Serial Number 09/659,959

Filing Date 12 September 2000

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CODE 00CC
ARLINGTON VA 22217-5660

Attorney Docket No. 78608

AN ALUMINUM HYPOCHLORITE ELECTROCHEMICAL SYSTEM

STATEMENT OF GOVERNMENT INTEREST

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of royalties thereon or therefor.

BACKGROUND OF THE INVENTION

(1) Field of the Invention

The present invention relates to an electrochemical battery system based upon an aluminum anode and a hypochlorite cathode.

(2) Description of the Prior Art

Presently, the high power density primary battery based on aluminum and silver oxide alkaline half cells provides sufficient energy for vehicle propulsion. The major advantage of this electrochemical system is the extraordinary current densities, on the order of 1600 mA/cm^2, which are readily achieved. These high current densities are indicative of facile electron transfer in both the anodic and the cathodic redox couples.

The high current densities in the alkaline aluminum - silver oxide cathodic couple may be attributed to the anomalous solid phase mobility of Ag^+. Unlike other cations, the silver cation travels rapidly not only through the liquid phase but also through the solid phase of its salts. Therefore, as AgO is reduced, Ag^+ can continually travel to the electrode interface, preventing surface passivation and permitting continuous facile electron transfer.

The major disadvantage of the alkaline aluminum silver oxide primary battery is the significant costs of the silver cathodes. Other cathodes may be considered; however, for the intended vehicle propulsion goals, alternative cathodic reactions are compared to the high cell voltage and extraordinary current densities accessible with the AgO cathode.

The patent literature contains a number of patents to a variety of different electrochemical power cells. For example, U.S. Patent No. 4,132,837 to Soffer illustrates high energy output primary and secondary electrochemical cells having a light metal anode, such as lithium metal, a cathode and a non-aqueous electrolyte comprising an aprotic solvent having dissolved therein an electrically conductive salt and a macroheterocyclic compound complexed with the cation moiety of the salt.

U.S. Patent No. 4,269,911 to Fukuoka et al. illustrates an aluminum-halogen cell comprising aluminum as an anode active material and a halogen compound as a cathode active material characterized in that the layer containing the cathode active material further comprises at least one stabilizer selected from the group consisting of magnesium halides, zinc halides, organic carboxylic acids and their anhydrides, aluminum or more basic metallic salts of perhaloid acids and quaternary ammonium salts.

U.S. Patent No. 5,718,986 to Brenner illustrates a cell or battery which is environmentally benign and which has an electrolyte containing a solution of an alkali metal chlorite or hypochlorite, an anode of magnesium or aluminum and an inert cathode.

Despite the existence of these electrochemical cells, there remains a need for an electrochemical system which yields an increased voltage level and which may be used to power vehicles.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide an electrochemical cell or battery system that is capable of extraordinary power densities.

It is a further object of the present invention to provide an electrochemical cell or battery system as above which is competitive with aluminum-silver oxide batteries in terms of power density and energy capacity.

It is still a further object of the present invention to provide an electrochemical cell or battery system which is less expensive to produce than other electrochemical cells or battery systems.

It is another object of the present invention to provide an electrochemical cell or battery system that has utility in propulsion systems.

The foregoing objects are attained by the electrochemical cell or battery system of the present invention.

In accordance with the present invention, an electrochemical cell or battery system comprises an anode formed from an aluminum containing material, a cathode formed from a hypochlorite solution phase catholyte material, and an electrolyte. The electrolyte may be an aqueous alkaline solution, seawater, or an aqueous alkaline solution with seawater. The electrochemical cell, in a preferred embodiment of the present invention, is formed from an aluminum containing material and an inert electrode substrate capable of carrying out the reduction of hypochlorite.

BRIEF DESCRIPTION OF THE DRAWINGS

Other details of the electrochemical cell or battery system of the present invention, as well as other objects and advantages attendant thereto are set forth in the following detailed description and the accompanying drawings, wherein:

FIG. 1 shows an electrochemical cell in accordance with the present invention;

FIG. 2 is a graph illustrating the results of full cell polarization tests with a reticulated nickel with palladium electrocatalyst, an alkaline electrolyte solution containing 3.0M NaOH, a sodium hypochlorite catholyte containing 0.7M NaOCl, at 55°C, and using an XA5-P aluminum alloy anode;

FIG. 3 is a graph illustrating nickel foil vs. reticulated nickel full cell polarization tests using an XA5-P aluminum alloy anode, an alkaline electrolyte solution containing 3.0M NaOH, a sodium hypochlorite catholyte containing 0.7M NaOCl, at a temperature of 55°C; and

FIG. 4 is a graph illustrating tests on the activation of the aluminum anode in the presence of varying hypochlorite concentrations.

DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

In accordance with the present invention, an electrochemical cell or battery system 10 is composed of bipolar electrodes 14, each having an anode 36 formed from aluminum or an aluminum alloy on one side. The other side of each electrode 14 is preferably formed with an electrocatalyst 38 capable of carrying out the reduction of hypochlorite. The hypochlorite is an aqueous solution phase catholyte material, which serves as the cathode. A suitable aqueous hypochlorite solution contains from about 0.35 to 0.7 Molar (M) sodium hypochlorite. An alkaline, seawater, or alkaline with seawater electrolyte is required to achieve high current densities. A suitable alkaline electrolyte comprises an aqueous solution containing sodium hydroxide from an effective amount to 3.0 (M).

A distribution manifold 16 is provided for introducing the electrolyte and the catholyte material into the space 18 between the electrodes. An outlet manifold 20 is provided for removing spent catholyte material and spent electrolyte.

As shown in FIG. 1, the electrical output produced by the electrodes 14 may be used to power a desired load 40.

In operation, the electrochemical cell or battery system 10 must be maintained at a temperature which enhances the performance of the electrochemical couple. a suitable operational temperature is about 55°C.

In the proposed new electrochemical system, the anode and cathode half reactions for the aluminum hypochlorite (Al - Ocl^-) couple in aqueous alkaline electrolyte are as follows (versus the standard hydrogen electrode potential, SHE):

Electrochemical Reactions for the Al-Ocl^-:

Anode

$$2Al(s)+8OH^-(aq)\rightarrow AlO_2^-(aq)+4H_2O(1)+6e^- \qquad E°=-2.34V$$

Cathode

$$3OCl^-(aq)+3H_2O(1)+6e^-\rightarrow 3Cl^-+6OH^-(aq) \qquad E°=0.81V$$

Overall Reaction:

$$2Al(s)+3OCl^-(aq)+2OH^-(aq)\rightarrow 2AlO_2^-(aq)+H_2O(1)+3Cl^-(aq) \qquad E°=3.15V$$

Unfortunately, the following parasitic reactions occur:

Corrosion Reaction:

$$2Al(s)+ 2H_2O(1)+2OH^-(aq)\rightarrow 2AlO_2^-(aq)+3H2\uparrow(g)$$

Direct Reaction:

$$2Al(s)+3OCl^-(aq)+2OH^-(aq)\rightarrow 2AlO_2^-(aq)+3Cl^-+H_2O(l)$$

Decomposition Reaction:

$$2OCl^-\rightarrow ClO_2^-+Cl^-$$

They reduce the theoretical open circuit potentials and inhibit the electrochemical performance.

Electrochemical Reactions for the Al-AgO:

Anode

$$2Al(s)+8OH^-(aq)\rightarrow 2AlO_2^-(aq)+4H_2O(l)+6e^- \quad E^\circ=-2.34V$$

Cathode

$$3AgO(s)+3H_2O(l)+6e^-\rightarrow 3Ag(s)+6OH^-(aq) \quad E^\circ=0.35V$$

Overall Reaction

$$2Al(s)+3AgO(s)+2OH^-(aq)\rightarrow 2AlO_2^-(aq)+H_2O(l)+3Ag(s) \quad E^\circ=2.69V$$

This theoretical aluminum hypochlorite voltage of 3.15 volts is 0.46 volts greater than the comparable aluminum-silver oxide cell. Initial tests have shown that polarization losses are less than in the comparable silver oxide system indicating that an electrochemical system of the present invention will support very high current densities.

The theoretical charge capacities and energy densities for the two electrochemical couples are listed below in Table I.

TABLE I - SUMMARY OF THE TWO ELECTROCHEMICAL COUPLES

System	Theoretical Cell Potential (Volts vs SHE)	Theoretical Charge Capacity (AH/kg)	Theoretical Energy Density (WH/kg)
Al-OCl^-	3.15	450	1417
Al-AgO	2.69	318	855

Operational potential of the aluminum hypochlorite electrochemical cell is contingent upon the ability to electrochemically, and not chemically, access the storage capacity of the aluminum and to access the capacity of the hypochlorite at various current densities. FIG. 2 presents a polarization profile during the reduction of hypochlorite at a porous nickel substrate catalyzed with palladium using an alkaline electrolyte containing 3.0M NaOH, an aqueous hypochlorite solution containing 0.7M OCl^-, and an XA5-P aluminum anode. The operational temperature of the cell was 55°C. FIG. 2 shows the corresponding cell potential (volts) at various applied current densities.

A higher surface area electrocatalytic cathode further diminishes the hypochlorite polarization losses. This is demonstrated in FIG. 3, in which a hypochlorite polarization utilizing a reticulated nickel substrate coated with palladium is compared with a polarization utilizing planar nickel surface also plated with palladium. The electrolyte solution used to perform the tests contained 3.0M NaOH. The sodium hypochlorite solution contained 0.7M NaOCl.

Several test regimes were conducted to optimize the sodium hydroxide concentration, the sodium hypochlorite concentration, and the temperature of the electrolyte. The testing revealed that sodium hypochlorite on its own was not enough to activate the aluminum anode; however, sodium hypochlorite in conjunction with sodium hydroxide revealed current densities on a half-cell basis that was increased 8-fold. FIG. 4 pictures these results. Current densities up to 1600 mA/cm^2 were observed on the half-cell basis for an aluminum anode. The notations on FIG. 4 indicate the following: AVG=average of several runs, the sodium hydroxide concentration [NaOH], sodium hypochlorite concentration [NaOCl], and the temperature in $^{\circ}C$. For example, AVG-0,0.35,55 means averaged runs, 0M NaOH, 0.35M NaOCl, $55^{\circ}C$.

The electrochemical cell or battery system of the present invention is useful for propulsion applications for undersea vehicles such as torpedoes, UUVs or AUVs. The theoretical voltage of the battery system of the present invention is greater than that of the aluminum/silver oxide or the aluminum hydrogen peroxide battery with the added advantage that it is lower in cost and the components are readily available as commercial off-the shelf items.

While the anode of the present invention has been described as being made from an aluminum material, alternative anodes include those composed of lithium, calcium or magnesium or alloys thereof. Hypochlorite forms other than sodium hypochlorite may also be utilized, including calcium hypochlorite and lithium hypochlorite. Alternative electrocatalyst materials capable of rapid reduction of the hypochlorite redox couple, including those with high surface area and those made from low cost materials will affect the cell performance. Alternative electrocatalyst materials include silver and nickel with a palladium/iridium combination.

It is apparent that there has been provided in accordance with the present invention an aluminum hypochlorite electrochemical system, which fully satisfies the means, objects and advantages set forth hereinbefore. While the invention has been described in the context of specific embodiments thereof, many alternatives, variations, and modifications will become apparent to those skilled in the art after reviewing the present disclosure. Therefore, it is intended to embrace such alternatives, variations, and modifications.

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AN ALUMINUM HYPOCHLORITE ELECTROCHEMICAL SYSTEM

ABSTRACT OF THE DISCLOSURE

The present invention relates to an electrochemical cell which has utility in propulsion systems of undersea vehicles. The electrochemical cell comprises an anode formed from an aluminum containing material, a cathode formed from a hypochlorite solution phase catholyte material, and an electrolyte. The electrolyte may be an aqueous alkaline solution, seawater, or an aqueous alkaline solution with seawater. The anode, in a preferred embodiment of the present invention, is formed from a bipolar electrode having an aluminum containing material and an electrocatalyst capable of carrying out the reduction of the hypochlorite.

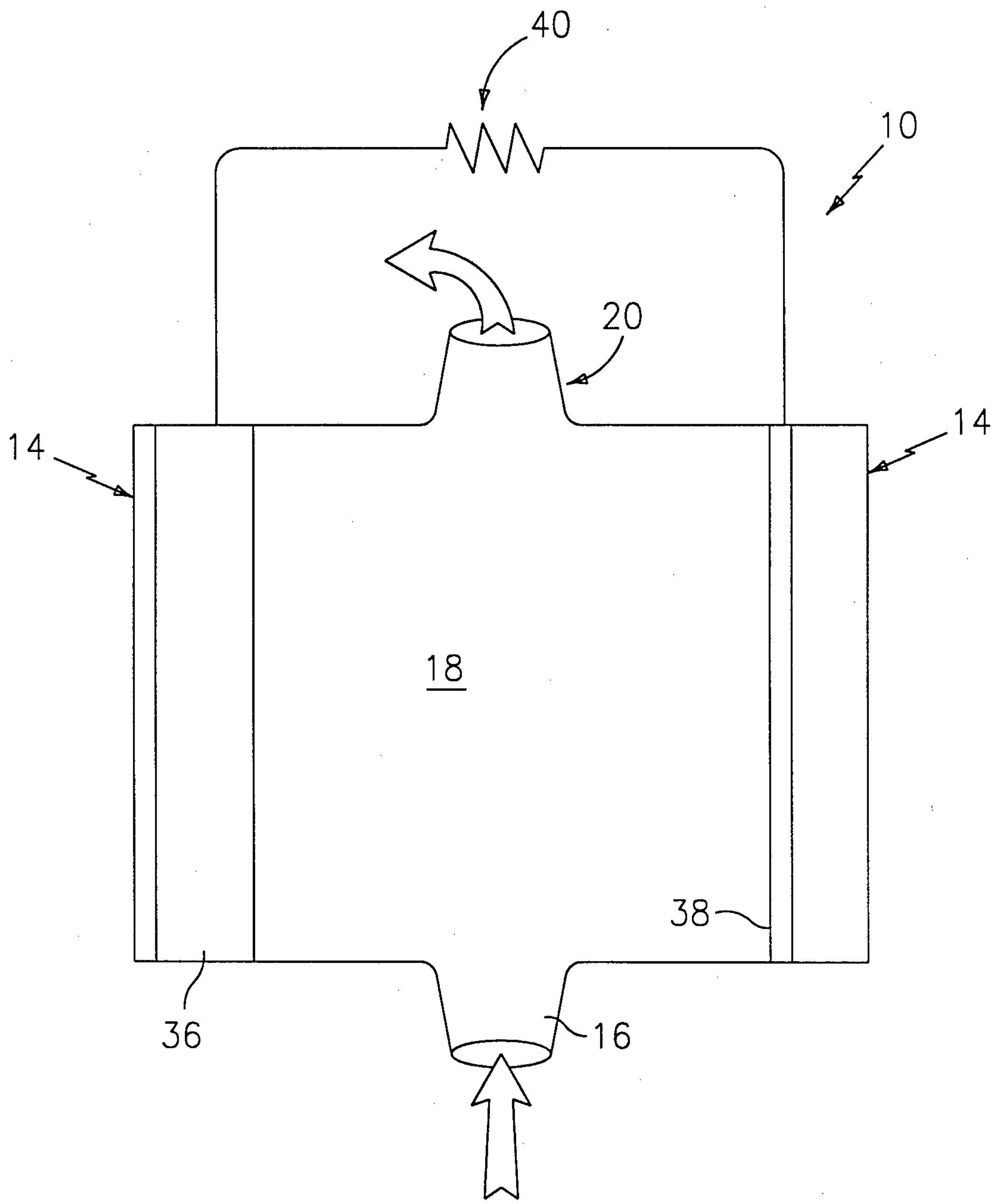
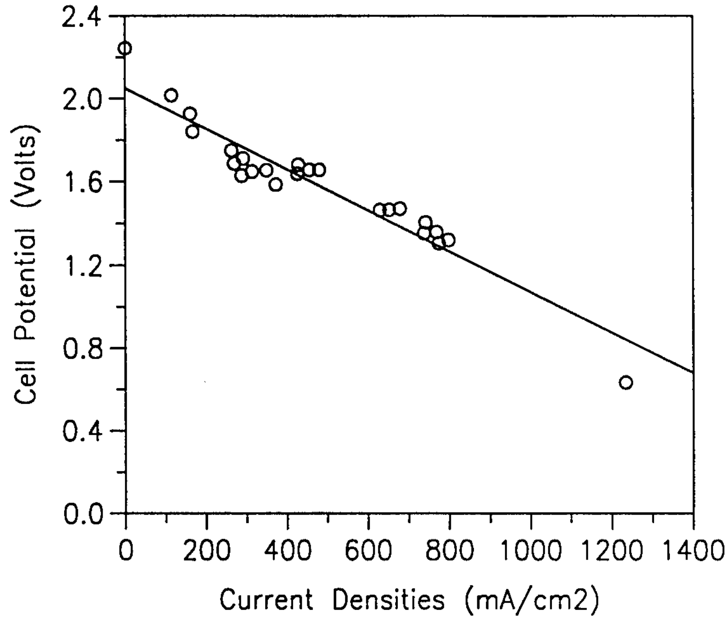
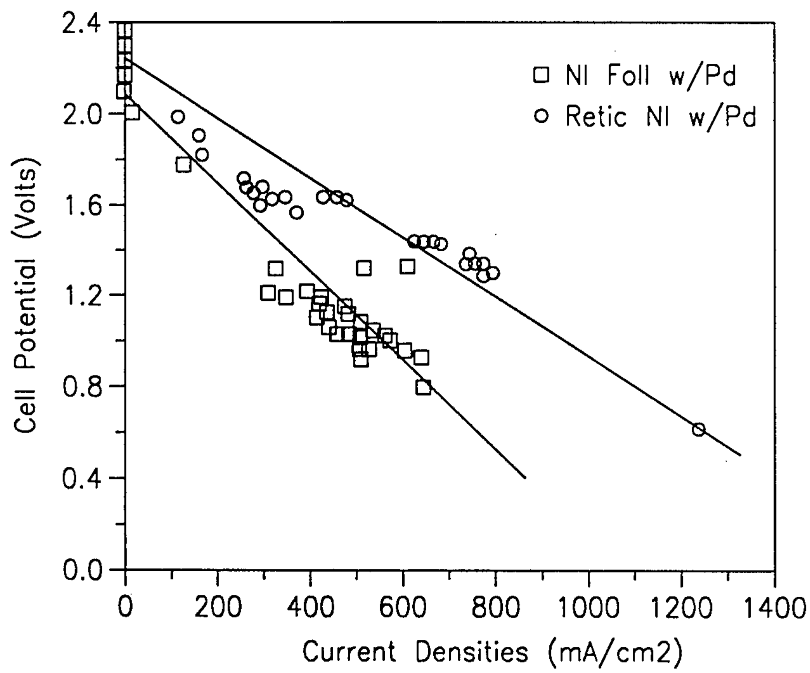


FIG. 1



2.4
2.0
1.6
1.2
0.8
0.4
0.0
Cell Potential (Volts)
0
200
400
600
800
1000
1200
1400
Current Densities (mA/cm2)

FIG. 2



2.4
2.0
1.6
1.2
0.8
0.4
0.0
Cell Potential (Volts)
NI Foil w/Pd
Retic NI w/Pd
0
200
400
600
800
1000
1200
1400
Current Densities (mA/cm2)

FIG. 3

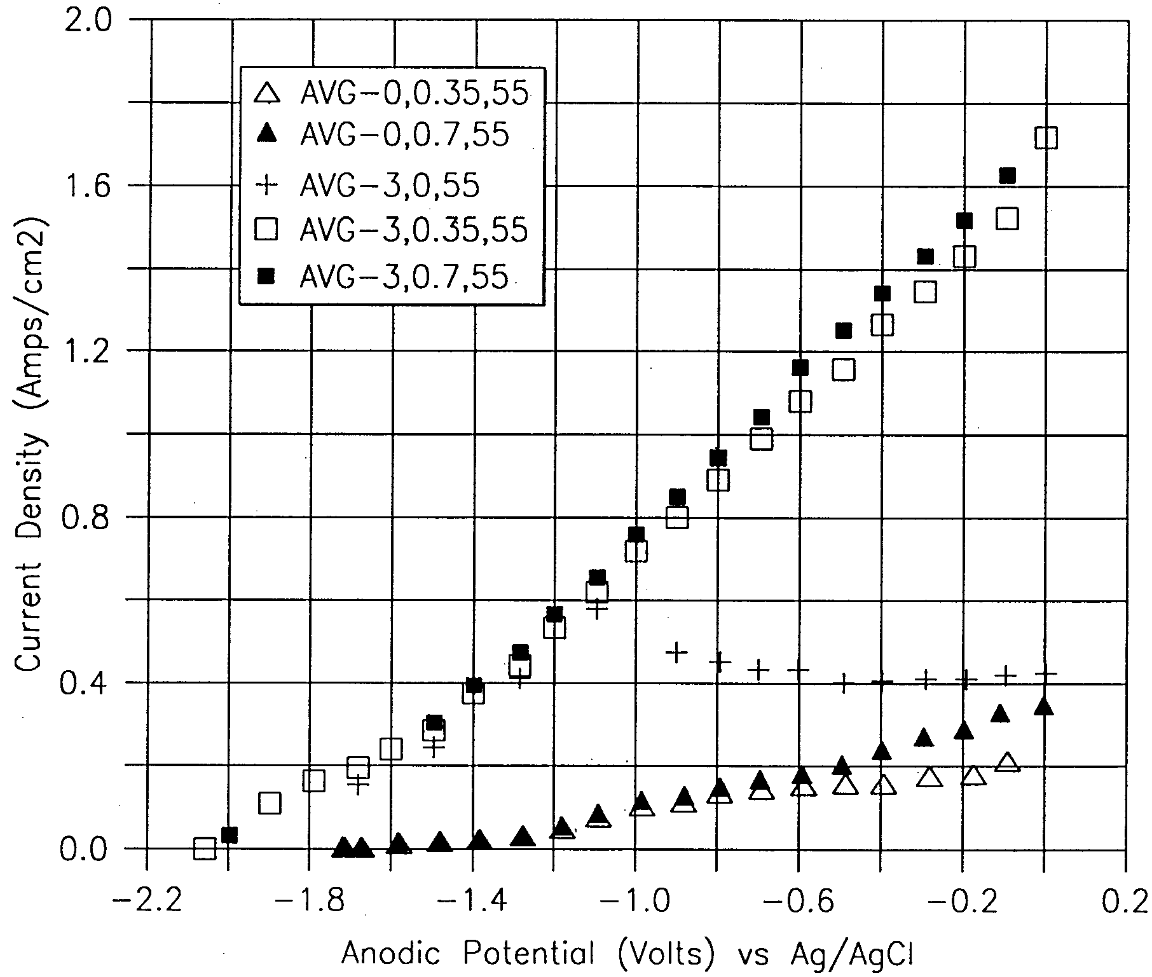

AVG−0,0.35,55
AVG−0,0.7,55
AVG−3,0,55
AVG−3,0.35,55
AVG−3,0.7,55
Current Density (Amps/cm2)
2.0
1.6
1.2
0.8
0.4
0.0
−2.2
−1.8
−1.4
−1.0
−0.6
−0.2
0.2
Anodic Potential (Volts) vs Ag/AgCl

FIG. 4