Journal of Applied Electrochemistry (2005) 35:581–587
DOI 10.1007/s10800-005-1822-5

High surface area, supported precious metal cathodes utilizing metal microfibrous collectors for application in chlor-alkali cells

RYAN A. NICKELL and BRUCE J. TATARCHUK*
Department of Chemical Engineering, Center for Microfibrous Materials Manufacturing, 230 Ross Hall, Auburn University, AL 36849, USA
*(*author for correspondence, e-mail: brucet@eng.auburn.edu; phone: +334-844-2023; fax: +334-844-2065)*

Received 07 June 2004; accepted in revised form 27 January 2005

Key words: activated hydrogen cathode, chlor-alkali, composite electrode, electrocatalysis, low overpotential

Abstract

Activated cathodes were prepared from papermaking techniques for use in a membrane type chlor-alkali cell. These cathodes consisted of a nickel fiber matrix, which entrapped a platinum electrocatalyst supported on activated carbon fiber. Following optimizations of the void volume, thickness, catalyst loading, carbon support, and substrate–support ratio, these cathodes performed at an overpotential of only 58 mV @ 3 kA m^{-2} in a cell containing 30 wt% NaOH at 80 °C. In addition to I/V performance, cathodes were characterized for catalyst dispersion and support surface area. When testing was discontinued, activated cathodes had demonstrated stability for greater than 60 days in a custom cell designed for continuous, steady-state operation.

1. Introduction

Recently, the chlor-alkali industry has witnessed an increased awareness of market fragility. Plagued by overcapacity, rising natural gas prices, and an overall slow economy, the industry witnessed chlorine prices as low as $70/ton in late 2001 [1]. While the industry is currently recovering and actually expected to grow through 2006, the situation has led to the shutdown of inefficient plants and an increased concern for profit margins [2]. Because electricity accounts for ~50% of production costs, the situation presents a unique opportunity to introduce activated cathodes, which offer dramatically reduced electrical consumption and, as a result, a more competitive market position [3].

Over the past few years, Auburn University has been engaged in the development of microfibrous materials to improve the performance of batteries, capacitors, gas diffusion electrodes, heterogeneous catalysis, chem-bio filtration units, and other applications [4–7]. Microfibrous materials offer a unique opportunity to expose materials with their maximum surface area in a structure that is conductive, durable, and customizable in terms of void, volume, shape, and thickness. In this application, novel cathodes based on nickel microfiber and activated carbon fiber are prepared from cost-efficient, wet-lay papermaking techniques. Nickel microfibers provide a three-dimensional and highly conductive matrix that entraps activated carbon fibers supporting a high performance electrocatalyst. The high surface area of the carbon fibers provides a means to support the catalyst with relatively high dispersion. The nickel fiber matrix provides its own reaction surface as well as an effective mechanism for transferring current to and from the much higher surface area carbon and precious metal electrocatalyst. The following discussion describes the performance and nature of these activated microfibrous cathodes according to a variety of factors: void fraction, substrate:support ratio, catalyst loading, thickness, type of carbon support, and long-term stability.

2. Experimental

2.1. *Preform fabrication*

Microfiber based preforms containing 4 μm Ni 200 fiber (Micro Metals, Inc.), activated carbon fiber, and 1 g of softwood cellulose were prepared according to a modification of TAPPI Standard 205 (Technical Association of the Pulp and Paper Industry, Inc.) [8]. The metal:carbon ratio varied between 2.5:0.5 and 1:2 (g Ni:g C). The activated carbons represented a range in surface areas from 1300 to 2500 m^2/g and included Toyobo KF-1600, SpectraCorp SACF-25, and Charcoal Cloth FM 1/250. Using a Timi type disintegrator (Lorentzen & Wettre Canada, Inc.), the activated carbon, nickel fiber, and cellulose were blended for 1.75×10^6 revolutions (counter setting of 70,000) in 2 l of tap water. The resulting dispersion was poured into a CA385 sheet machine

(Lorentzen & Wettre Canada, Inc.) filled to approximately 1/2 capacity with tap water. After filling the sheet machine to full capacity and re-agitating the dispersion with a metal bar (2.54 × 0.635 × 76.2 cm), a sheet was formed and removed according to TAPPI standards. These preforms ("active layers") were labeled accordingly and dried overnight at 60 °C in air. In the same manner, additional preforms ("overlayers") were prepared with 0.75 g 4 μm nickel and 0.25 g of softwood cellulose. To facilitate adhesion between the layers during sintering, overlayers were pressed at 133 MPa. Active layers were pressed at 221 MPa between titanium spacers having a gap of 0.097 mm.

2.2. *Preform sintering and electrode assembly*

The microfibrous preforms were subjected to a sintering process to pyrolyze the cellulose, reduce metal oxides, bond the nickel fibers, and entrap the carbon fibers. Using a template and precision shears, active layers and overlayers were cut into circles measuring 1.91 and 2.22 cm, respectively. In the general manner of Figure 1, the layers were sintered onto nickel foil for support and current collection. Refrac screen prevented movement of the microfiber layers during sintering. A thin layer of alumina felt was included to prevent bonding of the nickel fiber and refrac screen. Electrode assemblies were placed in a custom quartz U-tube and sintered in a vertical furnace at either 900 °C or 1000 °C for 2 h in hydrogen (BOC Gases, 99.9%) flowing at 150 ml/min. Following sintering, each electrode was removed from the supportive screens and placed in an ultrasonic bath filled with distilled and deionized water for a period of 30 min. The ultrasonic treatment provided for the removal of soot and loose carbon particulate. Before sintering and after ultrasonic treatment, electrode materials were dried overnight at 105 °C before weighing to the nearest 0.0001 g (Sartorius 180-D scale). This mass balance provided information relevant to carbon retention and total void fraction. Electrode volume was determined with a micrometer and calipers.

2.3. *Catalyst application and characterization*

Sintered electrodes were prepared with 5–20 wt% platinum on carbon according to a pseudo-incipient wetness technique [9]. According to the technique, a catalyst salt was concentrated in solution based on the total electrode void, V_T. This void included the intracarbon void, V_c and the bulk void, V_b. Intracarbon void was calculated from the product of the post-sinter carbon mass, m_c, and the carbon pore volume, υ_p. Pore volume and surface area were measured via the static volumetric adsorption of nitrogen according to ASTM D 3663–92 [10]. Nitrogen was adsorbed on the carbons following heat treatment identical to that of the sintering process. Bulk void was calculated from the product of the total volume and the bulk void fraction was given by

$$\epsilon_b = 1 - \frac{1}{(\mathrm{CA})l}\left[\frac{m_{\mathrm{Ni}}}{\rho_{\mathrm{Ni}}} + \frac{m_c}{\rho_{cb}}\right] \tag{1}$$

where CA = cross sectional area of the electrode, l = electrode thickness, m = species mass, and ρ = density. The bulk density of carbon, ρ_{cb}, was calculated from the relation of Equation 2, where the total volume exhibited macroscopically by 1 g of carbon was the sum of the volumes of both the microscopic pores and the solid carbon itself.

$$\frac{1}{\rho_{cb}} = \frac{1}{\rho_{ca}} + V_p \tag{2}$$

where ρ_{ca} = amorphous carbon density of 1.8–2.1 g cc^{-1} [11]. A value of 1.92 g cc^{-1} was measured in this laboratory and used in all relevant calculations.

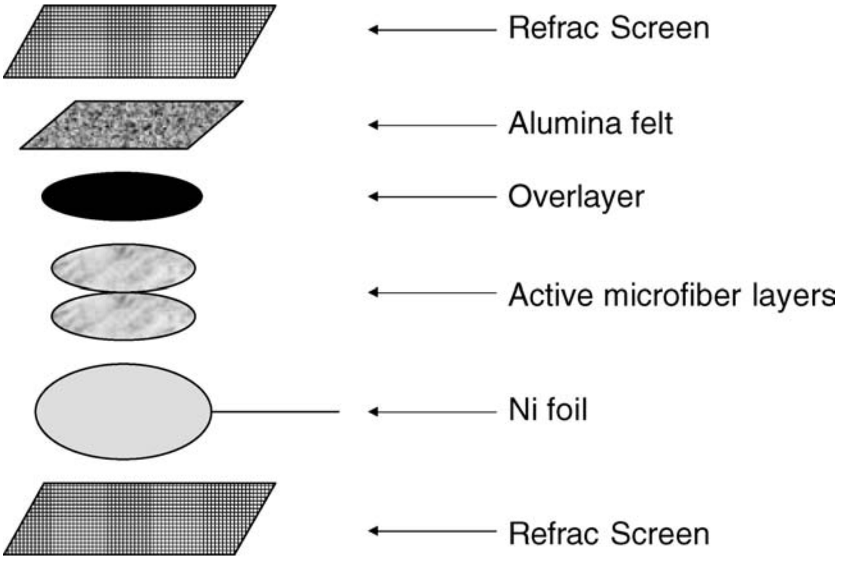

Fig. 1. Typical manner in which microfiber preforms were assembled for sintering into a composite electrode structure.

For each electrode type, a solution of tetraammine platinum (II) nitrate (TAPN, 99.995%, Aldrich) was prepared according to Equation 3.

$$[\mathrm{Cat}_{\mathrm{soln}}] = \left[\frac{m_{\mathrm{c}}\mathscr{X}_{\mathrm{cat}}}{V_{\mathrm{T}}}\right]\left[\frac{\mathrm{MW}_{\mathrm{Salt}}}{\mathrm{ME}_{\mathrm{Pt}}}\right] Y_{\mathrm{Pt}} \tag{3}$$

where MW = molecular weight, x_{cat} = support loading (wt%), and Y_{Pt} = Platinum salt yield (mol Pt/mol salt). Following overnight drying at 105 °C, the TAPN solution was applied to each electrode in a dropwise manner until the point of incipient wetness. Drying the impregnated electrodes slowly at a temperature of 40 °C facilitated the slow concentration and crystallization of TAPN in the carbon pore structure. Following additional drying at 105 °C, catalyst uptake was determined gravimetrically to the nearest 0.0001 g. Catalyst preparation was concluded by calcining the electrodes at 400 °C in helium (99.999% BOC Gases, 100 ml min^{-1}) for 2 h before reducing in hydrogen (99.999% BOC Gases, 150 ml min^{-1}) for 2 h at the same temperature. Samples were calcined in helium, since studies have associated this treatment with improved dispersion values over those from a reduction in hydrogen, alone [12]. Following calcination and reduction, the dispersions of selected samples were characterized via hydrogen chemisorption, oxygen chemisorption, and hydrogen–oxygen titration. Chemisorption procedures were performed in accordance with ASTM D 3908–88 [13]. Dispersion calculations were based upon the assumption of linear and bridge bonding stoichiometries for the hydrogen and oxygen species, respectively [14].

2.4. *I/V performance*

Polarization performance was measured in a custom glass H-cell which contained 155 ml of anolyte, 180 ml of catholyte, and a Nafion 117 separator. Anolyte and catholyte solutions were prepared to concentrations of 300 g l^{-1} NaCl and 30 wt% NaOH, respectively, using crystalline stock (Fisher Scientific, ACS) and distilled/deionized water. To protect the DSA anode (6.45 cm^2, Chemetics, Inc.) and increase current efficiency, the brine's pH was adjusted to a value of 3.5 using dilute HCl. Microfibrous cathodes were mounted in a Teflon shield assembly, which exposed a geometric area of 2.018 cm^2 for electrolysis. Cathode polarization was measured against a custom Hg/HgO reference electrode filled with 30 wt% caustic and in thermal equilibrium with the bulk cell. During testing, a temperature of 80 °C was maintained with a 1.2 amp heat tape, K-type thermocouple and an Omega CN77533-C2 temperature controller. Electronic hardware included an EG & G PAR 273A potentiostat, an Omega WB-31 White Box, and a Dell Dimension 4100 microcomputer running Windmill 4.3 DAQ Software (Windmill Software, Ltd.). Microfibrous electrodes were galvanostatically polarized at values of 3, 4, and 5 kA m^{-2} for two cycles from high to low current. At each current density, the stable IR compensated voltage was recorded for no less than twenty minutes and then averaged to obtain a final value. Averaging eliminated approximately 8 mV of noise associated with cycling of the temperature controller. This average overpotential for a given electrode at a given current density typically varied 2 mV.

2.5. *Stability testing*

Long-term stability of the activated cathode design was assessed in a custom reactor capable of operating unattended and at steady state. The reactor consisted of fused Pyrex glass compression joints (Ace-Glass, 7646–14, ca. 4 cm ID) and appropriate fittings for inletting reactants, exhausting products, and measuring temperature. These compression joints supported DSA anode, Nafion 117 membrane, and either steel cathode or activated microfibrous cathode. Using peristaltic pumps, acidified brine and deionized water were fed to the anode and cathode compartments at approximate flowrates of 0.55 ml min^{-1} and 0.25 ml min^{-1}, respectively. The cell was operated at a current density of 3 kA m^{-2}. Approximately every 24 h, the eluting caustic concentration (wt%) was determined from density measurements calculated from the mass of a 10 ml sample measured to nearest 0.1 ml and 0.0001 g. Data conversion from wt% to density was facilitated by the following relation valid between 17 and 38 wt% and based on published data [11].

$$[\mathrm{NaOH}]_{\mathrm{wt\%}} = 93.501\rho_{\mathrm{g/ml}} - 94.041 \tag{4}$$

Microscopic examination, gravimetric analysis, and voltage monitoring were used to characterize electrode stability.

3. Results

3.1. *Activated cathodes with differing catalyst supports*

Table 1 illustrates surface area and pore volume measurements on activated carbons following treatment in a typical hydrogen sintering environment (900 °C, 250 ml min^{-1}). Measured values of surface area and pore volume differ little from those reported by the manufacturers for virgin material; therefore, the sintering process does not appear to adversely affect the carbon's morphology. Table 2 illustrates dispersion values for platinum electrocatalyst supported on these same activated carbons when entrapped in a microfibrous electrode and prepared via pseudo-incipient wetness. Dispersions were measured on electrodes containing a nickel overlayer, two activated layers with 10–11% Pt on carbon, and an overall void fraction of 77–81%.

Activated layers were cut from perform having a 1.5:1.5 ratio of nickel to carbon fiber (grams). Dispersions ranged

Table 1. Comparison of manufacturer's data and experimentally determined data for surface area and pore volume of activated carbons used in composite electrodes

Manufacturer	Product	Surface area /m^2 g^{-1}		Pore volume /cc g^{-1}	
		Manufacturer	Experimental	Manufacturer	Experimental
Spectracorp, Inc.	SACF-25	2500	2306	1.2	1.12
Toyobo America, Inc.	KF-1600	1600	1681	NR	0.80
Charcoal Cloth, Ltd.	FM-1/250	1300	1081	0.50	0.54

Table 2. Dispersion of platinum electrocatalyst in activated cathodes containing 10 wt% Pt on carbon

Manufacturer	Product	Dispersion /%		
		H_2 Chemisorption	O_2 Chemisorption	H_2O_2 Titration
Spectracorp, Inc.	SACF-25	25	22	29
Toyobo America, Inc.	KF-1600	24	20	23
Charcoal Cloth, Ltd.	FM-1/250	30	29	28

from 20 to 30% with no one carbon showing clearly higher dispersions. Such a result suggests that the dispersion is primarily a function of preparation technique rather than support morphology. I/V performance of these activated cathodes is illustrated in Figure 2 for a current density range of 3–5 kA m^{-2}. Superior performance is obtained with a support of intermediate surface area, Toyobo KF-1600. Because higher surface areas are generally associated with increased microporosity, poorer performance of the Spectracorp material is best explained by poor catalyst accessibility.

3.2. *Activated cathodes with differing substrate:support ratios*

Figure 3 illustrates the retention of Toyobo KF-1600 in two layer activated cathodes as a function of both the sintering temperature and the substrate:support ratio. Both increased temperature and substrate loading are associated with an increase in the kinetics of carbon gasification. This observation concurs with previous work utilizing stainless steel microfibers [15]. Carbon retentions at 1000 °C are at least 21% lower than those at 900 °C. At a given temperature, nickel fiber catalyzes the carbon gasification, as higher substrate loadings are intuitively associated with an increased number of physical nickel–carbon contacts. Due to the imperfect assumption of zero cellulose retention, a slightly negative retention is observed at 1000 °C for the highest substrate loading. The data of Figure 3 suggest difficulty in achieving a combination of high void and high carbon loading. Figure 4 illustrates the I/V performance of these activated cathodes with a catalyst loading of 10–12% and an overall void fraction of 74–77%. Best performance is observed with the "balanced" nickel:carbon ratios of 1.5:1.5 and 2:1. Figure 4 shows only a small improvement in overpotential with the 2:1 ratio; however, the lower catalyst requirements of the 2:1 ratio

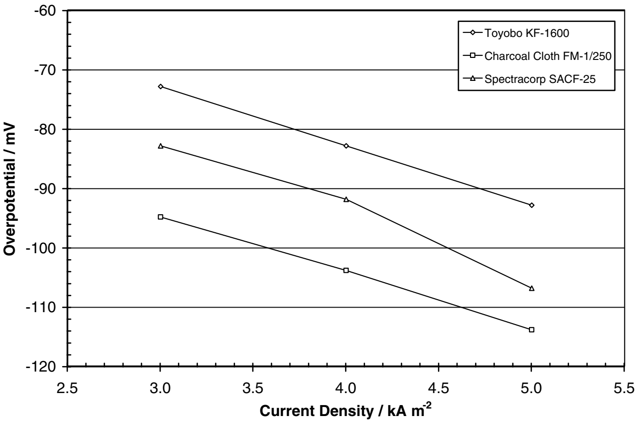

Fig. 2. I/V performance of activated cathodes with differing carbon supports. Cathodes contain two active layers with 10–12 wt% Pt on carbon and a void fraction of 74–77%.

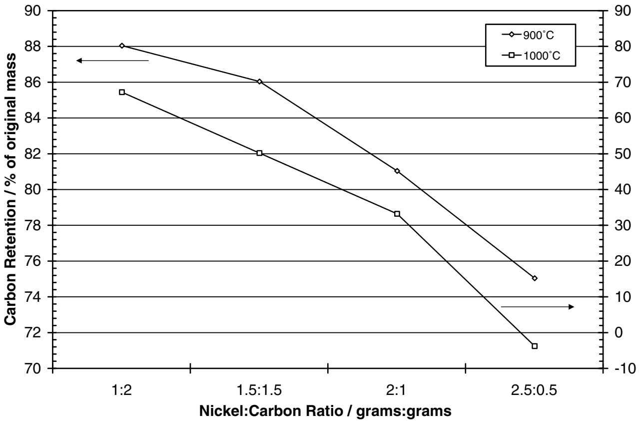

Fig. 3. Retention of activated carbon in composite electrodes as a function of the sintering temperature and the nickel:carbon ratio of the perform.

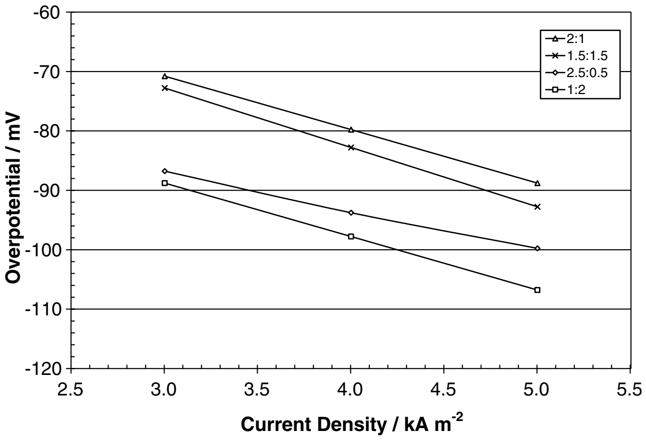

Fig. 4. I/V performance of activated cathodes having two active layers and ~10 wt% Pt on carbon but differing substrate:support ratios.

clearly qualify it as preferable from a cost standpoint. Inferior performance of the other ratios is best explained by either inadequate catalyst loading or an inadequate amount of nickel fiber for transporting current.

3.3. *Activated cathodes of differing void fraction*

Figure 5 illustrates the polarization performance of activated cathodes built with two active layers having 4 μm nickel fiber and Toyobo KF-1600 fiber in a 2:1 ratio. Catalyst loading varied from 10–12 wt% Pt on carbon. Within the studied range, lower void fractions are associated with improved I/V performance. In the absence of carbon fiber, other work from this laboratory has shown minimal overpotential with a high void fraction up to 94% [16]. In that case, a high void fraction appears to offer improved release of generated gas bubbles. In this case, higher voids are inherently associated with a reduced number of physical nickel fiber-carbon fiber electrical contacts. Consequently, activated cathodes benefit more from the improved intraelectrode conductivity rather than the restricted gas release at low values of the bulk void fraction.

3.4. *Activated cathodes of increased catalyst loading and thickness*

Beyond selection of the optimal catalyst support, void fraction, and substrate:support ratio, two opportunities remain for further reducing the cathodic overpotential. Either the catalyst loading may be increased, or the number of active layers having a given catalyst loading may be increased. Figure 6 illustrates results for the first case, where the number of catalyst layers remains at two, but the catalyst loading has been changed from approximately 5–20 wt%. Across the range of measured current densities, higher catalyst loadings are indeed associated with lower overpotential and reach a value of 68 mV at a current density of 3 kA m^{-2} . Regarding the second case, Figure 7 illustrates I/V performance for activated cathodes with a nominal catalyst loading of 11–12% but a varying number of microfibrous layers. At a current density of 3 kA m^{-2}, the hydrogen evolution

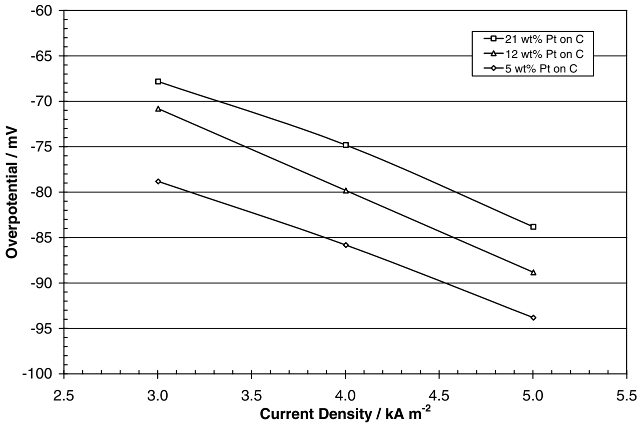

Fig. 6. I/V performance of activated microfiber cathodes with differing catalyst loadings. Void fraction = 73–75%, two active layers.

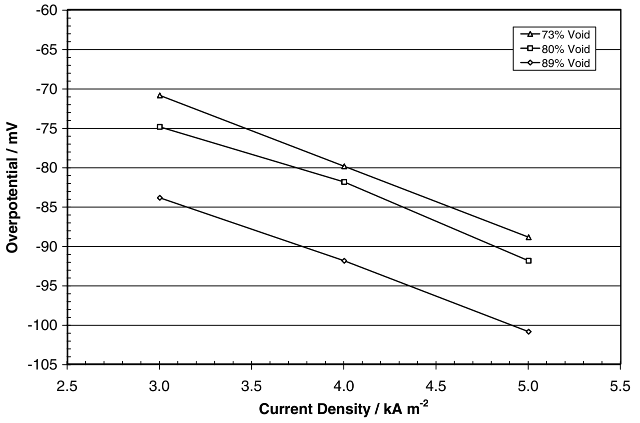

Fig. 5. I/V performance of activated cathodes with differing void fraction. Cathodes contain two active layers with 10–12 wt% Pt on Toyobo KF-1600 activated carbon.

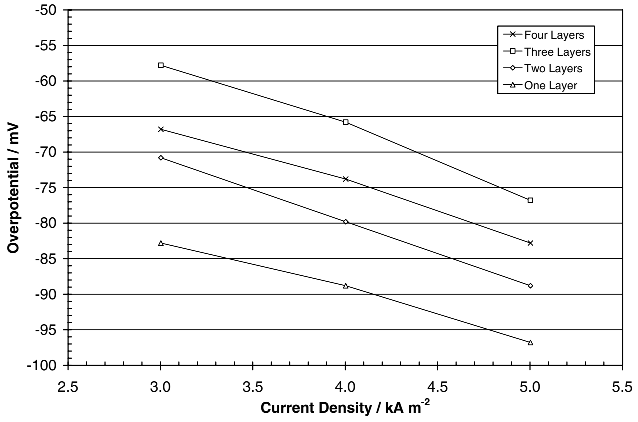

Fig. 7. I/V performance of activated microfiber cathodes with an increasing thickness or number of active layers. Void fraction = 73–75%, ~10 wt% Pt on carbon.

overpotential for a three layer structure is only 58 mV. This result represents the lowest overpotential obtained in this study. Of particular interest is the four layer cathode with inferior overpotential to a three layer configuration; yet, this result is not surprising in context of those results for void fraction. Performance of the four layer structure is best understood as a limitation of the microfibrous structure to offer adequate electrical conductivity through the structure's thickness.

3.5. *Activated cathode stability*

Stability measurements were taken on mild steel cathode and on activated cathode having a typical structure of one overlayer and two active layers. Active layers contained Spectracorp activated carbon with a 10% catalyst loading and were prepared from preform with a substrate:support ratio of 1.5:1.5. Overlayers were prepared to a diameter of 5 cm; and active layers, to a diameter of 4 cm. Following sintering, the cathode structure was not ultrasounded to remove loose carbon particulate.

Figure 8 shows baseline performance of the electrolysis cell over a 1 week period with mild steel cathode operated at 3 kA m^{-2}. Following a 24 h period, stable and steady-state performance was observed at an average potential of 9.5 V.

Eluted caustic was produced having a concentration of 26–28 wt%. The high value of the observed voltage was attributed to the large inter-electrode gap and use of Nafion 117 rather than the more efficient Nafion 90209 membrane. However, the voltage behavior was deemed acceptable since the experiment's purpose was to establish those characteristics of stable baseline operation rather than optimal reactor design. Figure 9 illustrates the performance of the microfibrous cathode design over a two month period. During the first 48 h of electrolysis, the electrode structure shed carbon in the catholyte and the voltage rose accordingly. After 48 h, the carbon shedding ceased and the cell operated for approximately two months at a stable potential of 9.3 V. Cell operation ceased due to caustic leaking from the FETFE o-rings and pitting the glassware. Following electrolysis, inspection of the microfibrous cathode revealed no visual signs of deterioration.

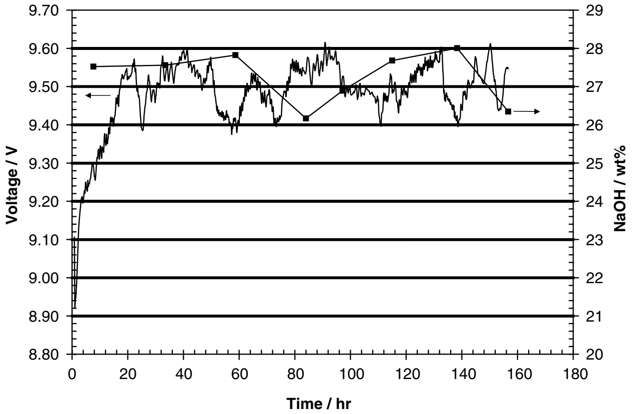

Fig. 8. Extended polarization test of mild steel cathode to assess baseline performance of a continuous flow, bench-scale chlor-alkali reactor.

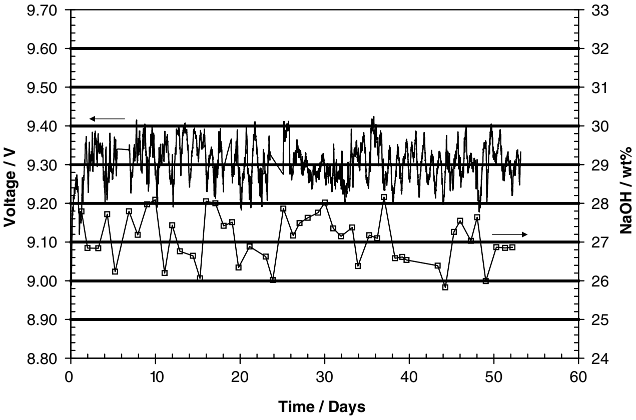

Fig. 9. Extended polarization test of a prototype activated microfibrous cathode in a continuous flow, bench-scale chlor-alkali reactor. Cathode contained two active layers with 10% Pt on SACF-25 activated carbon.

4. Conclusions

Wet-lay papermaking techniques have been utilized for the preparation of activated cathodes from nickel microfiber and activated carbon fiber supporting a platinum electrocatalyst. The preparation technique has allowed for extensive flexibility in optimizing facets of the structure including void fraction, carbon type, catalyst loading, thickness, and substrate:support ratio. Based on the techniques described herein, the design factors have been manipulated to create a cathode with only 58 mV of overpotential at 3 kA m^{-2} in 30 wt% caustic at 80 °C. This overpotential is realized from a structure of 73% void, which contains two active layers of Toyobo KF-1600 carbon fiber (~10 wt% Pt) and 4 μm nickel fiber in a 2:1 ratio. Flexibility of the chosen design approach is, perhaps, best illustrated by the fact that an overpotential reduction of 37 mV was directly associated with the optimization process. More simply, 37 mV of difference was observed between the best and worst microfibrous structures; thus, flexibility of the design proved important. A simple membrane chlor-alkali reactor was constructed for extended testing of the cathode design. For a period of 60 days, the microfibrous cathode design proved stable and operated at an overpotential far superior to that of mild steel cathode.

Acknowledgements

The authors wish to thank Mr. Wendell Sandlin, Glass Shop Manager, Department of Chemistry, Auburn University. His expertise with glassware proved

indispensable for realizing much of the apparatus described herein.

References

1. M.C. Blackburn, *Pulp Paper* **76** (2002) 25.
2. E. Van Savage, *Chem. Mkt. Rep.* **263** (2003) 1.
3. M.S. Vreeke, D.T. Mah and C.M. Doyle, *J. Electrochem. Soc.* **145** (1998) 3671.
4. C.J. Marion, D.R. Cahela, S. Ahn and B.J. Tatarchuk, *J. Power Sources* **47** (1994) 297.
5. G.M. Swain and B.J. Tatarchuk, *J. Electrochem. Soc.* **140** (1993) 1026.
6. D.R. Cahela and B.J. Tatarchuk, *IECON Proc.* **3** (1997) 1080.
7. S. Ahn and B.J. Tatarchuk, *J. App. Electrochem.* **27** (1997) 9.
8. Technical Association of the Pulp Industry. in 'Forming Handsheets for Physical Tests of Pulp, Standard T-205, TAPPI Testing Procedures: Standards and Provisional Methods, and Useful Methods,' TAPPI Pub., Atlanta GA (1971).
9. M.W. Meffert, PhD Dissertation. Auburn University, Auburn AL (1998).
10. ASTM Committee D-32, in 'Standard Test Method for the Surface Area of Catalyts', Std. D 3663–92, Annual Book of ASTM Standards (1999).
11. R.C. Weast (Ed.), *Handbook of Chemistry and Physics, B-101, D-256*, 57th, (CRC Press, Boca Raton, 1976).
12. F. Rodriguez-Reinoso, I. Rodriguez-Ramos, C. Moreno-Castilla, A. Guerrero-Ruiz and J.D. Lopez-Gonzalez, *J. Catalysis* **99** (1986) 171.
13. ASTM Committee D-32, in 'Standard Test Method for Hydrogen Chemisorption on Supported Platinum on Alumina Catalyts By Volumetric Vacuum Method,' Std. D 3908–88, Annual Book of ASTM Standards (1999).
14. G.R. Wilson and W.K. Hall, *J. Catalysis* **17** (1970) 190.
15. B.J. Tatarchuk, M.F. Rose, A. Krishnagopalan, J.N. Zabasajja and D. Kohler, U.S. Patent 5 096 663 (1992).
16. R.A. Nickell, PhD Dissertation. Auburn University, Auburn AL (2003).