

PATENT SPECIFICATION

(11) 1 529 371

1 529 371

- (21) Application No. 52331/75 (22) Filed 22 Dec. 1975
(31) Convention Application No. 535 716
(32) Filed 23 Dec. 1974 in
(33) United States of America (US)
(44) Complete Specification published 18 Oct. 1978
(51) INT CL² H01M 6/16, 10/40
(52) Index at acceptance H1B 1040 202 404 438 440 446 614A 616



(54) NONAQUEOUS ELECTROCHEMICAL CELL HAVING AN ELECTROLYTE CONTAINING CROTONITRILE

(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 GEORGE EARL BLOMGREN and GERALD HENRY NEWMAN), 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 metal anode, a solid cathode and a liquid organic electrolyte comprising crotonitrile in combination with a protective type cosolvent and a selected solute.

The development of high energy battery systems requires the compatibility of an electrolyte possessing desirable electrochemical properties with highly active anode materials, such as lithium, calcium, sodium and the like, and the efficient use of high energy density cathode materials, such as fluorinated carbon, copper sulfide and the like. 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 non-aqueous 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 γ -butyrolactone, or the like. 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 solvents is known and recommended for use but the selection of a suitable solvent has been particularly troublesome since many of the solvents which can be used to prepare electrolytes sufficiently conductive to permit effective ion migration through the solution are reactive with the highly reactive anodes described above. Consequently, many investigators 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, such as fluorinated carbon, 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. U.S. Patents 3,536,532 and 3,700,502 disclose nonaqueous cells employing solid fluorinated carbon $[(CF_3)_n]$ as the active cathode material in conjunction with a light metal anode and a conventional nonaqueous electrolyte.

French Patent 2,124,388 discloses a nonaqueous electrolyte using dioxolane as the solvent.

British Patent Application No. 33361/75 Patent Specification No. 1,513,419 discloses a nonaqueous electrolyte comprising sulfolane or its liquid alkyl-substituted

10

2

1,529,371

2

derivatives in combination with a low viscosity cosolvent and an ionizable solute. British Patent Specification No. 1,498,519 discloses a nonaqueous electrolyte based on 3-methyl-2-oxazolidone in combination with a low viscosity cosolvent and a conductive solute.

U.S. Patent 3,567,515 to Maricle et al discloses a nonaqueous cell system wherein sulfur dioxide is employed to form what is referred to as a "passivating" film on a highly active metal, such as lithium, said film being some form of metal-sulfur dioxide complex or reaction product which prevents substantial further attack of sulfur dioxide on the metal. In a similar manner, an article titled "Kinetics of the Solid Lithium Electrode in Propylene Carbonate" appearing in the J. Electro-chemical Society, Vol. 117, No. 3, March 1970, discloses that propylene carbonate may form a film on lithium metal through the reaction between the lithium and the propylene carbonate.

A Final Report dated September, 1967 under a Contract No.

DA-28-043-AMS-02304-(E)-USAECON

discloses the use of propylene carbonate as a good solvent for use in nonaqueous cells along with the listing of many other possible solvents. Crotonitrile is listed as a possible solvent; however, it was found that when it was in contact with lithium, the rate of corrosion of lithium was excessive. Therefore, crotonitrile was not pursued as a solvent having comparable properties to propylene carbonate.

It is thus known in the art that 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 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.

Accordingly, by practice of the present invention there may be provided:—

- (i) A nonaqueous cell employing among other components a liquid organic electrolyte comprising crotonitrile in combination with a protective cosolvent and a solute.
- (ii) A nonaqueous cell which utilizes a metal anode, such as lithium, a solid cathode such as $(CF_3)_2$, copper sulfide, copper oxide, nickel fluoride or silver chloride, and a liquid organic electrolyte comprising crotonitrile in combination with a protective cosolvent and a solute.
- (iii) An electrolyte solvent system for nonaqueous solid cathode cells comprising crotonitrile in combination with a protective cosolvent, a low viscosity cosolvent and a solute.
- (iv) A nonaqueous cell which utilizes a metal anode, a solid cathode and a liquid organic electrolyte based on crotonitrile in combination with a protective cosolvent such as propylene carbonate and a solute such as $LiClO_4$.

According to the present invention there is provided a nonaqueous cell comprising a metal anode, a solid cathode and a nonaqueous electrolyte comprising crotonitrile, a protective cosolvent and an ionizable solute, the ionizable solute being compatible and non-reactive with the crotonitrile, protective cosolvent, anode and cathode.

The invention provides a novel high energy density nonaqueous cell comprising a metal anode, a solid cathode and a liquid organic electrolyte comprising crotonitrile, a protective cosolvent and an ionizable solute. If the viscosity of the protective cosolvent is of a magnitude that it decreases the solution conductivity of the electrolyte below $10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$, then a low viscosity cosolvent is preferably added along with the protective cosolvent to achieve an electrolyte conductivity of at least about $10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$.

As used herein, a protective cosolvent shall mean at least one cosolvent which when mixed with crotonitrile and an ionizable solute to form a liquid electrolyte for use in a nonaqueous cell, the cosolvent will effectively form a protective barrier for

protecting the metal anode of the cell against excessive corrosion by crotonitrile, so that chemical or physical interaction between the anode metal and the electrolyte solution is substantially prevented.

An essential component of the liquid electrolyte of this invention is crotonitrile which has the properties shown in Table 1. Crotonitrile is also known or has been referred to as crotononitrile.

TABLE 1.

Molecular Weight: 67.09
Melting Point: -51.1°C
Boiling Point: 120°C
Density (20°C): 0.8239 g/cm^3
Dielectric Constant (20°C): 28.1
Viscosity (25°C): ~ 0.476 centipoise.

An ionizable solute of LiClO_4 , mixed in various concentrations in crotonitrile exhibited the laboratory measured properties shown in Table 2.

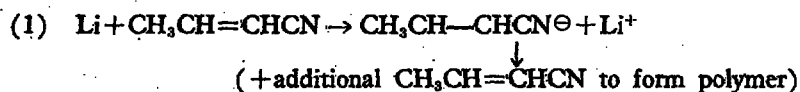
TABLE 2.

Concentration LiClO ₄ (Moles/liter)	Specific Conductivity (Ohm ⁻¹ cm ⁻¹)	Density (g/cm ³)	Viscosity (Centipoise)
0.5	8.832×10^{-3}	0.847	0.610
1.0	11.260×10^{-3}	0.883	0.886
2.0	11.400×10^{-3}	0.908	2.170

When a crotonitrile-LiClO₄ electrolyte was used in a lithium anode cell, a chemical reaction occurred between crotonitrile and the unprotected highly active lithium anode. This undesirable reaction continued until polymerization of the crotonitrile occurred which resulted in progressive thickening of the electrolyte until finally a solid was formed.

Thus, although the measured solution conductivity and viscosity appeared to indicate that crotonitrile in combination with an ionizable solute would be a suitable electrolyte for nonaqueous cells using metal anodes, the opposite was observed.

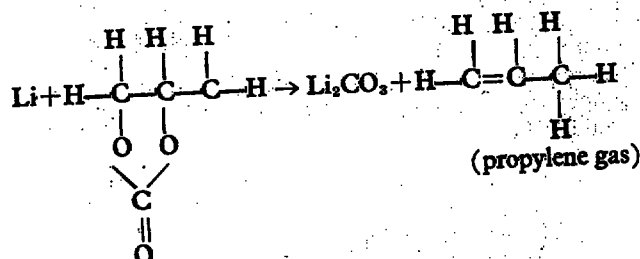
Although not wanting to be bound by theory, it is thought that the following reaction occurs between a highly active surface such as lithium and liquid crotonitrile solvent:



The crotonitrile radical ion (indicated by $\ominus$) then reacts with other crotonitrile molecules in an anionic polymerization process to produce a polymer of progressively increasing molecular weight until finally a solid is formed. This process continues even after the lithium has been completely consumed so long as there are additional crotonitrile molecules present and there is no other material present in the system which could terminate the reaction.

According to this invention, crotonitrile can be successfully employed in non-aqueous cells employing metal anodes if a protective cosolvent is added in conjunction with the crotonitrile. An example of a good protective cosolvent is propylene carbonate. It is believed that when lithium is contacted with the protective cosolvent propylene carbonate, the following reaction occurs to a limited extent so as to effectively form a thin protective barrier on the lithium surface:

(2)



S

10

15

20

2

•

•

Patents Nos. 3,536,532 and 3,700,502, solid fluorinated carbon electrodes are extremely stable and resistive to chemicals over the range of values of x from 0 to about 1. Preferably, $(CF_x)_n$ cathodes wherein x varies from 0.8 to 1.1 would be admirably suited for use with the specific electrolyte of the invention because this range represents the best available energy density of the cathode materials.

The ionizable solute for use in this invention may be a simple salt ($LiClO_4$) or double salt or mixtures thereof, which will produce an ionically conductive solution when dissolved in one or more solvents. Suitable solutes are complexes of inorganic or organic Lewis acids and inorganic ionizable salts. One of the requirements for utility is that the salts, whether simple or complex, be compatible with crotonitrile and the cosolvent(s) being employed and that they yield a solution which is sufficiently ionically conductive, e.g., at least about 10^{-4} ohm $^{-1}$ cm $^{-1}$. Generally, an amount of at least about 0.5 M (moles/liter) would be sufficient for most cell applications.

According to the Lewis or electronic concept of acids and bases, many substances 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).

A suggested reaction mechanism for the manner in which these complexes function in a solvent is described in detail in U.S. Patent 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.

Typical suitable Lewis acids include aluminum fluoride, aluminum bromide, aluminum chloride, antimony pentachloride, zirconium tetrachloride, phosphorus pentachloride, phosphorus pentafluoride, boron fluoride, boron chloride, boron bromide, and arsenic pentafluoride.

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 preferable double salt, for example, is that formed by the combination of aluminum chloride and lithium chloride to yield lithium aluminum tetrachloride. Other preferable double salts would be lithium tetrafluoroborate ($LiBF_4$), lithium hexafluoroarsenate ($LiAsF_6$), lithium hexafluorophosphate ($LiPF_6$) and potassium hexafluoroarsenate ($KAsF_6$).

A main criterion in selecting an ionizable salt is that it be compatible and non-reactive with the crotonitrile, the protective cosolvent and the electrodes of the cell. Likewise, the nonaqueous electrolyte should preferably be substantially inert with respect to the anode metal while at the same time the anode should preferably not be so completely passivated that when the cell is placed on discharge, delay in the flow of current would result.

Although it should be understood that not all combinations of crotonitrile, protective cosolvent(s) and solutes will function as efficient electrolytes in all anode/cathode cell systems, once the anode and cathode components of a nonaqueous cell are selected, it is within the skill of an artisan to select a suitable protective cosolvent and solute to be used with the crotonitrile of this invention to yield an electrolyte that will function efficiently in a nonaqueous cell system. For example, propylene carbonate is a good protective cosolvent and when added to a 1M solution of $LiClO_4$ with different concentrations of crotonitrile, the conductivity was found to vary as shown in Table 3. This shows that as the concentration of propylene carbonate increases, the conductivity decreases.

TABLE 3.

1M $LiClO_4$ with	Conductivity (m-mho/cm)
100% CN	11.36
10% PC—90% CN	10.94
20% PC—80% CN	10.54
30% PC—70% CN	10.13

Preferable nonaqueous cell systems according to this invention are shown in Table 4.

TABLE 4

Anode	Cathode	Crotonitrile Plus	Solute
Li	$(CF_x)_n$	Propylene Carbonate	$LiClO_4$ or $LiAsF_6$
Li	CuS	Propylene Carbonate	$LiClO_4$ or $LiAsF_6$
Li	CuO	Propylene Carbonate	$LiClO_4$ or $LiAsF_6$
Li	$(CF_x)_n$	Ethylene Carbonate	$LiClO_4$ or $LiAsF_6$
Li	CuS	Ethylene Carbonate	$LiClO_4$ or $LiAsF_6$
Li	CuO	Ethylene Carbonate	$LiClO_4$ or $LiAsF_6$
Li	$(CF_x)_n$	Propylene Glycol Sulfite	$LiClO_4$ or $LiAsF_6$
Li	CuS	Propylene Glycol Sulfite	$LiClO_4$ or $LiAsF_6$
Li	CuO	Propylene Glycol Sulfite	$LiClO_4$ or $LiAsF_6$

The present invention will now be further illustrated by way of the following Examples.

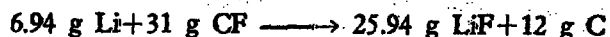
EXAMPLE I.

Nonaqueous button cells having a diameter of 1.7 inches (4.32 cm) and height of 0.36 inch (0.91 cm) were fabricated using either a CuS or $(CF_x)_n$ solid cathode, an electrolyte of 1M solution of $LiClO_4$ in crotonitrile, and a lithium anode. Specifically, each cell was constructed by placing a solid cathode in a nickel container followed by superimposing thereon a separator containing one milliliter of the electrolyte and composed of two layers of fibrous glass and a layer of "Celgard 2400" material, said latter material being a registered trademark of Celanese Corp. for wettable microporous polypropylene. A lithium electrode composed of a lithium sheet pressed onto and into an expanded nickel screen was placed on top of the separator followed by a fibrous glass pad, said pad being employed to contain additional electrolyte, if needed. The cell was closed at the top by a nickel lid which was seated upon an annular polypropylene gasket having an "L"-shaped cross section, which in turn rested on the peripheral surface of the container. A peripheral crimp seal was then made between the lid, gasket and container, thereby sealing the cell.

On different current drains to a specific cutoff voltage, the discharge capacity of the cathode, cathode efficiency and average discharge voltage to cutoff were obtained for each cell and are shown in Table 5. 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. The term "cathode limited" is intended to mean that the cathode will be completely consumed during discharge of the cell while some of the other active components of the cell will not be completely consumed. In other words, there is less cathode material present in the cell than would be required to completely discharge the cell.

For example, the theoretical efficiency of CF ($x=1$) as a cathode material in a lithium anode cell discharging at a 1 milliamperere per square centimeter drain to a 1.5 volt cutoff, is calculated as follows:

Assuming the reaction:



(equiv. wt.) (1 equiv. wt.) (1 equiv. wt.) (1 equiv. wt.)

then if 1 gram (g) CF is used the fraction of the equivalent weight is $1/31$. Since one

Faraday of electricity is obtained from one equivalent weight, then the AH per equivalent weight is calculated as follows:

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

Therefore, $1/31$ equivalent weight $\times 26.8$ AH/equivalent weight = 0.864 AH. This 0.864 AH or 864 mAh is the theoretical capacity of 1 gram of CF material when used as a cathode in a lithium anode cell and, by using this calculation technique, the cathode efficiency of $(CF_x)_n$ material and the other cathode materials can be calculated when such are used as cathodes in cells having various electrolytes.

As shown by the test data in Table 5, the discharge capacity and cathode efficiency of the cells containing crotonitrile as the sole solvent were very low thus demonstrating that crotonitrile would be unacceptable for nonaqueous cell systems if used as the only solvent.

TABLE 5

Cell Sample	Cathode	Current Drain (mA/cm ²)	Cutoff Voltage (Volts)	Theoretical Capacity (mAh)	Discharge Capacity (mAh)	% cathode Eff.	Average Discharge Voltage (Volts)
1	CuS	5.0	1.0	1025.0	120	11.4	—
2	CuS	5.0	1.0	1014.0	51	5.0	—
3	CuS	1.0	1.0	1008.0	212	21.0	1.6
4	CuS	1.0	1.0	1014.0	251	24.7	1.6
5	CuS	1.0	1.0	1014.0	310	30.5	1.8
6	CuS	0.1	1.0	1014.0	82	8.1	1.8
7	CuS	0.1	1.0	1014.0	68	6.7	1.8
8	CuS	0.1	1.0	997.0	99	9.9	1.8
9	$(CF_x)_n$	5.0	1.5	738.0	427	57.8	2.0
10	$(CF_x)_n$	5.0	1.5	718.3	352	49.0	2.0
11	$(CF_x)_n$	5.0	1.5	792.1	201	25.4	1.8
12	$(CF_x)_n$	1.0	1.5	733.1	486	66.3	2.1
13	$(CF_x)_n$	1.0	1.5	800.3	449	56.1	2.2
14	$(CF_x)_n$	1.0	1.5	839.7	430	51.2	2.2
15	$(CF_x)_n$	0.1	1.5	813.9	231	28.4	2.3
16	$(CF_x)_n$	0.1	1.5	780.6	298	38.2	2.3
17	$(CF_x)_n$	0.1	1.5	806.9	153	19.0	2.2

EXAMPLE II.

Several similar type button cells were produced as described in Example I except that the electrolyte was 1 M solution of LiClO_4 with different concentrations of crotonitrile and propylene carbonate. The cathode used in each of these cells was a solid $(\text{CF}_3)_x$ cathode wherein the x value varied from 0.85 to 1.0.

On a discharge drain ranging from 0.1 mA/cm^2 to 5.0 mA/cm^2 to a 1.5 volt cutoff, the average discharge voltage, cathode efficiency and discharge capacity to cutoff were obtained for each cell and are shown in Table 6. The test data in Table 6 clearly illustrate the high cathode utilization obtainable when using an electrolyte based on crotonitrile in combination with propylene carbonate and LiClO_4 . The test data also show that the concentration of the propylene carbonate can vary from 10 to 30 volume per cent of the solvent mixture and still provide a good electrolyte for use in nonaqueous lithium cells.

TABLE 6

Cell Sample	Electrolyte System	Current Drain (mA/cm^2)	Theoretical Capacity (mAH)	Discharge Capacity (mAH)	% cathode Eff.	Average Discharge Voltage (Volts)
1	10% PC-90% CN	5.0	656	120	18.3	1.9
2	10% PC-90% CN	5.0	701	90	12.8	2.0
3	10% PC-90% CN	5.0	676	200	29.5	2.0
4	10% PC-90% CN	1.0	781	609	78.0	2.3
5	10% PC-90% CN	1.0	787	692	87.9	2.3
6	10% PC-90% CN	1.0	767	703	91.6	2.3
7	10% PC-90% CN	0.1	761	630	82.8	2.3
8	10% PC-90% CN	0.1	800	560	70.0	2.2
9	10% PC-90% CN	0.1	749	440	58.8	2.6
10	20% PC-80% CN	1.0	827	661	80.0	2.2
11	20% PC-80% CN	1.0	872	779	89.3	2.2
12	20% PC-80% CN	1.0	735	531	72.3	2.1
13	30% PC-70% CN	1.0	781	580	74.4	2.2
14	30% PC-70% CN	1.0	833	690	82.8	2.2
15	30% PC-70% CN	1.0	807	540	66.9	2.3

EXAMPLE III.

Several similar type button cells were produced as described in Example I except that different cathodes were used along with different concentrations of crotonitrile and propylene carbonate in the LiClO_4 electrolyte solution.

The discharge capacity, average discharge voltage and cathode efficiency were obtained for each cell using a 1 mA/cm^2 drain to a specific cutoff voltage as shown in Table 7. As is known in the art, CuS cells will discharge in two steps and thus the data obtained for the CuS cells reflect the two-step discharge.

As demonstrated from the data in Table 7, crotonitrile in combination with propylene carbonate and an ionizable solute produces an electrolyte admirably suited for use in nonaqueous cells employing highly active metal anodes.

Cathode efficiencies of slightly over 100% for the NiF_2 cathode cells are believed to be within the limits of experimental error and are not believed to be significant.

TABLE 7

1M LiClO_4 - Various Cathodes - Discharge Rate 1.0 mA./cm²

Cell Sample	System	Theoretical Capacity (mAh)	Discharge Capacity (mAh)	% cathode Efficiency	Average Discharge Voltages (Volts)	
					1st Step	2nd Step
1	CuS	1008	680	67.5	1.9	1.0
2	10% PC-90% CN	1008	780	77.3	1.9	1.3
3	2-Step Discharge		790	78.3	1.9	1.2
	0.5 Volt Cutoff					
4	AgCl	826	580	70.2		2.6
5	10% PC-90% CN	809	565	69.8		2.6
6	1-Step Discharge		575	68.2		2.6
	1.5 Volts Cutoff					
7	AgCl	826	583	70.6		2.6
8	5% PC-95% CN	809	586	72.4		2.6
9	1-Step Discharge		572	70.7		2.6
	1.5 Volts Cutoff					
10	CuO	715	350	49.0		1.0
11	10% PC-90% CN	703	430	61.0		1.0
12	1-Step Discharge		360	51.0		0.9
	0.6 Volt Cutoff					
13	NiF_2	643	668	104.0		1.42
14	10% PC-90% CN	678	684	104.0		1.42
	1-Step Discharge					
	1.0 Volt Cutoff					

5 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. 5

WHAT WE CLAIM IS:—

10 1. A nonaqueous cell comprising a metal anode, a solid cathode and a nonaqueous electrolyte comprising crotonitrile, a protective cosolvent and an ionizable solute, the ionizable solute being compatible and non-reactive with the crotonitrile, protective cosolvent, anode and cathode. 10

2. The nonaqueous cell of claim 1 wherein said protective cosolvent is selected from propylene carbonate, ethylene carbonate, γ -butyrolactone, nitrobenzene, methyl acetate, sulfolane, 3-methyl sulfolane, methyl formate, dimethyl sulfoxide, propylene glycol sulfite and diethyl sulfite. 15

3. A nonaqueous cell as claimed in claim 2 wherein said protective cosolvent is propylene carbonate.

4. A nonaqueous cell as claimed in any of claims 1 to 3 wherein the metal-



17

9

1,529,371

9

Cathode efficiencies of slightly over 100% for the NiF_2 cathode cells are believed to be within the limits of experimental error and are not believed to be significant.

TABLE 7

1M LiClO_4 - Various Cathodes - Discharge Rate 1.0 mA/cm²

Cell Sample	System	Theoretical Capacity (mA·H)	Discharge Capacity (mA·H)	% cathode Efficiency	Average Discharge Voltages (Volts)	
					1st Step	2nd Step
1	CuS	1008	680	67.5	1.9	1.0
2	10% PC-90% CN 2-Step Discharge 0.5 Volt Cutoff		780	77.3	1.9	1.3
3			790	78.3	1.9	1.2
4	AgCl	826	580	70.2		2.6
5	10% PC-90% CN 1-Step Discharge 1.5 Volts Cutoff		565	69.8		2.6
6			575	68.2		2.6
7	AgCl	826	583	70.6		2.6
8	5% PC-95% CN 1-Step Discharge 1.5 Volts Cutoff		586	72.4		2.6
9			572	70.7		2.6
10	CuO	715	350	49.0		1.0
11	10% PC-90% CN 1-Step Discharge 0.6 Volt Cutoff		430	61.0		1.0
12			360	51.0		0.9
13	NiF_2	643	668	104.0		1.42
14	10% PC-90% CN 1-Step Discharge 1.0 Volt Cutoff		684	104.0		1.42

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:—

1. A nonaqueous cell comprising a metal anode, a solid cathode and a nonaqueous electrolyte comprising crotonitrile, a protective cosolvent and an ionizable solute, the ionizable solute being compatible and non-reactive with the crotonitrile, protective cosolvent, anode and cathode.

2. The nonaqueous cell of claim 1 wherein said protective cosolvent is selected from propylene carbonate, ethylene carbonate, γ -butyrolactone, nitrobenzene, methyl acetate, sulfolane, 3-methyl sulfolane, methyl formate, dimethyl sulfoxide, propylene glycol sulfite and diethyl sulfite.

3. A nonaqueous cell as claimed in claim 2 wherein said protective cosolvent is propylene carbonate.

4. A nonaqueous cell as claimed in any of claims 1 to 3 wherein the metal-



10

1,529,371

10

anode is selected from lithium, sodium, potassium, calcium, magnesium and their alloys.

5. A nonaqueous cell as claimed in claim 4 wherein the metal anode is lithium.

5

6. A nonaqueous cell is claimed in any of claims 1 to 5 wherein the solid cathode is selected from $(CF_3)_n$, copper sulfide, nickel fluoride, copper oxide, manganese dioxide, lead dioxide, iron sulfide, copper chloride, silver chloride and sulfur.

5

7. A nonaqueous cell as claimed in any of claims 1 to 6 wherein said electrolyte contains, in addition to the protective cosolvent, a low viscosity cosolvent selected from tetrahydrofuran, dioxolane, dimethoxyethane, dimethyl isoxazole and dioxane.

10

8. A nonaqueous cell as claimed in any of claims 1 to 7 wherein the solute is selected from lithium aluminum tetrachloride, lithium tetrafluoroborate, lithium hexafluoroarsenate, lithium hexafluorophosphate, potassium hexafluoroarsenate and lithium perchlorate.

10

15

9. A nonaqueous cell as claimed in any of claims 1 to 8 wherein the protective cosolvent is used in a concentration of from 1 to 50 volume percent of the solvent mixture.

15

10. A nonaqueous cell as claimed in claim 9 wherein the protective cosolvent is used in a concentration of from 4 to 30 volume percent of the solvent mixture.

20

11. A nonaqueous cell as claimed in claim 1 wherein said anode is lithium, said cathode is $(CF_3)_n$ and said protective cosolvent is propylene carbonate.

20

12. A nonaqueous cell as claimed in claim 1 wherein said anode is lithium, said cathode is copper sulfide and said protective cosolvent is propylene carbonate.

25

13. A nonaqueous cell as claimed in claim 1 wherein said anode is lithium, said cathode is nickel fluoride and said protective cosolvent is propylene carbonate.

14. A nonaqueous cell as claimed in claim 1 wherein said anode is lithium, said cathode is copper oxide and said protective cosolvent is propylene carbonate.

25

15. A nonaqueous cell as claimed in claim 1 wherein said anode is lithium, said cathode is silver chloride and said protective cosolvent is propylene carbonate.

30

16. A nonaqueous cell as claimed in claim 1 and substantially as hereinbefore described with reference to either Example II or III.

30

W. P. THOMPSON & CO.,
Coopers Buildings, 12 Church Street,
Liverpool L1 3AB,
Chartered Patent Agents.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1978.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.