

Investigation of a Sodium Hypochlorite Catholyte for an Aluminum Aqueous Battery System

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A solution-phase sodium hypochlorite (NaOCl) cathode for use in an aluminum-based seawater battery is presented. This catholyte attains a high power density, a positive redox potential, and a high Faradaic current capacity. NaOCl is also inexpensive, stable, and environmentally safe/friendly. Four aluminum alloys and 99.999% pure aluminum, serving as anodes, were tested in 3.0, 5.0, and 8.0 M NaOH solutions at the temperatures 45, 55, 65, and 80 °C. The catholyte concentration and temperature effects were optimized, and the best electrocatalyst was chosen to carry out the NaOCl reduction. Optimization experiments were carried out on a half-cell basis using a potentiostat in a three-electrode configuration with Ag/AgCl as the reference electrode and a carbon rod as the counter electrode. Full-cell testing incorporating the optimum conditions was performed with a flowing electrolyte apparatus. A catholyte concentration of 0.70 M NaOCl proved optimum in combination with 3.0 M NaOH at the temperature 55 °C and 5.0 M NaOH at the temperature 65 °C. The temperature 45 °C was not high enough for aluminum activation, the 80 °C data did not show an improvement over the 65 °C data, and polarization was not dramatically enhanced in 8.0 M NaOH. Nickel foil and porous nickel separately electroplated with palladium were found to be the most effective electrocatalysts. Full-cell data demonstrates a successful electrochemical system with current densities approaching 1200 mA/cm² and voltages above 1.0 V.

Introduction

The aluminum silver oxide (Al–AgO) battery^{1,2} has been widely used and recognized as one of the most high-power and -energy density systems for underwater propulsion systems. In terms of power and energy, this battery has the theoretical cell potential 2.69 V versus a standard hydrogen electrode (SHE),³ the theoretical charge capacity 318 A h/kg, and the theoretical energy density 855 W h/kg. The aluminum anode^{4–6} has been chosen in previous studies due to its availability, weight considerations, cost efficiency, and its high current-carrying capability. However, a disadvantage of the Al–AgO system is the cost of the AgO cathode. It is this drawback that has led to further investigations of alternate cathodes to replace AgO in an aluminum-based alkaline battery system.

The selection of such a cathode must meet certain criteria, which include the storage of large Faradaic current capacities, high voltages, and the ability to deliver stored energy very rapidly. These criteria have led to the development of solution-phase cathodes, the so-called catholytes, as possible cathodes for aluminum-based seawater batteries. Several catholytes exist and have been previously investigated, including ferricyanide,⁷ permanganate,⁸ and hydrogen peroxide.⁹ Sodium hypochlorite (NaOCl) as a solution-phase cathode is another possibility which has not been investigated. In terms of molecular weight, that of sodium hypochlorite (74.44 g/mol) is lower than those of both potassium ferricyanide (215.02 g/mol) and potassium

permanganate (158.03 g/mol). From a theoretical energy capacity standpoint, the Al–NaOCl system has a higher theoretical energy capacity (1417 W h/kg) than Al–K₃Fe(CN)₆ (285 W h/kg) but is comparable to Al–H₂O₂ (1760 W h/kg) and Al–KMnO₄ (1400 W h/kg). NaOCl is also environmentally safe, inexpensive, and readily available.

Each Al–catholyte system has distinct advantages and disadvantages. The ferricyanide system⁷ is the most predictable and reproducible and therefore is often used in electrochemical modeling. However, in this system there is a mixture of ferricyanide and ferrocyanide. Ferricyanide is unstable in sodium hydroxide solutions and becomes increasingly insoluble as the NaOH concentration increases. The presence of a mixed species reduces the available material necessary for reaction, so that the charge capacity is too low for high-energy-density systems. The permanganate system⁸ can achieve high currents with corresponding high voltages (e.g. 1.8 V at 1200 mA/cm²). In common with the ferricyanide system, the permanganate solubility decreases with increasing NaOH concentration. Additionally, permanganate converts to manganate at high NaOH concentrations, temperatures above 100 °C are required for cell activation, and precipitation of manganese dioxide limits the system performance. Hydrogen peroxide⁹ represents a more recent and simple system with a lightweight catholyte; the system is still currently under investigation. Unfortunately, there are safety issues which must be addressed when handling concentrated H₂O₂ (>50%). Concomitantly, hydrogen peroxide decomposes with increasing temperature, producing gases which must be monitored. Compared to the previous systems, sodium hypochlorite is a low-cost, environmentally safe, yet possibly high-performance system with simple electrochemical reactions and no safety issues.

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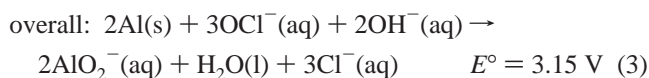
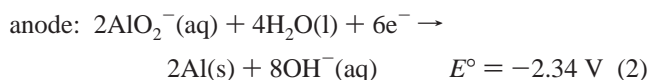
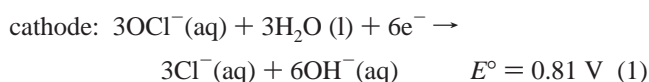
TABLE 1: Comparison of Al-Catholyte Electrochemical Systems^a

system	theoretical cell potential (V vs SHE)	theoretical charge capacity (A h/kg)	theoretical energy density (W h/kg)
Al-H ₂ O ₂	3.23	681	1760
Al-NaOCl	3.15	450	1417
Al-KMnO ₄	2.94	476	1400
Al-AgO	2.69	318	855
Al-K ₃ Fe(CN) ₆	2.83	101	285

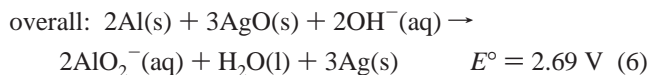
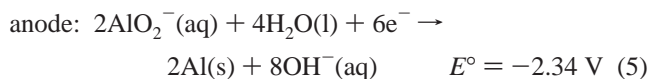
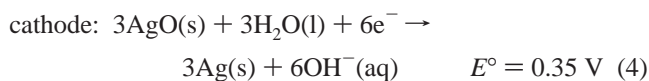
^a Theoretical refers to per kilogram of stored reactant.

Table 1 compares theoretical cell potentials, charge capacities, and energy densities for several Al-catholyte systems including the Al-OCl⁻ and Al-AgO systems. These calculations were performed assuming standard conditions of 1 atm of pressure and 25 °C. Table 1 illustrates that, on a theoretical basis, the aluminum hypochlorite system should surpass the aluminum silver oxide system in terms of cell potential, charge capacity, and energy density. Additionally, the total weight of the aluminum hypochlorite system is less on the basis of kilograms of active material required for the reaction than that of the aluminum silver oxide system.

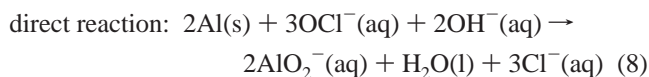
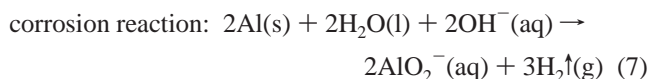
The redox potentials^{5,10} versus SHE associated with the Al-OCl⁻ system are as follows.



Reactions 1–3 demonstrate that the Al-OCl⁻ system is capable of attaining a higher potential than that associated with the Al-AgO system.



Unfortunately these theoretical open circuit potentials for both systems are reduced and the electrochemical performance is inhibited by the following parasitic reactions.⁵



Corrosion reaction 7 occurs due to the direct interaction between sodium hydroxide and the aluminum anode, resulting in the production of sodium aluminate and hydrogen gas.^{11,12} The direct reaction 8 also produces sodium aluminate in addition to chloride ions. Thus both parasitic reactions produce the

intermediate aluminate species, which is water soluble. The sodium aluminate produced ultimately leads to the production of aluminum hydroxide, which can cause clogging of the battery system and degraded cell performance.

The goal of this investigation was to reduce parasitic reactions 7 and 8 while maintaining cell potentials close to theoretical values and simultaneously achieving high Coulombic efficiencies for both the anode and cathode. Reaching this goal required optimization of the concentrations of sodium hydroxide/seawater electrolyte and sodium hypochlorite catholyte^{13–15} and of temperature.

Experimental Section

Chemicals included sodium hydroxide (ACS grade, 99.9%, Aldrich Chemical Co.), sodium hypochlorite (10–13 vol %, George Mann Inc.), and sea salt (ASTM-D 1141-52, Lake Products). The maximum stabilized concentration of commercially available NaOCl is 1.4 M (13%).

Aluminum alloys and pure aluminum (ALCAN International Limited, Kingston, Ontario, Canada) were used as working electrode materials. Metal foils (nickel, silver, and copper, Aldrich Chemical Co.) and porous nickel (RETIC Ni, ELTECH Inc.) were used as electrocatalysts. RETIC Ni contains 80 pores per inch, is 1.52 mm thick with a density of 0.4 gm/in.², and has a surface area equal to 10 times that of planar nickel. Both Ni foil and porous Ni plated with palladium (Tanuary Plating Company) were also used as electrocatalysts.

An EG&G PAR Model 371 potentiostat and an EG&G PAR Model 379 digital coulometer were used for the 0.5 cm² half-cell tests. External potential and current readings were observed using a Model 2830 digital multimeter by B+K Precision. Data were acquired using the software system Superscope, manufactured by GW Instruments of Somerville, MA.

The Model 371 potentiostat was used in a three-electrode configuration. The working electrodes (WEs) are described in a preceding paragraph. A silver-silver chloride electrode (Ag/AgCl, Fisher Scientific) served as the reference electrode (RE), and the counter electrode (CE) was a carbon rod (type L-3089/Grade AGKSP, Bay Carbon, Inc.).

EG&G flat specimen cell holders (Model K0105) were used to obtain half-cell data. The button cell holder or WE contains a hole (0.800 cm in diameter) in the center, exposing 0.5 cm² of the anode material. A rubber "O" ring and the electrode sample were placed in the holder. A stainless steel nut was then screwed into the liner to hold the electrode disk tightly against the face of the holder and to make good contact. The holder was then sealed with a cap. A stainless steel rod, 10 in. long, was inserted through the top of the holder to make contact with the metal liner. A glass sleeve, extending from the holder to 2 in. from the top of the rod, was placed around the rod. The top of the steel rod is threaded, which allows for a nut to screw down to the rod to hold the glass sleeve securely in place. It is at the stainless steel rod that the connection is made to the potentiostat. Once the cell holder was loaded with clean and weighed material, it was lowered into the electrolyte. All connections (WE, RE, CE) were made to the potentiostat prior to testing.

Seawater electrolyte solutions consisted of either 3.0, 5.0, or 8.0 M NaOH and 40 g/L of sea salt. The prepared solutions were placed in a 650 mL beaker with a stirring bar. A thermolyne (Type 1000 Series) hot plate was used to heat the solutions to temperatures of 45, 55, 65, or 80 °C. Once the desired temperature was reached, catholyte was added and testing began. The temperature of 80 °C is the maximum



Figure 1. Flowing electrolyte apparatus.

temperature that is appropriate on a total systems basis. Beyond this temperature, electrolyte boiling occurs.

Anodic polarizations were conducted by applying a potential ranging from -2.2 to 0.0 V versus Ag/AgCl and recording the current in milliamperes. The potentials were scanned at 10 mV/s. The maximum current carrying capacity of the potentiostat was 1 A. The potential range applied for the electrocatalyst and hypochlorite polarizations was 0.4 to -1.0 V versus Ag/AgCl. The measured current for half-cell experiments was converted to current density by dividing the current by the electrode area of 0.5 cm², resulting in mA/cm². The data collected included half-cell voltages, current, initial and final temperatures, and initial and final open circuit voltages. Some of the data are presented as polarization graphs where potential (V vs Ag/AgCl) is displayed on the x -axis and current density (mA/cm²) on the y -axis. All experiments were performed in triplicate and the data averaged.

Full-cell testing was performed utilizing a flowing electrolyte system, as shown in Figure 1. This apparatus consists of a 2-L electrolyte tank set into an electrothermal unimantle. An Isomatec pump system is used to pump the seawater electrolyte through the flow loop. A Polstat constant-temperature circulator is used to maintain a constant temperature of the seawater electrolyte. The cell holder is made of plexiglass and has electrode dimensions of 1.5 in. by 8 in., as shown in Figure 2a. The apparatus also contains a gas-monitoring device (cm³/min), pressure gauges to monitor seawater electrolyte flow and to alert when blockages occur, multimeters, and a data acquisition system. Data were collected using Laboratory Notebook TM and analyzed using Microsoft Excel, Cricket Graph, and Quatro Pro.

At the start of an experiment, seawater electrolyte is pumped at the fixed flow rate 250 cm³/min from the reservoir to an inlet located at the bottom of the cell. The seawater electrolyte exits the cell at the top and returns to the reservoir, where it is recirculated. The temperatures of the electrolyte reservoir, cell inlet, and cell outlet are recorded. Changes in cell inlet and outlet temperatures were especially monitored; this temperature change indicates how efficiently the cell is operating. Large temperature changes are associated with high gassing, high corrosion, and low efficiencies. Temperature changes of 10 °C are reasonable for high-rate systems such as the one reported here.

Figure 2b illustrates the configuration for a single cell. The dimensions of the electrodes (anode and electrocatalyst) are 1.5 in. in width and 8 in. in height. The anode and electrocatalyst

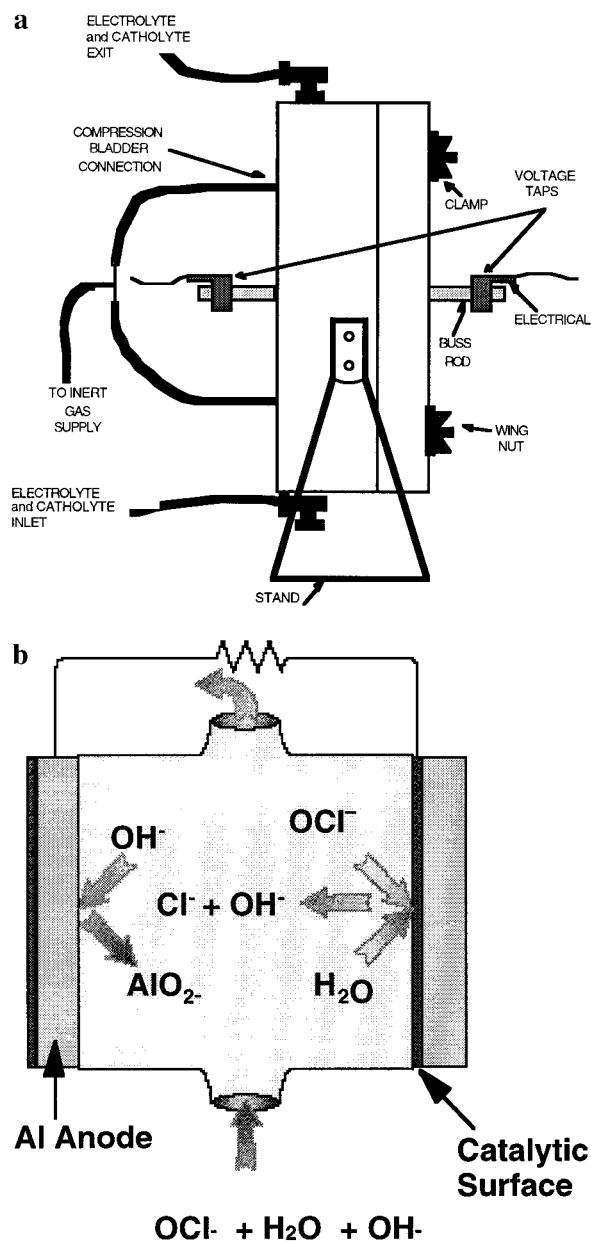


Figure 2. Flow cell: (a) 1.5 in. by 8 in. cell holder; (b) single-cell configuration.

are set up side by side with a fixed gap between them. A separator, which is not shown in Figure 2b, maintains the cell gap between the electrodes. The electrode area for the full cell is 77.4 cm². The effective electrode area, excluding the masking by the separator, is 68.3 cm²; this is the number that was used to convert current to current density in full-cell experiments. The separator used is VEXAR, a polyethylene woven material that is 0.635 mm thick. NaOH seawater electrolyte and NaOCl catholyte enter the inlet at the bottom of the cell. Hypochlorite reacts with the catalytic surface of the electrocatalyst to carry out the reduction of OCl⁻, thereby producing Cl⁻ and OH⁻ ions. The hydroxide ions react with the aluminum anode, producing aluminate. The NaOH seawater electrolyte/catholyte is continuously pumped through the cell, exiting through the outlet at the top of the cell.

Results and Discussion

Anode Characterization: Seawater Electrolyte Concentration and Temperature Variations. Experiments were

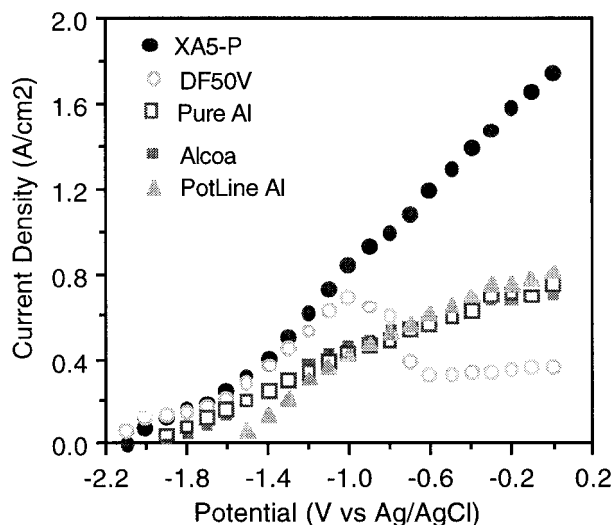


Figure 3. Polarization curves for several aluminum anodes in 3.0 M NaOH and at 65 °C.

undertaken to determine if additives or alloying materials in the aluminum anode were critical or if more inexpensive grades of aluminum would be acceptable. Additives such as Sn, Ga, Mg, and Pb alloyed to aluminum have been found to aid in activation through depassivation of the oxide layer and gas reduction.^{16,17} Passivation is the result of the formation of an impermeable oxide layer on the metal surface which protects the underlying metal from further oxidation. Current density decreases as the voltage is varied at the onset of passivation and then reaches a constant value when passivation of the metal surface is complete. Gallium increases the voltage range over which aluminum is activated by breaking down the oxide layer. Lead increases the atmospheric/chemical corrosion resistance and Coulombic efficiencies of the aluminum; however, it also decreases the voltage. The high overpotential of tin for the production of hydrogen gas suppresses corrosion reaction 7 and improves the voltage. Magnesium renders the aluminum sample more malleable.

Five different aluminum anodes were evaluated. Four of the anodes were aluminum alloys: DF50V,¹⁸ XA5-P,¹⁸ Alcoa #500, and potline aluminum. Aluminum alloys DF50V and XA5-P contain the additives Mg, Sn, and Ga. Alcoa #500 aluminum contains numerous additives in addition to Mg, Sn, and Ga. The exact amounts/percentages were not available from the manufacturer (Alcan International) for proprietary reasons. However, the manufacturer would confirm that the Ga percentage was greater in XA5-P, that the Mg percentage was greater in DF50V, and that the Sn percentage was the same in both XA5-P and DF50V. Potline aluminum is an impure form of aluminum obtained from mined bauxite. The fifth anode was 99.999% pure aluminum, containing no alloying additives.¹⁹

Experiments were also designed to determine the optimum NaOH concentrations²⁰ in addition to the optimum operating temperature. Sodium hydroxide concentrations of 3.0, 5.0, and 8.0 M were evaluated at temperatures of 45, 55, 65, and 80 °C at each aluminum anode. Polarization curves were used to compare current density (mA/cm²) versus potential (V) at the three NaOH concentrations and the four temperatures at each aluminum anode. Comparison of these polarization curves enabled the identification of the best aluminum anodes and optimum NaOH concentration and temperature. Figure 3 is an example of polarization curves recorded at each aluminum anode at 65 °C and in 3.0 M NaOH. Passivation occurs only at the DF50V aluminum anode under these experimental conditions.

TABLE 2: Current Densities (mA/cm²) at 3.0, 5.0, and 8.0 M NaOH for Each Aluminum Anode Considered at the Designated Temperature^a

Al	NaOH	temp			
		45 °C	55 °C	65 °C	80 °C
XA5P	3 M	*440 ± 3	*620 ± 10	1770 ± 15	*1820 ± 38
	5 M	*680 ± 12	1820 ± 5	1900 ± 46	2000 ± 5
	8 M	*560 ± 9	*700 ± 14	1980 ± 6	2000 ± 3
DF50V	3 M	*350 ± 10	*350 ± 27	*700 ± 13	1950 ± 19
	5 M	*200 ± 9	*580 ± 20	*1450 ± 9	1980 ± 3
	8 M	*350 ± 10	*600 ± 14	*220 ± 4	*400 ± 5
pure Al	3 M	450 ± 7	650 ± 13	780 ± 6	1200 ± 3
	5 M	480 ± 24	800 ± 28	1100 ± 7	*1200 ± 12
	8 M	*400 ± 14	650 ± 16	900 ± 38	*1000 ± 16
Alcoa	3 M	450 ± 7	600 ± 15	700 ± 13	*900 ± 22
	5 M	500 ± 15	650 ± 13	1020 ± 7	*1300 ± 8
	8 M	*380 ± 6	600 ± 24	900 ± 16	*1380 ± 15
potline Al	3 M	380 ± 9	590 ± 10	800 ± 20	1200 ± 3
	5 M	420 ± 10	650 ± 26	980 ± 13	1500 ± 9
	8 M	*350 ± 6	590 ± 8	900 ± 18	1450 ± 26

^a An * is used to indicate where passivation occurred. ± signifies the standard deviation.

Table 2 summarizes the polarization results. The highest current density achieved during a polarization experiment is recorded as a function of temperature and sodium hydroxide concentration. Thus, for each aluminum sample and for a specific temperature, three current densities are listed which correspond to the measured current densities at 3.0, 5.0, and 8.0 M NaOH, respectively. The standard deviation is indicated by the ± value. The numbers with asterisks (*) signify the highest current density achieved before passivation.

Aluminum alloy XA5-P passivated at 45 °C in the three NaOH concentrations considered with low current densities ranging from 440 to 680 mA/cm². At 55 °C, passivation occurred only in 3.0 and 8.0 M NaOH, whereas in 5.0 M NaOH the highest current density of 1820 ± 5 mA/cm² was achieved for this temperature. No passivation occurred at 65 °C; however, similar current densities of 1900 ± 46 and 1980 ± 6 mA/cm² were achieved in 5.0 and 8.0 M NaOH, respectively. At 80 °C, XA5-P passivated only in 3.0 M NaOH and a current density of 2000 mA/cm² was observed in both 5.0 and 8.0 M NaOH. The inconsistency in behavior observed in 3.0 M NaOH and at 80 °C is under further investigation.

The DF50V aluminum alloy passivated at all temperatures in 8.0 M NaOH and also at 45, 55, and 65 °C in 3.0 and 5.0 M NaOH. Current densities were generally low, ranging from 200 to 700 mA/cm², except at 65 °C in 5.0 M NaOH, where a current density of 1450 ± 9 mA/cm² was observed. At 80 °C, no passivation was observed in 3.0 and 5.0 M NaOH and large current densities of 1950 ± 38 and 1980 ± 3 mA/cm², respectively, were achieved.

No passivation of pure aluminum occurred in 3.0 M NaOH at the specified temperatures; current densities increased with temperature, reaching a maximum of 1200 ± 3 mA/cm² at 80 °C. In 5.0 M NaOH, pure aluminum passivated only at 80 °C, where a maximum current density of 1200 ± 12 mA/cm² was attained. Within experimental error, this is the same current density which was achieved in 3.0 M NaOH, where passivation was absent. Passivation also occurred in 8.0 M NaOH at temperatures of 45 and 80 °C, where the largest current density was 1000 ± 16 mA/cm² at the latter temperature. The performance of Alcoa aluminum was similar to that of pure aluminum.

Potline aluminum passivated only at 45 °C in 8.0 M NaOH with a current density of 350 ± 6 mA/cm². A maximum current

TABLE 3: Current Densities (mA/cm²) at Pure Aluminum, XA5-P Aluminum Alloy, and DF50V Aluminum Alloy for Each Catholyte Concentration at the Designated Temperature^a

NaOCl	Al sample	temp			
		45 °C	55 °C	65 °C	80 °C
0.35 M	pure Al	*30 ± 1	*35 ± 1	*35 ± 3	*48 ± 1
	XA5-P	200 ± 1	220 ± 3	220 ± 2	260 ± 1
	DF50V	200 ± 4	200 ± 5	275 ± 2	320 ± 4
0.70 M	pure Al	*28 ± 1	*25 ± 0	*22 ± 2	*22 ± 3
	XA5-P	280 ± 3	350 ± 3	400 ± 3	440 ± 7
	DF50V	340 ± 1	360 ± 4	440 ± 1	480 ± 4
1.40 M	pure Al	*50 ± 1	*48 ± 2	*48 ± 2	*50 ± 1
	XA5-P	550 ± 6	560 ± 7	680 ± 3	700 ± 8
	DF50V	600 ± 4	650 ± 6	690 ± 1	780 ± 4

^a An * is used to indicate where passivation occurred. ± signifies the standard deviation.

density of 1500 ± 9 mA/cm² was observed in 5.0 M NaOH at 80 °C, where no passivation occurred.

There is a clear trend of an increase in current density, and hence activation, with temperature at NaOH concentrations evaluated for XA5-P aluminum, pure aluminum, Alcoa aluminum, and potline aluminum. For DF50V aluminum, current density remained essentially the same at 45 and 55 °C before increasing at 65 and 80 °C in 3.0 M NaOH. In 5.0 M NaOH, there was an increase in current density with temperature at the DF50V aluminum anode. The behavior of DF50V aluminum in 8.0 M NaOH was sporadic as the temperature increased.

In general, experiments performed at the 8.0 M NaOH level resulted in a decrease in current density of the aluminum samples evaluated at a specific temperature. At 80 °C, slight enhancements in current density were observed over those at 65 °C. Overall, maximum current densities occurred in the presence of 3.0 and 5.0 M NaOH and at the temperatures 55 and 65 °C. Of the aluminum samples evaluated, aluminum alloy XA5-P outperformed the others. Alloy DF50V passivated the most as the NaOH concentration and temperature were changed; the only exceptions occurred at 80 °C in 3.0 and 5.0 M NaOH. Pure aluminum, potline aluminum, and Alcoa aluminum samples performed similarly and exhibited the lowest current densities as NaOH concentration and temperature were varied.

The enhanced cell performance observed for XA5-P can be attributed to the greater percentage of gallium than found in DF50V. Although gallium is also present in Alcoa aluminum, the presence of many other additives appears to hinder the cell performance of this sample. Potline aluminum did not perform well under the test conditions due to its impure state.

Pure aluminum also demonstrated lower current densities. However, the monitoring of its performance was continued in order to serve as a benchmark against which XA5-P and DF50V could be compared as catholyte concentrations and electrocatalysts were investigated.

Catholyte Concentration Characterization. A series of experiments at the temperatures 45, 55, 65, and 80 °C were performed to determine an optimum NaOCl concentration in the absence of NaOH. NaOCl concentrations of 0.35, 0.70, and 1.40 M were used in the presence of seawater. Pure aluminum, XA5-P aluminum, and DF50V aluminum served as the anode. Polarization graphs similar to Figure 3 were generated. Table 3 summarizes the polarization results. The highest current densities achieved during the polarization experiments are recorded as a function of temperature and catholyte concentration. Thus, for each NaOCl concentration and for a specific temperature, three current densities are listed which correspond to the measured current densities at pure aluminum, XA5-P

aluminum, and DF50V aluminum, respectively. The standard deviation is indicated by the ± value. The numbers with asterisks (*) signify the highest current density achieved before passivation.

The first number under each temperature in Table 3 corresponds to current densities recorded at a pure aluminum anode. For this anode, there is no activation at any of the designated temperatures; aluminum passivation occurs at current densities between 22 and 50 mA/cm². Thus, some type of impermeable layer must be forming on the surface of pure aluminum to show passivation at all temperatures and NaOCl concentrations considered. The exact nature of the surface layer is under investigation.

Current densities are significantly larger for aluminum alloy XA5-P, as shown by the second number under each temperature in Table 3. No passivation was observed at the three NaOCl concentrations and four temperatures considered. At a specific NaOCl concentration, there was an approximate 1.1-fold increase in current density for each 10 °C increase in temperature. However, the effect of NaOCl concentrations at individual temperatures led to an approximate 1.6-fold increase in current density from 0.35 to 0.70 M NaOCl and a 1.7-fold increase from 0.70 to 1.40 M. A 4-fold change in NaOCl concentration from 0.35 to 1.40 M led to an approximate 2.8-fold increase in current density at each specified temperature.

For aluminum alloy DF50V, current densities are indicated by the third number under each temperature in Table 3. These current densities are generally slightly larger than those observed for XA5-P. Similar to the case for alloy XA5-P, no passivation was observed at the three NaOCl concentrations and four temperatures considered, and the increase in current density was approximately 1.1-fold at a specific NaOCl concentration. Additionally, the effect of NaOCl concentrations at individual temperatures led to an approximate 1.6-fold increase in current density from 0.35 to 0.70 M NaOCl and a 1.7-fold increase from 0.70 to 1.40 M. A 4-fold change in NaOCl concentration from 0.35 to 1.40 M led to an approximate 2.8-fold increase in current density at each specified temperature. These observations were also noted for XA5-P.

The data in Table 3 demonstrate that none of the NaOCl concentrations considered are large enough at any temperature to activate the pure aluminum anode. However, NaOCl concentrations of 0.7 and 1.4 M do show current densities between 440 and 780 mA/cm² at 80 °C for aluminum alloys XA5-P and DF50V. Since these current densities are not large enough for high-rate applications where current densities greater than 1000 mA/cm² are required, the effect of both NaOH and NaOCl on current density magnitude was investigated for increases in current density.

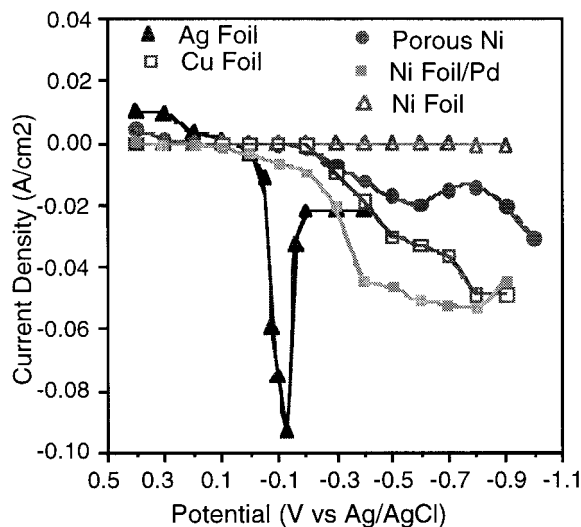
NaOCl and NaOH Concentration Effects. Table 4 summarizes the polarization results for XAP-5 Al, DF50V Al, and pure aluminum at 55 °C as a function of NaOCl concentration in the absence and presence of 3.0 M NaOH. For each aluminum sample and for a specific NaOCl concentration, two current densities are listed which correspond to the measured current densities in the presence of 0 M NaOH and 3.0 M NaOH, respectively. The numbers with asterisks (*) represent the highest current density achieved before passivation, and ± signifies the standard deviation.

For XAP-5 aluminum, catholyte alone activates the anode to a current density of 220 mA/cm² compared to the passivation which occurs at a current density of 620 mA/cm² in the presence of 3.0 M NaOH only. When a combination of 0.35 M NaOCl and 3.0 M NaOH is used, no passivation occurs and a

TABLE 4: Current Densities (mA/cm²) at 0 and 3.0 M NaOH for Each Aluminum Anode at the Designated NaOCl Concentration at 55 °C^a

Al sample	NaOH	NaOCl		
		0 M	0.35 M	0.70 M
XAP-5	0 M		220 ± 2	350 ± 3
	3 M	*620 ± 10	1780 ± 14	1780 ± 13
DF50V	0 M		200 ± 5	360 ± 4
	3 M	*350 ± 27	1380 ± 13	1420 ± 18
pure Al	0 M		*35 ± 1	*25 ± 0
	3 M	650 ± 13	*350 ± 10	*420 ± 12

^a An * is used to indicate where passivation occurred. ± signifies the standard deviation.

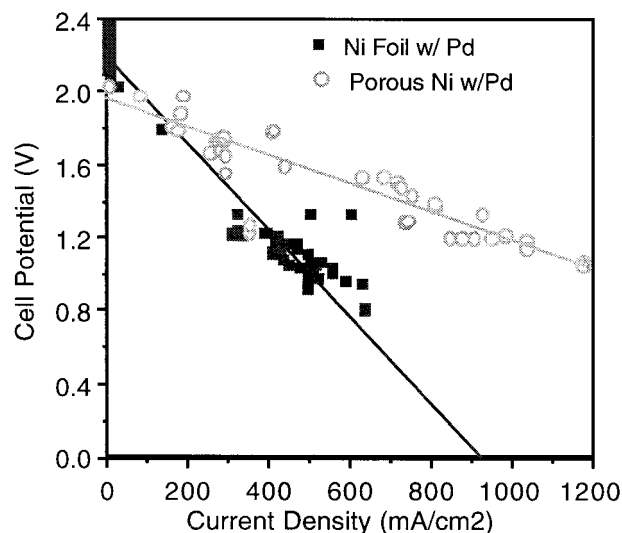
**Figure 4.** Electrolyte determinations in 3.0 M NaOH and 0.35 M NaOCl at 55 °C.

significantly enhanced current density of 1780 mA/cm² is observed; this is approximately three times larger than the current density observed in 3.0 M NaOH alone and approximately eight times larger than the current density observed in 0.35 M NaOCl alone. Fourfold and 7-fold increases were noted for DF50V aluminum, which achieved a current density of 1380 mA/cm² under identical combination conditions. For pure aluminum, a current density of 350 mA/cm² was observed in a 0.35 M NaOCl and 3.0 M NaOH combination. An increase in NaOCl concentration to 0.70 M, with NaOH concentration fixed at 3.0 M, did not result in significant changes in current density.

The goal of achieving 1000 mA/cm² was attained with 3.0 M NaOH and 0.35 and 0.70 M NaOCl. Any additional increase in the NaOH or NaOCl concentrations would only impact negatively on the system in terms of corrosion and decomposition reactions.

Electrocatalysts. Silver foil, nickel foil, copper foil, and porous nickel were investigated as possible catalysts for the reduction of NaOCl. Nickel foil was first electroplated with palladium,⁹ and porous nickel was used with and without palladium. Porous Ni was used to determine if this high-surface-area material, representing a 10-fold increase in surface area over that of a strictly planar surface, would significantly reduce mass-transfer-limiting processes occurring at the catalyst surface compared to the anode surface.

Figure 4 demonstrates that Ag foil performed ideally from 0.4 to -0.1 V before passivation occurred at -0.1 V. Ni foil showed zero current-carrying capability over the potential range

**Figure 5.** Measured voltages as a result of applying a constant current at 55 °C. The full cell included 3.0 M NaOH, seawater electrolyte, 0.70 M NaOCl, XA5-P as the anode, and either Ni foil with Pd or porous Ni with Pd as the electrocatalyst. The lines were generated using linear regression.

0.4 to -1.0 V. Cu foil, Ni foil with Pd, and porous Ni all demonstrated an increase in cathodic current density, as expected over the potential range. Copper was not investigated further due to its excessive gassing during testing. Porous nickel and nickel foil were both chosen as the preferred backbones for the electrolytic palladium surface in the sodium hypochlorite reduction.

Full-Cell Testing. The previous sets of experiments indicate that optimum parameters include [NaOH] = 3.0–5.0 M, [NaOCl] = 0.35–0.70 M, temperatures = 55–65 °C, electrocatalyst = Ni as a substrate, and XA5-P as the anode. Several combinations of optimum conditions were tested in a full-cell configuration.

Figure 5 shows full-cell polarization profiles at the temperature 55 °C, 3.0 M NaOH, and 0.70 M NaOCl when the electrocatalyst is either Ni foil or porous Ni plated with Pd. Open circuit voltages between 2.0 and 2.4 V were measured. Ni foil/Pd demonstrated a current density range from 0 to 700 mA/cm² with corresponding voltages of 2.4–0.8 V. In comparison, porous Ni/Pd demonstrated an increase in current density from 0 to 1200 mA/cm² with corresponding voltages of 2.0–1.0 V.

Figure 6 illustrates the constancy of the measured voltage with time at a constant current of 28 A (410 mA/cm²) for a cell consisting of the electrocatalyst Ni foil with Pd, a XA5-P Al anode, [NaOH] = 3.0 M, [NaOCl] = 0.70 M, and *T* = 55 °C. A steady voltage of 1.27 V was observed for the 17 min (1020 s) test duration. This measured voltage is consistent with the results shown in Figure 5. The efficiency of the XA5-P Al anode was calculated to be 52% from Coulombic calculations and initial and final aluminum weights. The measured total gas generated for 17 min was 330 cm³, leading to a gassing rate of 19.4 cm³/min.

An experiment similar to that shown in Figure 6 was performed with a porous Ni with Pd electrocatalyst. For a constant current of 55 A (800 mA/cm²), a steady voltage of 1.35 V was measured, which is verified by the data shown in Figure 5. The aluminum efficiency was found to be 61%, and the total gas generated was 391 cm³ for 17.3 min or a gassing rate of 22.6 cm³/min.

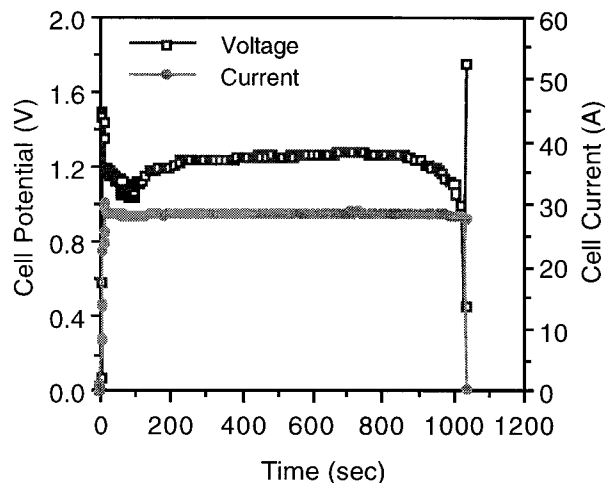


Figure 6. Voltage versus time in response to a constant current applied at 55 °C. The full cell included 3.0 M NaOH, seawater electrolyte, 0.70 M NaOCl, XA5-P as the anode, and Ni Foil with Pd as the electrocatalyst.

Summary

The use of sodium hypochlorite in an aluminum-based seawater battery system has been demonstrated. The battery system consisted of an aluminum anode, a sodium hydroxide and seawater electrolyte, an electrocatalyst, and a sodium hypochlorite catholyte. Several aluminum alloys and pure aluminum were considered as possible anodes. The aluminum alloy XA5-P was found to consistently attain the highest anodic current densities in 3.0 and 5.0 M NaOH solutions at the temperatures 55 and 65 °C. Optimum NaOCl concentrations of 0.35 and 0.70 M were demonstrated. Nickel foil and porous nickel electroplated with palladium proved to be the most effective electrocatalysts for the NaOCl reduction. Crucial to the performance of this particular aluminum-based battery is the combination of NaOH and NaOCl electrolytes. Sodium hypochlorite alone was insufficient to activate the aluminum anode. However, when combined with sodium hydroxide, an 8-fold increase in current density over that observed in sodium hypochlorite alone was obtained. Full-cell testing resulted in current densities up to 1200 mA/cm² with corresponding voltages above 1.0 V. With Ni foil/Pd as the electrocatalyst, an aluminum efficiency of 52% was calculated and minimal gas was generated. The most promising result was obtained with porous Ni/Pd as the electrocatalyst, where 61% aluminum efficiency was found in response to a constant current of 55 A (800 mA/cm²), which generated a steady voltage of 1.35 V.

These results demonstrate the viability of Al–NaOCl electrochemistry in developing a seawater battery for high-rate underwater applications.

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