

"NON-AQUEOUS CELLS"

The invention relates to a nonaqueous cell utilizing an active metal anode, a nonaqueous electrolyte solution comprising a solute dissolved in at least one organic solvent and a manganese dioxide-containing solid cathode containing a minor amount of manganese carbonate to improve pulse voltage capability at low temperatures such as -10°C .

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 electrolyte systems based on organic solvents.

The term "nonaqueous electrolyte" in the prior art refers to an electrolyte which is composed of a solute, for example, a salt or a 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 - (gamma)butyrolactone. The term "Periodic Table" as used herein refers to the Periodic Table of the Elements as set forth on the inside front cover of the Handbook of Chemistry and Physics, 63rd Edition, CRC Press Inc., Boca Raton, Florida, 1982-1983.

Although manganese dioxide has been mentioned as a cathode for cell applications, manganese dioxide inherently contains an unacceptable amount of water, both of the adsorbed and bound (absorbed) 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 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. It is therefore 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.

5 In order to reduce the water content in manganese dioxide, several processes have been developed. For example, U.S. Patent 4,133,856
discloses a process for producing an MnO_2 electrode (cathode) for nonaqueous cells whereby the
10 MnO_2 is initially heated within a range of 350°C to 430°C so as to substantially remove both the adsorbed 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°C to 350°C prior to its assembly into a cell. British
15 Patent 1,199,426 also discloses the heat treatment of MnO_2 in air at 250°C to 450°C to substantially remove its water component.

U.S. Patent 4,285,122 discloses a process whereby a homogeneous mass of particulate manganese
20 dioxide is heat-treated and then contacted with an organic solvent that substantially fills the pores of the manganese dioxide with a layer of the organic solvent which effectively decreases the affinity or propensity of the manganese dioxide for readsorbing
25 moisture.

U.S. Patent 4,379,817 discloses a process whereby the walls of the pores of manganese dioxide are coated by vapor-depositing an organic solvent thereon to reduce the manganese dioxide's affinity
30 for adsorbing moisture when exposed to a moisture-containing environment for a fixed time period.

Although manganese dioxide with reduced water content is better suited for nonaqueous cell systems, it was noted that cells employing this type of active material had a tendency to show increased internal impedance during storage. This condition is accompanied by poor closed circuit voltage, poor high and low temperature shelf life, poor cell voltage maintenance characteristics, and poor pulse rate and discharge capabilities.

10 European Patent Application No.83111812.0
(Publication No.0110344) discloses a nonaqueous cell employing a solid cathode comprising manganese dioxide, a binder, a conductive agent and at least one compound selected from the group consisting of
15 alkaline earth metal hydroxides such as $Mg(OH)_2$, $Ca(OH)_2$, $Ba(OH)_2$ and $Sr(OH)_2$ and alkaline earth metal carbonates, such as $MgCO_3$, $CaCO_3$, $BaCO_3$ and $SrCO_3$ to suppress or minimize the increase in the internal impedance of the cell which may occur during storage
20 or discharge.

United States Patent Specification No.4,465,747 discloses a nonaqueous cell employing a manganese dioxide-containing solid cathode having a minor amount of an alkali metal or an alkaline earth metal additive
25 such as Li_2SiO_3 , $Li_2B_4O_7$, Li_2MoO_4 , Li_3PO_4 or Li_2WO_4 to suppress the build-up of internal impedance in the cell during storage and discharge that may occur with electrolyte degradation.

It has now been found possible to provide an additive for a manganese dioxide-containing cathode intended for use in a nonaqueous cell that will improve the pulse voltage capability of the cell at low temperatures such as -10°C ., more particularly to provide a nonaqueous cell employing among other components a manganese dioxide-containing solid cathode having a minor amount of an additive of manganese carbonate (MnCO_3) to improve the pulse voltage capability at -10°C .

According to the present invention there is provided a nonaqueous cell which comprises an active metal anode, a nonaqueous electrolyte solution comprising a solute dissolved in at least one organic solvent and a solid cathode comprising manganese dioxide, a binder and a conductive agent, the cathode containing a minor amount of manganese carbonate.

The manganese carbonate additive used in the present invention should desirably be incorporated in the MnO_2 -containing cathode by an amount between about 0.1 and about 5 weight percent based on the dry weight of the cathode, preferably, between about 0.5 and about 3 weight percent and more preferably about 1 to about 2 weight percent. An amount of the additive below 0.1 weight percent will be ineffective to

substantially improve the low temperature pulse voltage capability. An amount of the additive above 5 weight percent would generally provide needless excess of the additive for improving the low temperature pulse voltage capability while also decreasing the volume available for the active cathode material for given size cells. It will be appreciated that the range of the additive will also depend upon the type of manganese dioxide employed.

- 10 To suppress or minimize an increase in the internal impedance of the cell which may occur during normal storage or discharge, an additive may be included in the manganese dioxide cathode as disclosed in European Patent Application No. 83111812.0
- 15 (Publication No.0110344) and United States Patent Specification No. 4,465,747. Specifically European Patent Application No.83111812.0 discloses a nonaqueous cell employing a manganese dioxide cathode which contains a minor amount of at least one compound
- 20 selected from the group consisting of alkaline earth metal hydroxides such as $Mg(OH)_2$, $Ca(OH)_2$, $Ba(OH)_2$ and $Sr(OH)_2$ and alkaline earth metal carbonates, such as $MgCO_3$, $CaCO_3$, $BaCO_3$ and $SrCO_3$ to suppress or minimize the increase in the internal impedance of the cell
- 25 which may occur during storage or discharge. United States Patent Specification No.4,465,747 discloses a nonaqueous cell employing a manganese dioxide cathode which contains a minor amount of an additive selected from the group consisting of the borates, silicates,

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molybdates, phosphates, aluminates, niobates, tantalates, titanates, vanadates, zirconates, manganates (Mn^{+4}), cobaltates, and tungstates of alkali metals or alkaline earth metals wherein the alkali metal is selected from the group consisting of lithium, potassium, rubidium and cesium and wherein the alkaline earth metal is selected from the group consisting of magnesium, calcium, strontium, and barium to suppress or minimize the increase in the internal impedance of the cell which may occur during storage or discharge. Suitable additives disclosed in this application include lithium metasilicate (Li_2SiO_3), lithium tetraborate ($Li_2B_4O_7$), lithium molybdate (Li_2MoO_4), lithium orthophosphate (Li_3PO_4), lithium orthosilicate (Li_4SiO_4), lithium metaborate ($LiBO_2$), lithium tungstate (Li_2WO_4), lithium niobate ($LiNbO_3$), lithium tantalate ($LiTaO_3$), lithium zirconate (Li_2ZrO_3), lithium metavanadate ($LiVO_3$), lithium titanate (Li_2TiO_3) and lithium aluminate ($LiAlO_2$). The preferred additives would be lithium metasilicate, lithium tetraborate, lithium orthophosphate, lithium molybdate and lithium tungstate.

The additive to the manganese dioxide-containing cathode to suppress or minimize the increase in the internal impedance of the cell which may occur during normal storage or discharge can be incorporated in the cathode by an amount between about 0.05 and about 10 weight percent based on the dry weight of the cathode, preferably, between about 0.1 and about 3 weight percent and

more preferably about 1 weight percent. It will be appreciated that the range of the additive will also depend upon the type of manganese dioxide employed. Of the additives disclosed in the United States Patent Specification and European Patent Application referred to hereinabove, $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ are the most preferred to be used along with the additive used in the present invention. The manganese carbonate additive and any additional additive if used can be blended directly with the dry cathode mix or can be added during the aqueous processing of the wet cathode mix. The dry mix is then molded into cathode pellets using conventional techniques.

The water inherently contained in both the 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 atmospheres, higher temperatures may be employed.

Preferably, the manganese dioxide should be heat-treated to remove its water content in the crystal lattice to below about 1 weight percent and then it can be mixed with a conductive agent such as graphite, carbon or the like and a binder such as Teflon (trademark for polytetrafluoroethylene), ethylene acrylic acid copolymer or the like to

produce a solid cathode. If desired, a small amount of the electrolyte can be incorporated into the manganese dioxide mix. In addition, another active cathode material such as a poly-carbon fluoride may also be added.

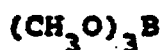
An added possible benefit in the removal of substantially all the water from manganese dioxide is that if small amounts of water are present in the cell's electrolyte then the manganese dioxide will adsorb the main portion of that water from the electrolyte and thereby prevent or substantially delay 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.

Useful highly active metal anode materials include aluminum, the alkali metals, alkaline earth metals and alloys of alkali metals or alkaline earth metals with each other and other metals. The term "alloy" as used herein and in the appended claims is intended to include mixtures, solid solutions, such as lithium-magnesium, and intermetallic compounds, such as lithium monoaluminide. The preferred anode materials are lithium, sodium, potassium, magnesium, calcium and alloys thereof.

Useful organic solvents employed alone or mixed with one or more other solvents for use in this invention include the following classes of compounds:

Alkylene nitriles: e.g., crotonitrile
(liquid range, -51.1°C to 120°C)

Trialkyl borates: e.g., trimethyl borate,



(liquid range, -29.3 to 67°C)

Tetraalkyl silicates: e.g., tetramethyl silicate,



Nitroalkanes: e.g., nitromethane, CH_3NO_2

(liquid range, -17 to 100.8°C)

Alkyl nitriles: e.g., acetonitrile, CH_3CN

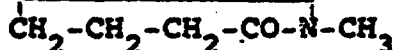
(liquid range, -45 to 81.6°C)

10 Dialkylamides: e.g., dimethylformamide,



(liquid range, -60.48 to 149°C)

Lactams: e.g., N-methylpyrrolidone,



15 (liquid range, -16 to 202°C)

Tetraalkylureas: e.g., tetramethylurea,



(liquid range, -1.2 to 166°C)

Monocarboxylic acid esters: e.g., ethyl acetate

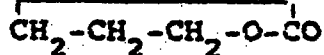
20 (liquid range, -83.6 to 77.06°C)

Orthoesters: e.g., trimethylorthoformate,



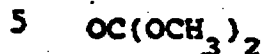
(boiling point, 103°C)

Lactones: e.g., γ (gamma)-butyrolactone.



(liquid range, -42 to 206°C)

Dialkyl carbonates: e.g., dimethyl carbonate.



(liquid range, 2 to 90°C)

Alkylene carbonates: e.g., propylene carbonate.



(liquid range, -48 to 242°C)

10 Monoethers: e.g., diethyl ether

(liquid range, -116 to 34.5°C)

Polyethers: e.g., 1,1- and 1,2-dimethoxyethane

(liquid ranges, -113.2 to 64.5°C and -58 to 83°C, respectively)

15 Cyclic ethers: e.g., tetrahydrofuran

(liquid range, -65 to 67°C); 1,3-dioxolane

(liquid range, -95 to 78°C)

Nitroaromatics: e.g., nitrobenzene

(liquid range, 5.7 to 210°C)

20 Aromatic carboxylic acid halides: e.g., benzoyl chloride

(liquid range, 0 to 197°C); benzoyl bromide

(liquid range, -24 to 218°C)

Aromatic sulfonic acid halides: e.g., benzene

25 sulfonyl chloride (liquid range, 14.5 to 251°C)

Aromatic phosphonic acid dihalides: e.g., benzene
phosphonyl dichloride (boiling point, 258°C)

Aromatic thiophosphonic acid dihalides: e.g.,
benzene thiophosphonyl dichloride (boiling point,
5 : 124°C at 5 mm)

Cyclic sulfones: e.g., sulfolane,

$\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-SO}_2$ (melting
point, 22°C); 3-methylsulfolane (melting
point, -1°C)

10 Alkyl sulfonic acid halides: e.g., methanesulfonyl
chloride
(boiling point, 161°C)

Alkyl carboxylic acid halides: e.g., acetyl chloride
(liquid range, -112 to 50.9°C); acetyl
15 bromide (liquid range, -96 to 76°C);
propionyl chloride (liquid range, -94 to
80°C)

Saturated heterocyclics: e.g., tetrahydrothiophene
(liquid range, -96 to 121°C);
20 3-methyl-2-oxazolidone (melting point,
15.9°C)

Dialkyl sulfamic acid halides: e.g., dimethyl
sulfamyl chloride (boiling point, 80°C at 16mm)

Alkyl halosulfonates: e.g., ethyl chlorosulfonate
25 (boiling point, 151°C)

Unsaturated heterocyclic carboxylic acid halides:
e.g., 2-furoyl chloride (liquid range, -2 to 173°C)

5 Five-membered unsaturated heterocyclics: e.g.,
3,5-dimethylisoxazole (boiling point, 140°C); 1-methylpyrrole (boiling point, 114°C); 2,4-dimethylthiazole (boiling point, 144°C);
furan (liquid range, -85.65 to 31.36°C)

10 Esters and/or halides of dibasic carboxylic acids:
e.g., ethyl oxalyl chloride (boiling point, 135°C).

Mixed alkyl sulfonic acid halides and carboxylic acid halides:
15 e.g., chlorosulfonyl acetyl chloride (boiling point, 98°C at 10mm)

Dialkyl sulfoxides: e.g., dimethyl sulfoxide (liquid range, 18.4 to 189°C)

20 Dialkyl sulfates: e.g., dimethylsulfate (liquid range, -31.75 to 188.5°C)

Dialkyl sulfites: e.g., dimethylsulfite (boiling point, 126°C)

Alkylenesulfites: e.g., ethylene glycol sulfite (liquid range, -11 to 173°C)

Halogenated alkanes: e.g., methylene chloride
(liquid range, -95 to 40°C);

1,3-dichloropropane (liquid range, -99.5 to
120.4°C)

5 The preferred solvents are sulfolane;
tetrahydrofuran; methyl-substituted tetrahydrofuran;
1,3-dioxolane; 3-methyl-2-oxazolidone; propylene
carbonate; γ (gamma)-butyrolactone; ethylene
glycol sulfite; dimethylsulfite; dimethyl sulfoxide;
10 and 1,1- and 1,2-dimethoxyethane. Of the preferred
solvents, the best are sulfolane; 3-methyl-2-
oxazolidone; propylene carbonate; 1,1- and
1,2-dimethoxyethane, and 1,3-dioxolane because they
appear more chemically inert to battery components
15 and have wide liquid ranges, and especially because
they permit highly efficient utilization of the
cathode materials.

Low viscosity cosolvents which can be used
include tetrahydrofuran (THF), methyl-substituted
20 tetrahydrofuran (Me-THF), dioxolane (DIOX),
dimethoxyethane (DME), dimethyl isoxazole (DMI),
diethyl carbonate (DEC), ethylene glycol sulfite
(EGS), dioxane, dimethyl sulfite (DMS) or the like.
Specifically, the total amount of the low viscosity
25 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.

The ionizing solute for use in the
30 invention may be a simple or double salt or mixtures
thereof, for example, LiCF_3SO_3 , LiBF_4 and
 LiClO_4 , which will produce an ionically conductive

5 solution when dissolved in one or more solvents.
Preferred solutes are complexes of inorganic or
organic Lewis acids and inorganic ionizable salts.
The only requirements for utility are that the
10 salts, whether simple or complex, be compatible with
the solvent or solvents being employed and that they
yield a solution which is sufficiently ionically
conductive. According to the Lewis or electronic
concept of acids and bases, many substances which
15 contain no active hydrogen can act as acids or
acceptors of electron doublets. The basic concept
is set forth in the chemical literature (Journal of
the Franklin Institute, Vol. 226 - July/December,
1938, pages 293-313 by G.N Lewis).

20 A suggested reaction mechanism for the
manner in which these complexes function in a
solvent is described in detail in U.S. Patent No.
3,542,602 wherein it is suggested that the complex
or double salt formed between the Lewis acid and the
ionizable salt yields an entity which is more stable
than either of the components alone.

25 Typical Lewis acids suitable for use in the
present invention include aluminum fluoride,
aluminum bromide, aluminum chloride, antimony
pentachloride, zirconium tetrachloride, phosphorus
pentachloride, boron fluoride, boron chloride, boron
bromide, phosphorous pentafluoride, arsenic
pentafluoride and antimony pentafluoride.

30 Ionizable salts useful in combination with
the Lewis acids include lithium fluoride, lithium
chloride, lithium bromide, lithium sulfide, sodium
fluoride, sodium chloride, sodium bromide, potassium
fluoride, potassium chloride and potassium bromide.

It will be obvious to those skilled in the art that the double salts formed by a Lewis acid and an inorganic ionizable salt may be used as such or the individual components may be added to the solvent separately to form the double salt or the resulting ions in situ. One such double salt, for example, is that formed by the combination of aluminum chloride and lithium chloride to yield lithium aluminum tetrachloride.

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EXAMPLE 1

Several miniature cells having a nominal 20 mm diameter and nominal 1.6 mm height were constructed. Each cell contained 0.022 gram lithium as the anode; 0.36 gram of a particulate cathode mix containing MnO_2 in the weight percent shown in Table 1. 3 weight percent acetylene black, 3 weight percent polytetrafluoroethylene and the weight percent of the selected additive shown in Table 1, all percentages based on the dry weight of the cathode; and about 0.092 milliliters of an electrolyte consisting of about 50 volume percent propylene carbonate, 50 volume percent dimethoxyethane (DME) and containing 1 M LiCF_3SO_3 . Additional miniature cells were constructed as above except that they did not contain any additive.

The closed circuit voltages (Initial Volts. Fresh) of three cells of each type were observed 2 seconds after initiation of a 400-ohm discharge load. The average of the three cells was calculated and the results are shown in Table I.

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Three cells of each type were then discharged across a 30K-ohm load with a superimposed 400-ohm pulse load (once per day, 3 days per week, for two seconds) at 21°C. The voltages were

5 recorded with time to a 2.0 volt cutoff for both the background load and the pulse discharge load.

The above two tests were repeated for cells stored at 60°C for 40 days and the data calculated (Initial Volts, Stored) are shown in Table 1.

10 For the above test, the average milliamperere hour (mAh) outputs to 2.0 volts (background and pulse loads) for three fresh cells of each type were also calculated and are shown in Table 1. The same

15 data for cells that were stored at 60°C for 40 days are shown in Table 1.

TABLE 1

Sample Cells	Additive	Initial Volts		Discharge Capacity (mAh) to 2.0 V			
		Wt% MnO ₂	Fresh (volt)	Stored (volt)	*Background Load Fresh Stored	**Pulse Load Fresh Stored	
A	NONE (control)	94	2.94	2.48	83 69	62 44	
B	1% MnCO ₃	93	2.82	2.13	75 67	64 33	
C	1% MnCO ₃ / 1% Ca(OH) ₂	92	2.84	2.81	75 77	64 49	
D	3% MnCO ₃ / 1% Ca(OH) ₂	90	2.90	2.81	79 76	66 51	

* to 2.0 volt cutoff on 30-K ohm background load.

** to 2.0 volt cutoff on 400-ohm pulse load.

EXAMPLE 2

Several miniature cells were produced as in Example 1 with or without an additive as shown in Table 2. Fresh cells were chilled at -10°C for 4 hours and then discharged across a 400-ohm pulse load for two seconds. The average closed circuit voltage (fresh) at 2 seconds observed for three cold cells of each type is shown in Table 2. The cells were then continuously discharged across a 30K-ohm load at 21°C for 11 days after which they were again chilled at -10°C for four hours. The cold cells were then discharged across a 400-ohm pulse load for 2 seconds and the average closed circuit voltage at 2 seconds was calculated for three cells of each type. The results obtained (11 days) are shown in Table 2. The cells were then continuously discharged across a 30K-ohm load at 21°C for an additional 11 days after which they were again chilled at -10°C for four hours. The cold cells were then discharged across a 400-ohm pulse load for 2 seconds and the average closed circuit voltage at 2 seconds was calculated for three cells of each type. The results obtained (22 days) are shown in Table 2.

TABLE 2

		<u>Pulse Voltage (volts)</u>			
	<u>Cell Sample</u>	<u>Additive</u>	<u>Fresh</u>	<u>11 Days</u>	<u>22 Days</u>
5	E	None	2.55	2.24	1.89
	F	1% MnCO ₃	2.56	2.31	2.16
	G	1% Ca(OH) ₂	2.46	2.14	1.92
	H	1% Ca(OH) ₂ / 1% MnCO ₃	2.67	2.24	2.00
10	I	1% Ca(OH) ₂ / 3% MnCO ₃	2.48	2.20	1.81

The data observed from Examples 1 and 2 demonstrate that the additives used in the present invention can improve the -10°C pulse voltage for MnO_2 -containing cells. The data also demonstrate that the additive used in the present invention (MnCO_3) can be used with another additive such as Ca(OH)_2 , such other additive incorporated to improve the pulse voltage and capacity maintenance on storage. Thus, the combination of the additive of the present invention along with an additional additive such as Ca(OH)_2 can be used to simultaneously improve the -10°C pulse voltage capability and the pulse voltage and capacity maintenance on storage. Accordingly, where the cells are expected to be stored for a long period of time, it would be preferable to add an additional additive, such as Ca(OH)_2 , to the cathode for the reasons discussed above.

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CLAIMS

1. A nonaqueous cell which comprises an active metal anode, a nonaqueous electrolyte solution comprising a solute dissolved in at least one organic solvent and a solid cathode
5 comprising manganese dioxide, a binder and a conductive agent, the cathode containing a minor amount of manganese carbonate.
2. A nonaqueous cell as claimed in claim 1, in which the manganese carbonate in the cathode is present in an amount between about 0.1 weight percent
10 and about 5 weight percent based on the dry weight of the cathode.
3. A nonaqueous cell as claimed in claim 2, in which the manganese carbonate is present in an amount between about 0.5 weight percent and about 3 weight
15 percent based on the dry weight of the cathode.
4. A nonaqueous cell as claimed in any of claims 1 to 3, in which the cathode contains 0.05 to 10 weight per cent, based on the dry weight of the cathode, of an additive selected from alkaline earth
20 metal hydroxides; alkaline earth metal carbonates; the borates, silicates, molybdates, phosphates, aluminates, niobates, tantalates, titanates, vanadates, zirconates, manganates (Mn +4), cobaltates, and tungstates of alkali metals or alkaline earth
25 metals wherein the alkali metal is selected from lithium, potassium, rubidium and cesium and wherein the alkaline earth metal is selected from magnesium, calcium, strontium, and barium and mixtures thereof.
5. A nonaqueous cell as claimed in claim 4, in
30 which the additive is selected from lithium metasilicate, lithium tetraborate, lithium molybdate, lithium orthophosphate, lithium tungstate, $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$.



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6. A nonaqueous cell as claimed in claim 5, in which the additive is Ca(OH)_2 .

7. A nonaqueous cell as claimed in any of claims 4 to 6 in which the additive in the cathode is present in an amount between about 0.1 weight percent and about 3 weight percent based on the dry weight of the cathode.

8. A nonaqueous cell as claimed in any of claims 1 to 7, in which the active metal anode is selected from lithium, sodium, potassium, magnesium, calcium, aluminium and alloys thereof.

9. A nonaqueous cell as claimed in any of claims 1 to 8, in which the organic solvent is selected from sulfolane; 1,3-dioxolane; 3-methyl-2-oxazolidone; propylene carbonate; γ (gamma)-butyrolactone; ethylene glycol sulfite; dimethylsulfite; dimethyl sulfoxide; and 1,1- and 1,2-dimethoxyethane.

10. A nonaqueous cell as claimed in any of claims 1 to 9, in which any water inherently present in the manganese dioxide is substantially removed.

11. A nonaqueous cell as claimed in any of claims 1 to 10, in which the manganese dioxide is heat treated to remove its water content in the crystal lattice to below about 1 weight percent.

12. A nonaqueous cell according to claim 1, substantially as hereinbefore described with particular reference to Example 1 or 2.
