

SPECIFICATION

Non-aqueous cells employing heat-treated manganese dioxide cathodes

- 5 The development of high energy battery systems requires the compatibility of an electrolyte possessing desirable electrochemical properties with highly reactive anode materials, such as lithium, sodium, and the like and the efficient use of high energy density cathode materials, such as manganese dioxide. The use of aqueous electrolytes is precluded in these systems since the anode materials are sufficiently active to react with water chemically. It has therefore been necessary, in order to realize the high energy density obtainable through use of these highly reactive anodes and high energy density cathodes, to turn to the investigation of nonaqueous electrolyte systems and more particularly to nonaqueous organic electrolyte systems. 10
- The term "nonaqueous organic electrolyte" in the prior art refers to an electrolyte which is composed of a solute, for example, a salt or complex salt of Group I-A, Group II-A or Group III-A elements of the Periodic Table, dissolved in an appropriate nonaqueous organic solvent. Conventional solvents include propylene carbonate, ethylene carbonate or γ -butyrolactone. The term "Periodic Table" as used herein refers to the Periodic Table of the Elements as set forth on the inside back cover of the Handbook of Chemistry and Physics, 48th Edition, the Chemical Rubber Co., Cleveland, Ohio, 1967-1968. 15
- 20 A multitude of solutes is known and recommended for use but the selection of a suitable solvent has been particularly troublesome since many of those solvents which are used to prepare electrolytes sufficiently conductive to permit effective ion migration through the solution are reactive with the highly active anodes mentioned above. Most investigators in this area, in search of suitable solvents, have concentrated on aliphatic and aromatic nitrogen- and oxygen-containing compounds with some attention given to organic sulfur-, phosphorus- and arsenic-containing compounds. The results of this search have not been entirely satisfactory since many of the solvents investigated still could not be used effectively with high energy density cathode materials, such as manganese dioxide (MnO_2), and were sufficiently corrosive to lithium anodes to prevent efficient performance over any length of time. 25
- 30 Although manganese dioxide has been mentioned as a possible cathode for cell applications, manganese dioxide inherently contains an unacceptable amount of water, both of the absorbed and bound (adsorbed) types, which is sufficient to cause anode (lithium) corrosion along with its associated hydrogen evolution. This type of corrosion that causes gas evolution is a serious problem in sealed cells, particularly in miniature type button cells. In order to maintain overall battery-powered electronic devices as compact as possible, the electronic devices are usually designed with cavities to accommodate the miniature cells as their power source. The cavities are usually made so that a cell can be snugly positioned therein thus making electronic contact with appropriate terminals within the device. A major potential problem in the use of cell-powered devices of this nature is that if the gas evolution causes the cell to bulge then the cell could become wedged within the cavity. This could result in damage to the device. Also, if electrolyte leaks from the cell it could cause damage to the device. Thus it is important that the physical dimensions of the cell's housing remain constant during discharge and that the cell will not leak any electrolyte into the device being powered. 35 40
- 45 U.S. Patent 4,133,856 discloses a process for producing a MnO_2 electrode (cathode) for nonaqueous cells whereby the MnO_2 is initially heated within a range of 350° to 430°C so as to substantially remove both the absorbed and bound water and then, after being formed into an electrode with a conductive agent and binder, it is further heated in a range of 200° to 350°C prior to its assembly into a cell. British Patent 1,199,426 also discloses the heat treatment of MnO_2 in air at 250° to 450°C to substantially remove its water component.
- 50 U.S. Patents 3,871,916; 3,951,685, and 3,996,069 disclose a nonaqueous cell employing a 3-methyl-2-oxazolidone-based electrolyte in conjunction with a solid cathode selected from $(\text{CF}_3)_n$, CuO , FeS_2 , Co_3O_4 , V_2O_5 , Pb_3O_4 , In_2S_3 , and CoS_2 .
- While the theoretical energy, i.e., the electrical energy potentially available from a selected anode-cathode couple, is relatively easy to calculate, there is a need to choose a nonaqueous electrolyte for a couple that permits the actual energy produced by an assembled battery to approach the theoretical energy. The problem usually encountered is that it is practically impossible to predict in advance how well, if at all, a nonaqueous electrolyte will function with a selected couple. Thus a cell must be considered as a unit having three parts: a cathode, an anode, and an electrolyte, and it is to be understood that the parts of one cell are not predictably interchangeable with parts of another cell to produce an efficient and workable cell. 55 60
- It is an object of the present invention to provide a manganese dioxide nonaqueous cell employing an active metal anode.
- The invention provides a novel high energy density nonaqueous cell comprising a highly active metal anode, a manganese dioxide-containing cathode and a liquid organic electrolyte comprising 3-methyl-2-oxazolidone together with a conductive solute with or without at least 65

one cosolvent having a viscosity lower than that of 3-methyl-2-oxazolidone and wherein the manganese dioxide has a water content of less than 1 weight percent based on the weight of the manganese dioxide. Preferably the water content should be lower than 0.5 weight percent and most preferably below 0.2 weight percent.

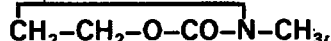
5 The water inherently contained in both electrolytic and chemical types of manganese dioxide can be substantially removed by various treatments. For example, the manganese dioxide can be heated in air or an inert atmosphere at a temperature of 350°C for about 8 hours or at a lower temperature for a longer period of time. Care should be taken to avoid heating the manganese dioxide above its decomposition temperature which is about 400°C in air. In oxygen atmosphere, higher temperatures may be employed. To make it suitable for use in the cell of this invention the manganese dioxide should be heated for a sufficient period of time to ensure that the water content is reduced below 1 weight percent, preferably below about 0.5 and most preferably below about 0.2 weight percent based on the weight of the manganese dioxide. An amount of water above about 1 weight percent would react with the highly active metal anode, such as lithium, and cause it to corrode thereby resulting in hydrogen evolution. As stated above this could result in physical distortion of the cell and/or electrolyte leakage from the cell during storage or discharge.

To effectively remove the undesirable water from MnO_2 , or MnO_2 mixed with a conductive agent and a suitable binder, to the level necessary to practice this invention, it is believed necessary that both the absorbed and bound water be substantially removed. After the water removal treatment has been completed, it is essential that the manganese dioxide be shielded to prevent absorption of water from the atmosphere. This could be accomplished by handling the treated manganese dioxide in a dry box or the like. Alternatively, the treated manganese dioxide or the manganese dioxide combined with a conductive agent and a suitable binder could be heat treated to remove water that could have been absorbed from the atmosphere.

Preferably, the manganese dioxide should be heat treated to remove its water content to below 1 weight percent and then it can be mixed with a conductive agent such as a graphite, or carbon and a binder such as Teflon (trademark for polytetrafluoroethylene) or ethylene acrylic acid polymer to produce a solid cathode electrode. If desired, a small amount of electrolyte can be incorporated into the manganese dioxide mix.

An added possible benefit in the removal of substantially all the water from manganese dioxide is that if small amounts of water are present in the cell's electrolyte then the manganese dioxide will absorb the main portion of that water from the electrolyte and thereby prevent or substantially delay the reaction of the water with the anode such as lithium. In this situation, the manganese dioxide will act as an extracting agent for the water impurities in the organic solvents.

The electrolyte for use in this invention is a 3-methyl-2-oxazolidone-based electrolyte. Liquid organic 3-methyl-2-oxazolidone material, (3Me2OX)



is an excellent nonaqueous solvent because of its high dielectric constant, chemical inertness to battery components, wide liquid range and low toxicity.

45 However, it has been found that when metal salts are dissolved in liquid 3Me2Ox for the purpose of improving the conductivity of 3Me2Ox, the viscosity of the solution may be too high for its efficient use as an electrolyte for some nonaqueous cell applications other than those requiring very low current drains. Thus, in some applications in accordance with this invention, the addition of a low viscosity cosolvent would be desirable if 3Me2Ox is to be used as an electrolyte for nonaqueous cells which can operate or perform at a high energy density level. Specifically, in order to obtain a high energy density level in accordance with this invention, it is essential to use a heat-treated MnO_2 cathode along with a highly active metal anode. Thus this invention is directed to a novel high energy density cell having a highly active metal anode, such as lithium, a heat-treated MnO_2 cathode, and an electrolyte comprising 3Me2Ox in combination with a conductive solute with or without at least one low viscosity cosolvent.

The low viscosity cosolvents if used in this invention include tetrahydrofuran (THF), dioxolane (DIOX), dimethoxyethane (DME), propylene carbonate (PC), dimethyl isoxazole (DMI), diethyl carbonate (DEC), ethylene glycol sulfite (EGS), dioxane and dimethyl sulfite (DMS). Dimethoxyethane (DME), dioxolane (DIOX) and propylene carbonate (PC) are preferred cosolvents because of their compatibility with metal salts dissolved in liquid 3Me2Ox and their chemical inertness to cell components. Specifically, the total amount of the low viscosity cosolvent added could be between about 20% and about 80% based on total solvent volume, i.e. exclusive of solute, so as to lower the viscosity to a level suitable for use in a high drain cell.

Conductive solutes (metal salts) for use in this invention with the liquid 3Me2Ox may be selected from MCF_3SO_3 , MBF_4 , MC10_4 , and $\text{MM}'\text{F}_8$ wherein M is lithium, sodium or potassium,

and M' is phosphorus, arsenic or antimony. The addition of the solute is necessary to improve conductivity of 3Me2Ox so that said 3Me2Ox can be used as the electrolyte in nonaqueous cell applications. Thus the particular salt selected has to be compatible and nonreactive with 2Me2Ox and the electrodes of the cell. The amount of solute to be dissolved in the liquid 3Me2Ox should be sufficient to provide good conductivity, e.g., at least $10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$. Generally an amount of at least 0.5 molar would be sufficient for most cell applications.

Highly active metal anodes suitable for this invention include lithium (Li), potassium (K), sodium (Na), calcium (Ca), magnesium (Mg), aluminium (Al), and their alloys. Of these active metals, lithium would be preferred because in addition to being a ductile, soft metal that can easily be assembled in a cell, it possesses the highest energy-to-weight ratio of the group of suitable anode metals.

The present invention of a high energy density cell with a 3-Me2Ox-based electrolyte, a solid MnO_2 -containing cathode having less than 1 weight percent water and a highly active metal anode will be further illustrated in the following examples.

EXAMPLE 1

Thermogravimetric analyses (TGA) were made of various samples of commercial manganese dioxide. Some of the samples were analyzed as obtained, other samples were heat treated at 350°C for 8 hours, and other samples were heat treated at 350°C for 8 hours and then blended with carbon and Teflon to produce cathode mixes. The data obtained from the thermogravimetric analyses (TGA) are shown in Table I. The data clearly show that commercial types of manganese dioxide contain large amounts of water. In addition, the data show that even after the manganese dioxide had been heat treated as specified above, it will absorb water from the atmosphere even after only a small period of time.

TABLE I

Percent Weight Loss at Various Temperatures as Indicated by TGA
Total % Weight Loss at Temp. °C (Cumulative)

Sample Description	100	200	250	300	350	400
*Tekkosha MnO ₂ , as received	1.0	2.1	2.7	3.5	4.4	5.1
Tekkoshas as above, but dried at 350°C., 8 hrs; exposed to room atmosphere 5 mins. in sample transfer	0.2	0.3	0.3	0.3	0.4	0.6
**Cathode mix taken directly from dry box; exposed to room atmosphere 5 mins. in sample transfer	0.3	0.4	0.5	0.7	1.1	—
Cathode mix exposed to room atmosphere	0.3	0.5	0.5	—	—	—
Cathode mix same as above but exposed to room atmosphere an additional 17 hrs. ***	0.6	0.8	0.8	0.9	1.1	1.9
***Sedema MnO ₂	1.4	2.1	2.4	2.6	2.9	3.7

*Tekkosha MnO₂ is commercial electrolytic MnO₂.

**Cathode mix—heat treated Tekkosha MnO₂ + carbon black + graphite + Teflon

***Sedema MnO₂ is commercial chemical MnO₂

****Room humidity, 35-50%

EXAMPLE II

Each of two falt-type cells was constructed utilizing a nickel metal base having therein a shallow depression into which the cell contents were placed and over which a nickel metal cap was placed to close the cell. The contents of each sample cell consisted of 1.0 inch (2.54 cm) diameter lithium discs consisting of five sheets of lithium foil having a total thickness of 0.10 inch (0.254 cm), about 4 ml of an electrolyte consisting of about 40 vol.% dioxolane, about 30 vol.% dimethoxyethane (DME), about 30 vol.% 3Me2Ox plus about 0.1% dimethelisoxazole (DMI) and containing 1M LiCF₃SO₃, a 1.0 inch (2.54 cm) diameter porous nonwoven polypropylene separator having a thickness of 0.01 inch (0.0254 cm) which absorbed some of the electrolyte and two grams of cathode mix compressed to form a cathode having an apparent interfacial area of 5 square centimeters. In the first cell the cathode mix consisted of Tekkosha electrolytic MnO₂ heat treated at 350°C for 20 hours, carbon black, and Teflon. The second cell employed the same type of components as in the first cell except that the Tekkosha MnO₂ was untreated. Each cell was discharged across a 1200-ohm load to a 1-volt cutoff and the cathode efficiencies assuming a 1-electron reaction were calculated along with the overall energy densities. The data obtained are shown in Table II.

TABLE II

Cathode	Efficiency* 1-electron	Cathode Energy	
		Density (Wh/in ³)	(J/cm ³)
Heat Treated MnO ₂	81.0%	72.8	15,993.1
Unheated MnO ₂	48.2%	35.2	7,732.9

*Coulombic

EXAMPLE III

Ten miniature button cells were constructed using a lithium anode, an electrolyte consisting of about 40 vol.% dioxolane, about 30 vol.% DME, about 30 vol.% 3Me2Ox plus about 0.1% DMI and containing 1 M LiCF₃SO₃, and a cathode containing 80 wt.% unheated or heat-treated MnO₂, 1.5 wt.% carbon black, 13.5 wt.% graphite, and 5.0 wt.% ethylene acrylic acid binder. The heat-treated MnO₂ was heated at a temperature of 350°C for 18 hours under an argon atmosphere. Each cell (0.452 inch (1.148 cm) diameter; 0.166 inch (0.422 cm) height) contained 0.3045 gram of the untreated MnO₂-containing cathode mix, or 0.3036 gram of the heat-treated MnO₂-containing cathode mix, 0.037 gram of lithium, a polypropylene separator, and 140 µl of the electrolyte. Each cell was placed on a continuous 6200-ohm background load and was pulsed on a 250-ohm load for 2 seconds once a week. Upon reaching a cutoff voltage of 1 volt, the cell capacity and cathode coulombic efficiency for each cell were calculated and are shown in Table III.

TABLE III

Cell Sample	MnO ₂	Cell Capability (mAh)	Cathode Efficiency (% 1 _e)
1	Heat Treated	37.6	50.0
2	Heat Treated	30.2	40.3
3	Heat Treated	39.2	52.2
4	Heat Treated	46.0	61.4
5	Heat Treated	41.4	55.3
6	Not Heated	6.1	8.2
7	Not Heated	26.4	35.5
8	Not Heated	34.2	45.7
9	Not Heated	10.9	14.5
10	Not Heated	4.9	6.6

EXAMPLE IV

Two cells were constructed similar to cells in Example II except that 1.5 ml of the electrolyte was used and in the first cell the cathode mix (33% porosity) consisted of 80 wt.% Tekkosha MnO₂, 10 wt.% carbon black and 10% Teflon, and in the second cell the cathode mix (45%

porosity) was the same except that the MnO_2 was electrolytic MnO_2 made by Union Carbide Corporation. The MnO_2 in each cell was heat treated and then blended into cathode pellets which were dried at 120°C in vacuum. The nominal interfacial electrode area for each electrode was 2 square centimeters. The cells were continuously discharged across a 3000-ohm load and the cathode coulombic efficiency of utilization to a 2.0 volt cutoff was calculated to be 88% for the Tekkosha MnO_2 containing cell and 99% for the other cell.

EXAMPLE V

Several 0.455 inch (1.156 cm) diameter, 0.165 inch (0.419 cm) high cells were constructed using 0.36 gram of cathode mix containing 86 wt.% Tekkosha MnO_2 , 8.5 wt.% carbon black, 2.5 wt.% graphite, and 3.0 wt.% Teflon; 0.03 gram lithium anode; and 140 μl of the electrolyte used in Example III. The MnO_2 , prior to forming the cathode mix, was heat treated at 350°C for 8 hours. Thereafter the molded cathode mix pellets were exposed to various levels of humidity for various lengths of time and then assembled into cells. The bulge measurements, if any, and the leakage, if any, after storage for various periods of time as shown in Table IV. The bulge measurement is the deviation in mils or millimeters of the height of the cell from the original height of the cell due to anode corrosion and/or gas evolution within the cell. Leakage is any electrolyte visually observable at the seal area of the cell. The cells were then discharged across a 15,000 ohm load until the voltage dropped to 2.4 volts. The average milliampere hours capacity delivered by the cells in each sample group is also shown in Table IV.

The data shown in Table IV demonstrate that the cells in which the heat-treated MnO_2 cathodes have been exposed to substantial levels of humidity begin to show bulging within 24 hours. Some decrease in bulge with time may be due to some of the gas escaping through the cover/gasket/container interface when leakage occurs.

TABLE IV (non-metric)

Group Sample	% Humidity	MnO ₂ Cathode Exposure Time	Average Bulge (mils) after Storage					Leakage*	mAh
			1 day	7 days	1 month	2 months	3 months		
1	<1	2 hrs.	—	—	0	—1	0	0/100	65
2	3+	2 hrs.	+3	+10	+2	+1	+2	0/45	61
3	2.7	2 hrs.	-0.7	-1	+0.2	0	-1	5/16	72
4	14	30 mins.	+10	+6	+4	+4	+3	15/20	66
5	14	2 hrs.	+14	+12	+9	+8	+7	6/20	62
6	15	25 mins.	+12	+6	+3	—	+3	—	—
7	19	50 mins.	+18.5	+22.5	+16	+14	+13	27/46	29
8	26	30 mins.	+11	+6	+4	+4	+3	7/20	68
9	26	2 hrs.	+17	+15	+10	+11	+10	6/19	58
10	27	40 mins.	+21	+21	+15	+10	+11	27/47	36
11	69	20-30 mins.	+23	+22	+18	+16	+15	7/19	41
12	72	45 mins.	+21	+24	+17	+14	+4	37/50	31

*the first number is the number of cell where electrolyte was observed and the second number is the total number of cells in the group

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TABLE IV (METRIC)

Group Sample	% Humidity	MnO ₂ Cathode Exposure Time	Average Bulge (millimeters) after storage					Leakage*	mAh
			1 day	7 days	1 month	2 months	3 months		
1	<1	2 hrs.	—	—	0	—0.025	0	0/100	65
2	3+	2 hrs.	+0.076	+0.25	+0.051	+0.025	+0.2	0/45	61
3	2.7	2 hrs.	—0.018	—0.025	+0.0051	0	—0.025	5/16	72
4	14	30 mins.	+0.25	+0.15	+0.1	+0.1	+0.076	15/20	66
5	14	2 hrs.	+0.36	+0.3	+0.23	+0.2	+0.18	6/20	62
6	15	25 mins.	+0.3	+0.15	+0.076	—	+0.076	—	—
7	19	50 mins.	+0.47	+0.57	+0.41	+0.36	+0.33	27/46	29
8	26	30 mins.	+0.28	+0.15	+0.1	+0.1	+0.076	7/20	68
9	26	2 hrs.	+0.43	+0.38	+0.25	+0.28	+0.25	6/19	58
10	27	40 mins.	+0.53	+0.53	+0.38	+0.25	+0.28	27/47	36
11	69	20-30 mins.	+0.58	+0.56	+0.46	+0.41	+0.38	7/19	41
12	72	45 mins	+0.53	+0.61	+0.43	+0.36	+0.1	37/50	31

*the first number is the number of cell where electrolyte was observed and the second number is the total number of cells in the group

CLAIMS

1. A nonaqueous cell comprising an active metal anode, a manganese dioxide-containing cathode and a liquid organic electrolyte comprising 3-methyl-2-oxazolidone together with a solute and wherein the manganese dioxide has a water content of less than 1 weight percent based on the weight of the manganese dioxide. 5
2. A nonaqueous cell as claimed in claim 1 wherein the water content is less than 0.5 weight percent based on the weight of the manganese dioxide.
3. A nonaqueous cell as claimed in claim 2 wherein the water content is less than 0.2 weight percent based on the weight of the manganese dioxide. 10
4. A nonaqueous cell as claimed in any one of claims 1 to 3 wherein the cathode comprises manganese dioxide, a conductive agent and a binder.
5. A nonaqueous cell as claimed in claim 4 wherein the conductive agent is carbon or graphite and the binder is polytetrafluorethylene or ethylene acrylic acid polymer.
6. A nonaqueous cell as claimed in any one of claims 1 to 5 wherein at least one cosolvent is contained in the liquid organic electrolyte. 15
7. A nonaqueous cell as claimed in claim 6 wherein said solvent is selected from tetrahydrofuran, dioxolane, dimethoxyethane, dimethyl isoxazole, diethyl carbonate, propylene carbonate, ethylene glycol sulfite, dioxane and dimethyl sulfite.
8. A nonaqueous cell as claimed in any one of claims 1 to 7 wherein said solute is selected from MCF_3SO_3 , MBF_4 , MC10_4 , and $\text{MM}'\text{F}_6$ wherein M is lithium, sodium or potassium and M' is phosphorus, arsenic or antimony. 20
9. A nonaqueous cell as claimed in any one of claims 1 to 8 wherein said active metal anode is selected from lithium, potassium, sodium, calcium, magnesium, aluminum and alloys thereof. 25
10. A nonaqueous cell as claimed in any one of claims 1 to 6 wherein the anode is lithium and the electrolyte is LiCF_3SO_3 dissolved in 3-methyl-2-oxazolidone, dioxolane, dimethoxyethane and dimethyl isoxazole.
11. A nonaqueous cell as claimed in any one of claims 1 to 6 wherein the anode is lithium and the electrolyte is LiBF_4 dissolved in 3-methyl-2-oxazolidone and dimethoxyethane. 30
12. A nonaqueous cell as claimed in any one of claims 1 to 6 wherein the anode is lithium and the electrolyte is LiCF_3SO_3 dissolved in 3-methyl-2-oxazolidone and dimethoxyethane.
13. A nonaqueous cell as claimed in any one of claims 1 to 6 wherein the anode is lithium and the electrolyte is LiCF_3SO_3 dissolved in 3-methyl-2-oxazolidone and propylene carbonate.
14. A nonaqueous cell as claimed in claim 1 and substantially as hereinbefore described with reference to any one of the Examples II to IV. 35



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