

1

2

3,258,368

ORGANIC ELECTROLYTE FOR MAGNESIUM PRIMARY CELLS

John L. Robinson, Freeland, and Peter F. King, Midland, Mich., assignors to The Dow Chemical Company, Midland, Mich., a corporation of Delaware
No Drawing. Filed May 20, 1963, Ser. No. 281,788
3 Claims. (Cl. 136-100)

This invention relates to a novel electrolyte for use in magnesium primary cells and more particularly is concerned with an aqueous carboxylic acid salt electrolyte for such cells.

Aqueous solutions of inorganic salts, e.g. halides, sulfates and perchlorates, long have been used as electrolytes for primary cells which utilize magnesium as the anode. (The term magnesium as used herein is meant to include magnesium and magnesium base alloys containing at least about 70 weight percent magnesium.) These electrolytes provide a working potential of the magnesium anode versus saturated calomel electrode of from about -1.3 to about -1.5 volts. However, when employed in a magnesium primary cell, the useful or energy producing reaction is accompanied by a wasteful anode corrosion reaction. As a result, with such electrolytes the magnesium anode operates at a maximum coulombic efficiency of from about 65 to about 75 percent. Also, with these electrolytes, the corrosion pattern is non-uniform, i.e. rough and pitted. Therefore, a considerable excess anode metal thickness is needed to prevent anode perforation during useful cell life. In addition to the loss of a considerable portion of the magnesium anode, the corrosion reaction consumes water such that in the case of "dry cells" excess water must be employed in the cathode formulation. Further, hydrogen is evolved at such rates that special venting must be provided in construction of the cells. Also, the magnesium hydroxide formed by this wasteful reaction deposits adjacent the anode and occupies almost twice the volume of magnesium consumed. In dry cells, therefore, this anticipated product build-up must be overcome by providing special cell design and construction to provide for controlled expansion or containment of the cell volume.

When chromic acid electrolytes are utilized in magnesium primary cells, the wasteful corrosion reaction during operation can be held to a minimum and operating anode efficiencies of 90 percent or more obtained. With this latter electrolyte, however, the working potential of the magnesium anode versus the saturated calomel electrode is from 0 to about -0.10 volt. Thus over 1.2 volts of active working anode potential is sacrificed to obtain the high anode efficiency with the chromic acid electrolytes.

Now, unexpectedly it has been found that both high anode efficiencies and high working potentials are realized in primary cells employing a magnesium anode when alkali metal and alkaline earth metal salts of certain aliphatic and aromatic carboxylic acids are employed as the electrolyte in such cells.

It is a principal object of the present invention to provide an electrolyte for primary cells employing a magnesium anode which gives high anode efficiency and high working potentials.

It is also an object of the present invention to provide an electrolyte for use in a magnesium anode containing primary cell the use of which is accompanied by a desirable uniform corrosion pattern of the anode during operation and wherein corrosion products produced in the cell result substantially completely from the useful electrical power producing reaction.

It is a further object of the present invention to provide an electrolyte for magnesium primary cells which substantially eliminates hydrogen generation during cell operation.

It is another object of the present invention to provide a magnesium primary cell having an electrolyte in which there is substantially no heat generated from the wasteful chemical corrosion reaction.

These and other objects and advantages readily will become apparent from the detailed description presented hereinafter.

In accordance with the present invention, high anode efficiencies and working potentials are realized for magnesium primary cells employing an aqueous solution of an alkali metal or alkaline earth metal salt of certain aliphatic carboxylic or aromatic carboxylic acids as an electrolyte. The term "alkali metal" as used herein is meant to include lithium, sodium, potassium, rubidium and cesium and the term "alkaline earth metal" as used herein is meant to include magnesium, calcium, strontium and barium.

In general, the aliphatic carboxylic acid salts which preferably are employed as electrolytes for magnesium primary cells contain from 1 to about 5 carbon atoms in the carbon chain. Further, these salt forming acids are either saturated or unsaturated and straight or branched chain. Saturated aliphatic acids which are either mono- or polycarboxylated are suitable for use in the present invention provided there is at least one methylene or methyl radical or group present for each carboxy group ($-\text{COOH}$) in the parent acid. The terms "methyl group" or "methyl radical" and "methylene group" or "methylene radical" as used herein means ($-\text{CH}_3$) and



respectively as well as substituted groups wherein one or more of the H atoms have been replaced by another group. To illustrate, the salts of malonic acid and of hydroxy substituted acids such as citric acid, glycolic acid, tartaric acid and malic acid, for example, are suitable for use as electrolytes with magnesium cells. Additionally, salts of unsaturated aliphatic carboxylic acids having at least one carboxylate group for each



group also can be employed. However, substituent groups which are strong polarizers such as halo, nitro, phenolic, etc., cannot be used.

In general, it has been found with these aliphatic carboxylic alkali metal and alkaline earth metal salt electrolytes that cell efficiency increases slowly with increasing carbon chain length. This increase is offset, however, by a corresponding rise in polarization and decrease in the active potential with increase in carbon chain. With carbon chains of longer than about 5 carbon atoms detrimental polarization and reduced electrolyte solubility may occur.

Aromatic carboxylic acid salts suitable for use as electrolytes are those materials having two or more carboxy groups present on each ring of the acid. Illustrative members include, for example phthalic acid, isophthalic acid and pyromellitic acid. The aromatic acids also can contain other substituent groups which are not strong polarizers.

With magnesium primary cells, ordinarily the aqueous electrolyte concentration is from about 0.5 to about 5 normal, based on the carboxylate anion. Preferably the electrolyte concentration ranges from about 1 to about 4 normal. For a specific primary cell construction, generally the present novel electrolyte is employed in about

3

the same concentration as the inorganic halide electrolyte normally employed therein. Further, with a dry-type cell, chromates or other traditional inhibitors can be used in conjunction with the present organic electrolytes to extend shelf storage life (i.e., open circuit corrosion control) of the cell.

The electrolytes of this invention are used in a conventional manner in a magnesium primary cell as the electrolyte is adapted to any primary cell construction employing a magnesium anode or anodes. In cell construction, however, with the present novel electrolyte there is no need to use excess anode above theoretical as is needed with conventional halide electrolytes which give irregular non-uniform corrosion with pitting. Also, elaborate gas venting systems are not required in cells employing the present novel electrolyte.

The following examples will serve to further illustrate the present invention but are not meant to limit it thereto.

EXAMPLE 1

A number of electrochemical tests evaluating the present electrolyte were carried out in a standard one-compartment electrolysis cell having a magnesium alloy anode having a nominal composition of about 1.8% Al, 1.3% Zn, 0.15% Ca, balance Mg suspended between one inch square parallel platinum cathodes. The cell volume was about 200 cubic centimeters. The nominal anode dimensions were 1.25 inches x 0.25 inch x 0.146 inch to give an area of approximately 1.05 square inches (i.e., 6.8 sq. cm.). A Luggin capillary probe was inserted next to the anode and the anode potential vs. saturated calomel was recorded with either a Brown electronic recorder or a Sanborn oscillograph. Constant currents were achieved with 24 to 600 volt power sources in series with large "swamping" resistors.

Both anode efficiency and operating anode potentials were determined.

For the efficiency measurements, anode weight losses were determined after passage of approximately 20 ampere minutes at various impressed current densities. The working potentials also were measured at various impressed current densities.

Table I, which follows, presents the results of electrical potential measurements and anode efficiencies obtained with a number of electrolytes at various applied currents.

TABLE I

Run No.	Electrolyte Solute	Normality Aqueous Electrolyte	Potential vs. Sat'd. Calomel (-volts)			Anode Efficiency (percent)	
			Applied Current Milliamperes			Applied Current, Milliamperes	
			5	20	100	20	100
1	Magnesium Acetate	1.0	1.45	1.43	1.43	82	89
2	Potassium Acetate	1.0	1.52	1.44	1.40	83	87
3	Calcium Acetate	1.0	1.45	1.43	1.42	83	87.5
4	Magnesium Propionate	1.0	1.39	1.32	1.16	81	88.5
5	Calcium Malonate	1.0	1.50	1.45	1.45	67.5	67.5
6	Sodium Succinate	1.0	1.46	1.40	1.40	81.5	80
7	Calcium Acrylate	1.0	1.35	1.30	1.25	84	90.5
8	Sodium Maleate	1.0	1.43	1.34	1.39	80	88
9	Sodium Malate	1.0	1.40	1.37	1.27	90.5	92
10	Potassium Tartrate	1.0	1.49	1.35	1.12	90.5	95.5
11	Magnesium Glycolate	1.0	1.48	1.47	1.39	83	81.5
12	Trisodium Citrate	1.0	1.51	1.45	1.28	94.5	96.5
13	Dipotassium Phthalate	1.0	1.50	1.37	1.25	89.5	83
14	Sodium Adipate	1.0	1.55	1.49	1.32	86.5	97
15	Sodium Pimelate	1.0	1.44	1.33	1.27	91	91
16	Disodium Isophthalate	1.0	1.48	1.37	1.12	92	92.5
17	Tetrasodium Pyromellitate	1.0	1.45	1.38	1.27	92	93
18	Disodium Malate	1.0	1.41	1.36	1.26	90	93

EXAMPLE 2

Steel jacketed "D" size primary cells were fabricated in accordance with the cell embodiment described and set forth in U.S. 2,845,471. These cells utilized AZ21X1 magnesium alloy anodes of composition set forth herein-

4

before. The anodes were about 1.5 inches high by about from 0.022 to about 0.025 inch thick and weighed from about 3.8 to about 4.1 grams. The cells had about 30 hours total operating life to an 0.75 volt end voltage through 10 ohms resistance. A batch of cathode mix was formulated by dry blending about 850 grams of African MnO_2 , 30 grams BaCrO_4 and 120 grams Shawinigan acetylene black. The dry blend was wetted with about 530 milliliters of a predetermined electrolyte per 1000 grams of dry mix. An amount of the resulting wet cathode mix ranging from about 48 to about 52 grams was used in each cell. Cells were discharged continuously at a temperature of about 70° F. through 10 ohms resistance to an 0.75 volt end voltage. Table II summarizes the results of a number of tests made with magnesium acetate electrolyte of various normalities. For control purposes, a cell similarly constructed but employing conventional 3 normal MgBr_2 also was subjected to the same test.

Table II

Run No.	Electrolyte Normality	Cell Capacity, hrs.	Anode Efficiency, percent
1	0.5	14	82
2	1.0	21.5	83
3	1.4	26.0	86
4	2.0	30.0	88
5	2.5	31.0	87
6	3.0	27.5	86
7	4.0	25.0	85
8	5.0	4.5	67
9	6.0	2.0	62
10 (control)	3 N MgBr_2	23	64

EXAMPLE 3

Cells were prepared as described in Example 2 except that an aqueous solution of 0.9 N magnesium pyromellitate or 1.3 N magnesium isophthalate was used as electrolyte. Discharging these cells through a 10 ohm drain to 0.75 end voltage resulted in anode efficiencies of 80% for the magnesium pyromellitate and 79% for the magnesium isophthalate electrolytes respectively.

EXAMPLE 4

Cells having an operational life of from about 140-150 hours to 1.0 volt through a 50 ohm drain were prepared using the same construction as described in Example 2 except that the cathode mix was about 82%

5

Control cells employing 3 N magnesium bromide electrolyte were similarly prepared and tested. Table III shows the results of these tests.

Table III

Run No.	Anode Material	Electrolyte	Cell Capacity, Hrs.	Anode Efficiency, Percent
1-----	AZ21X1 alloy----	Magnesium acetate----	140	76
2-----	do-----	MgBr ₂ (control)-----	142	62

A second series of similar cells was prepared wherein high purity magnesium was utilized as anode material instead of the aluminum-zinc containing magnesium alloy. These cells were tested to a 1.0 volt end voltage through a 10 ohm resistor.

Table IV presents the results of this run.

Table IV

Run No.	Anode Material	Electrolyte	Anode Efficiency, Percent
1-----	High purity Mg-----	Magnesium acetate----	82
2-----	do-----	MgBr ₂ (control)-----	61

Various modifications can be made in the present invention without departing from the spirit or scope thereof for it is understood that we limit ourselves only as defined in the appended claims.

We claim:

1. In a magnesium battery having a high anode effi-

6

ciency and potential which includes a magnesium anode, a cathode, an aqueous electrolyte, a chromate inhibitor and a current collector, the improvement which comprises; providing an aqueous carboxylic acid salt electrolyte the solute of which is a member selected from the group consisting of alkali metal and alkaline earth metal salts of aliphatic and aromatic carboxylic acids and further characterized in that the aliphatic acids have a carbon chain length of from 1 to about 5 carbon atoms and there is at least one radical selected from the group consisting of methylene and methyl present for each carboxy group of said aliphatic acid and the aromatic carboxylic acid salts have at least two carboxy groups present on each ring of said aromatic acid, and wherein the solute concentration in said electrolyte ranges from about 0.5 to about 5 normal.

2. The magnesium battery as defined in claim 1 wherein the solute of the aqueous carboxylic acid salt electrolyte is magnesium acetate and the concentration of said magnesium acetate in said electrolyte ranges from about 1 to about 4 normal.

3. The magnesium battery as defined in claim 2 having a manganese dioxide cathode and a carbon current collector.

References Cited by the Examiner

UNITED STATES PATENTS

2,245,528	6/1941	Loder	260—524
2,993,946	7/1961	Lozier	136—90
3,057,944	10/1962	Ruetschi et al.	136—154 X
3,095,331	6/1963	Davis	136—154 X

WINSTON A. DOUGLAS, *Primary Examiner*.

B. J. OHLENDORF, *Assistant Examiner*.