrolysis energy consumed by each half-cell in the combination cell was determined from the measured half-cell voltage (SHE) plus 50 pct of the membrane voltage and compared to the voltage of the independently operated cell. On that basis, the electrolysis energy was decreased from 3.43 to 1.14 $\text{kW}\cdot\text{h/kg}$ for Zn electrowinning and from 2.97 to 1.32 $\text{kW}\cdot\text{h/kg}$ for NaClO_4 production.

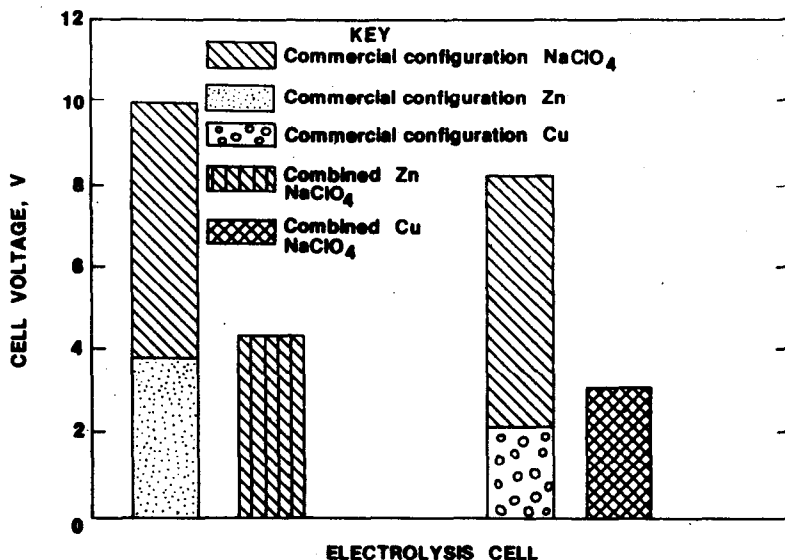


Figure 5 - Comparison of cell voltages in commercial configuration and combined cells

Copper Electrowinning. Figure 5 also shows that a 64-pct decrease in cell voltage can be obtained using Cu electrowinning in combination with NaClO_4 production. Using cathode and anode current densities of 3 and 15 A/dm^2 , respectively, the cell voltage for the combination cell was 2.95 V compared to 8.23 V for the sum of the voltages for the independent cells. The cationic membrane contributed 0.21 V to the cell voltage. The electrolysis energy was decreased from 2.00 to 0.24 $\text{kW}\cdot\text{h/kg}$ for Cu electrowinning. Energy for NaClO_4 production was decreased the same as when coupled with Zn electrowinning, from 2.97 to 1.32 $\text{kW}\cdot\text{h/kg}$.

Membrane

Physical separation of the two half-cells and electrical contact between them were accomplished using a cationic membrane similar to that used in electrodialysis cells (figure 1). Electrolysis current was conducted through this membrane by means of H^+ and Na^+ migrating from the anolyte to the catholyte. Since H^+ is produced at the anode during electrolysis, an equilibrium is established between the concentrations of H^+ and Na^+ in the anolyte and the percentage of the current transported through the membrane by these ions. Figure 6 shows the advancement towards this equilibrium condition starting with an anolyte containing 4.7M $NaClO_3$ and 1.6M $NaClO_4$. After 18.1 A·h of electrolysis, the $H^+ : Na^+$ ratio in the anolyte was ≈ 0.5 ($H^+ = 2.3M$, $Na^+ = 4.5M$) and ≈ 95 pct of the current was transported by the H^+ . As a result of the ion-selective characteristics of the membrane at equilibrium, the $NaClO_4$ was retained in the anolyte while the acidity of the catholyte was markedly increased. This allows for the processing and recovery of the anolyte and for subsequent use of the catholyte in a leaching or an acid-stripping step to replenish the metal ions removed by electrowinning.

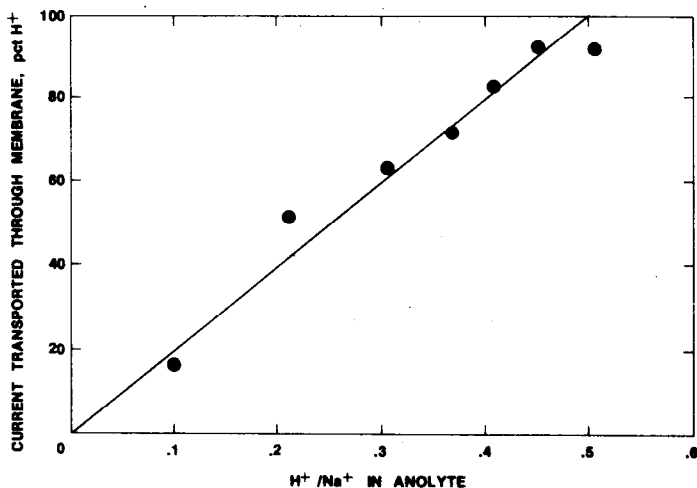


Figure 6 - Effect of the (H^+) to (Na^+) ratio in the anolyte on the transport of electrolysis current through the membrane.

Since the results shown in figure 6 indicate that the most efficient and practical operation of the combination cell occurs when the anolyte is $\sim 2M$ in acidity rather than nearly neutral as in commercial cells, the effects of highly acidic conditions on the anode current efficiency and anolyte stability were also determined. Using an initial anolyte concentration of 4.7M $NaClO_3$ and 1.6M $HClO_4$ rather than 4.7M $NaClO_3$ and 1.6M $NaClO_4$,

in combination with Zn electrowinning, the current efficiency for the anode reaction continued to be greater than 90 pct during an electrolysis at 15 A/dm². The anolyte remained stable for acid levels as high as 2.8M HClO₄.

In addition to a determination of the H⁺ and Na⁺ transported through the membrane, further investigations were made regarding the extent of diffusion through the membrane by the other ions. Table III shows the extent of ionic diffusion for several ions during 2.3 A·h of electrolysis. Less than 1 pct of the initial concentrations of Zn²⁺, Cu²⁺, ClO₃⁻, and ClO₄⁻ diffused through the membrane, while ≈3.7 pct of the SO₄²⁻ diffused.

Table III. Ionic Diffusion During Electrolysis

Anolyte Ion	Concentration, g/L		Catholyte Concentration, g/L		Diffusion, pct of Initial
	Initial	Final	Initial	Final	
Cu ²⁺	0	0.3	60	30	0.50
Zn ²⁺	0	0.8	140	110	0.57
ClO ₃ ⁻	392	350	0	1.7	0.43
ClO ₄ ⁻	167	209	0	1.6	1.0
SO ₄ ²⁻	0	11.0	300	289	3.7

The cationic permselective membrane exhibited excellent stability in the combined electrowinning-electrochemical cell, having been used successfully for 280 h of electrolysis, corresponding to the passage of 325 A·h through the membrane.

Summary

Laboratory studies to more efficiently utilize electrolysis energy by combining electrowinning with electrochemical production of sodium perchlorate have led to the following conclusions:

1. Each half-cell can function simultaneously at compatible current densities and temperatures without decreasing the reaction current efficiencies.
2. The electrolysis voltage in the combination cell can be decreased by more than 60 pct compared to the sum of the voltages of the independently operated cells.
3. A cationic permselective membrane can be used to effectively separate the anolyte and catholyte.
4. Hydrogen ions carry a predominantly greater percentage of the current through the membrane than the sodium ions at an anolyte acidity level near 2M. Consequently the sodium perchlorate product is retained in the anolyte for processing and recovery, and the acidity is increased in the catholyte for subsequent use in a metal ion regeneration step.

References

1. A. J. Appleby, and B. Pichon, "The Mechanism of the Electrochemical Oxidation of Sulfur Dioxide in Sulfuric Acid Solutions," J. Electroanal. Chem., 95 (1979), pp. 59-71.
2. Gerald F. Pace, and John C. Stauter, "Direct Electrowinning of Copper from Synthetic Pregnant Leach Solutions Utilizing SO₂ and Graphite Anodes - Pilot Plant Results," CIM Trans., v. LXXVII (1974), pp. 51-57.
3. Zdenek Samec, and Jan Weber, "Study of the Oxidation of SO₂ Dissolved in 0.5 M H₂SO₄ on a Gold Electrode - I Stationary Electrode," Electrochimica Acta, v. 20 (1975), pp. 403-412.
4. Zdenek Samec, and Jan Weber, "Study of the Oxidation of SO₂ Dissolved in 0.5 M H₂SO₄ on a Gold Electrode - II A Rotating Disc Electrode," Electrochimica Acta, v. 20 (1975), pp. 413-419.
5. E. T. Seo, and D. T. Sawyer, "Electrochemical Oxidation of Dissolved Sulfur Dioxide at Platinum and Gold Electrodes," Electrochimica Acta, v. 10 (1965), pp. 239-252.
6. K. Weisener, "The Electrochemical Oxidation of Sulfur Dioxide at Porous Catalyzed Carbon Electrodes in Sulfuric Acid," Electrochimica Acta, v. 18 (1973), pp. 185-189.
7. R. J. Allen, W. Juda, R. W. Lindstrom, and H. G. Petros, "Energy Savings by Means of Fuel Cell Electrodes in Electro-Chemical Industries," Prototech Company (New Highlands, Mass.), U.S. Dept. of Energy, Contract No. ET-78-C-02-4881, Report C00-4881-6 (1979), p. 72.
8. Amiram Bar-Ilan, Walter Juda, Robert J. Allen, and Robert W. Lindstrom, "Energy Savings by Means of Fuel Cell Electrodes in Electro-Chemical Industries." Prototech Co. (New Highlands, Mass.), U.S. Dept. of Energy, Contract No. DE-AC02-78ET25309, Report C00-4881-16 (1980), p. 37.
9. Walter Juda, and Robert L. Novak, "Method of Electrodeposition Using Catalyzed Hydrogen," U.S. Pat. 3,793,165, Feb. 19, 1974.
10. Mohammad Farooque, and Robert W. Coughlin, "Anodic Coal Reaction Lowers Energy Consumption of Metal Electrowinning," Nature, 280 (5724) (1979), pp. 666-668.
11. Mohammad Farooque, and Robert W. Coughlin, "Electrochemical Gasification of Coal (investigation of operating conditions and variables)," Fuel, 58 (10) (1979), pp. 705-712.
12. A. M. Pande, K. N. Gupta, and V. A. Atelkar, "Single Cell Extraction of Zinc and Manganese Dioxide from Zinc Sulfide Concentrate and Manganese Ores," Hydromet., v. 9 (1982), pp. 57-68.
13. B. Verbaan, and B. Mullinder, "The Simultaneous Electrowinning of Manganese Dioxide and Zinc from Purified Neutral Zinc Sulfate at High Current Efficiencies," Hydromet., v. 7 (1981), pp. 339-352.

14. Battelle Lab, "A Survey of Electrochemical Metal Winning Processes," Battelle Columbus Lab. (Columbus, Ohio), prepared for Argonne Nat. Lab. under Contract No. 31-109-38-4212, ANL/OEPM-79-3, 1979, available from NTIS, Springfield, Va.
15. Castle Technology Corporation, "Survey of Electrochemical Production of Inorganic Compounds," Argonne Nat. Lab. (Argonne, Ill.), prepared for U.S. Dept. of Energy under Contract No. W-31-109-38-5054, ANL/OEPM-80-3, available from NTIS, Springfield, Va.
16. O. deNora, P. Gallone, C. Traini, and G. Meneghini, "On the Mechanism of Anodic Chlorate Oxidation," J. Electrochem. Soc., v. 116 (1) (1969), pp. 146-151.
17. J. C. Schumacher, "Perchlorates - Their Properties, Manufacture and Uses," ACS Monograph Series, Reinhold Publishing Corp., New York, N.Y., 1960.
18. Proceedings of the Workshop on Energy Conservation in Industrial Electrochemical Processes. Argonne Nat. Lab., prepared for U.S. Energy Research and Development Administration under Contract W-31-109-ENG-38, ANL/OEPM-77-1, 1976, available from NTIS, Springfield, Va.
19. Khchiro Sugino, and Shigeru Aoyagi, "Studies on the Mechanism of the Electrolytic Formation of Perchlorate," J. Electrochem. Soc., v. 103 (3) (1956), pp. 166-170.
20. C. H. Cotterill, and J. M. Cigan, eds., "AIME World Symposium on Mining and Metallurgy of Lead and Zinc--Extractive Metallurgy of Lead and Zinc," Port City Press, Inc., Baltimore, Md., v. 2 (1970).
21. C. L. Mantell, "Electrochemical Engineering," Chemical Engineering Series, McGraw-Hill Book Co., Inc., New York, N.Y., 1960.
22. J. C. Yannopoulos, and J. C. Agarwal, eds., "AIME International Symposium on Copper Extraction and Refining--Extractive Metallurgy of Copper," Port City Press, Baltimore, Md., v. 2 (1976).
23. D. J. MacKinnon, and V. I. Lakshmanan, "Recent Advances in Copper Electrowinning," Canmet Report 76-10, January 1976.
24. V. A. Ettel, B. V. Tilak, and A. S. Gendron, "Measurement of Cathode Mass Transfer Coefficients in Electrowinning Cells," J. Electrochem. Soc., Vol. 121, No. 7 (1974), pp. 867-872.
25. V. A. Ettel, A. S. Gendron, and B. V. Tilak, "Electrowinning Copper at High Current Densities," Metallurgical Transactions B, Vol. 6B, March 1975, pp. 31-35.
26. W. W. Harvey, M. R. Randlett, and K. I. Bangerskis, "High Current Density Copper Electrowinning in a Series Cell. Part II: Electrowinning," Journal of Metals, Aug. (1975), pp. 19-24.