

PATENT SPECIFICATION

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(54) NONAQUEOUS CELL

(71) We, UNION CARBIDE CORPORATION, a corporation organized and existing under the laws of the State of New York, United States of America, of 270 Park Avenue, New York, State of New York 10017, United States of America, (assignee of MARVIN LEE KRONENBERG), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to a nonaqueous cell utilizing a highly active metal anode, a solid cathode selected from CuO, FeS₂, Co₃O₄, V₂O₅, Pb₃O₄, In₂S₃ and CoS₂, and a liquid organic electrolyte based on 3-methyl-2-oxazolidone in conjunction with a low viscosity cosolvent and a conductive solute.

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 and sodium, and the efficient use of high energy density cathode materials, such as FeS₂. 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.

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 δ -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.

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 reactive anodes described 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 extremely high energy density cathode materials and were sufficiently corrosive to lithium anodes to prevent efficient performance over any length of time.

U. S. Patent 3,547,703 to Blomgren et al discloses the use of a nonaqueous battery electrolyte employing a solute dissolved in ethylene glycol sulfite.

In an article appearing in Abstracts of the Third International Conference on Nonaqueous Solvents, July 5-7, 1972, Michigan State University, an abstract by H. L. Hoffman, Jr. and P. G. Sears discloses that 3-methyl-2-oxazolidone has been found to be a good non-aqueous solvent because of its ease of synthesis and purification, stability, attractive physical properties, broad dissolving power and coordinating ability. The article mainly related to the disclosure that the basic physical and chemical characteristics of 3-methyl-2-oxazolidone qualified it as a good potential nonaqueous solvent.

U. S. Patent 3,871,916, filed on April 22, 1974 by the same applicant as the subject

invention, discloses a nonaqueous cell utilizing a highly active metal anode, a solid (CF₃)_n cathode and a liquid organic electrolyte based on 3-methyl-2-oxazolidone in conjunction with a low viscosity cosolvent and a selected solute.

U.S. Patents 3,769,092 to V. L. Dechenaux and 3,778,310 to B. H. Garth disclose nonaqueous cell systems wherein copper oxide electrodes in conjunction with specific organic electrolytes and highly active metal anodes have been used.

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 such 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.

By practice of the present invention there may be provided a nonaqueous cell which utilizes a highly active metal anode, a solid cathode selected from CuO, FeS₂, Co₃O₄, V₂O₅, Pb₃O₄, In₂S₃ and CoS₂, and a liquid organic electrolyte consisting essentially of 3-methyl-2-oxazolidone in combination with a low viscosity cosolvent and a solute.

By practice of the present invention there may also be provided a nonaqueous cell which utilizes a highly active metal anode, a cathode selected from CuO, FeS₂, Co₃O₄, V₂O₅, Pb₃O₄, In₂S₃ and CoS₂, and a liquid organic electrolyte consisting essentially of 3-methyl-2-oxazolidone in combination with a low viscosity cosolvent and a solute that will yield a cathode efficiency above 50% and preferably above 75% during discharge as based on a drain of 1 mA/cm² to 1.0 volt cutoff using a lithium anode cell.

The invention provides a novel high energy density nonaqueous cell comprising a highly active metal anode, a solid cathode selected from CuO, FeS₂, Co₃O₄, V₂O₅, Pb₃O₄, In₂S₃ and CoS₂, and a liquid organic electrolyte comprising 3-methyl-2-oxazolidone in combination with at least one low viscosity cosolvent and a conductive solute.

Highly active metal anodes suitable for this invention include lithium (Li), potassium (K), sodium (Na), calcium (Ca), magnesium (Mg) 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 solid cathodes for use in this invention may be made by any suitable method known to those skilled in the battery art. For those cathode materials that have relatively low conductivity, it will be necessary to have a conductive additive mixed with the materials prior to pressing or otherwise molding them into cathode structures. Generally, these types of cathode materials can be mixed with a 5 to 10% by weight conductive additive, such as carbon black, and with a 2 to 10% by weight resin binder, such as polytetrafluoro-ethylene powder, and then pressed into a finished cathode structure having from 7 to 20% by weight combined conductive carbon and binder. U. S. Patents 3,639,174, 3,655,585, 3,686,038 and 3,778,310, and British Patent 1,346,890 are cited as being representative of disclosures for making solid cathodes suitable for use in this invention.

Liquid organic 3-methyl-2-oxazolidone material, (3Me20x), $\text{CH}_2\text{---CH}_2\text{---O---CO---N---CH}_3$, is an excellent nonaqueous solvent because of its high dielectric constant, chemical inertness to battery components, wide liquid range (i.e. is liquid over a wide temperature range), and low toxicity.

However, it has been found that when metal salts are dissolved in liquid 3Me20x for the purpose of improving the conductivity of 3Me20x, the viscosity of the solution becomes too high for its efficient use as an electrolyte for nonaqueous cell applications other than those requiring very low current drains. Thus, in accordance with this invention, the addition of a low viscosity cosolvent is necessary if 3Me20x 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 solid cathode as specified above 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 solid cathode selected from CuO, FeS₂, Co₃O₄, V₂O₅, Pb₃O₄, In₂S₃ and CoS₂ and an electrolyte comprising 3Me20x in combination with at least one low viscosity cosolvent and a conductive solute. The cathode efficiency of the subject invention, as based on the percentage of the theoretical capacity of the cathode material available in a cell operating on a drain of 1 milliampere per square centimeter to a 1.0 volt cutoff using a lithium anode, will be above 50% and preferably above 75% according to this invention.

The low viscosity cosolvents for use in this invention include tetrahydrofuran (THF), dioxolane, dimethoxyethane (DME), dimethyl isoxazole (DMI), diethyl carbonate (DEC), ethylene glycol sulfite (EGS), dioxane and dimethyl sulfite (DMS). Tetrahydrofuran and dioxolane are preferred cosolvents because of their compatibility with metal salts dissolved in liquid 3Me2Ox and their chemical inertness to cell components. The total amount of the low viscosity cosolvent added should preferably be from 20% to 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 cell.

Conductive solutes (metal salts) for use in this invention with the liquid 3Me2Ox may be selected from the group MCF_3SO_3 , MSCN , MBF_4 , MC10_4 and $\text{MM}'\text{F}_6$ 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 preferably to be compatible and non-reactive with 3Me2Ox and the electrodes of the cell. The amounts of solute to be dissolved in the liquid 3Me2Ox should be sufficient to provide good conductivity, e.g., at least about $10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$. Generally an amount of at least about 0.5 M would be sufficient for most cell applications.

The present invention of a high energy density cell with a 3Me2Ox-based electrolyte, a solid cathode selected from the group recited above and a highly active metal anode will be further illustrated in the following examples.

EXAMPLE I

The viscosity of several samples of 3Me2Ox, with and without a conductive solute and/or a low viscosity cosolvent, were obtained using a Cannon-Fenske viscometer. The data obtained are shown in Table 1 and clearly demonstrate the high viscosity of a solution of 3Me2Ox containing a dissolved conductive solute. As shown in sample 2, when one mole of LiC10_4 is added to one liter of 3Me2Ox, the viscosity of the solution was found to be 6.61 centistokes. In sample 6, when one mole of the same metal salt, LiC10_4 , was added to one liter of equal parts of 3Me2Ox and tetrahydrofuran (THF), the viscosity of the solution was found to be only 2.87. Thus it is clearly shown that the viscosity of a solution of 3Me2Ox and a metal salt can be decreased by the addition of a specifically selected low viscosity cosolvent.

TABLE 1

Sample	Solvent and Salt	Viscosity (Centistokes)
1	3Me2Ox; no salt	2.16
2	3Me2Ox; 1M LiC10_4	6.61
3	3Me2Ox; 1M LiBr	7.58
4	50-50 3Me2Ox, THF; no salt	1.05
5	50-50 3Me2Ox, THF; 1M LiAsF_6	3.59
6	50-50 3 Me2Ox, THF; 1M LiC10_4	2.87
7	25-75 3 Me2Ox, THF; 1M LiAsF_6	2.08
8	25-75 3Me2Ox, dioxolane; 1M LiAsF_6	1.83
9	25-75 3Me2Ox, THF; 1M LiC10_4	1.99

EXAMPLE II

Each of six flat-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 a 1.0 inch diameter lithium disc consisting of five sheets of lithium foil having a total thickness of 0.10 inch, about 4 ml of a specific electrolyte as shown in Table 3, a 1.0 inch diameter porous nonwoven poly-propylene separator (0.01 inch thick) which absorbed some of the electrolyte, and a solid FeS_2 cathode mix compressed onto and into a porous 1.0 inch diameter cathode collector.

The FeS_2 electrodes were made of a mixture of FeS_2 , acetylene black and a polytetrafluoroethylene binder compression-molded onto both sides of a nickel expanded mesh. The FeS_2 and acetylene black were first micromilled together, then blended with water, ethanol and a polytetrafluoroethylene emulsion (obtained commercially from Du Pont as Teflon emulsion designated T-30-B) in the proportions shown in Table 2 prior to draining off the excess liquid and compression molding (at 18,000 psi) onto the expanded

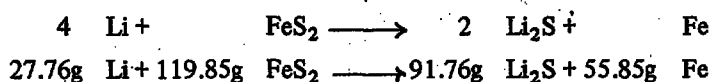
metal carrier or mesh. "Teflon" is a Trade Mark. Each finished FeS_2 electrode contained about 1.9 grams of the cathode mix and had a thickness of about 0.04 inch with a diameter of about 1.0 inch.

TABLE 2

Materials	Amount	% In Finished Electrode
FeS_2	20.0 g	87.5
"Teflon" emulsion	2.86 g	7.5
Acetylene black	1.14 g	5.0
Ethanol	20.0 ml	—
H_2O	110.0 ml	—

5 The total thickness of the anode, cathode plus cathode collector and separator for each cell measured about 0.15 inch. The average discharge voltage and discharge capacity on various current drains to a 1.0 volt cutoff were obtained for each cell and are shown in Table 3. Since the cells were cathode-limited, the cathode efficiency was calculated as a percentage based on the theoretical capacity of the cathode material available in each cell.

10 For example, the theoretical efficiency of FeS_2 as a cathode material in a lithium anode cell discharging at a 1 milliampere per square centimeter drain to a 1.0 volt cutoff is calculated as follows: Assuming the reaction:



then if 1 gram (g) FeS_2 is used, the fraction of the equivalent weight is $\frac{1}{29.96}$. Since one Faraday of electricity is obtained from one equivalent weight, then the AH per equivalent weight is calculated as follows:

$$\frac{96,500}{3600} \times \frac{\text{coulombs/Faraday}}{\text{coulombs/AH}} = 26.8 \text{ AH/equivalent weight.}$$

Therefore, $29.96 \text{ equivalent weight} \times 26.8 \text{ AH/equivalent weight} = 0.894 \text{ AH}$. This 0.894 AH or 894 AH. This 0.894 AH or 894 mAh is the theoretical capacity of 1 gram of FeS_2 material when used as a cathode in a lithium anode cell and by using this value as a reference, the cathode efficiency of FeS_2 material can be calculated when used as a cathode in a cell having various electrolytes.

As evidenced by the test data shown in Table 3, the cathode efficiency of the cells ranged from 69.0% to 89.7%, thus demonstrating that using the teachings of the subject invention efficient, high energy density FeS_2 nonaqueous cells can be made.

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TABLE 3

Sample	Electrolyte-Solvent	Electrolyte Salt	Current Density (mA/cm ²)	Average Discharge Voltage (Volt)	Theoretical Capacity (mAh)	Average Discharge Capacity to 1.0V Cutoff (mAh)	Cathode Efficiency (%)
1	30 vol.%(v/o) 3Me2Ox 70 v/o THF	2M LiBF ₄	1.0	1.24	1172	855	73.0
2	30 v/o 3Me2Ox 40 v/o Dioxolane 30 v/o DME + Trace of DMI	2M LiAsF ₆	1.0	1.20	1174	810	69.0
3	"	1M LiCF ₃ SO ₃	0.8	1.27	1168	835	71.5
4	"	2M LiCF ₃ SO ₃	0.8	1.25	1178	913	77.5
5	"	2M LiBF ₄	0.2	1.44	1194	1071	89.7
6	"	1M LiBF ₄	0.2	1.45	1196	997	83.4

EXAMPLE III

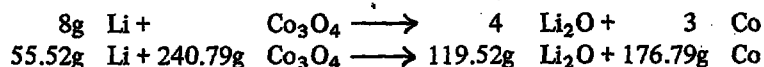
Three flat type cells were constructed as described in Example II except that the solid cathode was Co_3O_4 which was made as described in Example II for FeS_2 using the proportions shown in Table 4 and the electrolyte employed in each cell is as shown in Table 5.

TABLE 4

<u>Materials</u>	<u>Amount</u>	<u>% In Finished Electrode</u>
Co_3O_4	20.0 g	87.5
"Teflon" emulsion	2.86 g	7.5
Acetylene Black	1.14 g	5.0
Ethanol	20.0 ml	—
H_2O	110.0 ml	—

5 The average discharge voltage and discharge capacity on various current drains to a 1.0 volt cutoff were obtained for each cell and are shown in Table 5.

As in the previous example, the cells were cathode-limited and thus the theoretical efficiency of Co_3O_4 as a cathode material in a lithium cell discharging at a 1 milliampere per square centimeter drain to a 1.0 volt cutoff is calculated as follows:
Assuming the reaction:



then if 1 gram (g) Co_3O_4 is used, the fraction of the equivalent weight is $\frac{1}{30.1}$. Since one Faraday of electricity is 26.8 AH/equivalent weight, then $\frac{1}{30.1}$ equivalent weight x 26.8 AH/equivalent weight = 0.890 AH.

This 0.890 AH or 890 mAh is the theoretical capacity of 1 gram of Co_3O_4 material when used as a cathode in a lithium anode cell and by using this value as a reference, the cathode efficiency of Co_3O_4 material can be calculated when used as a cathode in a cell having various electrolytes.

The test data shown in Table 5 wherein the cathode efficiency of the cells ranged from 71.4% to 80.9%, demonstrated that using the teachings of the subject invention, efficient, high energy density Co_3O_4 nonaqueous cells can be made.

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TABLE 5

Sample	*Electrolyte Salt	Average Discharge Voltage (volt)	Theoretical Capacity (mAh)	Discharge Capacity to 1.00 Cutoff (mAh)	Cathode Efficiency (%)
1 **	2 M LiBF ₄	1.08	1182	844	71.4
2 **	2 M LiBF ₄	1.15	1336	1081	80.9
3 ***	1 M LiCF ₃ SO ₃	1.17	1543	1195	77.4

* Electrolyte Solvent 30 vol % (V/o) 3Me20x
40 V/o Dioxolane
30 V/o DME
Trace of DMI

** Current density 0.8 mA/cm²

*** Current density 0.2 mA/cm²

EXAMPLE IV

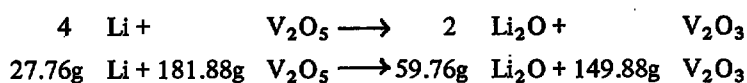
Two flat type cells were constructed as described in Example II except that the solid cathode was V₂O₅ which was made as described in Example II for FeS₂ using the proportions shown in Table 6 and the electrolyte employed in each cell is as shown in Table 7.

TABLE 6

Materials	Amount	% In Finished Electrode
V ₂ O ₅	20.0 g	87.5
"Teflon" emulsion	2.86 g	7.5
Acetylene Black	1.14 g	5.0
Ethanol	20.0 ml	—
H ₂ O	110.0 ml	—

The average discharge voltage and discharge capacity on a 0.8 milliamperes per square centimeter drain to a 1.0 volt cutoff were obtained for each cell and are shown in Table 7.

As in the previous examples, the cells were cathode-limited and thus the theoretical efficiency of V₂O₅ as a cathode material in a lithium cell discharging at a 1 milliamperes per square centimeter drain to a 1.0 volt cutoff is calculated as follows:
Assuming the reaction:



then if 1 gram (g) V₂O₅ is used, the fraction of the equivalent weight is $\frac{1}{45.47}$. Since one Faraday of electricity is 26.8 AH/equivalent weight, then $\frac{1}{45.47}$ equivalent weight x 26.8 AH/equivalent weight = 0.589 AH. This 0.589 AH or 589 mAh is the theoretical capacity of 1 gram of V₂O₅ material when used as a cathode in a lithium anode cell and by using this value as a reference, the cathode efficiency of V₂O₅ material can be calculated when used as a cathode in a cell having various electrolytes.

The test data shown in Table 7 wherein the cathode efficiency of the cells varied between 68.4% and 67.6% demonstrated that using the teachings of the subject invention, efficient, high energy density V_2O_5 nonaqueous cells can be made.

TABLE 7

Sample	Electrolyte	Average Discharge Voltage (volt)	Theoretical Capacity (mAh)	Discharge Capacity to 1.0 Volt Cutoff (mAh)	Cathode Efficiency (%)
1 *	1M $LiCF_3SO_3$ in 30 v/o 3Me2Ox 40 v/o Dioxolane 30 v/o DME Trace of DMI	1.90	500	342	68.4
2 *	2M $LiCF_3SO_3$ in 50 v/o 3Me2Ox 50 v/o Dioxolane	1.70	503	340	67.6

* Current density 0.8 mA/cm²

EXAMPLE V

Three flat type cells were constructed as described in Example II except that the solid cathode was Pb_3O_4 which was made as described in Example II for FeS_2 using the proportions shown in Table 8 and the electrolyte employed in each cell is as shown in Table 9.

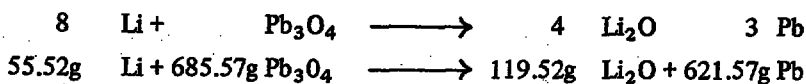
TABLE 8

Sample	Materials	Amount	% In Finished Electrode
1 and 2	Pb_3O_4	30.0 g	92
	"Teflon" emulsion	1.63 g	3
	Acetylene Black	1.63 g	5
	Ethanol	30 ml	—
3	H_2O	110.0 ml	—
	Pb_3O_4	30.0 g	92
	"Teflon" emulsion	1.63 g	3
	Lead Powder	1.63 g	5
	Ethanol	30.0 ml	—
	H_2O	110.0 ml	—

The average discharge voltage and discharge capacity on various current drains to a 1.0 volt cutoff were obtained for each cell and are shown in Table 9.

As in the previous examples, the cells were cathode-limited and thus the theoretical efficiency of Pb_3O_4 as a cathode material in a lithium cell discharging at a 1 milliamperere per square centimeter drain to a 1.0 volt cutoff is calculated as follows:

Assuming the reaction:



then if 1 gram (g) Pb_3O_4 is used, the fraction of the equivalent weight is $\frac{1}{85.7}$. Since one Faraday of electricity is 29.8 AH/equivalent weight then $\frac{1}{85.7}$ equivalent weight $\times$ 26.8 AH/equivalent weight = 0.312 AH. This 0.312 AH or 312 mAh is the theoretical capacity of 1 gram of Pb_3O_4 material when used as a cathode in a lithium anode cell and by using this value as a reference, the cathode efficiency of Pb_3O_4 material can be calculated when used as a cathode in a cell having various electrolytes.

The test data shown in Table 9 wherein the cathode efficiency of the cells ranged from 72.5% to 99.8%, demonstrated that using the teachings of the subject invention, efficient, high energy density Pb_3O_4 nonaqueous cells can be made.

TABLE 9

Sample	Electrolyte	Average Discharge Voltage (volt)	Theoretical Capacity (mAh)	Discharge Capacity to 1.0 volt Cut off	Cathode Efficiency (%)
1 *	1M LiCF_3SO_3 in 30 v/o 3Me20x 40 v/o Dioxolane 30 v/o DME	1.39	563	562	99.8
2 *	1M LiBF_4 in 50 v/o 3Me20x 50 v/o Trimethyl phosphite	1.38	563	550	97.7
3***	1M LiCF_3SO_3 in 30 v/o 3Me20x 40 v/o Dioxolane 30 v/o DME Trace DMI	1.19	792	574	72.5

* Current density 0.2 mA/cm²

** Current density 0.8 mA/m²

EXAMPLE VI

Two flat type cells were constructed as described in Example II except that the solid cathode was In_2S_3 which was made as described in Example II for FeS_2 using the proportions shown in Table 10 and the electrolyte employed in each cell is as shown in Table 11.

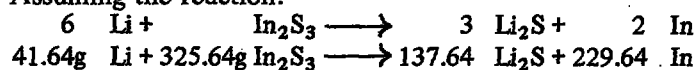
TABLE 10

Materials	Amount	% In Finished Electrode
In ₂ S ₃	20.0 g	87.5
"Teflon" emulsion	2.86 g	7.5
Acetylene Black	1.14 g	5.0
Ethanol	20.0 ml	—
H ₂ O	110.0 ml	—

The average discharge voltage and discharge capacity on a 0.2 milliamperes per square centimeter drain to a 1.0 volt cutoff were obtained for each cell and are shown in Table 11.

As in the previous examples, the cells were cathode-limited and thus the theoretical efficiency of In₂S₃ as a cathode material in a lithium cell discharging at a 1 milliamperes per square centimeter drain to a 1.0 volt cutoff is calculated as follows:

Assuming the reaction:



then if 1 gram (g) In₂S₃ is used, the fraction of the equivalent weight is $\frac{1}{54.27}$. Since the Faraday of electricity is 26.8 AH/equivalent weight, then $\frac{1}{54.27}$ equivalent weight x 26.8 AH/equivalent weight = 0.49 AH.

This 0.494 AH or 494 mAh is the theoretical capacity of 1 gram of In₂S₃ material when used as a cathode in a lithium anode cell and by using this value as a reference, the cathode efficiency of In₂S₃ material can be calculated when used as a cathode in a cell having various electrolytes.

The test data shown in Table II wherein the cathode efficiency of the cells varied between 59% and 95%, demonstrated that using the teachings of the subject invention, efficient, high energy density In₂S₃ nonaqueous cells can be made.

TABLE II

Sample	Electrolyte	Average Discharge Voltage (volt)	Theoretical Capacity (mAh)	Discharge Capacity to 1.0 Volt Cut off (mAh)	Cathode Efficiency (%)
1 *	2M LiBF ₄ in 30 v/o 3Me20x 40 v/o Dioxolane 30 v/o DME Trace DMI	1.30	522	496	95
2 *	1M LiCF ₃ SO ₃ in 30 v/o 3Me20x 40 v/o Dioxolane 30 v/o DME Trace DMI	1.34	516	304	59

* Current density 0.2 mA/cm²

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EXAMPLE VII

Four flat cells were constructed as described in Example II except that the solid cathode was CoS_2 which was made as described in Example II for FeS_2 using the proportions shown in Table 12 and the electrolyte employed in each cell is as shown in Table 13.

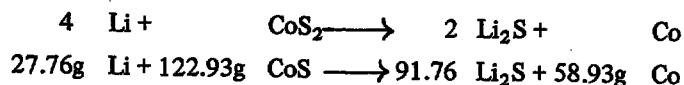
TABLE 12

Materials	Amount	% In Finished Electrode
CoS_2	20.0 g	84.70
"Teflon" emulsion	1.63 g	6.91
Acetylene Black	1.98 g	8.39
Ethanol	20.0 ml	—
H_2O	110.0 ml	—

The average discharge voltage and discharge capacity on a 0.2 or a 0.8 milliamperes per square centimeter drain to a 1.0 volt or 1.2 volt cutoff were obtained for each cell and are shown in Table 13.

As in the previous examples, the cells were cathode-limited and thus the theoretical efficiency of CoS_2 as a cathode material in a lithium cell discharging at a 1 milliamperes per square centimeter drain to a 1.0 volt cutoff is calculated as follows:

Assuming the reaction:



then if 1 gram (g) CoS_2 is used, the fraction of the equivalent weight is $\frac{1}{30.73}$. Since one Faraday of electricity is 26.8 AH/equivalent weight, then $\frac{1}{30.73}$ equivalent weight x 26.8 AH/equivalent weight = 0.872 AH.

This 0.872 AH or 872 mAh is the theoretical capacity of 1 gram of CoS_2 material when used as a cathode in a lithium anode cell and by using this value as a reference, the cathode efficiency of CoS_2 material can be calculated when used as a cathode in a cell having various electrolytes.

The test data shown in Table 13 wherein the cathode efficiency of the cells varied between 86.8% and 93.5% demonstrated that using the teachings of the subject invention, efficient, high energy density CoS_2 nonaqueous cells can be made.

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TABLE 13

Sample	Electrolyte	Average Discharge Voltage (volt)	Theoretical Capacity (mAh)	Discharge Capacity to 1.0 or 1.2 volt Cut off	Cathode Efficiency (%)
1 *	2 M LiBF ₄ in 30 v/o 3Me20x 40 v/o Dioxolane 30 v/o DME Trace DMI	1.48	633	592 (1.2 V cut off)	93.5
2**	Same as No. 1	1.37	643 (1.0 V cut off)	588	91.4
3 *	1M LiCF ₃ SO ₃ 30 v/o 3 Me20x 40 v/o Dioxolane 30 v/o DME Trace DMI	1.48	682 cut off)	592	86.8
4 *	Same as No. 3	1.33	635 (1.0V cut off)	560	88.2

* Current density 0.2 mA/cm²

**Current density 0.8 mA/cm²

EXAMPLE VIII

Each of four flat-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 a 1.0 inch diameter lithium disc consisting of five sheets of lithium foil, having a total thickness of 0.10 inch, about 4 ml of a specific electrolyte as shown in Table 15, a 1.0 inch diameter porous nonwoven polypropylene separator (0.01 inch thick) which absorbed some of the electrolyte, and a solid CuO cathode mix compressed onto and into a porous 1.0 inch diameter cathode collector.

The copper oxide electrodes were made of a mixture of CuO (made by the reaction of fine copper powder in air at an elevated temperature of about 400°C for about 15 hours), acetylene black and a polytetrafluoroethylene binder compression-molded onto both sides of a nickel expanded mesh. The CuO and acetylene black were first micromilled together, then blended with water, ethanol and a polytetrafluoroethylene emulsion (obtained commercially from Du Pont as Teflon emulsion designated T-30-B) in the proportions shown in Table 14 prior to draining off the excess liquid and compression molding (at 18,000 psi) onto the expanded metal carrier or mesh. Each finished CuO electrode contained about 1.9 grams of the cathode mix and had a thickness of about 0.04 inch with a diameter of about 1.0 inch.

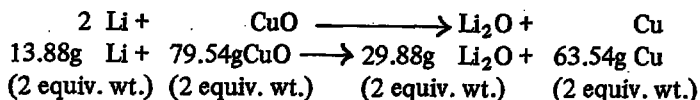
TABLE 14

Materials	Amount	% in Finished Electrode
Cu O	20.0 g	87.5
"Teflon" emulsion	2.86 g	7.5
Acetylene black	1.14 g	5.0
Ethanol	20.0 ml	—
H ₂ O	110.0 ml	—

The total thickness of the anode, cathode plus cathode collector and separator for each cell measured about 0.15 inch. The open circuit voltage and discharge capacity to a 1.0 volt cutoff were obtained for each cell and are shown in Table 15. Samples 1 and 3 in Table 15 relate to cells that were discharged on a 1.0 milliamperere per square centimeter drain to a 1.0 volt cutoff. Since the cells were cathode-limited, the cathode efficiency was calculated as a percentage based on the theoretical capacity of the cathode material available in each cell.

For example, the theoretical efficiency of CuO as a cathode material in a lithium anode cell discharging at a 1 milliamperere per square centimeter drain to a 1.0 volt cutoff, is calculated as follows:

Assuming the reaction:



then if 1 gram (g) CuO is used, the fraction of the equivalent weight is $\frac{1}{39.77}$. Since one Faraday of electricity is obtained from one equivalent weight, then the AH per equivalent weight is calculated as follows:

$$\frac{96,500}{3600} \frac{\text{coulombs/Faraday}}{\text{coulombs/AH}} = 26.8 \text{ AH/equivalent weight.}$$

Therefore, $\frac{1}{39.77}$ equivalent weight x 26.8 AH/equivalent weight = 0.676 AH. This 0.676 AH or 676 mAh is the theoretical capacity of 1 gram of CuO material when used as a cathode in a lithium anode cell and, by using this value as a reference, the cathode efficiency of CuO material can be calculated when used as a cathode in a cell having various electrolytes.

As demonstrated by the test data shown in Table 15, the cathode efficiency of the cells ranged from 75.1% to 81.8% depending on the cosolvent(s) used. Thus using the teachings of the subject invention, efficient, high energy density CuO nonaqueous cells can be made.

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TABLE 15

Sample	Electrolyte-Solvent	Electrolyte Salt	O.C.V. (Volt)	Theoretical Capacity (mAh)	Disch. Cap. to 1.0V Cut off (mAh)	Cathode Eff. %
1	30 vol. % (v/o) 3 Me 20x 70 v/o THF	2 M LiBF ₄	2.75	1063	870	81.8%
2 *	30 v/o 3Me 20x 70 v/o THF	1 M LiBF ₄	2.95	1088	817	75.1%
3	30 v/o 3Me 20x 30 v/o DME 40 v/o Dioxolane	2 M LiBF ₄	3.0	965	750	77.7%
4 **	30 v/o 3Me 20x 40 v/o THF 30 v/o DME	2 M LiBF ₄	2.85	1072	834	77.8%

* after 5 days on 5-mA current drain the cell was discharged across a 300-ohm load at $\sim 0.8 \text{ mA/cm}^2$

** after 6 days on 5-mA current drain the cell was discharged across a 300-ohm load at $\sim 0.8 \text{ mA/cm}^2$

EXAMPLE IX

Two flat type cells were constructed as described in Example VIII, using the same cell components except that the electrolyte employed in each cell is as shown in Table 16. Each cell was tested as described in Example VIII and the discharge capacity and cathode efficiency observed for each cell are shown in Table 16. As evidenced by the data in Table 16, high cathode utilization can be obtained from CuO cathodes when using an electrolyte based on 3Me20x in combination with a selected low viscosity cosolvent and a selected salt in accordance with this invention.

TABLE 16

Sample	Electrolyte Solvent Containing 2M LiClO ₄	Theoretical capacity (mAh)	Discharge Capacity to 1.0v Cut off (mAh)	Cathode Eff. %
1*	30 v/o 3Me20x 70 v/o THF	979	750	76.6
2**	30 v/o 3 Me20x 40 v/o Dioxolane 30 v/o DME	990	840	84.8

* open circuit voltage 2.8 volts

** open circuit voltage 2.6 volts

EXAMPLE X

A flat-type cell was constructed as described in Example VIII, using the same cell components except that the electrolyte employed in the cell was 2M LiAsF₆ in a mixture of 40v/o dioxolane, 30v/o DME and 30v/o 3Me20x. The cell, tested on a 1.0 milliampere per square centimeter drain to a 1.0 volt cutoff, delivered a discharge capacity of 765 mAh.

Based on a theoretical capacity of 994 mAh, the cathode efficiency of the cell was 76.9%. Again this test showed that high cathode utilization can be obtained from a CuO cathode in a nonaqueous cell system when using a liquid organic electrolyte consisting essentially of 3Me20x in combination with at least one selected low viscosity cosolvent and a selected metal salt.

EXAMPLE XI

Six flat type cells were constructed as described in Example VIII, using the same cell components except that the electrolyte employed in each cell is as shown in Table 17. Each cell was discharged across a 300-ohm load to a 1.0 volt cutoff. The discharge capacity and cathode efficiency observed for each cell (samples 1-5) are shown in Table 17 and clearly illustrate the high cathode utilization obtainable from CuO cathodes when using an electrolyte based on 3Me20x in combination with a selected low viscosity cosolvent and a selected salt. The test data for sample 6 in Table 17 shows that when the electrolyte consisted of 1M LiCF₃SO₃ in pure dioxolane, the cell could not be usefully discharged when coupled to a 300-ohm load. Although the reason for this is not precisely known, it could partially be due to the fact that the conductivity of the pure dioxolane electrolyte was measured as being $2.5 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$ while the conductivity of the 50:50 dioxolane-2Me20x electrolyte was measured as being $6.5 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$.

TABLE 17

Sample	Electrolyte-Solvent	Electrolyte Salt	O.C.V. (Volt)	Theoretical Capacity (mAh)	Disch. Cap. to 1.0V Cut off (mAh)	Cathode Eff. %
1	50 vol. % (v/o) 3Me2Ox 50 v/o dioxolane	1 M LiCF ₃ SO ₃	2.75	970	757	78
2	50 v/o 3Me2Ox 50 v/o dioxolane	2 M LiCF ₃ SO ₃	2.40	1016	790	77.8
3	50 v/o 3Me2Ox 50 v/o THF	2 M LiCF ₃ SO ₃	2.60	993	705	71
4	30 v/o 3Me2Ox 40 v/o dioxolane 30 v/o DME	1 M LiCF ₃ SO ₃	2.80	1019	857	84.1
5	30 v/o 3Me 2Ox 40 v/o dioxolane 30 v/o DME	2 M LiCF ₃ SO ₃	2.75	1006	841	83.6
6*	dioxolane	1 M LiCF ₃ SO ₃	2.55	—	—	—

* would not discharge across 300-ohm load

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

WHAT WE CLAIM IS:-

- 5 1. A nonaqueous cell comprising a highly active metal anode, a solid cathode selected from CuO , FeS_2 , Co_3O_4 , V_2O_5 , Pb_3O_4 , In_2S_3 and CoS_2 , and a liquid organic electrolyte comprising 3-methyl-2-oxazolidone in combination with at least one low viscosity cosolvent and a conductive solute. 5
- 10 2. A nonaqueous cell as claimed in claim 1 wherein said low viscosity cosolvent is selected from tetrahydrofuran, dioxolane, dimethoxyethane, dimethyl isoxazole, diethyl carbonate, ethylene glycol sulfite dioxane and dimethyl sulphite. 10
3. A nonaqueous cell as claimed in claim 2 wherein said low viscosity cosolvent is tetrahydrofuran.
- 15 4. A nonaqueous cell as claimed in claim 2 wherein said low viscosity cosolvent is dioxolane. 15
5. A nonaqueous cell as claimed in any one of the preceding claims wherein said conductive solute is selected from MCF_3SO_3 , MSCN , 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 6. A non aqueous cell as claimed in claim 5 wherein said conductive solute is selected from LiBF_4 , LiC10_4 and LiCF_3SO_3 . 20
7. A nonaqueous cell as claimed in any one of the preceding claims wherein said active metal anode is selected from lithium, potassium, sodium, calcium, magnesium and alloys thereof.
- 25 8. A nonaqueous cell as claimed in claim 7 wherein said active metal anode is lithium. 25
9. A nonaqueous cell as claimed in any one of the preceding claims wherein said low viscosity cosolvent is used in an amount of 20% to 80% based on total solvent volume.
10. A nonaqueous cell as claimed in any one of the preceding claims wherein the cathode efficiency, as based on the percentage of the theoretical capacity of the cathode material available in a cell operating on a drain of $1\text{mA}/\text{cm}^2$ to a 1.0 volt cutoff using a lithium anode is above 50%. 30
11. A nonaqueous cell as claimed in claim 10 wherein the cathode efficiency is above 75%. 30
12. A nonaqueous cell as claimed in claim 1 substantially as hereinbefore described with reference to any one of Examples II to VII.
- 35 13. A nonaqueous cell as claimed in claim 1 substantially as hereinbefore described with reference to any one of Examples VIII to XI. 35

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

WHAT WE CLAIM IS:-

- 5 1. A nonaqueous cell comprising a highly active metal anode, a solid cathode selected from CuO , FeS_2 , Co_3O_4 , V_2O_5 , Pb_3O_4 , In_2S_3 and CoS_2 , and a liquid organic electrolyte comprising 3-methyl-2-oxazolidone in combination with at least one low viscosity cosolvent and a conductive solute. 5
- 10 2. A nonaqueous cell as claimed in claim 1 wherein said low viscosity cosolvent is selected from tetrahydrofuran, dioxolane, dimethoxyethane, dimethyl isoxazole, diethyl carbonate, ethylene glycol sulfite dioxane and dimethyl sulphite. 10
3. A nonaqueous cell as claimed in claim 2 wherein said low viscosity cosolvent is tetrahydrofuran.
- 15 4. A nonaqueous cell as claimed in claim 2 wherein said low viscosity cosolvent is dioxolane. 15
5. A nonaqueous cell as claimed in any one of the preceding claims wherein said conductive solute is selected from MCF_3SO_3 , MSCN , 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 6. A non aqueous cell as claimed in claim 5 wherein said conductive solute is selected from LiBF_4 , LiC10_4 and LiCF_3SO_3 . 20
7. A nonaqueous cell as claimed in any one of the preceding claims wherein said active metal anode is selected from lithium, potassium, sodium, calcium, magnesium and alloys thereof.
- 25 8. A nonaqueous cell as claimed in claim 7 wherein said active metal anode is lithium. 25
9. A nonaqueous cell as claimed in any one of the preceding claims wherein said low viscosity cosolvent is used in an amount of 20% to 80% based on total solvent volume.
10. A nonaqueous cell as claimed in any one of the preceding claims wherein the cathode efficiency, as based on the percentage of the theoretical capacity of the cathode material available in a cell operating on a drain of $1\text{mA}/\text{cm}^2$ to a 1.0 volt cutoff using a lithium anode is above 50%. 30
11. A nonaqueous cell as claimed in claim 10 wherein the cathode efficiency is above 75%. 30
12. A nonaqueous cell as claimed in claim 1 substantially as hereinbefore described with reference to any one of Examples II to VII.
- 35 13. A nonaqueous cell as claimed in claim 1 substantially as hereinbefore described with reference to any one of Examples VIII to XI. 35

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