

CELL CORROSION REDUCTION

This invention relates to methods utilized in the reduction of corrosion and gassing in aqueous electrochemical cells particularly in alkaline type cells having zinc anodes.

A problem in aqueous electrochemical cells has been the evolution of hydrogen gas in the sealed cell container. Such gassing has resulted in corrosion, leakage of the electrolyte from the cell, cell container deformation and rupture, and a possible hazard when the cell is disposed of in a fire. Various expedients have been utilized in preventing, minimizing and controlling such hydrogen gas evolution and its consequences. Such expedients have included mechanical means such as vents and additional volume for storing the hydrogen without excessive pressure build up. Chemical expedients have included: corrosion and gassing inhibitors such as lead, indium, tin, cadmium, bismuth, thallium, and gallium; hydrogen getters such as rare metals supported on oxides such as platinum supported on aluminum oxide or palladium or finely dispersed nickel mixed with polytetrafluoroethylene and manganese dioxide, and hydrides such as LaNiH ; hydrogen recombination with oxygen particularly utilized in nickel cadmium cells;

and removal of chemicals such as chlorides from the surface of the anode metal which tend to accelerate corrosion. The most common, most effective and the oldest expedient (particularly in alkaline electrolyte cells) has been the utilization of mercury to amalgamate the anode metal such as zinc to increase the normally high hydrogen overpotential and to provide for a uniform equipotential surface on the anode metal. Recently, with the increase of environmental concerns, reduction or elimination of mercury without substantial concomitant increase in cell corrosion or gassing has been vigorously pursued.

It is an object of the present invention to provide a means for reduction or elimination of mercury in cell anodes without loss of corrosion protection and increase in cell gassing.

This and other objects, features and advantages of the present invention will become more evident from the following discussion.

Generally the present invention comprises a method for making an electrochemical cell subject to reduced gassing by means of utilization of specific materials in specific states; such materials and the cell itself. The method is particularly applicable to a cell having an anode comprised of a mercury amalgamated powdered metal such as zinc. In the method of the present

invention the powdered metal is substantially formed into individual single crystals and a small amount of one or more of indium, cadmium, gallium, thallium, bismuth, tin, and lead is added to the anodic material i.e. the powdered metal (amalgamated or unamalgamated) or to mercury which is then amalgamated with the powdered metal. The mercury and the additives, in this latter procedure, generally form a surface alloy on each of the particles.

Though the use of single crystal anode material and the use of an indium and/or other additives have separately been known to effectively permit some reduction of mercury content in the anode without detrimental increase in gassing, the effect of the combination has unexpectedly been discovered to be considerably more than additive. Thus, in cells having amalgamated single crystal zinc anodes, the amount of mercury in the amalgam can be effectively reduced from about 6-7% to about 4%. Similarly the utilization of an indium additive with polycrystalline zinc amalgam anodes permits the reduction of mercury from about 6-7% to about 3.5%. However, in accordance with the present invention, a combination of the two, i.e. a single crystal zinc amalgam with an indium additive unexpectedly permits the effective reduction of the

mercury to about 1.5%. As a matter of course, combination of chemical gas reduction expedients does not usually provide an additive effect nor does excessive utilization of additives

The single crystals of zinc are preferably prepared as described in copending application No. 8406662. Such procedure involves the formation of a thin skin crucible on each of the zinc particles by oxidation in air at a temperature just below the melting point (419°C) of the zinc, heating of the skin enclosed zinc particles in an inert atmosphere above the melting point of the zinc and slow cooling thereafter with removal of the oxide skins. Zinc particles sizes generally range between 80 and 600 microns for utility in electrochemical cells and such method provides an effective means for making single crystal particles of such small dimensions.

Generally the amounts of indium or other additive added to the anode metal amalgam may range between 25-5000 ppm and preferably between 100-1000 ppm. Such material may be directly added to the mercury itself. For example indium is highly soluble in mercury and can be directly added thereto in the form of powder or granules. Alternatively, the additive may be plated on the surface of the anode metal from salts of the additive prior to amalgamation with mercury. Such salts include the halides, particularly chlorides, oxides and

acetates of the materials such as indium. It has been discovered that the additives such as indium whether by addition to the mercury or by plating on the single crystal anode metal particles do not in fact disrupt the single crystal nature thereof to any detrimental extent as may have been expected.

The amount of mercury in the anode amalgam may range from 0 - 4% depending upon the cell utilization and the degree of gassing to be tolerated.

The amalgamated single crystal metal particles with additives such as indium are then formed into anodes for electrochemical cells particularly alkaline electrochemical cells. Such cells generally have anodes of zinc and cathodes of materials such as manganese dioxide, silver oxide, mercuric oxide and the like. Electrolytes in such cells are generally alkaline and usually comprise hydroxide solutions such as of sodium or potassium hydroxide. Other anode metals capable of being formed into single crystal powders and which are useful in electrochemical cells include Al, Cd, Ca, Cu, Pb, Mg, Ni, and Sn. It is understood that with anodes of these metals the additive is not the same as the anode active material but is less electrochemically active.

The effects of the present invention can be more clearly evidenced by consideration of comparative gassing rates and discharge capacities as shown in the following examples. It is understood that such examples are for illustrative purposes and are not to be construed as a limitation on the present invention. In the examples as well as throughout this discussion all parts are parts by weight unless otherwise indicated.

EXAMPLE 1

Zinc powder amalgams containing 1.5% mercury are made with polycrystalline zinc alone, polycrystalline zinc with 0.1% indium as an additive element with the mercury, single crystal zinc, and single crystal zinc with 0.1% indium as an additive element with the mercury. Equal amounts of the amalgam powders are then placed in equal amounts of 37% KOH alkaline solution (typical electrolyte solution of alkaline cells) and tested for gassing at a temperature of 71°C. The amount of gassing, measured in microliters/gram per day ($\mu\text{L/g-day}$) and the rate reduction factors (with the polycrystalline zinc control being 1) are set forth in Table 1.

TABLE 1

ANODE MATERIAL	GASSING RATE	RATE REDUCTION FACTOR
Polycrystalline zinc, 1.5% Hg	295	1
Polycrystalline zinc, 1.5% Hg 0.1% indium	105	2.8
Single crystal zinc, 1.5% Hg	140	2.1
Single crystal zinc, 1.5% Hg 0.1 indium	30	9.8

A rate reduction factor (if any) would at most have been expected to be about 5.9 (2.8×2.1) for a combined utilization of single crystal zinc and indium with a gassing rate reduction to about 50 $\mu\text{L/g-day}$. The combination however synergistically reduces the gassing to about double the expected reduction.

EXAMPLE 2

Fifteen amalgams of single crystal zinc particles with various combinations of additive materials of indium, thallium, gallium and lead are prepared and tested for corrosion. The additive materials are plated on the zinc particles from salts thereof. All the amalgams contain 1.5% by weight of mercury. The amounts of each of the additive materials (designated by "+", and "-" if not present) are 0.1% indium (In), 0.01% thallium (Tl), 0.005% gallium (Ga), and 0.04% lead (Pb).

Two grams of each of the amalgams are placed in a 37% KOH electrolyte solution with gassing at the end of 24 and 48 hours being measured at 90° as being representative of corrosion. As controls two amalgams are made with one containing no additive material but with 1.5% mercury and the other containing polycrystalline zinc with 7% mercury similar to that commonly used in alkaline type cells. Results of such tests are given in Table 2.

TABLE 2

ADDITIVE ELEMENT				VOLUME OF GAS (mL), 90°C	
In	Tl	Ga	Pb	24 Hours	48 Hours
+	-	-	-	0.17	0.51
-	+	-	-	0.13	0.49
-	-	+	-	0.42	1.35
-	-	-	+	0.40	1.15
+	+	-	-	0.13	0.36
+	-	+	-	0.17	0.47
+	-	-	+	0.15	0.42
-	+	+	-	0.12	0.40
-	+	-	+	0.12	0.56
-	-	+	+	0.40	1.13
+	+	+	-	0.13	0.42
+	+	-	+	0.11	0.32
-	+	+	+	0.15	0.60
+	-	+	+	0.14	0.44
+	+	+	+	0.10	0.28
-	-	-	- (control)	0.41	1.39
Control 7% Hg-polycrystalline Zn				0.16	0.43

Indium and/or thallium as shown in the above table provide the most efficacious reduction of gassing and are thus preferred embodiments of the present invention. However increase in percentage of gallium or

lead is expected to provide similar effects. Other materials similar in effect to indium such as cadmium, tin and bismuth may be similarly expected to provide the enhanced effect of the present invention.

EXAMPLE 3

Seven zinc amalgams containing 1.5% Hg are prepared with three being comprised of single crystal zinc (made as described above) and four being comprised of polycrystalline zinc. The amalgams containing single crystal zinc comprise two having 0.1% indium (one added to the mercury prior to amalgamation and the other being plated on the zinc particle surfaces prior to amalgamation) and one having no indium. The polycrystalline zinc amalgams include three without lead for direct comparison with the single crystal zinc which contains no lead and one polycrystalline amalgam with lead as commonly utilized in electrochemical cells. The lead free polycrystalline amalgams are directly analagous to the three single crystal zinc amalgams. The polycrystalline leaded zinc amalgam contains 0.02% indium. A control of polycrystalline zinc with lead and 7% mercury (as commonly utilized in alkaline cells) is

also prepared. Two gram samples of each of the above amalgams are tested for gassing at elevated temperatures (71°C and 90°C) for varying time periods with total gas volume and gassing rates being comparatively determined as set forth in Table 3 below.

EXAMPLE 4

Cells are made with the amalgams described in Example 3 of single crystal zinc with 0.1% indium (both types), polycrystalline zinc with 0.1% indium plated on the zinc particles, polycrystalline zinc with 0.02% indium added to the mercury, and a control of polycrystalline zinc with no indium and 7% mercury (a typical alkaline cell). Each of the cells of AA standard size contains a 2.7 gram anode (1.75% starch graft copolymer gelling agent), 2.6 grams of a 37% KOH electrolyte and a manganese dioxide cathode with the cell being anode limited. Five cells are tested for gassing for varying periods at 71°C without discharge and five are similarly tested but after partial discharge at 3.9 ohm for one hour. Total gas volume and gassing rates are set forth in Table 3 below.

TABLE 3A
SINGLE CRYSTAL ZINC

	No Indium 1.5% Hg	0.1% Indium in 1.5% Hg	0.1% Indium + 1.5% Hg
<u>GAS VOLUME mL/2g AMALGAM (OUT-OF-CELL)</u>			
<u>DAYS (71°C)</u>			
7	1.55	0.44	0.41
14	3.52	0.95	0.98
21	5.88	1.57	1.70
28	7.75	2.25	2.36
<u>IN-CELL (UNDISCHARGED)</u>			
0	--	0.17	0.19
7	--	0.48	0.37
14	--	0.56	0.58
28	--	0.92	0.94
<u>IN-CELL (DISCHARGED AT 3.9 OHM FOR ONE HOUR)</u>			
0	--	0.21	0.18
7	--	0.31	0.30
14	--	0.43	0.42
28	--	1.01	0.98
<u>HOURS AT 90°C (OUT-OF-CELL)</u>			
24	0.53	0.20	0.20
48	1.88	0.68	0.69
<u>GASSING RATE uL/g-day (OUT-OF-CELL)</u>			
<u>DAYS (71°C)</u>			
0-7	111	31	29
7-14	141	36	41
14-21	169	44	51
21-28	133	49	47
0-14	126	34	35
14-28	151	46	49
0-28	138	40	42
<u>IN-CELL (UNDISCHARGED)</u>			
0-7	--	16	10
7-14	--	4	11
0-14	--	10	10
14-28	--	10	10
0-28	--	10	10
<u>IN-CELL (DISCHARGED AT 3.9 OHM FOR ONE HOUR)</u>			
0-7	--	5	6
7-14	--	6	6
0-14	--	6	6
14-28	--	15	15
0-28	--	11	11

TABLE 3B
POLYCRYSTALLINE ZINC (No Pb)

	<u>No Indium</u> <u>1.5% Hg</u>	<u>0.1% Indium</u> <u>in 1.5% Hg</u>	<u>0.1% Indium</u> <u>+ 1.5% Hg</u>
<u>GAS VOLUME mL/2g AMALGAM (OUT-OF-CELL)</u>			
<u>DAYS (71°C)</u>			
7	4.10	1.50	1.45
14	7.73	2.52	2.68
21	--	3.60	3.96
28	--	4.64	5.11
<u>IN-CELL (UNDISCHARGED)</u>			
0	--	--	--
7	--	--	0.40
14	--	--	0.76
28	--	--	1.00
<u>IN-CELL (DISCHARGED AT 3.9 OHM FOR ONE HOUR)</u>			
0	--	--	0.28
7	--	--	0.60
14	--	--	1.02
28	--	--	2.53
<u>HOURS AT 90°C</u>			
<u>(OUT-OF-CELL)</u>			
24	1.89	0.47	0.60
48	4.73	1.21	1.49
<u>GASSING RATE uL/g-day (OUT-OF-CELL)</u>			
<u>DAYS (71°C)</u>			
0-7	293	107	104
7-14	259	73	88
14-21	-	77	91
21-28	-	74	82
0-14	276	90	96
14-28	-	76	87
0-28	-	83	91
<u>IN-CELL (UNDISCHARGED)</u>			
0-7	-	-	7
7-14	-	-	19
0-14	-	-	13
14-28	-	-	6
0-28	-	-	10
<u>IN-CELL (DISCHARGED AT 3.9 OHM FOR ONE HOUR)</u>			
0-7	-	-	17
7-14	-	-	22
0-14	-	-	20
14-28	-	-	40
0-28	-	-	30

TABLE 3C
POLYCRYSTALLINE ZINC (WITH Pb)

	<u>0.02% Indium</u> <u>1.5% Hg</u>	<u>No Indium</u> <u>7% Hg control</u>
<u>GAS VOLUME mL/2g AMALGAM (OUT-OF-CELL)</u>		
<u>DAYS (71°C)</u>		
7	1.21	0.49
14	2.49	0.92
21	3.91	1.42
28	5.29	1.96
<u>IN-CELL (UNDISCHARGED)</u>		
0	0.29	0.28
7	0.78	0.37
14	0.94	0.47
28	1.28	0.71
<u>IN-CELL (DISCHARGED AT 3.9 OHM FOR ONE HOUR)</u>		
0	0.23	0.18
7	0.91	0.39
14	1.25	0.49
28	4.37	1.00
<u>HOURS AT 90°C</u> <u>(OUT-OF-CELL)</u>		
24	0.50	0.17
48	1.20	0.56
<u>GASSING RATE uL/g-day (OUT-OF-CELL)</u>		
<u>DAYS (71°C)</u>		
0-7	86	35
7-14	91	31
14-21	101	36
21-28	99	39
0-14	89	33
14-28	100	37
0-28	94	35
<u>IN-CELL (UNDISCHARGED)</u>		
0-7	26	5
7-14	8	5
0-14	17	5
14-28	9	6
0-28	13	6
<u>IN-CELL (DISCHARGED AT 3.9 OHM FOR ONE HOUR)</u>		
0-7	36	11
7-14	18	5
0-14	27	8
14-28	83	13
0-28	55	11

EXAMPLE 5

Cells are made as in Example 4 and are each discharged to various cutoff-voltages with a 3.9 ohm load with the capacities in service hours set forth in Table 4 below.

TABLE 4 (Discharge Characteristics)
(Service Hours at 3.9 ohms)

CUT-OFF VOLTAGES	SINGLE CRYSTAL ZINC		POLYCRYSTALLINE ZINC		
	0.1% In +1.5% Hg	0.1% In in 1.5% Hg	0.02% In 1.5% Hg	0.1% In + 1.5% Hg	No In 7% Hg Ctrl
1.2	0.660	0.668	0.533	0.688	0.623
1.1	1.6161	1.638	1.457	1.712	1.553
1.0	2.826	2.859	2.480	2.926	2.598
0.9	3.535	3.652	3.235	3.619	3.295
0.8	3.800	3.967	3.498	3.883	3.599
0.65	3.986	4.179	3.594	4.020	3.684

It is evident from the above examples and tables that the single crystal zinc with one or more additives of the present invention is markedly effective in permitting large mercury reductions without increase in cell gassing while at the same time enhancing cell discharge characteristics when such cells are compared to the current commercial alkaline cells having high mercury amalgam content.

It is understood that the above examples are for illustrative purposes only and details contained therein are not to be construed as limitations on the present invention. Changes in cell construction, materials, ratios and the like may in fact be made without departing from the scope of the present invention.

CLAIMS:

1. An electrochemical cell comprising an anode, a cathode and an aqueous electrolyte characterised in that said anode comprises particles of discrete single crystals of anode metal and one or more additives comprising indium, cadmium, gallium, thallium, bismuth, tin and lead wherein the or each said additive is present in said anode in a range of 25-5000 ppm, each said additive being different from and less electrochemically active than the anode metal.
2. The cell of claim 1 wherein said range is between 100-1000 ppm.
3. The cell of claim 1 or 2 wherein said anode comprises discrete single crystal anode metal particles and one or more of indium, thallium, gallium and lead.
4. The cell of claim 3 wherein said anode comprises discrete single crystal anode metal particles and indium.
5. The cell of claim 1, 2, 3 or 4 wherein said anode metal is zinc.
6. The cell of any preceding claim wherein said electrolyte is comprised of an alkaline solution.



7. The cell of any preceding claim wherein said anode further comprises mercury.

8. The cell of claim 7 wherein said mercury is present in said anode in amounts of up to 4% by weight thereof.

9. The cell of claim 7 wherein said mercury is present in said anode in amounts of up to 1.5% by weight thereof.

10. A method for making an aqueous electrochemical cell subject to reduced gassing said method comprising the steps of making discrete individual single crystal particles of the metal utilized as the active anode of said cell, adding one or more additives selected from indium, cadmium, gallium, thallium, bismuth, tin and lead to said single crystal particles, and utilizing said single crystal particles with said one or more additives as the anode of said cell, each said additive being different from and less electrochemically active than the anode metal.

11. The method of claim 10 wherein said discrete individual single crystal metal particles are made by forming individual thin oxide coatings on polycrystalline metal particles by oxidation of said polycrystalline metal particles in air at a temperature



below the melting point of said metal, heating of said metal particles in an inert atmosphere above the melting point of said metal, slow cooling of the metal particles and removal of said coatings.

12. The method of claim 10 or 11 wherein said one or more additives each comprise from 25-5000 ppm of said anode.

13. The method of claim 12 wherein said one or more additives comprise from 100-1000 ppm.

14. The method of any of claims 10 to 13 wherein said metal is zinc.

15. The method of claim 14 wherein said single crystal zinc particles with said one or more additives are amalgamated with mercury.

16. The method of claim 15 wherein said single crystal zinc particles are alloyed with one or more additives of the group consisting of indium, thallium, gallium and lead.

17. The method of claim 16 wherein said mercury is present in said anode in amounts of up to 4% by weight thereof.



18. The method of claim 16 wherein said mercury is present in said anode in amounts of up to 1.5% by weight thereof.

19. The method of claim 16, 17 or 18 wherein said one or more additives are plated on said single crystal zinc particles prior to amalgamation of said particles with mercury.

20. The method of claim 16, 17 or 18 wherein said one or more additives are admixed with said mercury prior to amalgamation of said single crystal zinc particles with said mercury.

21. A composition of matter suitable for use in making an anode of an aqueous electrochemical cell with reduced gassing, said composition comprising discrete individual single crystal metal particles containing one or more additives comprising indium, cadmium, gallium, thallium, bismuth, tin and lead, wherein the or each said additive is present in said anode in a range of 25-5000 ppm, each said additive being different from and less electrochemically active than the anode metal.

22. The composition of matter of claim 21 wherein said discrete individual single crystal metal particles are amalgamated with mercury.



23. The composition of matter of claim 22 wherein said metal is zinc.

24. The composition of matter of claim 23 wherein said mercury is present in amounts up to 4% by weight thereof and said one or more additives each comprise from 100 to 1000 ppm of said composition.

25. The composition of matter of claim 24 wherein said one or more additives are selected from indium, thallium, gallium and lead.

26. An electrochemical cell subject to reduced gassing comprising an aqueous alkaline eletrolyte, a cathode and an anode compriseing mercury amalgamated single crystal zinc particles and indium with said mercury comprising up to 4% by weight of said anode and said indium comprising from 100 to 1000 ppm of said anode.

27. The cell of claim 26 wherein said mercury comprises up to 1.5% by weight of said anode, said cathode comprises manganese dioxide and said aqueous electrolyte comprises a potassium hydroxide solution.

28. The cell of claim 8 or 17 wherein said anode comprises single crystal zinc particles, mercury and lead.



29. The composition of matter of claim 25 wherein said additive is lead.

30. The method of making electrochemical cells, comprising making cell anodes of single crystal material, substantially as herein described with reference to any of examples 1 to 5, and assembling the anode with a cathode and aqueous electrolyte.

31. An electrochemical cell comprising a cathode, an aqueous electrolyte, and an anode of single crystal anode metal particles, substantially as herein described with reference to any of examples 1 to 5.



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