

Description

The invention relates to the use of a solid cathode material in a nonaqueous cell and to a nonaqueous cell containing said cathode material.

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. 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 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 organic electrolyte systems. A large number of nonaqueous organic electrolyte solutions is taught in the art as being suitable for a wide variety of cell systems.

Although a larger number of known solid cathode 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 program 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.

French Patent 2,381,395 discloses nonaqueous (organic) cells having cathodes of the formula MY_kX_z where M is a Group IIA, IIB, IVB VB, or VIIB element or a metal from a group including lead and iron, Y is a Group VA element such as bismuth and X is sulfur, selenium or tellurium, with k being 0 or 1 and z being 3 or more.

Patent Specification US—A—4158723 discloses an electric cell having lithium as a negative active material, an electrolyte solution of which the solvent is an aprotic liquid, and a positive active material comprising lead bismuthate, $Pb_2Bi_2O_9$, i.e. a compound of lead oxide, PbO , and bismuth oxide Bi_2O_3 . The positive active material is stated to be one which results from the combination of an oxide having the character of an acidic anhydride with the lead oxide PbO .

It is an object of the present invention to provide solid cathode materials for nonaqueous cell systems, and to provide a nonaqueous cell including such a cathode material.

According to the present invention a nonaqueous electrochemical cell system uses a solid cathode material which comprises the reaction product of bismuth, sulphur and iron or

lead wherein the bismuth is in excess of 1/3 of the moles of sulphur. Preferably the reaction product is in the proportions of two moles of bismuth, two moles of iron or lead and five moles of sulfur.

Although not wanting to be bound by theory, it is believed that based on the above proportions the following reactions occur:



It is thus believed that the materials are in the form of bismuth iron sulfide or bismuth lead sulfide.

As used herein, the term "mole" shall mean atomic weight such as gram-atoms. The reaction products of these cathode materials can be obtained by mixing together the appropriate moles of the specific components and then heating them at a sufficient temperature, e.g., about 550°C., in an enclosed vessel for a time sufficient to insure complete reaction. Upon cooling, the reaction product can be ground to a powder and, if desired, mixed with a binder or a conductive agent. Suitable binders would include polytetrafluoroethylene, polyethylene, polysulfone, polypropylene, polyamide and conductive agents would include carbon and graphite or metal powders. It would also be suitable to mix with the cathode material of this invention bismuth, iron or lead powder which will have the added benefits of permitting a greater densification of the reaction product and of enhancing voltage control.

The reaction product of the bismuth lead sulfide could also be prepared by employing an aqueous method which comprises reacting the proper proportions of bismuth and lead nitrates with an excess of sodium sulfide and then filtering the solution containing the precipitated reaction product through a coarse frit, followed by thorough washing, and drying for about three hours at 400°C.

If the bismuth is added in excess of 1/3 of the moles of sulfur some of the bismuth would remain in a metallic state, thus serving as a conductive additive.

The solid cathode materials formed by the reaction of bismuth, iron and sulfur and the reaction product of bismuth, lead and sulfur have been found to be ideally suited for use in nonaqueous cell systems.

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, 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 $(\text{CH}_3\text{O})_3\text{B}$ (liquid range -29.3 to 67°C.)

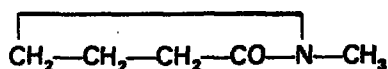
Tetraalkyl silicates: e.g., tetramethyl silicate, $(\text{CH}_3\text{O})_4\text{Si}$ (boiling point 121°C.)

Nitroalkanes: e.g., nitromethane, CH_3NO_2 (liquid range -17 to 100.8°C.)

Alkyl nitriles: e.g., acetonitrile, CH_3CN (liquid range -45 to 81.6°C.)

Dialkyl amides: e.g., dimethylformamide, $\text{HCON}(\text{CH}_3)_2$ (liquid range -60.48 to 149°C.)

Lactams: e.g., N-methylpyrrolidone,



(liquid range -16 to 202°C.)

Tetraalkylureas: e.g., tetramethylurea,

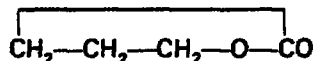


(liquid range -1.2 to 166°C.)

Monocarboxylic acid esters: e.g., ethyl acetate (liquid range -83.6 to 77.06°C.)

Orthoesters: e.g., trimethylorthoformate, $\text{HC}(\text{OCH}_3)_3$ (boiling point 103°C.)

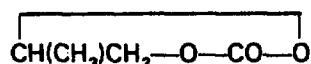
Lactones: e.g., γ -(gamma)butyrolactone,



(liquid range -42 to 206°C.)

Dialkyl carbonates: e.g., dimethyl carbonate, $\text{OC}(\text{OCH}_3)_2$ (liquid range 2 to 90°C.)

Alkylene carbonates: e.g., propylene carbonate,



(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.)

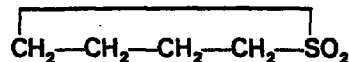
Aromatic carboxylic acid halides: e.g., benzoyl chloride (liquid range 0 to 197°C.); benzoyl bromide (liquid range -24 to 218°C.)

Aromatic sulfonic acid halides: e.g., benzene sulfonyl chloride (liquid range 14.5 to 251°C.)

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

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

Cyclic sulfones: e.g., sulfolane,



(melting point 22°C.); 3-methylsulfolane (melting point -1°C.)

Alkyl sulfonic acid halides: e.g., methane-sulfonyl 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-oxazolidone (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.)

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.); 2,4-dimethylthiazole (boiling point 144°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 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 -31.75 to 188.5°C.)

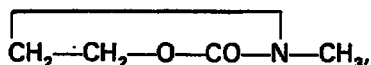
Dialkyl sulfites: e.g., dimethylsulfite (boiling point 126°C.)

Alkylene 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 (liquid range -99.5 to 120.4°C.)

Of the above, the preferred solvents are sulfolane; crotonitrile; nitrobenzene; tetrahydrofuran; methyl-substituted tetrahydrofuran; 1,3-dioxolane; 3-methyl-2-oxazolidone; propylene carbonate; γ -butyrolactone; ethylene glycol sulfite; dimethylsulfite; dimethyl sulfoxide; 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 and have wide liquid ranges, and especially because they permit highly efficient utilization of the cathode materials.

The best electrolyte for use in this invention is a 3-methyl-2-oxazolidone-based electrolyte. Liquid organic 3-methyl-2-oxazolidone material, (3Me2Ox)



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

However, it has been found that when metal salts are dissolved in liquid 3Me2Ox for the purpose of improving the conductivity of 3Me2Ox, the viscosity of the solution may be too high for its efficient use as an electrolyte for some nonaqueous cell applications other than those requiring very low current drains. Thus, in some applications in accordance with this invention, the addition of a low viscosity cosolvent would be desirable if 3Me2Ox is to be used as an electrolyte for nonaqueous cells which can operate or perform at a high energy density level.

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

The ionizing solute for use in the invention may be a simple or double salt or mixtures thereof, which will produce an ionically conductive 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 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 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 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.

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 and boron bromide.

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.

The invention will now be further illustrated by reference to the accompanying drawings and the following examples. In the drawings,

Figure 1 contains data showing the discharge characteristics of the cell disclosed and described in Example 1,

Figure 2 contains data showing the discharge characteristics of the cell disclosed and described in Example 2,

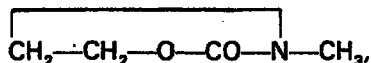
Figure 3 contains data showing the discharge characteristics of the cell disclosed and described in Example 3, and

Figure 4 contains data showing the discharge characteristics of the cell disclosed and described in Example 4.

Example 1

A flat-type cell was constructed utilizing a stainless steel metal base having therein a shallow depression into which the cell contents were placed and over which a stainless steel metal cap was placed to close the cell. The contents of each sample cell consisted of a 0.591 inch (1.501 cm) diameter lithium disc (0.114 g) having a total thickness of 0.050 inch (0.127 cm), about 1.5 ml of an electrolyte consisting of about 40 vol. % dioxolane, about 30 vol. % dimethoxyethane (DME), about 30 vol. % 3Me2Ox plus about 0.1% dimethylisoxazole (DMI) and containing 1 M LiCF_3SO_3 , and 0.875 inch (2.222 cm) diameter porous nonwoven polypropylene separator (0.01 inch or 0.0254 cm thick) which absorbed some of the electrolyte and 0.515 gram of a cathode mix compressed to form a cathode. The cathode mix consisted of 90% by weight of the chemically made reaction product of 2 moles of bismuth, 2 moles of lead and 5 moles sulfur and 10% by

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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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weight lead powder. The cell was discharged across a 15 K-ohm load and the voltage observed with time is shown as the curve in Figure 1. In addition, at various time periods, the cell was discharged across a 1 K-ohm load (pulse discharge for two seconds) and the voltage observed is shown as the points identified as "+" in Figure 1.

Example II

A flat-type cell was constructed as in Example I except that in the cathode mix the 10% by weight lead powder was replaced with 10% by weight graphite and the total cathode mix weight was 0.25 gram. The cell was tested as described in Example I and the data obtained are shown in Figure 2.

Example III

A flat-type cell was constructed as in Example I except that the cathode mix (0.455 gram) consisted of 85% by weight of the thermal reaction product of 2 moles bismuth, 2 moles lead and 5 moles sulfur, 10% by weight carbon and 5% by weight polytetrafluoroethylene as a binder. The cell was tested as described in Example I and the data obtained are shown in Figure 3.

Example IV

A flat-type cell was constructed as in Example I except that the cathode mix (0.505 gram) consisted of 90% by weight of the thermal reaction product of 2 moles bismuth, 2 moles iron and 5 moles sulfur, and 10% by weight of bismuth powder. The cell was tested as described in Example I and the data obtained are shown in Figure 4.

Claims

1. The use in a non-aqueous electrochemical cell of a solid cathode material comprising the reaction product of bismuth, sulphur and iron or lead characterised in that the bismuth is in excess of 1/3 of the moles of the sulphur.

2. The use as claimed in claim 1, characterised in that the reaction product is in the proportions of 2 moles of bismuth, 5 moles of sulphur and 2 moles of iron or lead.

3. The use as claimed in claim 1, characterised in that a conductive agent is present in the cathode material and that the conductive agent is bismuth in the metallic state resulting from using an excess of bismuth to form the reaction product.

4. The use as claimed in claim 2, characterised in that a conductive agent is added to the reaction product.

5. The use as claimed in claim 4 characterised in that said conductive agent is at least one material selected from graphite, carbon, lead, bismuth and iron.

6. The use as claimed in any of the preced-

ing claims, characterised in that a binder is added to the reaction product.

7. The use as claimed in claim 6, characterised in that the binder is at least one material selected from polytetrafluoroethylene, polyethylene, polysulfone, polypropylene and polyamide.

8. A nonaqueous cell comprising an active metal anode, an organic electrolyte solution and a solid cathode material, characterised in that the solid cathode material is a material as defined in any one of the preceding claims.

9. A nonaqueous cell as claimed in claim 8, characterised in that the solvent of the electrolyte is at least one solvent selected from sulfolane; crotonitrile; nitrobenzene; tetrahydrofuran; methyl-substituted tetrahydrofuran 1,3-dioxolane; 3-methyl-2-oxazolidone; propylene carbonate; γ -butyrolactone; ethylene glycol sulfite- dimethyl-sulfite; dimethyl sulfoxide; 1,1- and 1,2-dimethoxyethane; and dimethyl isoxazole.

10. A nonaqueous cell as claimed in claim 9, characterised in that the solvent of the electrolyte is 3-methyl-2-oxazolidone along with a low viscosity solvent selected from tetrahydrofuran; methyl-substituted tetrahydrofuran; dioxolane; dimethoxyethane; dimethylisoxazole; diethyl carbonate; ethylene glycol sulfite; dioxane; and dimethyl sulfite.

11. A nonaqueous cell as claimed in any one of claims 8 to 10, characterised in that said active anode is selected from lithium, sodium, potassium, calcium and alloys thereof.

Patentansprüche

1. Verwendung eines festen Kathodenmaterials, das das Reaktionsprodukt von Wismut, Schwefel und Eisen oder Blei enthält, in einer nicht-wässrigen elektrochemischen Zelle, dadurch gekennzeichnet, daß Wismut mehr als 1/3 der Mole des Schwefels aufweist.

2. Verwendung nach Anspruch 1, dadurch gekennzeichnet, daß das Reaktionsprodukt 2 Mol Wismut, 5 Mol Schwefel und 2 Mol Eisen oder Blei enthält.

3. Verwendung nach Anspruch 1, dadurch gekennzeichnet, daß ein leitfähiges Mittel im Kathodenmaterial vorhanden ist und daß das leitfähige Mittel Wismut im metallischen Zustand ist, was sich durch die Verwendung eines Überschusses an Wismut ergibt, um das Reaktionsprodukt zu bilden.

4. Verwendung nach Anspruch 2, dadurch gekennzeichnet, daß dem Reaktionsprodukt ein leitfähiges Mittel beigegeben wird.

5. Verwendung nach Anspruch 4, dadurch gekennzeichnet, daß dieses leitfähige Mittel aus wenigstens einem der Stoffe Graphit, Kohlenstoff, Blei, Wismut und Eisen ausgewählt ist.

6. Verwendung nach einem der vorangehenden Ansprüche dadurch gekennzeichnet, daß zum Reaktionsprodukt ein Bindemittel hinzugefügt wird.

weight lead powder. The cell was discharged across a 15 K-ohm load and the voltage observed with time is shown as the curve in Figure 1. In addition, at various time periods, the cell was discharged across a 1 K-ohm load (pulse discharge for two seconds) and the voltage observed is shown as the points identified as "+" in Figure 1.

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2. The use as claimed in claim 1, characterised in that the reaction product is in the proportions of 2 moles of bismuth, 5 moles of sulphur and 2 moles of iron or lead.

3. The use as claimed in claim 1, characterised in that a conductive agent is present in the cathode material and that the conductive agent is bismuth in the metallic state resulting from using an excess of bismuth to form the reaction product.

4. The use as claimed in claim 2, characterised in that a conductive agent is added to the reaction product.

5. The use as claimed in claim 4 characterised in that said conductive agent is at least one material selected from graphite, carbon, lead, bismuth and iron.

6. The use as claimed in any of the preced-

ing claims, characterised in that a binder is added to the reaction product.

7. The use as claimed in claim 6, characterised in that the binder is at least one material selected from polytetrafluoroethylene, polyethylene, polysulfone, polypropylene and polyamide.

8. A nonaqueous cell comprising an active metal anode, an organic electrolyte solution and a solid cathode material, characterised in that the solid cathode material is a material as defined in any one of the preceding claims.

9. A nonaqueous cell as claimed in claim 8, characterised in that the solvent of the electrolyte is at least one solvent selected from sulfolane; crotonitrile; nitrobenzene; tetrahydrofuran; methyl-substituted tetrahydrofuran 1,3-dioxolane; 3-methyl-2-oxazolidone; propylene carbonate; *p*-butyrolactone; ethylene glycol sulfite; dimethyl-sulfite; dimethyl sulfoxide; 1,1- and 1,2-dimethoxyethane; and dimethyl isoxazole.

10. A nonaqueous cell as claimed in claim 9, characterised in that the solvent of the electrolyte is 3-methyl-2-oxazolidone along with a low viscosity solvent selected from tetrahydrofuran; methyl-substituted tetrahydrofuran; dioxolane; dimethoxyethane; dimethylisoxazole; diethyl carbonate; ethylene glycol sulfite; dioxane; and dimethyl sulfite.

11. A nonaqueous cell as claimed in any one of claims 8 to 10, characterised in that said active anode is selected from lithium, sodium, potassium, calcium and alloys thereof.

Patentansprüche

1. Verwendung eines festen Kathodenmaterials, das das Reaktionsprodukt von Wismut, Schwefel und Eisen oder Blei enthält, in einer nicht-wässrigen elektrochemischen Zelle, dadurch gekennzeichnet, daß Wismut mehr als 1/3 der Mole des Schwefels aufweist.

2. Verwendung nach Anspruch 1, dadurch gekennzeichnet, daß das Reaktionsprodukt 2 Mol Wismut, 5 Mol Schwefel und 2 Mol Eisen oder Blei enthält.

3. Verwendung nach Anspruch 1, dadurch gekennzeichnet, daß ein leitfähiges Mittel im Kathodenmaterial vorhanden ist und daß das leitfähige Mittel Wismut im metallischen Zustand ist, was sich durch die Verwendung eines Überschusses an Wismut ergibt, um das Reaktionsprodukt zu bilden.

4. Verwendung nach Anspruch 2, dadurch gekennzeichnet, daß dem Reaktionsprodukt ein leitfähiges Mittel beigegeben wird.

5. Verwendung nach Anspruch 4, dadurch gekennzeichnet, daß dieses leitfähige Mittel aus wenigstens einem der Stoffe Graphit, Kohlenstoff, Blei, Wismut und Eisen ausgewählt ist.

6. Verwendung nach einem der vorangehenden Ansprüche dadurch gekennzeichnet, daß zum Reaktionsprodukt ein Bindemittel hinzugefügt wird.



7. Verwendung nach Anspruch 6, dadurch gekennzeichnet, daß das Bindemittel wenigstens aus einem der Stoffe Polytetrafluoroäthylen, Polyäthylen, Polysulfon, Polypropylen und Polyamid ausgewählt ist.

8. Nicht-wässrige Zelle, die eine aktive Metallanode, eine organische Elektrolytlösung und ein festes Kathodenmaterial aufweist, dadurch gekennzeichnet, daß das feste Kathodenmaterial einen Stoff darstellt, der in einem der vorangegangenen Ansprüche definiert ist.

9. Nicht-wässrige Zelle nach Anspruch 8, dadurch gekennzeichnet, daß das Lösungsmittel des Elektrolyten aus einem der Lösungsmittel aus Sulfolan, Crotonitril, Nitrobenzol, Tetrahydrofuran, Methyl-substituiertes Tetrahydrofuran, 1,3-Dioxolan, 3-Methyl-2-Oxazolidon, Propylenkarbonat, γ -Butyrolacton, Äthylenglykolsulfit, Dimethylsulfit, Dimethylsulfoxid, 1,1- und 1,2 Dimethoxyäthan und Dimethylisoxazol ausgewählt ist.

10. Nicht-wässrige Zelle nach Anspruch 9, dadurch gekennzeichnet, daß das Lösungsmittel des Elektrolyten 3-Methyl-2-Oxazolidon zusammen mit einem der niedrigviskosen Lösungsmittel Tetrahydrofuran, Methyl-substituiertes Tetrahydrofuran, Dioxolan, Dimethyläthan, Dimethylisoxazol, Diäthylkarbonat, Äthylenglykolsulfit, Dioxan und Dimethylsulfit ist.

11. Nicht-wässrige Zelle nach einem der Ansprüche 8—10, dadurch gekennzeichnet, daß die aktive Anode aus Lithium, Natrium, Kalium, Kalzium und deren Legierungen ausgewählt ist.

Revendications

1. Utilisation, dans une cellule électrochimique non aqueuse, d'un matériau cathodique solide comprenant le produit de réaction du bismuth, du soufre et du fer ou du plomb, caractérisée en ce que le bismuth est en excès d'un tiers du nombre de moles de soufre.

2. Utilisation suivant la revendication 1, caractérisée en ce que le produit de réaction est dans les proportions de 2 moles de bismuth, 5 moles de soufre et 2 moles de fer ou de plomb.

3. Utilisation suivant la revendication 1, caractérisée en ce qu'un agent conducteur est présent dans le matériau cathodique et en ce

que l'agent conducteur est le bismuth à l'état métallique, résultant de l'utilisation d'un excès de bismuth pour former le produit de réaction.

4. Utilisation suivant la revendication 2, caractérisée en ce qu'un agent conducteur est ajouté au produit réactionnel.

5. Utilisation suivant la revendication 4, caractérisée en ce que l'agent conducteur est au moins une matière choisie entre graphite, carbone, plomb, bismuth et fer.

6. Utilisation suivant l'une quelconque des revendications précédentes, caractérisée en ce qu'un liant est ajouté au produit de réaction.

7. Utilisation suivant la revendication 6, caractérisée en ce que le liant est au moins une matière choisie entre polytétrafluoréthylène, polyéthylène polysulfone, polypropylène et polyamide.

8. Cellule non aqueuse, comprenant une anode en métal actif, une solution organique d'électrolyte et un matériau cathodique solide, caractérisée en ce que le matériau cathodique solide est un matériau tel que défini dans l'une quelconque des revendications précédentes.

9. Cellule non aqueuse suivant la revendication 8, caractérisée en ce que le solvant de l'électrolyte est au moins un solvant choisi entre le sulfolane; le crotonitrile; le nitrobenzène; le tétrahydrofuranne; le tétrahydrofuranne à substituant méthyle; le 1,3-dioxolane; la 3-méthyl-2-oxazolidone; le carbonate de propylène; la γ -butyrolactone; le sulfite d'éthylène-glycol; le sulfite de diméthyle; le diméthylsulfoxyde; le 1,1- et le 1,2-diméthoxyéthane; et le diméthylisoxazole.

10. Cellule non aqueuse suivant la revendication 9, caractérisée en ce que le solvant de l'électrolyte est la 3-méthyl-2-oxazolidone utilisée conjointement avec un solvant à faible viscosité, choisi entre le tétrahydrofuranne; le tétrahydrofuranne à substituant méthyle; le dioxolane; le diméthoxyéthane; le diméthylisoxazole; le carbonate de diéthyle; le sulfite d'éthylène-glycol; le dioxanne; et le sulfite de diméthyle.

11. Cellule non aqueuse selon l'une quelconque des revendications 8 à 10, caractérisée en ce que l'anode active est choisie entre le lithium, le sodium, le potassium, le calcium et leurs alliages.

