

NONAQUEOUS CELL

The invention relates to a nonaqueous cell utilizing an active metal anode, a liquid electrolyte based on organic solvents and a cathode comprising
5 antimony trisulfide, and also to a solid cathode for such a cell.

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,
10 sodium, and the like and the efficient use of high energy density cathode materials. 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
15 in order to realize the high energy density obtainable through the 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
20 on organic solvents. A large number of nonaqueous electrolyte solutions based on organic solvents is taught in the art as being suitable for a wide variety of cell systems.

Although a large number of known solid cathode
25 materials is suitable for nonaqueous cell systems, there is always a need for new solid cathode materials

to help fill the demand created by the large number of battery-powered devices being marketed. For example, the toy industry has recently embarked upon a programme of marketing a multiplicity of computerized games some of which are educational in nature. Many of these devices require portable power sources and, therefore, any new cell system would be welcomed.

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.

It is an object of the present invention to provide new cathode materials for nonaqueous cell systems based on organic solvents.

The invention is directed to a new solid cathode material for nonaqueous electrolyte cell systems

based on organic solvents which cathode material comprises antimony trisulfide (Sb_2S_3).

The antimony trisulfide can be mixed with a conductive agent such as graphite, carbon or the like and a binder such as Teflon (trademark for polytetrafluoroethylene), ethyleneacrylic acid copolymer or the like to produce a solid cathode electrode. If desired in some applications, another active cathode material could be utilized with antimony trisulfide to form the cathode of the cell.

By use of the present invention there may be provided a solid cathode material for a liquid non-aqueous cell system based on organic solvents, a new nonaqueous cell system employing new solid cathode materials comprising antimony trisulfide, and a new nonaqueous cell system employing an active metal anode, an electrolyte based on e.g. 3-methyl-2-oxazolidone (3Me20x) as the organic solvent and an active cathode comprising antimony trisulfide.

Advantages of antimony trisulfide for use as an active cathode (electrochemically reducible) material in a nonaqueous electrolyte system based on organic solvents are:

- 1) A fully discharged antimony trisulfide (Sb_2S_3) cathode does not exhibit excessive expansion as do other cathodes such as FeS_2 .

2) A lithium/Sb₂S₃ cell will deliver substantially its entire 6-electron theoretical Sb₂S₃ capacity on low drain conditions (about 0.15 milliamperes per square centimetre).

5 3) A lithium/Sb₂S₃ cell will discharge at a substantially unipotential level.

4) A lithium/Sb₂S₃ cell will deliver a discharge voltage compatible with that of Zn/MnO₂ cells and Az/Ag₂O cells, thus making it interchangeable with
10 such cells.

5) Antimony trisulfide is located in many deposits throughout the world thus making it a readily available material for use in cell manufacture.

Useful highly active metal anode materials include
15 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-
20 magnesium and intermetallic compounds, such as lithium monoaluminide. The preferred anode materials are lithium, sodium, potassium, calcium and alloys thereof.

In nonaqueous cells, useful organic solvents employed alone or mixed with one or more other solvents
25 for use in preparing electrolytes employed in the cell of 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, $(\text{CH}_3\text{O})_3\text{B}$
(liquid range -29.3 to 67°C)
- 5 Tetraalkyl silicates: e.g. tetramethyl silicate,
 $(\text{CH}_3\text{O})_4\text{Si}$ (boiling point 121°C)
- Nitroalkanes: e.g., nitromethane, CH_3NO_2
(liquid range -17 to 100.8°C)
- Alkyl nitriles: e.g., acetonitrile, CH_3CN
10 (liquid range -45 to 81.6°C)
- Dialkylamides: e.g., dimethylformamide, $\text{HCON}(\text{CH}_3)_2$
(liquid range -60.48 to 149°C)
- Lactams: e.g., N-methylpyrrolidone,
 $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CO-N-CH}_3$ (liquid range -16 to 202°C)
- 15 Tetraalkylureas: e.g., tetramethylurea,
 $(\text{CH}_3)_2\text{N-CO-N}(\text{CH}_3)_2$ (liquid range -1.2 to 166°C)
- Monocarboxylic acid esters: e.g., ethyl acetate
(liquid range -83.6 to 77.06°C)
- Orthoesters: e.g., trimethylorthoformate, $\text{HC}(\text{OCH}_3)_3$
20 (boiling point 103°C)
- Lactones: e.g., γ (gamma)butyrolactone, $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-O-CO}$
(liquid range -42 to 206°C)
- Dialkyl carbonates: e.g., dimethyl carbonate,
 $\text{OC}(\text{OCH}_3)_2$ (liquid range 2 to 90°C)
- 25 Alkylene carbonates: e.g., propylene carbonate,
 $\text{CH}(\text{CH}_3)\text{CH}_2\text{-O-CO-O}$ (liquid range -48 to 242°C)

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)

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 210.8°C)

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 sulfonyl chloride (liquid range 14.5 to 251°C)

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

Aromatic thiophosphonic acid dihalides: e.g., benzene thiophosphoryl dichloride (boiling point 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).

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 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); 3-methyl-2-oxa-
5 zolidone (melting point 15.9°C)

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

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

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

Five-membered unsaturated heterocyclics: e.g.,
3,5-dimethylisoxazole (boiling point 140°C);
1-methylpyrrole (boiling point 114°C);
15 2,4-dimethylthiazole (boiling point 114°C)
furan (liquid range -85.65 to 31.36°C)

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
20 halides: e.g., chlorosulfonyl acetyl chloride
(boiling point 98°C at 10 mm).

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

Dialkyl sulfates: e.g., dimethylsulfate (liquid range
25 -31.75 to 188.5°C)

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

Alkyene sulfites: e.g, ethylene glycol sulfite

(liquid range -11 to 173°C)

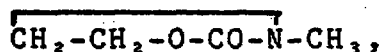
Halogenated alkanes: e.g, methylene chloride

(liquid range -95 to 40°C); 1,3-dichloropropane

5 (liquid range -99.5 to 120.4°C)

Of the above, the preferred solvents are sulfolane; tetrahydrofuran; 1, 3-dioxolane; 3-methyl-2-oxazolidone; propylene or ethylene carbonate; γ -butyrolactone; 1,2-dimethoxyethane and mixtures thereof because they
10 appear more chemically inert to battery components and have wide liquid ranges, and especially because they permit highly efficient utilization of the cathode materials.

A preferred electrolyte solution for use in this
15 invention is a 3-methyl-2-oxazolidone-based electrolyte solution. Liquid organic 3-methyl-2-oxazolidone material, (3Me2Ox)



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

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
25 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
5 electrolyte for nonaqueous cells which can operate or perform at a high energy density level.

The low viscosity cosolvents which can be used along with 3Me2Ox include tetrahydrofuran (THF), methyl-substituted tetrahydrofuran (met-THF),
10 dioxolane (DIOX), dimethoxyethane (DME), or the like. Dimethoxyethane (DME), dioxolane (DIOX) and tetrahydrofuran (THF) are preferred cosolvents because of their compatibility with metal salts dissolved in liquid 3Me2Ox and their chemical inertness to cell components.
15 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.

20 The ionizing solute for use in the invention may be a simple or double salt or mixtures thereof, e.g., LiCF_3SO_3 , or LiClO_4 , which will produce an ionically conductive solution when dissolved in one or more solvents. Useful solutes include complexes of
25 inorganic or organic Lewis acids and inorganic ionizable salts. The only requirements for utility are that the 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
5 which 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).

10 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
15 an entity which is more stable than either of the components alone.

Typical Lewis acids suitable for use in the present invention include aluminium fluoride, aluminium bromide, ~~aluminium~~ aluminium chloride, antimony pentachloride, zirconium
20 tetrachloride, phosphorus pentachloride, boron fluoride, boron chloride and boron bromide.

Ionizable salts useful in combination with the Lewis acids include lithium fluoride, lithium chloride, lithium bromide, lithium sulfide, sodium fluoride,
25 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
5 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 boron fluoride and lithium fluoride to yield lithium tetrafluoroborate.

A separator for use in this invention has to be
10 chemically inert and insoluble in the cell system and have a porosity so as to permit the liquid electrolyte to permeate through and contact the anode of the cell, thus establishing an ion transfer path between the anode and cathode.

15 The container housing for the cell can be made of stainless steel or some other conductive material that will not corrode or otherwise deteriorate when in contact with the cell materials.

The insulating member disposed between the cover
20 and the container has to be stable in the presence of the cell components and can be selected from such materials as polytetrafluoroethylene, fluorinated ethylene-propylene copolymer, polychlorotrifluoro-ethylene, perfluoro-alkoxy polymer, polyvinyl, poly-
25 ethylene, polypropylene, polystyrene, nylon, etc.

The sole figure of the accompanying drawing is a graph containing data showing the discharge

characteristics of the cell disclosed and described in the following example, and will be referred to in the example.

EXAMPLE

5 A flat-type cell was constructed utilizing a stainless steel base having therein a shallow depression into which the cell contents were placed and over which a spring-loaded stainless steel plate was placed. The contents of the cell consisted of
10 four 0.375 inch diameter lithium discs (0.174 gram) having a total thickness of 0.180 inch (representing excess anode material), about 0.5 ml of an electrolyte consisting of about 40 vol. % 1,3-dioxolane, about
15 30 vol. % 1,2-dimethoxyethane (DME), about 30 vol. % 3Me2Ox plus about 0.1% dimethylisoxazole (DMI) and containing 1 M LiCF_3SO_3 , a 0.45 inch diameter porous nonwoven polypropylene separator (0.01 inch thick) which absorbed some of the electrolyte and 0.302 gram
20 of a cathode mix compressed to form a cathode having a solids packing of 59%. The cathode mix consisted of 0.2266 gram of antimony trisulfide (Sb_2S_3), 0.0395 gram of graphite, 0.0085 gram of acetylene black and 0.0271 gram of polytetrafluoroethylene. The cell was discharged across a 15 K-ohm load and the voltage
25 observed with time is shown as the curve in the Figure. In addition, at various time periods, the cell was discharged across a 1 K-ohm load (pulse

-13-

discharge) for about 2 seconds, and the voltages observed are shown as the points identified as "+" in Figure 1. As evident from the Example, the cell of this invention had a relatively unipotential discharge
5 for more than 40 days and delivered 107 milliamperes-hours to a 1.2 volt cutoff. Based on a 6-electron discharge reaction for Sb_2S_3 , this cell delivered 100% of its theoretical capacity.

While the present invention has been described
10 with reference to many particular details thereof, it is not intended that these details shall be construed as limiting the scope of this invention.

CLAIMS

1. A nonaqueous cell comprising an anode, an electrolyte solution based on an organic solvent and a cathode, said cathode comprising antimony trisulfide (Sb_2S_3).

5 2. A cell as claimed in claim 1, wherein the cathode contains a binder.

3. A cell as claimed in claim 2, wherein the binder is polytetrafluoroethylene or ethylene-acrylic acid copolymer.

10 4. A nonaqueous cell as claimed in claim 1, 2 or 3, wherein the cathode contains a conductive agent.

5. A nonaqueous cell as claimed in claim 4, wherein the conductive agent is carbon or graphite.

15 6. A nonaqueous cell as claimed in any one of the preceding claims, wherein said anode is selected from the group consisting of lithium, potassium, sodium, calcium, magnesium and alloys thereof.

20 7. A nonaqueous cell as claimed in any one of the preceding claims, wherein the organic solvent comprises at least one solvent selected from the group consisting of sulfolane, tetrahydrofuran, 3-methyl-2-oxazolidone, 1,3-dioxolane, 1,2-dimethoxyethane, propylene carbonate, ethylene carbonate and γ -butyrolactone.



8. A nonaqueous cell as claimed in any one of claims 1 to 7, wherein the organic solvent comprises 3-methyl-2-oxazolidone, 1,3-dioxolane and 1,2-dimethoxyethane.

5 9. A nonaqueous cell as claimed in any one of claims 1 to 7, wherein the anode is lithium and the electrolyte solution comprises LiCF_3SO_3 dissolved in 3-methyl-2-oxazolidone, 1,3-dioxolane and 1,2-dimethoxyethane.

10 10. A nonaqueous cell as claimed in claim 1, substantially as hereinbefore described in the foregoing Example.

11. A solid cathode for a non-aqueous cell, comprising antimony trisulfide.

15 12. A solid cathode as claimed in claim 11, which also comprises a binder.

13. A solid cathode as claimed in claim 12, wherein the binder is polytetrafluoroethylene or ethylene-acrylic acid copolymer.

20 14. A solid cathode as claimed in any one of claims 11 to 13, which also comprises a conductive agent.

15. A solid cathode as claimed in claim 14, wherein said conductive agent is carbon or graphite.

16. A solid cathode as claimed in claim 11, substantially as hereinbefore described in the foregoing Example.

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