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3 AN ALUMINUM HYPOCHLORITE ELECTROCHEMICAL SYSTEM

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5 STATEMENT OF GOVERNMENT INTEREST

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

10
11 BACKGROUND OF THE INVENTION

12 (1) Field of the Invention

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

15 (2) Description of the Prior Art

16 Presently, the high power density primary battery based on
17 aluminum and silver oxide alkaline half cells provides sufficient
18 energy for vehicle propulsion. The major advantage of this
19 electrochemical system is the extraordinary current densities, on
20 the order of 1600 mA/cm², which are readily achieved. These high
21 current densities are indicative of facile electron transfer in
22 both the anodic and the cathodic redox couples.

23 The high current densities in the alkaline aluminum - silver
24 oxide cathodic couple may be attributed to the anomalous solid
25 phase mobility of Ag⁺. Unlike other cations, the silver cation
26 travels rapidly not only through the liquid phase but also

1 through the solid phase of its salts. Therefore, as AgO is
2 reduced, Ag⁺ can continually travel to the electrode interface,
3 preventing surface passivation and permitting continuous facile
4 electron transfer.

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

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

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

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

6 Despite the existence of these electrochemical cells, there
7 remains a need for an electrochemical system which yields an
8 increased voltage level and which may be used to power vehicles.
9

10 SUMMARY OF THE INVENTION

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

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

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

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

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

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

11
12 BRIEF DESCRIPTION OF THE DRAWINGS

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

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

19 FIG. 2 is a graph illustrating the results of full cell
20 polarization tests with a reticulated nickel with palladium
21 electrocatalyst, an alkaline electrolyte solution containing 3.0M
22 NaOH, a sodium hypochlorite catholyte containing 0.7M NaOCl, at
23 55°C, and using an XA5-P aluminum alloy anode;

24 FIG. 3 is a graph illustrating nickel foil vs. reticulated
25 nickel full cell polarization tests using an XA5-P aluminum alloy
26 anode, an alkaline electrolyte solution containing 3.0M NaOH, a

1 sodium hypochlorite catholyte containing 0.7M NaOCl, at a
2 temperature of 55°C; and

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

6 7 DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

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

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

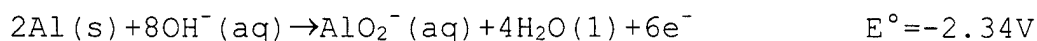
25 As shown in FIG. 1, the electrical output produced by the
26 electrodes 14 may be used to power a desired load 40.

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

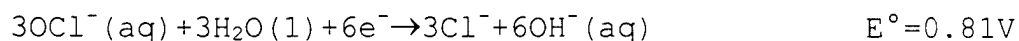
5 In the proposed new electrochemical system, the anode and
6 cathode half reactions for the aluminum hypochlorite (Al - Ocl⁻)
7 couple in aqueous alkaline electrolyte are as follows (versus the
8 standard hydrogen electrode potential, SHE):

9
10 Electrochemical Reactions for the Al-Ocl⁻:

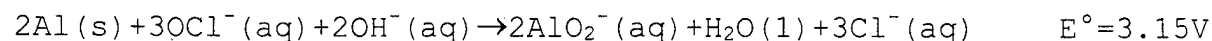
11 Anode



13 Cathode

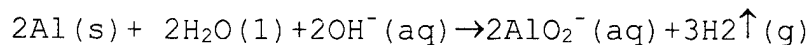


15 Overall Reaction:

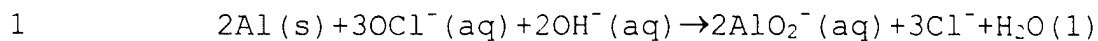


17 Unfortunately, the following parasitic reactions occur:

18 Corrosion Reaction:



20 Direct Reaction:



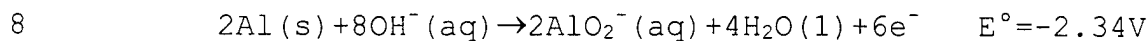
2 Decomposition Reaction:



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

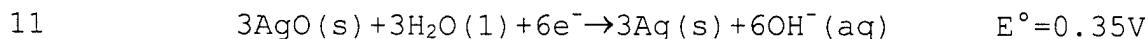
6 Electrochemical Reactions for the Al-AgO:

7 Anode



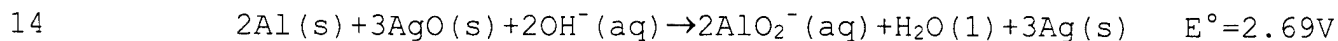
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10 Cathode



12

13 Overall Reaction



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

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

1

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

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

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

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

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

22 While the anode of the present invention has been described
23 as being made from an aluminum material, alternative anodes
24 include those composed of lithium, calcium or magnesium or alloys
25 thereof. Hypochlorite forms other than sodium hypochlorite may
26 also be utilized, including calcium hypochlorite and lithium

1 hypochlorite. Alternative electrocatalyst materials capable of
2 rapid reduction of the hypochlorite redox couple, including those
3 with high surface area and those made from low cost materials
4 will affect the cell performance. Alternative electrocatalyst
5 materials include silver and nickel with a palladium/iridium
6 combination.

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

1 Attorney Docket No. 78608

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3 AN ALUMINUM HYPOCHLORITE ELECTROCHEMICAL SYSTEM

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5 ABSTRACT OF THE DISCLOSURE

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

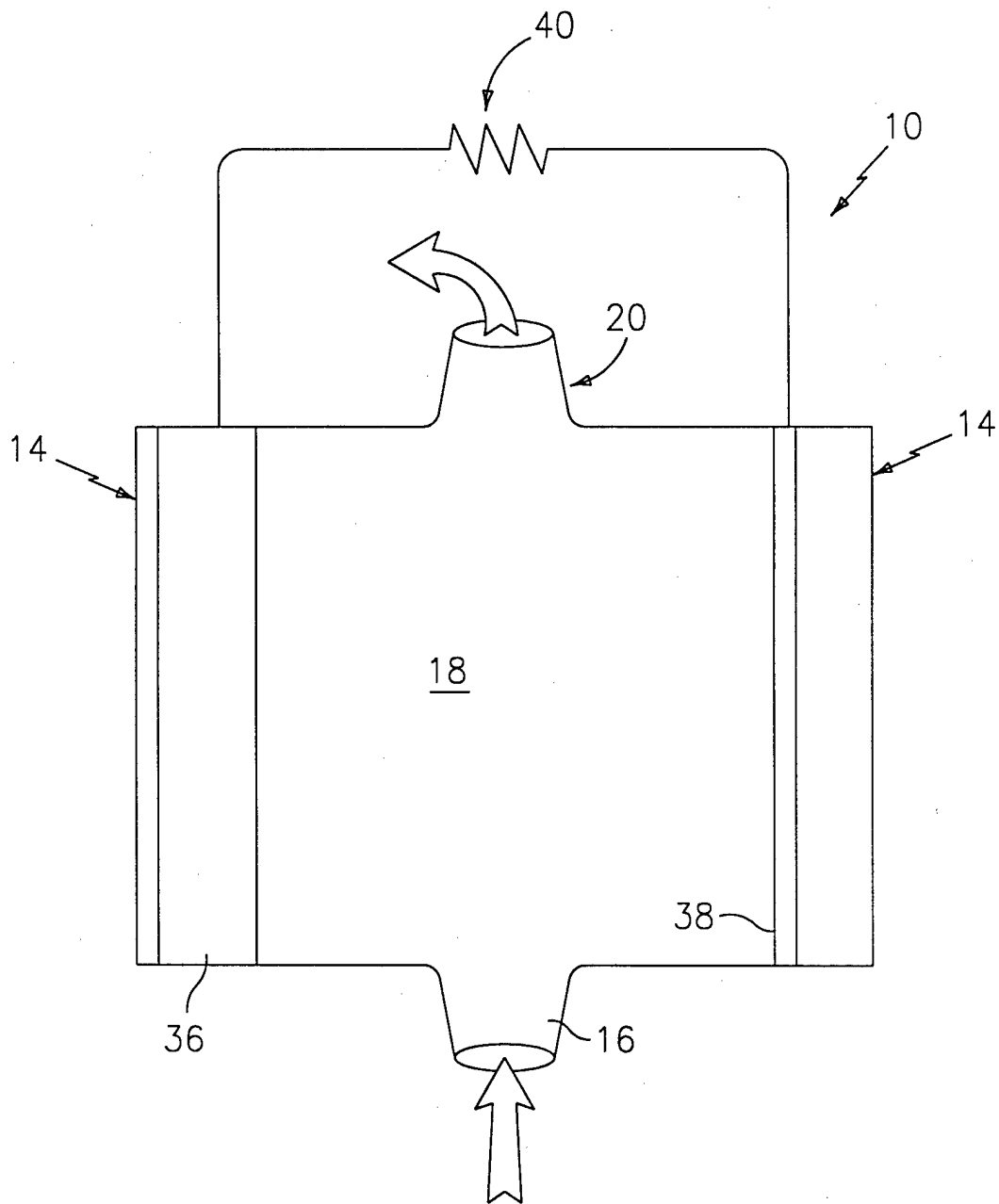


FIG. 1

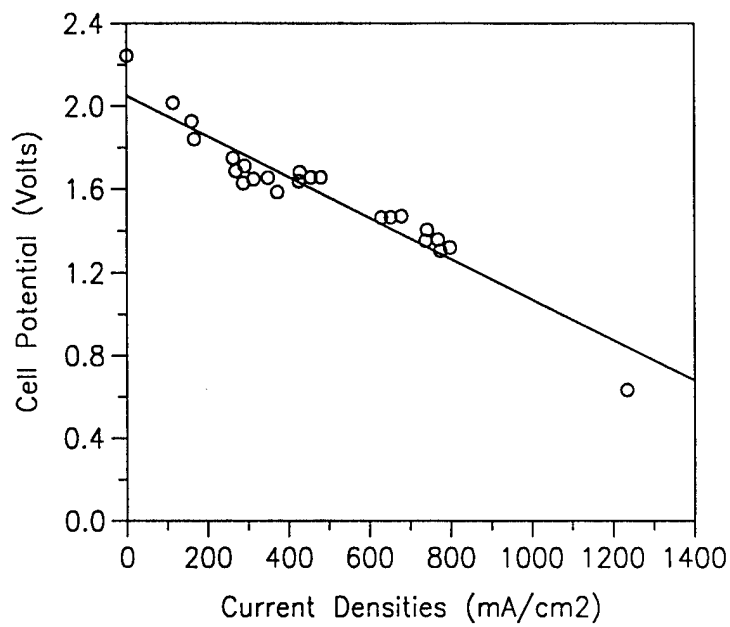


FIG. 2

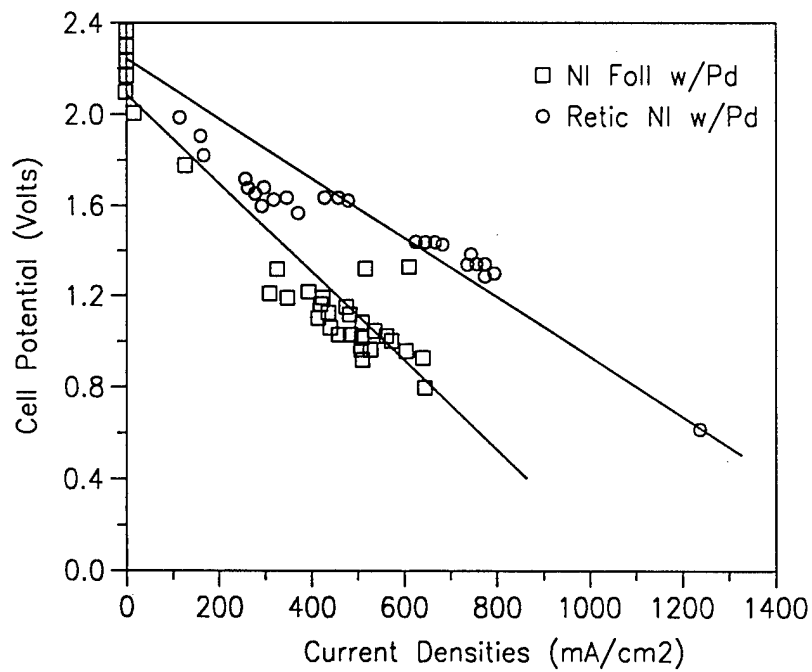


FIG. 3

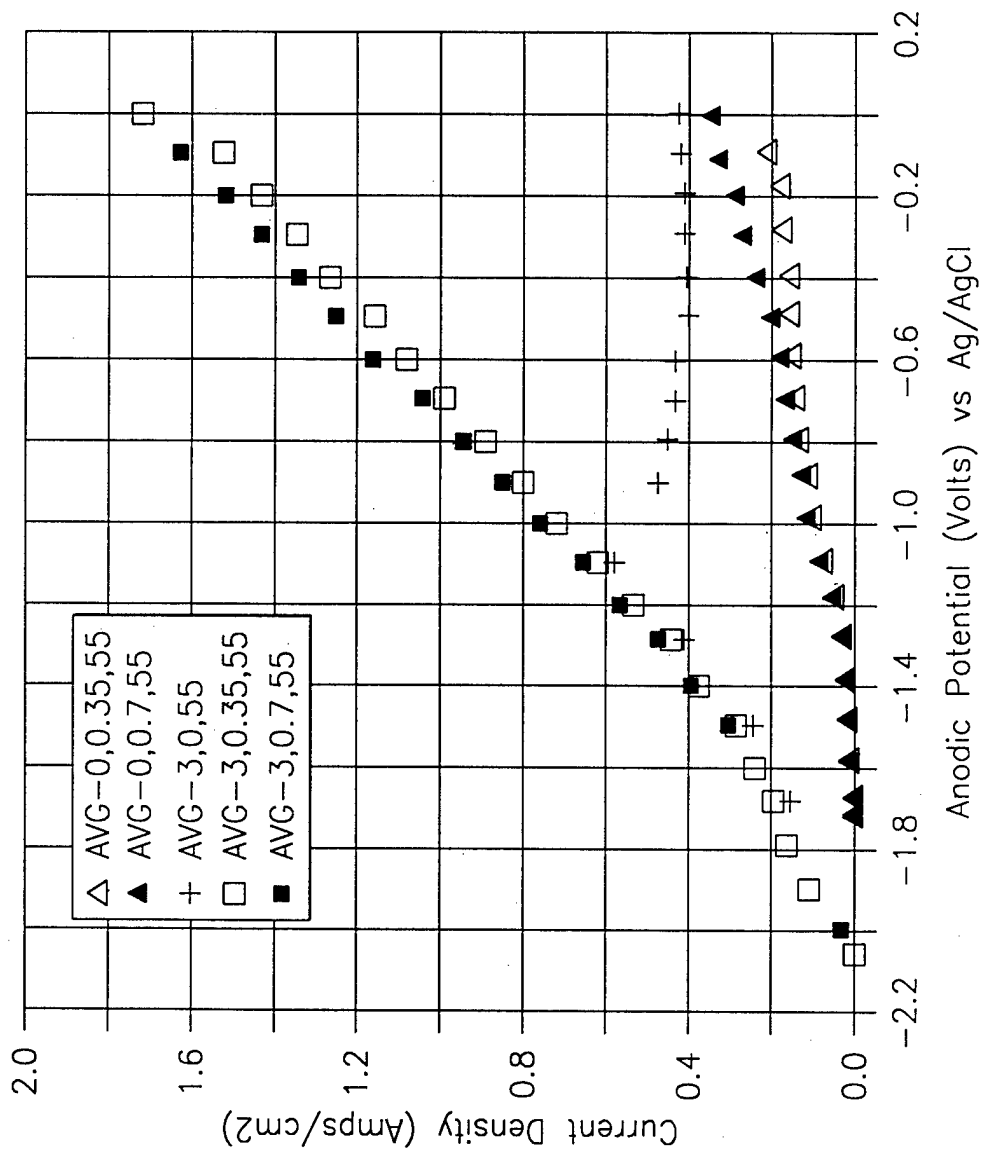


FIG. 4