Electrochemical and Integrated Process Opportunities for On-Site/On-Demand Generation of Chlorine Dioxide

Final Report – 08/02/1996 – 08/01/1999

B. J. Tatarchuk
G. Krishnagopalan
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Work Performed Under Contract No. DE-FC07-96ID13444

Final Report
DOE Project
DE-FC07-96ID13444

Project Description:

Electrochemical and Integrated- Process Opportunities for On-Site/ On- Demand Generation of Chlorine Dioxide

Project Period:

August 2, 1996 – August 1, 1999

Submitted:

January 30, 2000

By:

Dr. Bruce J. Tatarchuk
Dr. G. Krishnagopalan
Ryan A. Nickell

Auburn University
Center for Microfibrous Materials Manufacturing

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Project Summary

Due to continued evidence of environmental harm from elemental chlorine bleaching, the nation's paper industry continues to search for cost effective alternative bleaching. A practical and cost effective bleaching alternative is chlorine dioxide manufactured entirely from sodium chlorate.

Sodium chlorate is produced by the electrolysis of brine in an undivided cell with steel plate cathodes and dimensionally stable anodes. Although the overpotential at the anode is only 50 mV, the cathodic overpotential is 940 mV [1]. Thus, nearly one volt of electricity is wasted in driving hydrogen evolution at the cathode.

Auburn University's Center for Microfibrous Materials Manufacturing has demonstrated that high performance, three dimensional, microfibrous electrodes can improve the performance of capacitors, batteries, hybrid power cells, and electrolysis electrodes in a variety of applications [2,3]. The goal of this research was to apply this technology to a chlorate cell's cathode and reduce the overpotential between 200 and 400 mV. An economic analysis of the industry has shown that for every 100 mV reduction in overpotential, $100 per square meter of electrode can be saved annually.

Due to their enhanced surface area over plates, corrosion of microfibrous electrodes is a major issue in this research. Samples based on chromium protection (i.e. stainless steel) have proved unfeasible for chlorate application. However, samples based on stainless steel and nickel show dramatic performance improvements over industry status quo in chlor-alkali application. Building microfibrous electrodes on a titanium base protected with a silver coating alleviates the corrosion problem and provides 100

mV or more of overpotential reduction. Further reduction is realized by impregnating silver-titanium microfibrous mesh with a PVDF binder and dispersed platinum on activated carbon. The resulting electrodes are mechanically sound, active towards hydrogen evolution, and hold promise for practical industry use.

Introduction to the Chlorate Process and Research Justification

With continued expansion of the pulping industry and continued restriction of allowable waste, the need for alternative, environmentally benign bleaching agents is paramount. An alternative to elemental chlorine is chlorine dioxide, a compound made via sodium chlorate reduction [5]. Due to safety concerns, on site generation of chlorine dioxide is preferential to importing the product from an external source [4].
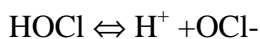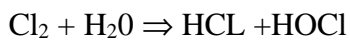
The most economical process (and the only currently practiced) for generating sodium chlorate is the electrolysis of brine in an undivided cell. The overall reaction is:

$$NaCl + 3H_2O \Rightarrow NaClO_3 + 3H_2 \qquad \text{-1.72V @ 25°C, pH=6.0, vs. SHE.}$$

The fundamental anodic reaction and theoretical potential for chlorine evolution are:

$$Cl\text{-} \Rightarrow Cl_2 + 2e\text{-} \qquad \text{-1.331V @ 80°C, [Cl-] = 150g/L.}$$

Chlorate is produced through the following reaction equilibria:

$$Cl_2 + H_2O \Rightarrow HCL + HOCl$$

$$HOCl \Leftrightarrow H^+ + OCl\text{-}$$

$$2HOCl + OCl\text{-} \Rightarrow ClO_3\text{-} + 2H^+ + 2Cl\text{-}$$

The fundamental cathodic reaction and theoretical potential for hydrogen evolution are:

$$2H^+ + 2e\text{-} \Rightarrow H_2 \qquad \text{-0.4199V @ 80°C, pH = 6.0}$$

All currently practiced processes use similar electrodes and materials of construction [5]. The highly corrosive nature of the chloride, chlorate, and hypchlorite ions requires titanium and/or Teflon reactor shells. All commercial reactors use DSA or dimensionally stable anodes, which provide an overpotential of only 50 mV; thus, there is no real opportunity to improve upon the anode's electrical requirements. Whether the electrodes exist in monopolar or bipolar arrangements determines whether mild steel or titanium is used as the cathode. Electrical requirements at the cathode are high; driving the reaction on steel requires an overpotential of 940 mV [1]. Titanium voltage requirements are higher. A high overpotential combined with the large and growing chlorate market translates into millions of wasted dollars in electricity. In 1995, 500,000 metric tons of chlorate were produced at $500/ mt. This figure translates into a 1995 production cost of 250 million dollars, 90% of which is electricity. New cathodes with overpotentials reduced by 200 – 300 mV will save greater than $135/mt.

The Center for Microfibrous Materials Manufacturing at Auburn University has shown expertise in the innovation of three dimensional microfibrous electrodes for applications ranging from capacitors to hybrid power sources to batteries to electrolysis. The goal of the currently discussed project has been to expand this innovation to the cathode of the sodium chlorate process.

Corrosion Issues With Microfibrous Electrodes in Sodium Chlorate

Microfibrous electrodes consist of random, micro-welded meshes of fibers ranging from 2 to 100 microns in diameter. This fiber size requires selection of a material with extremely high corrosion resistance such that the microfibrous electrode will not disintegrate in the chlorate reactor. After a thorough market survey, approximately ten materials were selected as having feasible resistance to the corrosive chlorate brine. These materials' corrosion performances were analyzed gravimetrically in year one, and the results are shown below.

Metal	Initial Mass (grams)	Final Mass (grams)		Mass Loss (grams)	Mass Loss (percent)
SS316L	0.01338	0.01327		0.00011	0.82
SS304	0.00773	0.0077		0.00003	0.39
Ni	0.08373	0.08306		0.00067	0.8
Zn	0.75267	0.74647		0.0062	0.82
Nb	0.377-92-	0.37729		0.00063	0.17
Nb/Ti	0.10882	0.1086		0.00022	0.2
Hastelloy B	0.03763	0.03684		0.00079	2.1
Hastelloy X	0.52637	0.51215		0.01422	2.7
lnconel600	0.15887	0.16033		-0.00146	-0.92
SS316L	0.33446	0.33337		0.00109	0.33
Pt	0.03541	0.0354		0.00001	0.03

Test conditions were the following:

Exposure time = 32 days   Brine Volume = 15 ml.

Temperature = 80°C   pH = 6.0

Brine composition: 450g/L $NaClO_3$, 110 g/L NaCl, 5g/L $Na_2Cr_2O_7$, 4g/L NaClO

The results show less than 1% mass loss for all materials except for the Hastelloys. The

Hastelloy materials exhibited less than 3% mass loss.

The aforementioned test is an incomplete summary of a material's corrosion

resistance. Faradic corrosion is an anodic process; therefore, a material polarized

cathodically has increased corrosion resistance. In order to test candidate electrode

materials under typical conditions, the materials must be placed in an operational chlorate

cell. As a result, the following batch chlorate cell was constructed.
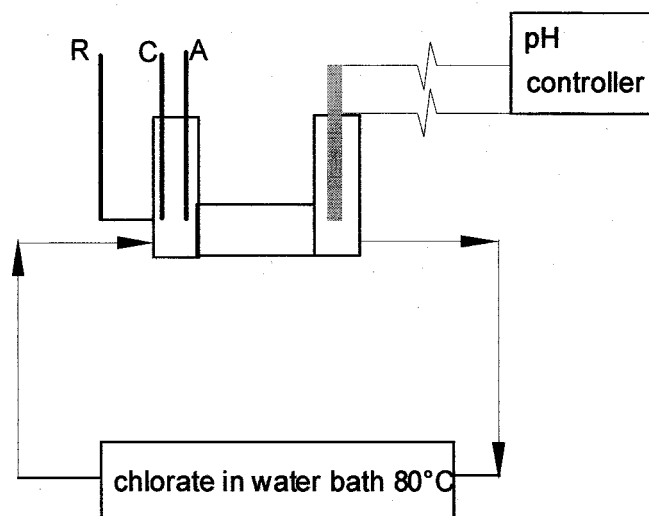

Figure 1: Batch Chlorate Cell

R, C, and A refer to the reference, cathode, and anode electrodes, respectively. Total

system capacity was 1 liter of chlorate brine, of which 250 ml. was located in the reaction

chamber. Brine was recirculated in Kynar tubing from an 80°C water bath to the reaction

chamber and back to the bath. A digital pH controller was used to add 1M HCL to the

system to maintain a pH of 6.0. Because stainless steel microfibers are readily available,

a 316L stainless steel foil was tested first. A $1in^2$ foil was placed in the cell at –1.024 V.

vs. S.C.E. for 120 hours. This potential is typical of a cathode operating at 200 mV less overpotential than current industry practice. Upon test completion, the stainless sample showed no mass loss; therefore, corrosion was insignificant.
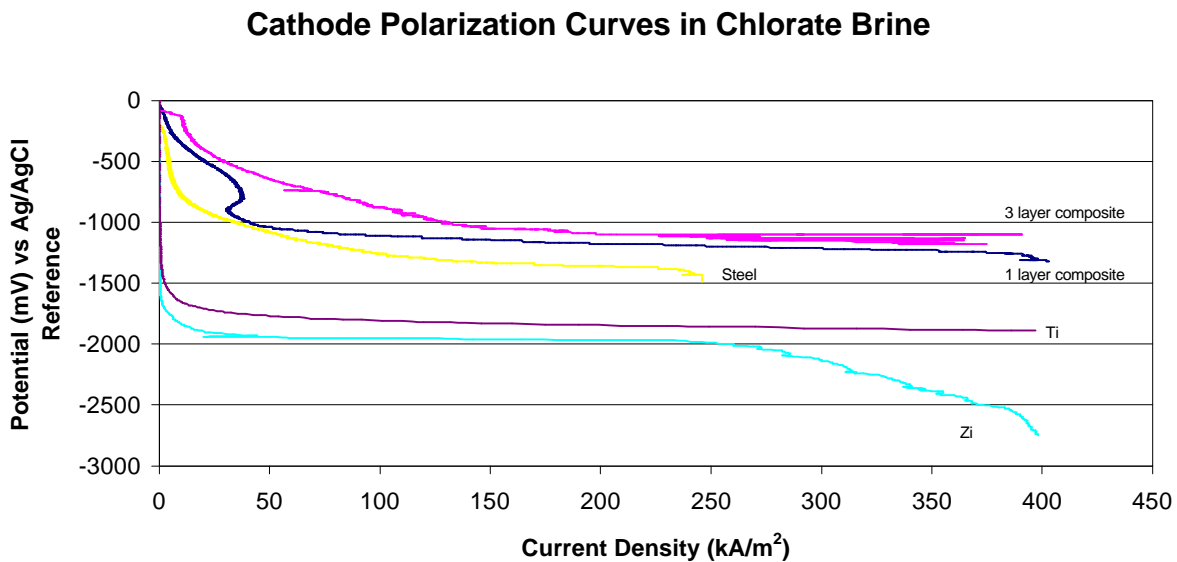
In order to test stainless steel performance in a microfibrous assembly, three SS316L microfibrous electrodes comprised of 2 micron fiber and either one to three layers of high surface area carbon were constructed. These electrodes were impregnated with a tetradiamineplatinate salt via an incipient wetness technique. The platinum salt was reduced to elemental platinum via helium calcination and hydrogen reduction. The resulting platinum loadings were between 10 and 13% grams Pt/gram C. The resulting electrodes consisted, then, of a stainless metal backing, one to three composite layers of carbon and metal fiber, and a facial layer of metal fiber. All these layers were intimately contacted and fused by sintering under a hydrogen atmosphere at 1100°C.

The microfibrous electrodes were placed a single, stirred, undivided, polarization cell and were not mechanically stable. Even under cathodic protection, the electrodes exhibited severe visual corrosion after immersion for less than 15 minutes. This corrosion result contradicted that of the gravimetric test involving the foil. Additional literature review and research revealed that the sintering process destroyed the corrosion resistance of the stainless steel [6]. Hastelloy metals and stainless steels both rely on the effective formation of a chromium oxide layer to stop the corrosion process. Unfortunately, sintering chromium-containing metals in the presence of carbon results in chromium's precipitation from the metal and the formation of chromium carbide. These results drastically reduced the database of candidate metals for microfibrous electrodes.

The decision was made to refocus the corrosion research on titanium class metals and alloys.

Titanium class metals include titanium, titanium alloys, and zirconium. All of these materials exhibit high strength, reasonable conductivity, and high corrosion resistance due to the formation of a protective oxide layer. In other words, these metals passivate under anodic or open circuit potential in a corrosive environment. In contrast, under cathodic potential, titanium does not passivate but forms titanium hydride, a brittle material with poor conductivity and mechanical properties. Thus, a titanium plate cathode of current industrial practice has a maximum lifetime of two years [5].

An additional penalty to shortened lifetime is an increased electrical requirement for chlorate cells operating with titanium cathodes. The following data generated during this project illustrates the point clearly.

Cathode Polarization Curves in Chlorate Brine

At the same current density, titanium cathodes consume around 300 mV more potential than mild steel cathodes. Zirconium cathodes show the worst performance overall.

Hydride formation on a microfibrous material is greatly accelerated due to a surface area thousands of times larger than a plate electrode of equivalent mass. Thus some type of hydride prevention is required for the creation of a high performance titanium based microfibrous electrode. An intense literature survey revealed that elements in column 1B of the periodic table (gold, silver, and copper) are impermeable to hydrogen penetration. U.S. patents 4,186,066 and 3,992,279 particularly discuss the application of these metals to titanium plates or screens to create hydrogen impermeability [7,8]. With this information, corrosion research shifted towards the discovery of materials and methods required for applying a micron thick layer of silver to titanium, creating a coherent bond between the two metals, and driving the formation of a $AgTi$ and/or $AgTi_3$ intermetallic.

As described in the quarterly reports, the task of successfully applying a silver coating to titanium proved difficult and the task extended well into year two. Initially, silver application was done via electroplating preceded by three complex processes for specimen preparation.

1) Bright dip to remove oxides

2) Activation soak to roughen substrate

3) Alternating current for electrochemical etch

4) Electroplating with LDC-4704 solution

The process worked well for titanium foils, and a conformal white silver coating was produced.

Samples of a commercially available titanium microfibrous mesh were obtained and used to evaluate the feasibility of adapting the aforementioned coating process to

metal fibers. The titanium samples were sinter bonded 50 – 100 micron fibers with an overall electrode thickness of ~2mm.
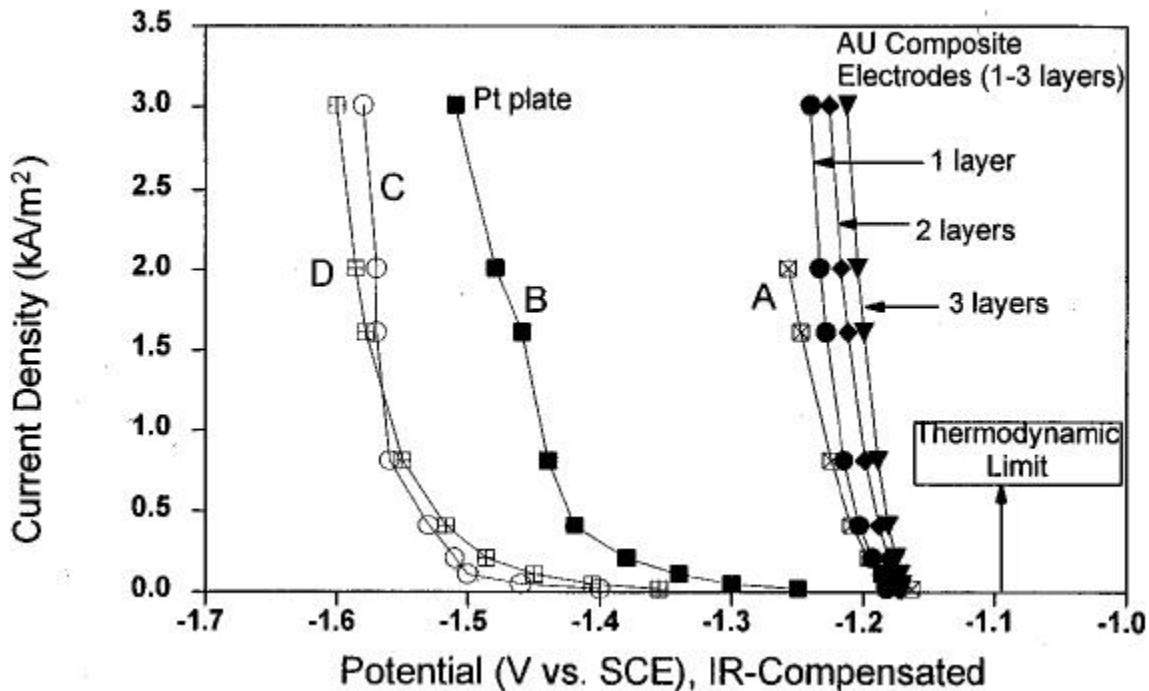
Unfortunately, the bright dip process caused disintegration of most titanium microfibrous samples.   Those samples that did not disintegrate had uneven and unacceptable silver coatings. After many quarters of research, it was discovered that replacing the three preparation steps by a single dip in concentrated hydrochloric acid was proper to prevent disintegration of the microfibrous electrode.

Further investigation concluded that a silver-titanium microfibrous structure was the optimal material to provide high corrosion resistance and high conductivity in a microfibrous structure. A number of electroless and electrolytic procedures were identified for successful application of an approximately 3 micron silver coating. Of the electroless techniques, Brashear silvering was deemed the most effective and practical. Of the electroplating techniques, cyanide based ones were the most effective and practical. Final selection between the electroless and electrolytic techniques will be largely based on the economics of a commercial operation.

Catalytic Performance and Electrode Development in Sodium Chlorate

The research was aimed at reducing the cathodic overpotential in a sodium chlorate cell by 300 mV or more. The research goal was accomplished by three main procedures: 1) Using microfibrous metals with enhanced surface area, 2) Using metals with high catalytic activity towards the hydrogen evolution reaction, and 3) Highly dispersing those metals which exhibit high catalytic activity.

Except for a cation exchange membrane, chlor-alkali cells are fundamentally identical to sodium chlorate cells. In both cells, hydrogen evolution occurs on the cathode. The catholyte in chlor-alkali cells is 30 wt% NaOH, which is non-corrosive towards both nickel and stainless steel. Previous research projects have provided the Auburn University Center for Microfibrous Materials Manufacturing with considerable expertise in designing nickel microfibrous materials [2,3]. As a result, the catalytic activity of a composite microfibrous material towards hydrogen evolution was tested in a chlor-alkali cell before a chlorate cell. The following figure shows polarization curves in 30 wt% sodium hydroxide at 75°C.
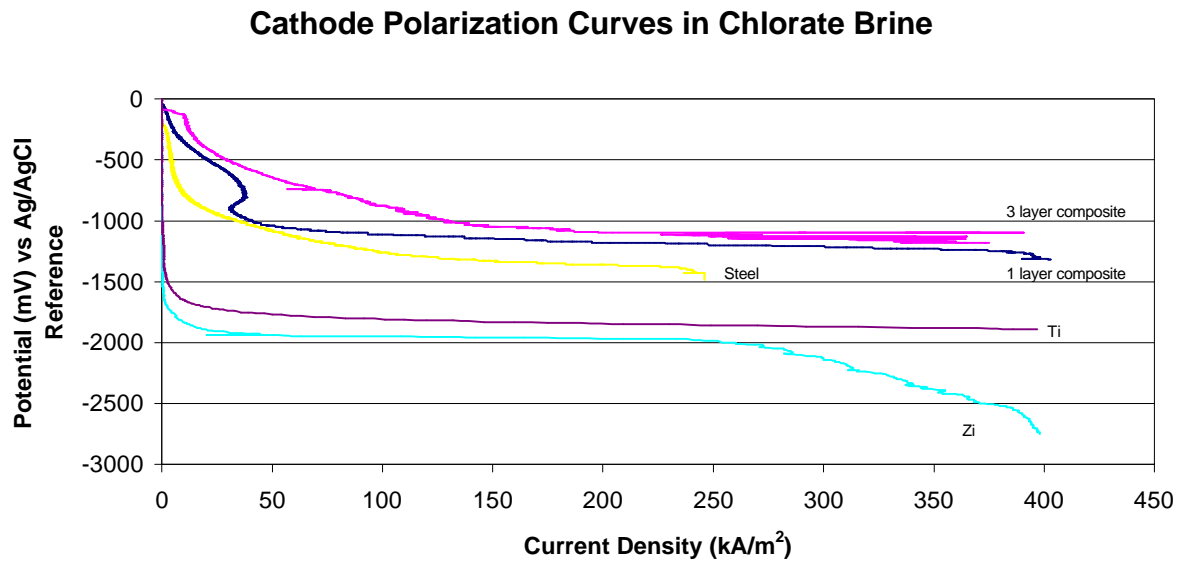
Legend:

A- Proprietary commercial activated cathode coating with low porosity (unstable in chlorate)
B- Platinum plate (stable in chlorate)
C- Roughened nickel commercial cathode (unstable in chlorate)
D- Steel plate (unstable in chlorate)

As the figure shows, Auburn University's microfibrous electrodes operated at a potential approximately 400 mV less than industry standard, mild steel cathodes. These composite electrodes were comprised of nickel metal fibers, activated carbon fibers, and highly dispersed platinum crystallites. Assembly of these materials was analogous to the sintering and incipient wetness technique previously mentioned. The figure shows that as the number of activated electrode layers increased (from 1 to 3), the Auburn University electrodes continued to improve in performance and were within 100 mV of the theoretical limit.
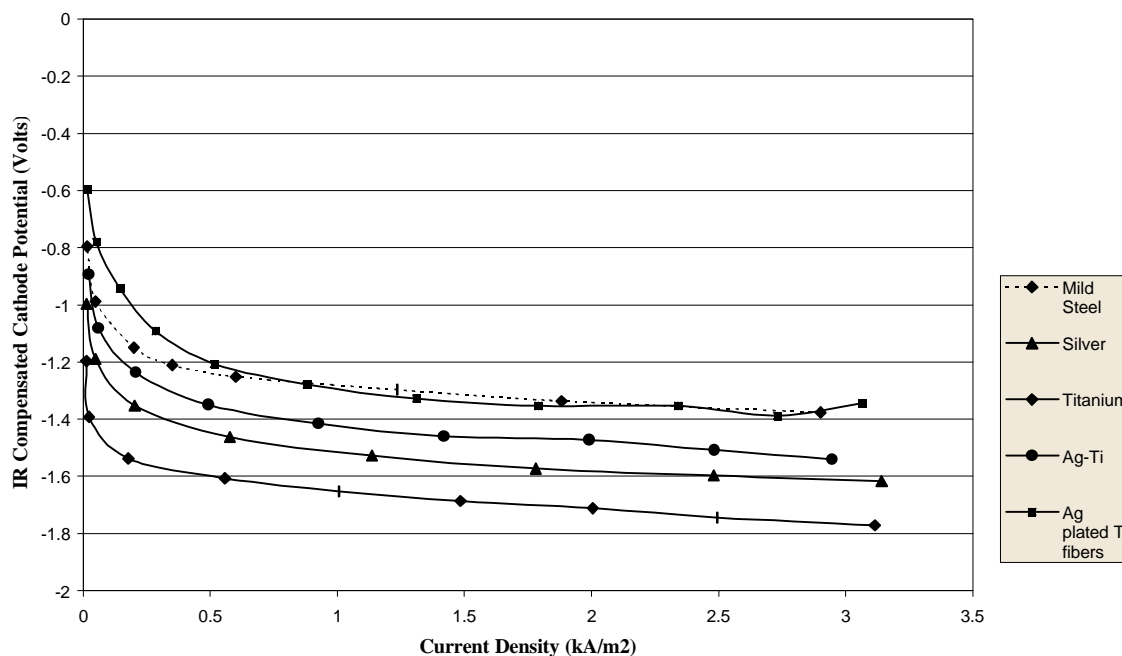
In order to show that the Auburn electrode technology also applied to hydrogen evolution in chlorate brine, polarization curves for titanium, zirconium, steel, and stainless steel microfibrous electrodes were acquired. The activated composite electrode layers contained 10% (by mass) platinum on carbon having a surface area greater than 1000 m^2/gram.

Cathode Polarization Curves in Chlorate Brine

In this particular example, a prototype Auburn University electrode showed 250 mV improvement over primary industry practice (steel). The prototype showed 500 mV improvement over secondary industry practice (titanium). Unfortunately, the corrosion investigations of this project proved these prototypes unstable in chlorate brine due to chromium carbide precipitation. As a result, catalyst optimization was focused around the material constraints of the silver- titanium intermetallic system.

The following polarization curves show the performance of titanium and silver in a sodium chlorate cell.

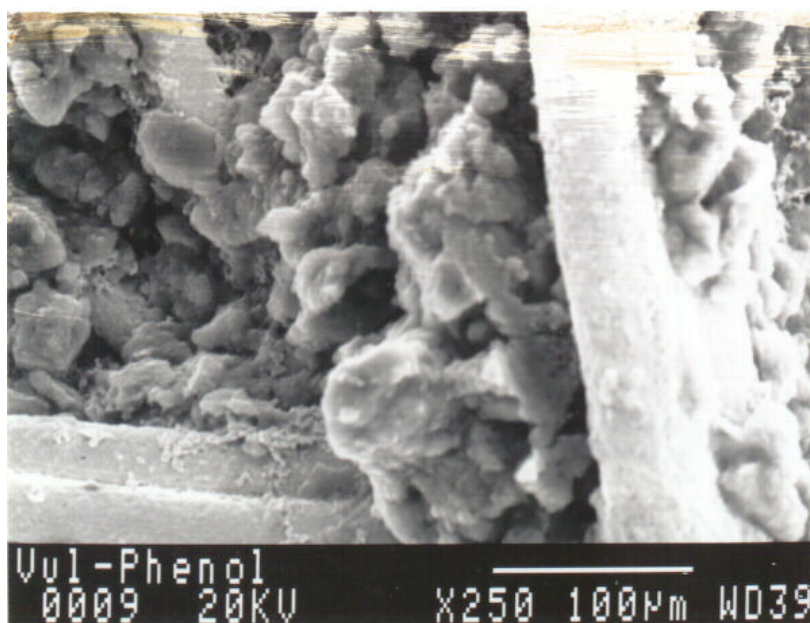**Polarization in Chlorate Brine, 80°C, pH=6.0**

As the figure shows, silver plates exhibit higher catalytic activity toward hydrogen evolution in chlorate brine than titanium plates. A silver-titanium intermetallic plate exhibits higher performance than that of either individual metal, although performance is still lackluster to steel. In order to meet the performance of steel, silver coated titanium composites were produced based on a commercially available sintered titanium product. Although the performance was only equal to steel at high current, low current performance was superior to steel.

In order for chlorate electrodes to achieve the high performance demonstrated in chlor-alkali, the electrodes must contain a highly dispersed electrocatalyst on a high surface area support. Typically, the catalyst support is added through wet lay papermaking technology at Auburn University's Center for Microfibrous Materials Manufacturing. The catalyst support is trapped in the electrode during the sintering process. Unfortunately, the solid state chemistry of titanium prohibits the sintering of
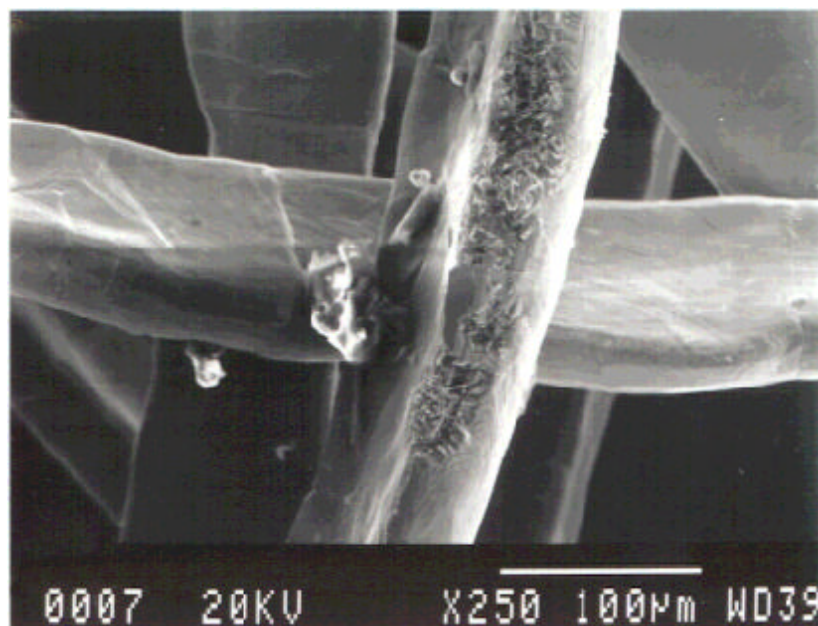
metal fibers in the presence of a carbon support. If titanium is sintered in carbon's presence, chemical combination results in titanium carbide, a material with poor properties for the current application.

The approach of the current research was, then, to sinter titanium fibers exclusive of carbon's presence, coat the fibers with silver, and anneal under an inert atmosphere to drive formation of the desired intermetallic. Subsequently, activated carbon particles containing highly dispersed electrocatalyst were trapped in the metal matrix with an appropriate binder. A major goal of the research was to discover a binder material inert to the corrosive chlorate broth, compatible with carbon, and practical for use.

A variety of binder systems were investigated including but not limited to carboxymethylcellulose (CMC), polyvinylalcohol, (PVA), teflon dispersion (T-30), phenolic resin, and PVDF resin. PVA and CMC exhibited severe usability problems due to agglomeration and viscosity. Teflon dispersion and phenolic resin both produced acceptable carbon entrapment after recipe optimization. A scanning electron micrograph of a microfibrous titanium electrode with entrapped (via phenolic resin) carbon particulate is shown below.

Vul-Phenol
0009 20KV   X250 100μm WD39

The SEM clearly shows a high surface area carbon in intimate contact with interlocking metal fibers. The roughened macroscopic surface of the carbon also contributes to effective catalyst exposure. Shown below is a picture of sintered microfibrous titanium product without the activated carbon layer.

0007 20KV   X250 100μm WD39

Electrochemical impedance spectroscopy was used to quantitatively determine the nature of contact between the activated carbon and metal fiber matrix. A commercial 40 micron nickel fiber mesh was sintered under a 1000°C hydrogen atmosphere to remove impurities and fuse the fiber matrix. The nickel electrodes were dipped in a phenolic resin/ solvent / activated carbon recipe developed during this project. After thermal solvent removal, the electrodes were placed in a 250 ml. impedance cell filled with 1M NaOH and outfitted with a platinum counter-electrode.

The theoretical capacitance of flat plate electrodes is ~25 $\mu F/cm^2$ from AC impedance spectroscopy. Microfibrous electrodes (without carbon) from this research yielded measurements on the order of 325 $\mu F/cm^2$. When impregnated with high surface area carbon (via phenolic resin), electrodes from this research yielded capacitances on the order of 24,510 $\mu F/cm^2$. Thus the research clearly showed performance increases due to enhanced metallic area. The research showed dramatic performance increases when a catalyzed carbon coating was added to the electrochemical circuit.

Further research by the Auburn University Center for Microfibrous Materials Manufacturing found that phenolic resin imposed a hydrophobic nature on the electrode and impeded electrolysis performance. Continued research discovered PVDF as the optimal binder material. Samples of PVDF placed in chlorate brine at 80°C showed no breakdown after 6 months of immersion. A fractional factorial method was used to determine the optimum mixture of carbon/ PVDF/ solvent to create a conformal coating without blocking interior accessibility of the microfibrous electrode. Samples were examined under an optical microscope and scored on visual quality. Sample scores ranged from 1 to 5 based on the following criteria:

1- Carbon dispersion unusuable; too viscous to apply
2- Carbon agglomerations between metal fibers, low loading
3- Carbon agglomerations between fibers, complete loading
4- Carbon clumping on electrode face, occluding interior accessibility
5- Uniform carbon coating on metal fibers; metal fibers appear black

A score of 5 was best, a score of 3 was acceptable, a score of 2 was fair, and any other number was unacceptable. Masses of PVDF and carbon were varied in the factorial while the amount of acetone solvent (7.91 ml) was held constant. Results from the factorial experiment are shown below.

Sample #	PVDF (grams)	Carbon (grams)	Visual Rating (1-5)
1	0.25	0.25	2
2	0.25	0.5	2.5
3	0.25	0.75	3
4	0.25	1	4
5	0.50	0.25	2
6	0.50	0.5	4
7	0.50	0.75	4
8	0.50	1	4
9	0.75	0.25	4
10	0.75	0.5	4
11	0.75	0.75	4
12	0.75	1	4

As the table shows, no scores of 5 were obtained from the research. Only one score of 3 was obtained; thus, an optimized method for applying carbon to the silver-titanium electrodes had been developed.

Economic Analysis and Electrode Manufacturing Costs

An economic window analysis was completed for the ongoing research. A brief summary of the work follows. The calculations are based on a 400mV potential savings at the cathode under typical chlorate cell operating conditions: 3.0V total, 3 kA/ m^2, and 95% current efficiency.

The amount of chlorate produced by a single square meter of electrode annually is:

$$(0.95)\left(\frac{3000C}{s \cdot m^2}\right)\left(\frac{equiv}{96,487C}\right)\left(\frac{mol}{6equiv}\right)\left(\frac{106.44\,g}{mol}\right)\left(\frac{mton}{1e6g}\right)\left(\frac{3600s}{hr}\right)\left(\frac{8760hr}{yr}\right) = \frac{16.53mton}{m^2 \cdot yr}$$

If sodium chlorate costs $400 per metric ton and 45% of this cost is due to power requirements, then it costs nearly $3000 per year to operate a single square meter of electrode.

$$\left(\frac{16.53mton}{m^2 \cdot yr}\right)\left(\frac{\$400}{mton}\right)(0.45) = \frac{\$2,974\,electricity}{m^2 \cdot yr}$$

If an optimized electrode allows a 400 mV reduction in the required electrolysis potential, then the following calculation shows that nearly $400 are saved each year for a single square meter of electrode in service.

$$\left(\frac{0.4V}{3.0V}\right)\left(\frac{\$2,974}{m^2 \cdot yr}\right) = \frac{\$396}{m^2 \cdot yr}$$

From this research, a good rule of thumb for calculating an electrode's ROI would be that a single square meter of microfibrous electrode would save $100 per year if the electrode lowered overpotential by 400 mV.

References

1) K. Viswanathan and B.V. Tilak, *J. Electrochem. Soc.*, *131*, 1551 (1984)

2) D. Kohler, J. Zabasajja, A. Krishnagopalan, and B. Tatarchuk, *J. Electrochem. Soc.*, *137*, 136 (1990)

3) D. Kohler, J. Zabasajja, F. Rose, and B. Tatarchuk, *J. Electrochem. Soc.*, *137*, 1750 (1990)

4) H. Vogt, J. Balej, J.E. Bennett, R. P. Wintzer, S.A. Sheikh, and P. Gallone, *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed., Vol. A6, 1986, p.483

5) John J. McKetta, *Encyclopedia of Chemical Processing and Design*, 1st ed., Vol. 51, 1995, p.126

6) Tony Wu, Master's Thesis, Auburn University, Auburn, Alabama (1991)

7) Titanium Industries, *U.S. Patent 4,186,066*

8) Kemanord Aktiebolag, *U.S. Patent 3,992,279*