

THF-based Electrolyte for Low Temperature Performance in Primary Lithium Batteries

BACKGROUND OF INVENTION

- [001] This invention relates to a nonaqueous electrolyte for a primary electrochemical cell, such as a lithium/iron disulfide cell. More specifically, an electrolyte including THF is contemplated.
- [002] Batteries are used to provide power to many portable electronic devices. In today's consumer-driven device market, standardized primary cell sizes (e.g., AA or AAA) and specific nominal voltages (typically 1.5 V) are preferred. Moreover, consumers frequently opt to use primary batteries for their low cost, convenience, reliability and sustained shelf life as compared to comparable, currently available rechargeable (i.e., secondary) batteries. Primary lithium batteries (those that contain metallic lithium or lithium alloy as the electrochemically active material of the negative electrode) are becoming increasingly popular as the battery of choice for new devices because of trends in those devices toward smaller size and higher power.
- [003] One type of lithium battery that is particularly useful for 1.5 V consumer devices is the lithium-iron disulfide (or LiFeS_2) battery, having the IEC designations FR6 for AA size and FR03 for AAA size. LiFeS_2 cells offer higher energy density, especially at high drain rates in comparison to alkaline, carbon zinc or other primary (i.e., non-rechargeable) battery systems. Such batteries use iron disulfide, FeS_2 (also referred to as pyrite or iron pyrite, which is the preferred mineral form of iron disulfide for battery applications), as the electrochemically active material of the positive electrode.
- [004] As a general rule, the electrolyte in any battery must be selected to provide sufficient electrical conductivity to meet discharge requirements over the desired temperature range. As demonstrated by U.S. Patent No. 4,129,691 to Broussely, increasing the solute (i.e., salt) concentration in a lithium battery electrolyte is expected to result in a corresponding increase in the conductivity and usefulness of that electrolyte. However, other limitations—such as the solubility of the solute in specific solvents, the formation of an appropriate passivating layer on lithium-based electrodes and/or the compatibility of the solvent with the electrochemically active or other materials in the cell—make the selection of an appropriate electrolyte system

difficult. As a non-limiting example, U.S. Patent No. 4,804,595 to Bakos describes how certain ethers are not miscible with solvents such as propylene carbonate. Additional electrolyte deficiencies and incompatibilities are well known and documented in this art, particularly as they relate to LiFeS_2 cells and lithium's reactivity with many liquids, solvents and common polymeric sealing materials.

[005] Ethers are often desirable as lithium battery electrolyte solvents because of their generally low viscosity, good wetting capability, good low temperature discharge performance and good high rate discharge performance, although their polarity is relatively low compared to some other common solvents. Ethers are particularly useful in cells with pyrite because they tend to be more stable as compared to higher voltage cathode materials in ethers, where degradation of the electrode surface or unwanted reactions with the solvent(s) might occur (e.g., polymerization). Among the ethers that have been used in LiFeS_2 cells are 1,2-dimethoxyethane ("DME") and 1,3-dioxolane ("DIOX"), whether used together as taught by U.S. Patent Nos. 5,514,491 or 6,218,054 or European Patent 0 529 802 B1, all to Webber, or used in whole or in part as a blend of solvents as suggested by U.S. Patent Nos. 7,316,868 to Gorkovenko (use of DIOX and 5-6 carbon 1,3-dialkoxyalkanes); 3,996,069 to Kronenberg (use of 3-methyl-2-oxazolidone and DIOX and/or DME); or U.S. Patent Publication No. 2008/0026296A1 to Bowden (use of sulfolane and DME).

[006] Other solvents not specifically containing DIOX or DME may also be possible, such as those disclosed in U.S. Patent No. 5,229,227 to Webber (use of 3-methyl-2-oxazolidone with polyalkylene glycol ethers such as diglyme). However, because of interactions among solvents, as well as the potential effects of solutes and/or electrode materials on those solvents, ideal electrolyte solvent blends and the resulting discharge performance of the cell are often difficult to predict without actually testing the proposed blend in a functioning electrochemical cell.

[007] A wide variety of solutes has been used in LiFeS_2 cell electrolytes, including lithium iodide (LiI), lithium trifluoromethanesulfonate (LiCF_3SO_3 or "lithium triflate"), lithium bistrifluoromethylsulfonyl imide ($\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ or "lithium imide"), lithium perchlorate (LiClO_4), lithium hexafluoroarsenate (LiAsF_6) and others. While electrolytes containing lithium triflate can provide fair cell electrical and discharge characteristics, such electrolytes have relatively low electrical conductivity. Furthermore, lithium triflate is relatively expensive.

Lithium iodide (LiI) has been used as an alternative to lithium triflate to both reduce cost and improve cell electrical performance, as discussed in the previously identified U.S. Patent No. 5,514,491 to Webber. One particular brand of AA- sized FR06 batteries sold by Energizer Holdings Inc. currently uses a nonaqueous electrolyte with 0.75 molar concentration of LiI salt in a solvent mixture containing DIOX and DME.

[008] Lithium iodide and lithium triflate salts have been used in combination to provide improved low temperature discharge performance, as described in related U.S. Patent Publication No. 2006/0046154 to Webber. As discussed therein, LiFeS₂ cells with a high ether content and LiI as a solute (either the sole solute or in combination with lithium triflate) may sometimes, on high rate discharge at low temperatures, exhibit a rapid drop in voltage at the beginning of discharge. The voltage can drop so low that a device being powered by the cell will not operate. Eliminating LiI as a solute and making lithium triflate the sole solute can solve this problem, but the operating voltage can then be too low on high rate and high power discharge at room temperature. And the use of perchlorates as the sole, primary salt or even as a co-salt may be problematic because of the potential health and safety issues posed by these compounds.

[009] Additives may be employed in the electrolyte to enhance certain aspects of a cell and/or its performance. For example, U.S. Patent No. 5,691,083 to Bolster describes the use of a very low concentration of potassium salt additives to achieve a desired open circuit voltage in cells with a cathode material including FeS₂, MnO₂ or TiS₂. U.S. Publication No. 2008/0026290 to Jiang discloses the use of an aluminum additive to slow the development of a passivation film on the surface of the lithium electrode. In each of these examples, the benefit of the additive(s) selected must be balanced against any deleterious reactions or effects (in terms of discharge performance, safety and longevity of the battery).

[0010] Finally, as mentioned above, it is believed higher concentrations of solute(s) normally improve the conductivity of the electrolyte. However, certain systems (typically in rechargeable lithium-sulfur battery systems where non-chalcogenic polysulfides are the preferred cathode material) utilize a "catholyte" where portions of the electrode itself dissolve into the electrolyte solution to provide ionic conductivity. In such systems, minimal to non-existent concentrations of lithium ions may be provided to a fully charged cell without compromising performance as taught by U.S. Patent No. 7,189,477 to Mikhaylik. Ultimately,

LiFeS₂ and other lithium electrochemical cells do not exhibit this propensity to provide ions from the electrodes to the electrolyte, thereby eliminating the usefulness of this approach in LiFeS₂ systems and more generally illustrating the pitfalls associated with blindly applying teachings from a given electrochemical system to another, dissimilar system.

DETAILED DESCRIPTION OF INVENTION

[0011] Unless otherwise specified, as used herein the terms listed below are defined and used throughout this disclosure as follows:

- [0012] ambient (or room) temperature – between about 20°C and about 25°C; unless otherwise stated, all examples, data and manufacturing information were provided/conducted at ambient temperature.
- [0013] anode – the negative electrode; more specifically, within the meaning of the invention, it consists essentially of lithium or an alloy containing at least 90% lithium by weight as the primary electrochemically active material.
- [0014] cathode – the positive electrode; more specifically, within the meaning of the invention, it comprises iron disulfide as the primary electrochemically active material, along with one or more rheological, polymeric and/or conductive additives, coated onto a metallic current collector.
- [0015] cell housing – the structure that physically encloses the electrochemically active materials, safety devices and other inert components which comprise a fully functioning battery; typically consists of a container (formed in the shape of a cup, also referred to as a “can”) and a closure (fitting over the opening of the container, typically consists of venting and sealing mechanisms for impeding electrolyte egress and moisture/atmospheric ingress).
- [0016] electrolyte – one or more solutes dissolved within one or more liquid, organic solvents; does not include any electrochemical systems where the cathode is expected to partially or completely dissolve in order to contribute ionic conductivity to the cell (i.e., a “catholyte” such as those utilized in lithium-sulfur batteries)

- [0017] jellyroll (or spirally wound) electrode assembly – strips of anode and cathode, along with an appropriate polymeric separator, are combined into an assembly by winding along their lengths or widths, e.g., around a mandrel or central core.
- [0018] nominal – a value, specified by the manufacturer, that is representative of what can be expected for that characteristic or property.
- [0019] percent discharge – the percentage of the capacity removed from a cell as a result of its intended use, but excluding capacity removed by deliberate conditioning or preliminary discharge performed by a manufacturer to make the cell more suitable for consumer use.
- [0020] salt – as part of the electrolyte, an ionizable compound, typically including lithium or some other metal, dissolved in one or more solutes.
- [0021] DIOX – 1,3-dioxolane
- [0022] DME – 1,2-dimethoxyethane
- [0023] THF – tetrahydrofuran
- [0024] 2MeTHF – 2-methyl tetrahydrofuran
- [0025] DMP – 1,2-dimethoxypropane
- [0026] PC – propylene carbonate
- [0027] EC – ethylene carbonate
- [0028] MA – methyl acetate
- [0029] EA – ethyl acetate
- [0030] LiTfSi or Li imide – lithium bis(trifluoromethylsulfonyl) imide
- [0031] Figures 1 through 9 contain information related to the embodiments disclosed in the Examples below. Figure 10 illustrates the components of a LiFeS₂ cell.

Cell Design

- [0032] The invention will be better understood with reference to FIG. 10, which shows a specific cell design that may be implemented. Cell 10 is an FR6 type cylindrical LiFeS₂ battery cell, although the invention should have equal applicability to FR03 or other cylindrical cells. Cell 10 has a housing that includes a container in the form of a can 12 with a closed bottom and an open top end that is closed with a cell cover 14 and a gasket 16. The can 12 has a bead or reduced diameter step near the top end to support the gasket 16 and cover 14. The gasket 16 is

compressed between the can 12 and the cover 14 to seal an anode or negative electrode 18, a cathode or positive electrode 20 and electrolyte within the cell 10.

[0033] The anode 18, cathode 20 and a separator 26 are spirally wound together into an electrode assembly. The cathode 20 has a metal current collector 22, which extends from the top end of the electrode assembly and is connected to the inner surface of the cover 14 with a contact spring 24. The anode 18 is electrically connected to the inner surface of the can 12 by a metal lead (or tab) 36. The lead 36 is fastened to the anode 18, extends from the bottom of the electrode assembly, is folded across the bottom and up along the side of the electrode assembly. The lead 36 makes pressure contact with the inner surface of the side wall of the can 12. After the electrode assembly is wound, it can be held together before insertion by tooling in the manufacturing process, or the outer end of material (e.g., separator or polymer film outer wrap 38) can be fastened down, by heat sealing, gluing or taping, for example.

[0034] An insulating cone 46 is located around the peripheral portion of the top of the electrode assembly to prevent the cathode current collector 22 from making contact with the can 12, and contact between the bottom edge of the cathode 20 and the bottom of the can 12 is prevented by the inward-folded extension of the separator 26 and an electrically insulating bottom disc 44 positioned in the bottom of the can 12.

[0035] Cell 10 has a separate positive terminal cover 40, which is held in place by the inwardly crimped top edge of the can 12 and the gasket 16 and has one or more vent apertures (not shown). The can 12 serves as the negative contact terminal. An insulating jacket, such as an adhesive label 48, can be applied to the side wall of the can 12.

[0036] Disposed between the peripheral flange of the terminal cover 40 and the cell cover 14 is a positive temperature coefficient (PTC) device 42 that substantially limits the flow of current under abusive electrical conditions. Cell 10 also includes a pressure relief vent. The cell cover 14 has an aperture comprising an inward projecting central vent well 28 with a vent hole 30 in the bottom of the well 28. The aperture is sealed by a vent ball 32 and a thin-walled thermoplastic bushing 34, which is compressed between the vertical wall of the vent well 28 and the periphery of the vent ball 32. When the cell internal pressure exceeds a predetermined level, the vent ball 32, or both the ball 32 and bushing 34, is forced out of the aperture to release pressurized gases from the cell 10. In other embodiments, the pressure relief vent can be an aperture closed by a rupture membrane, such as disclosed in U.S. Patent Application

Publication No. 2005/0244706, herein fully incorporated by reference, or a relatively thin area such as a coined groove, that can tear or otherwise break, to form a vent aperture in a portion of the cell, such as a sealing plate or container wall.

[0037] The terminal portion of the electrode lead 36, disposed between the side of the electrode assembly and the side wall of the can, may have a shape prior to insertion of the electrode assembly into the can, preferably non-planar that enhances electrical contact with the side wall of the can and provides a spring-like force to bias the lead against the can side wall. During cell manufacture, the shaped terminal portion of the lead can be deformed, e.g., toward the side of the electrode assembly, to facilitate its insertion into the can, following which the terminal portion of the lead can spring partially back toward its initially non-planar shape, but remain at least partially compressed to apply a force to the inside surface of the side wall of the can, thereby making good physical and electrical contact with the can.

Electrolyte

[0038] A nonaqueous electrolyte, containing water only in very small quantities as a contaminant (e.g., no more than about 500 parts per million by weight, depending on the electrolyte salt being used), is deposited into the cell housing during manufacture. Because the electrolyte is the primary media for ionic transfer in a LiFeS_2 cell, selection of an appropriate solvent and solute combination is critical to optimizing the performance of the cell. Moreover, the solute and solvents selected for the electrolyte must possess appropriate miscibility and viscosity for the purposes of manufacture and use of the resulting cell, while still delivering appropriate discharge performance across the entire spectrum of temperatures potentially experienced by most consumer batteries (i.e., about -40°C to 60°C). Furthermore, the electrolyte must be non-reactive and non-volatile (or at least possess a low enough boiling point to be practically retained by conventional polymeric seals and closure mechanisms).

[0039] Miscibility and viscosity of the solvents and the electrolyte is key to the manufacturing and operational aspects of the battery. All solvents used in the blend must be completely miscible to insure a homogeneous solution. Similarly, in order to accommodate the requirements of high volume production, the solvents must possess a sufficiently low viscosity to flow and/or be dispensed quickly.

[0040] Additionally, the solvents and the electrolyte must possess a boiling point appropriate to the temperature range in which the battery will most likely be exposed and stored (i.e., -40° C. to 60° C). More specifically, the solvent(s) must be sufficiently non-volatile to allow for safe storage and operation of the battery within this stated temperature range. Similarly, the solvents and the electrolyte must not react with the electrode materials in a manner that degrades the electrodes or adversely affects performance of the battery upon discharge. Suitable organic solvents that have been or may be used in LiFeS₂ cells have included one or more of the following: 1,3-dioxolane; 1,3-dioxolane based ethers (e.g., alkyl- and alkoxy-substituted DIOX, such as 2-methyl-1,3-dioxolane or 4-methyl-1,3-dioxolane; etc.); 1,2-dimethoxyethane; 1,2-dimethoxyethane-based ethers (e.g., diglyme, triglyme, tetraglyme, ethyl glyme, etc.); ethylene carbonate; propylene carbonate; 1,2-butylene carbonate; 2,3-butylene carbonate; vinylene carbonate; methyl formate; γ -butyrolactone; sulfolane; acetonitrile; N,N-dimethyl formamide; N,N-dimethylacetamide; N,N-dimethylpropyleneurea; 1,1,3,3-tetramethylurea; beta aminoenones; beta aminoketones; methyltetrahydrofurfuryl ether; diethyl ether; tetrahydrofuran ("THF"); 2-methyl tetrahydrofuran; 2-methoxytetrahydrofuran; 2,5-dimethoxytetrahydrofuran; 3,5-dimethylisoxazole ("DMI"); 1,2-dimethoxypropane ("DMP"); and 1,2-dimethoxypropane-based compounds (e.g., substituted DMP, etc.).

[0041] Salts should be nearly or completely soluble with the selected solvent(s) and, as with the discussion of solvent characteristics above, without any degradation or adverse effects. Examples of typical salts that have been or may be used in LiFeS₂ cells include LiI ("lithium iodide"), LiCF₃SO₃ ("lithium triflate"), LiClO₄ ("lithium perchlorate"), Li(CF₃SO₂)₂N ("lithium imide"), Li(CF₃CF₂SO₂)₂N and Li(CF₃SO₂)₃C. Other potential candidates are lithium bis(oxalato)borate, lithium bromide, lithium hexafluorophosphate, potassium hexafluorophosphate and lithium hexafluoroarsenate. Two key aspects of salt selection are that they do not react with the housing, electrodes, sealing materials or solvents and that they do not degrade or precipitate out of the electrolyte under the typically expected conditions to which the battery will be exposed and expected to operate (e.g., temperature, electrical load, etc.). It is possible to use more than one solute to maximize certain aspects of performance.

[0042] Ethers suitable for use in LiFeS₂ cells according to the invention were selected to include the following criteria: (1) large usable liquid range, especially very low melting point, (2) low viscosity, (3) good solvating properties for lithium salts, (4) good chemical and thermal

stability towards Li anode and FeS₂ cathode, and (5) toxicity that is similar to or better than DME and DIOX. Figure 1 shows a table of the solvents considered, including melting points, boiling points and viscosity. All of the solvents listed in Figure 1 are deemed to meet the criteria above.

[0043] THF, 2MeTHF, and DMP were evaluated using LiI and Li imide salts. Two approaches were used in determining the solvent ratios. Insofar as current, commercially available LiFeS₂ cells utilize a 65:35 DIOX:DME blend (by volume), DIOX and/or DME was replaced with one of the new ethers and cells were tested on low temperature performance. The second approach was to add a certain amount of the alternative solvent into the solvent blend 65DIOX:35DME (v/v). This approach was good for quick screening of many alternative solvents, although it did not offer any direct comparisons. The particulars of these approaches are summarized in Figure 2, and the lot numbers recited therein apply to the remainder of the Figures throughout this application.

[0044] For the solvent blends containing carbonates and acetates, only Li imide salts were used because the chemical reactions between LiI and carbonates convert LiI to insoluble Li₂CO₃. Note that carbonates and acetates were originally selected based on their usage in low temperature secondary lithium-ion cells, although as shown below, none were able to provide adequate service for primary lithium cells.

[0045] The salt concentration for all electrolytes was fixed at 0.75 moles of solute per liter of solvent blends at ambient temperature. All solvents had relatively low moisture to start with (5~50ppm) except for DMP, which had a moisture level of 2800 ppm for the as-received sample. Therefore, DMP was stored with 4Å molecular sieves to reduce its moisture. After storage, the moisture of DMP was reduced to 197ppm.

[0046] The fill volume of the electrolyte dispensed was 1.47ml for all lots. Cells were pre-discharged. All other aspects of the assembly and construction were consistent with the disclosure contained herein.

[0047] The electrolytes utilizing THF showed substantial, unexpected and dramatically improved performance at extremely low temperatures (i.e., -40° C) as compared to the previously recognized best low temperature electrolytes, such as those disclosed in United States Patent Publication Nos. 20060046152 and/or 20060046154. Significantly, these publications document the well-known problem of "sudden death" of cells at extremely low

temperature, although it will be readily appreciated that even in those publications no viable solution was known to provide substantial service at extremely low temperature and high rate.

[0048] In contrast, the invention solves the shortcomings of the prior art by providing a battery with substantial capacity at extremely low temperature. Moreover, the use of THF allows for the salt to be varied, whereas the prior art indicated that blend of LiI and lithium triflate was the best (and perhaps only) means of achieving any service at low temperature. Furthermore, the invention maintains the salt concentration at 0.75 M, which should assist in maintaining room temperature performance. In short, the THF allowed for more capacity and at lower temperatures than was previously known, while still providing adequate, if not par, service for most ambient temperature drain rates.

[0049] Thus, when this electrolyte is used in conjunction with a LiFeS_2 battery according to the configuration described above, extraordinary improvements are observed at extremely low temperatures. In many embodiments, double the amount of capacity can be expected. Moreover, these improvements can be realized without sacrificing performance at room temperature or on specialized discharge tests, such as the American National Standard Institute (ANSI) digital still camera pulse test.

Other Cell Components

[0050] The cell container is often a metal can with a closed bottom such as the can in FIG. 10. The can material will depend in part of the active materials and electrolyte used in the cell. A common material type is steel. For example, the can may be made of steel, plated with nickel on at least the outside to protect the outside of the can from corrosion. The type of plating can be varied to provide varying degrees of corrosion resistance or to provide the desired appearance. The type of steel will depend in part on the manner in which the container is formed. For drawn cans the steel can be a diffusion annealed, low carbon, aluminum killed, SAE 1006 or equivalent steel, with a grain size of ASTM 9 to 11 and equiaxed to slightly elongated grain shape. Other steels, such as stainless steels, can be used to meet special needs. For example, when the can is in electrical contact with the cathode, a stainless steel may be used for improved resistance to corrosion by the cathode and electrolyte.

[0051] The cell cover can be metal. Nickel plated steel may be used, but a stainless steel is often desirable, especially when the cover is in electrical contact with the cathode. The

complexity of the cover shape will also be a factor in material selection. The cell cover may have a simple shape, such as a thick, flat disk, or it may have a more complex shape, such as the cover shown in FIG. 10. When the cover has a complex shape like that in FIG. 10, a type 304 soft annealed stainless steel with ASTM 8-9 grain size may be used, to provide the desired corrosion resistance and ease of metal forming. Formed covers may also be plated, with nickel for example.

[0052] The terminal cover should have good resistance to corrosion by water in the ambient environment, good electrical conductivity and, when visible on consumer batteries, an attractive appearance. Terminal covers are often made from nickel plated cold rolled steel or steel that is nickel plated after the covers are formed. Where terminals are located over pressure relief vents, the terminal covers generally have one or more holes to facilitate cell venting.

[0053] The gasket is made from any suitable thermoplastic material that provides the desired sealing properties. Material selection is based in part on the electrolyte composition. Examples of suitable materials include polypropylene, polyphenylene sulfide, tetrafluoride-perfluoroalkyl vinyl ether copolymer, polybutylene terephthalate and combinations thereof. Preferred gasket materials include polypropylene (e.g., PRO-FAX® 6524 from Basell Polyolefins in Wilmington, DE, USA) and polyphenylene sulfide (e.g., XTEL™ XE3035 or XE5030 from Chevron Phillips in The Woodlands, TX, USA). Small amounts of other polymers, reinforcing inorganic fillers and/or organic compounds may also be added to the base resin of the gasket.

[0054] The gasket may be coated with a sealant to provide the best seal. Ethylene propylene diene terpolymer (EPDM) is a suitable sealant material, but other suitable materials can be used.

[0055] If a ball vent is used, the vent bushing is made from a thermoplastic material that is resistant to cold flow at high temperatures (e.g., 75°C). The thermoplastic material comprises a base resin such as ethylene-tetrafluoroethylene, polybutylene terephthalate, polyphenylene sulfide, polyphthalamide, ethylene-chlorotrifluoroethylene, chlorotrifluoroethylene, perfluoroalkoxyalkane, fluorinated perfluoroethylene polypropylene and polyetherether ketone. Ethylene-tetrafluoroethylene copolymer (ETFE), polyphenylene sulfide (PPS), polybutylene terephthalate (PBT) and polyphthalamide are preferred. The resin can be modified by adding a thermal-stabilizing filler to provide a vent bushing with the desired sealing and venting

characteristics at high temperatures. The bushing can be injection molded from the thermoplastic material. TEFZEL® HT2004 (ETFE resin with 25 weight percent chopped glass filler), polythalamide (e.g., AMODEL® ET 10011 NT, from Solvay Advanced Polymers, Houston, TX) and polyphenylene sulfide (e.g., e.g., XTEL™ XE3035 or XE5030 from Chevron Phillips in The Woodlands, TX, USA) are preferred thermoplastic bushing materials.

[0056] The vent ball itself can be made from any suitable material that is stable in contact with the cell contents and provides the desired cell sealing and venting characteristic. Glasses or metals, such as stainless steel, can be used. In the event a foil vent is utilized in place of the vent ball assembly described above (e.g., pursuant to U.S. Patent Application Publication No. 2005/0244706), the above referenced materials may still be appropriately substituted.

Electrodes

[0057] The anode comprises a strip of lithium metal, sometimes referred to as lithium foil. The composition of the lithium can vary, though for battery grade lithium, the purity is always high. The lithium can be alloyed with other metals, such as aluminum, to provide the desired cell electrical performance or handling ease, although the amount of lithium in any alloy should nevertheless be maximized and alloys designed for high temperature application (i.e., above the melting point of pure lithium) are not contemplated. Appropriate battery grade lithium-aluminum foil, containing 0.5 weight percent aluminum, is available from Chemetall Foote Corp., Kings Mountain, NC, USA.

[0058] Other anode materials may be possible, including sodium, potassium, zinc, magnesium and aluminum, either as co-anodes, alloying materials or distinct, singular anodes. Ultimately, the selection of an appropriate anode material will be influenced by the compatibility of that anode with LiI, the cathode and/or the ether(s) selected.

[0059] As in the cell in FIG. 10, a separate current collector (i.e., an electrically conductive member, such as a metal foil, on which the anode is welded or coated OR an electrically conductive strip running along the length of the anode) is not needed for the anode, since lithium has a high electrical conductivity. By not utilizing such a current collector, more space is available within the container for other components, such as active materials. Anode current collectors may be made of copper and/or other appropriate high conductivity metals so as long

as they are stable when exposed to the other interior components of the cell (e.g., electrolyte), and therefore also add cost.

[0060] The electrical connection must be maintained between each of the electrodes and the opposing terminals proximate to or integrated with the housing. An electrical lead 36 can be made from a thin metal strip connecting the anode or negative electrode to one of the cell terminals (the can in the case of the FR6 cell shown in FIG. 10). When the anode includes such a lead, it is oriented substantially along a longitudinal axis of the jellyroll electrode assembly and extends partially along a width of the anode. This may be accomplished embedding an end of the lead within a portion of the anode or by simply pressing a portion such as an end of the lead onto the surface of the lithium foil. The lithium or lithium alloy has adhesive properties and generally at least a slight, sufficient pressure or contact between the lead and electrode will weld the components together. The negative electrode may be provided with a lead prior to winding into a jellyroll configuration. The lead may also be connected via appropriate welds.

[0061] The metal strip comprising the lead 36 is often made from nickel or nickel plated steel with sufficiently low resistance (e.g., generally less than $15\text{m}\Omega/\text{cm}$ and preferably less than $4.5\text{m}\Omega/\text{cm}$) in order to allow sufficient transfer of electrical current through the lead and have minimal or no impact on service life of the cell. A preferred material is 304 stainless steel. Examples of other suitable negative electrode lead materials include, but are not limited to, copper, copper alloys, for example copper alloy 7025 (a copper, nickel alloy comprising about 3% nickel, about 0.65% silicon, and about 0.15% magnesium, with the balance being copper and minor impurities); and copper alloy 110; and stainless steel. Lead materials should be chosen so that the composition is stable within the electrochemical cell including the nonaqueous electrolyte. Examples of metals generally to be avoided but can be present as impurities in relatively minor amounts are aluminum, iron and zinc.

[0062] The cathode is in the form of a strip that comprises a current collector and a mixture that includes one or more electrochemically active materials, usually in particulate form. Iron disulfide (FeS_2) is a preferred active material although the invention is applicable to most cathode materials that are stable with LiI and have a potential vs. Li that is less than 2.8V, possibly including CuO , CuO_2 and oxides of bismuth (e.g., Bi_2O_3 , etc.). Notably, MnO_2 is not suitable because these cathodes have a potential that is too high when compared to the I_2/I^- redox couple.

[0063] In a LiFeS_2 cell, the active material comprises greater than 50 weight percent FeS_2 . The cathode can also contain one or more additional active materials mentioned above, depending on the desired cell electrical and discharge characteristics. More preferably the active material for a LiFeS_2 cell cathode comprises at least 95 weight percent FeS_2 , yet more preferably at least 99 weight percent FeS_2 , and most preferably FeS_2 is the sole active cathode material. FeS_2 having a purity level of at least 95 weight percent is available from Washington Mills, North Grafton, MA, USA; Chemetall GmbH, Vienna, Austria; and Kyanite Mining Corp., Dillwyn, VA, USA. A more comprehensive description of the cathode, its formulation and a manner of manufacturing the cathode is provided below.

[0064] The current collector may be disposed within or imbedded into the cathode surface, or the cathode mixture may be coated onto one or both sides of a thin metal strip. Aluminum is a commonly used material. The current collector may extend beyond the portion of the cathode containing the cathode mixture. This extending portion of the current collector can provide a convenient area for making contact with the electrical lead connected to the positive terminal. It is desirable to keep the volume of the extending portion of the current collector to a minimum to make as much of the internal volume of the cell available for active materials and electrolyte.

[0065] The cathode is electrically connected to the positive terminal of the cell. This may be accomplished with an electrical lead, often in the form of a thin metal strip or a spring, as shown in FIG. 10, although welded connections are also possible. The lead is often made from nickel plated stainless steel. Still another embodiment may utilize a connection similar to that disclosed in United States Patent Application Serial No. 11/439,835, which should publish on or after November 29, 2007, and/or United States Patent Application Serial No. 11/787,436, which should publish on or after October 16, 2008, both of which are commonly assigned to the assignee of this application and incorporated by reference herein. Notably, to the extent a cell design may utilize one of these alternative electrical connectors/current limiting devices, the use of a PTC may be avoided. In the event an optional current limiting device, such as a standard PTC, is utilized as a safety mechanism to prevent runaway discharge/heating of the cell, a suitable PTC is sold by Tyco Electronics in Menlo Park, CA, USA. Other alternatives are also available.

Separator

[0066] The separator is a thin microporous membrane that is ion-permeable and electrically nonconductive. It is capable of holding at least some electrolyte within the pores of the separator. The separator is disposed between adjacent surfaces of the anode and cathode to electrically insulate the electrodes from each other. Portions of the separator may also insulate other components in electrical contact with the cell terminals to prevent internal short circuits. Edges of the separator often extend beyond the edges of at least one electrode to insure that the anode and cathode do not make electrical contact even if they are not perfectly aligned with each other. However, it is desirable to minimize the amount of separator extending beyond the electrodes.

[0067] To provide good high power discharge performance it is desirable that the separator have the characteristics (pores with a smallest dimension of at least $0.005\ \mu\text{m}$ and a largest dimension of no more than $5\ \mu\text{m}$ across, a porosity in the range of 30 to 70 percent, an area specific resistance of from 2 to $15\ \text{ohm}\cdot\text{cm}^2$ and a tortuosity less than 2.5) disclosed in U.S. Patent No. 5,290,414, issued March 1, 1994, and hereby incorporated by reference.

[0068] Suitable separator materials should also be strong enough to withstand cell manufacturing processes as well as pressure that may be exerted on the separator during cell discharge without tears, splits, holes or other gaps developing that could result in an internal short circuit. To minimize the total separator volume in the cell, the separator should be as thin as possible, preferably less than $25\ \mu\text{m}$ thick, and more preferably no more than $22\ \mu\text{m}$ thick, such as $20\ \mu\text{m}$ or $16\ \mu\text{m}$. A high tensile stress is desirable, preferably at least 800, more preferably at least 1000 kilograms of force per square centimeter (kgf/cm^2). For an FR6 type cell the preferred tensile stress is at least $1500\ \text{kgf}/\text{cm}^2$ in the machine direction and at least $1200\ \text{kgf}/\text{cm}^2$ in the transverse direction, and for a FR03 type cell the preferred tensile strengths in the machine and transverse directions are 1300 and $1000\ \text{kgf}/\text{cm}^2$, respectively. Preferably the average dielectric breakdown voltage will be at least 2000 volts, more preferably at least 2200 volts and most preferably at least 2400 volts. The preferred maximum effective pore size is from $0.08\ \mu\text{m}$ to $0.40\ \mu\text{m}$, more preferably no greater than $0.20\ \mu\text{m}$. Preferably the BET specific surface area will be no greater than $40\ \text{m}^2/\text{g}$, more preferably at least $15\ \text{m}^2/\text{g}$ and most preferably at least $25\ \text{m}^2/\text{g}$. Preferably the area specific resistance is no greater than $4.3\ \text{ohm}\cdot\text{cm}^2$, more preferably no greater than $4.0\ \text{ohm}\cdot\text{cm}^2$, and most preferably no greater than 3.5

ohm-cm². These properties are described in greater detail in U.S. Patent Publication No. 2005/0112462, which is hereby incorporated by reference.

[0069] Separator membranes for use in lithium batteries are often made of polypropylene, polyethylene or ultrahigh molecular weight polyethylene, with polyethylene being preferred. The separator can be a single layer of biaxially oriented microporous membrane, or two or more layers can be laminated together to provide the desired tensile strengths in orthogonal directions. A single layer is preferred to minimize the cost. Suitable single layer biaxially oriented polyethylene microporous separator is available from Tonen Chemical Corp., available from EXXON Mobile Chemical Co., Macedonia, NY, USA. Setela F20DHI grade separator has a 20 μm nominal thickness, and Setela 16MMS grade has a 16 μm nominal thickness. Suitable separators with similar properties are also available from Entek Membranes in Lebanon, OR, USA.

Cell Construction and Manufacture

[0070] The anode, cathode and separator strips are combined together in an electrode assembly. The electrode assembly may be a spirally wound design, such as that shown in FIG. 10, made by winding alternating strips of cathode, separator, anode and separator around a mandrel, which is extracted from the electrode assembly when winding is complete. At least one layer of separator and/or at least one layer of electrically insulating film (e.g., polypropylene) is generally wrapped around the outside of the electrode assembly. This serves a number of purposes: it helps hold the assembly together and may be used to adjust the width or diameter of the assembly to the desired dimension. The outermost end of the separator or other outer film layer may be held down with a piece of adhesive tape or by heat sealing. The anode can be the outermost electrode, as shown in FIG. 10, or the cathode can be the outermost electrode. Either electrode can be in electrical contact with the cell container, but internal short circuits between the outmost electrode and the side wall of the container can be avoided when the outermost electrode is the same electrode that is intended to be in electrical contact with the can.

[0071] The cell can be closed and sealed using any suitable process. Such processes may include, but are not limited to, crimping, redrawing, colleting and combinations thereof. For example, for the cell in FIG. 10, a bead is formed in the can after the electrodes and insulator

cone are inserted, and the gasket and cover assembly (including the cell cover, contact spring and vent bushing) are placed in the open end of the can. The cell is supported at the bead while the gasket and cover assembly are pushed downward against the bead. The diameter of the top of the can above the bead is reduced with a segmented collet to hold the gasket and cover assembly in place in the cell. After electrolyte is dispensed into the cell through the apertures in the vent bushing and cover, a vent ball is inserted into the bushing to seal the aperture in the cell cover. A PTC device and a terminal cover are placed onto the cell over the cell cover, and the top edge of the can is bent inward with a crimping die to hold retain the gasket, cover assembly, PTC device and terminal cover and complete the sealing of the open end of the can by the gasket.

[0072] With respect to the cathode, the cathode is coated onto a metallic foil current collector, typically an aluminum foil with a thickness between 18 and 20 μm , as a mixture which contains a number of materials that must be carefully selected to balance the processability, conductivity and overall efficiency of the coating. This coating consists primarily of iron disulfide (and its impurities); a binder that is generally used to hold the particulate materials together and adhere the mixture to the current collector; one or more conductive materials such as metal, graphite and carbon black powders added to provide improved electrical conductivity to the mixture, although the amount of conductor depends upon the electrical conductivity of the active material and binder, the thickness of the mixture on the current collector and the current collector design; and various processing or rheological aids that are dependent upon the coating method, the solvent used and/or the mixing method itself.

[0073] The following are representative materials that may be utilized in the cathode mix formulation: pyrite (at least 95% pure); conductor (Pure Black 205-110 from Superior Graphite Chicago, IL, and/or MX15 from Timcal Westlake, OH); and binder/processing aids (styrene-ethylene/butylenes-styrene (SEBS) block copolymer, such as g1651 from Kraton Polymers Houston, TX, and Efka 6950 from Heerenveen, Netherlands). Small amounts of impurities may be naturally present in any of the aforementioned materials, although care should be taken to utilize the highest purity pyrite source available so as to maximize the amount of FeS_2 present within the cathode.

[0074] It is also desirable to use cathode materials with small particle sizes to minimize the risk of puncturing the separator. For example, FeS_2 is preferably sieved through a 230 mesh (62

μm) screen before use or the FeS_2 may be milled or processed as described in U.S. Patent Publication No. 2005/0233214, which is incorporated by reference herein. Other cathode mix components should be carefully selected with eye toward chemical compatibility/reactivity and to avoid similar particle-size-based mechanical failure issues.

[0075] The cathode mixture is applied to the foil collector using any number of suitable processes, such as three roll reverse, comma coating or slot die coating. The methods of coating described in U.S. Patent Application Serial No. 11/493,314, which should publish on or after January 31, 2008 and is incorporated by reference, could be used. One preferred method of making FeS_2 cathodes is to roll coat a slurry of active material mixture materials in a highly volatile organic solvent (e.g., trichloroethylene) onto both sides of a sheet of aluminum foil, dry the coating to remove the solvent, calender the coated foil to compact the coating, slit the coated foil to the desired width and cut strips of the slit cathode material to the desired length. The use of volatile solvents maximize the efficiency of recovering such solvents, although it is possible to utilize other solvents, including aqueous-based compositions, in order to roll coat the cathode mix described above.

[0076] After or concurrent with drying to remove any unwanted solvents, the resulting cathode strip is densified via calendering or the like to further compact the entire positive electrode. In light of the fact that this strip will then be spirally wound with separator and a similarly (but not necessarily identically) sized anode strip to form a jellyroll electrode assembly, this densification maximizes loading of electrochemical material in the jellyroll electrode assembly. However, the cathode cannot be over-densified as some internal cathode voids are need to allow for expansion of the iron disulfide during discharge and wetting of the iron disulfide by the organic electrolyte, as well as to avoid unwanted stretching and/or de-lamination of the coating.

Example 1

[0077] Cells were constructed in accordance with the information contained in Figures 1 and 2. These cells were cooled down from 21°C to 0° , -20° and -40°C . The cell impedance data was recorded by sweeping the frequency from 65kHz to 1Hz after 1 hour equilibration at each temperature.

[0078] In comparison to the “control” electrolyte having only DIOX and DME, the addition of THF, 2MeTHF, and DMP suppressed the cell OCV slightly while the addition of PC and EC into DIOX-containing solvents increased the cell OCV significantly. Cells using Li imide had slightly higher OCV than cells using LiI salt as well.

[0079] In terms of cell ohmic impedance, the control lot using 65:35 DIOX:DME (all ratios presented herein are volume ratios blended at room temperature) solvent blend had the lowest impedance when using LiI salt. THF and 2MeTHF increased impedance slightly if the solvent blend contained both DIOX and DME. However, impedance was very large for THF-DME and DIOX-THF-2MeTHF blends using LiI salt. In contrast, when the salt is switched from LiI to Li imide, many ether solvents that do not work well with LiCF₃SO₃ and LiClO₄ and even LiI (although to a lesser degree) will work well with Li imide salt for primary lithium cells, possibly due to the effects of ionic association. However, the carbonate- and acetate-based solvents gave somewhat higher impedance than any of the ether-based solvents when using Li imide, indicating that viscosity may play a significant role as well.

Example 2

[0080] A signature test was conducted with cells from Example 1 (including the cooling regimen described therein) being continuous discharged at progressively lower drain rates, with standardized rest periods after the cutoff voltage (for comparison's sake, both to a 1.0 and 0.9 volt cut) is attained. The cell is then tested at the next drain rate and test is run until complete. However, for the initial 1A discharge, a short current interrupt of 100mS for every 1 minute of discharge was used, during which the cell ohmic resistance can be observed. For all the low temperature tests, the test schedule also has a 5 hour delay built in to allow a minimum of 2-3 hour dwell time at the specified test temperature.

[0081] Figure 3 summarizes the service on the 1A step of the signature test at three different temperatures (21°, - 20° and - 40° C). When the salt was switched from LiI to Li imide, they performed the same as or only slightly worse than the control solvent lot. This is mainly due to the higher ionic dissociation of Li imide in the ether solvents than LiI. At - 20° C, the carbonate and acetate solvent blends gave essentially zero service on the 1A/-20° C test. At - 40° C, the majority of the lots, including the control (lot 1113), did not give any service time.

Among the lots that did show good service, the solvent blends containing THF were the best in terms of overall 1A performance at 21°, -20° and -40° C.

[0082] Given these results, THF was identified as the most promising solvent as compared to DME, 2MeTHF and DMP in terms of solving the sudden shutdown issues associated with the 1A/-40°C test and improving its performance on low/moderate rate test at -40° C.

[0083] For Li imide salt, the use of THF improved the performance on 1A/-40° C test without causing any negative impact on the performance both at 20° and -20° C. The solvent blends using solvents with low cation ion solvating power such as 2MeTHF can perform well very, likely due to the less tendency of ionic association for Li imide than for LiI salt in the THF and 2MeTHF-containing ether solvents.

[0084] The carbonate- and acetate-based electrolytes, which improved the low temperature performance of Li-ion cells, showed abysmal performance in Li/FeS₂ AA cells even at -20° C, likely due to the formation of very resistive SEI layers on the lithium anode surface.

[0085] Figures 4 through 7 illustrate detailed signature test data for all lots at 21°, -20°, and -40° C. Note that error bars are included where appropriate. At 21° C, the rate capability of all the electrolytes evaluated using L91-20 jellyrolls was very good except for lot 1114, which used 0.75M⁺ LiI dissolved in 35:30:35 DIOX:THF:2MeTHF solvent blend. The low-rate performance was very insensitive to the solvent used as can be seen from the gradual convergence of the discharged capacity towards between 2800 and 3000 mAh as the current was decreased to 10mA for all LiI lots except for lot 1114, which may have experienced problems in its manufacture. All Li imide lots showed performance equal to or slightly better than the LiI control lot. At -20° C, none of the alternative solvents improved the performance of LiI and Li imide electrolytes. However, at -40° C, some of the alternative solvent blends significantly improved the performance of Li imide and more so of LiI electrolytes even at low drains.

Example 3

[0086] Further tests were conducted with cells from Example 1 (including the cooling regimen described therein) but this time with LiI electrolytes using DIOX:DME:THF solvent blend with optimized compositions for best performance at low (-40°C) and ambient temperatures.

[0087] The cells in this example demonstrate an unexpected benefit on -40°C as compared to previous teachings (e.g., see reference by Mastuda et al. JES, 131, 2821).

[0088] The solvent compositions were optimized using Design Expert® version 7.1.3 by Stat-Ease, Inc. Thus, the following optimal solvent composition with emphasis on improving low temperature performance of the cell was 57.3 wt.% DIOX, 23.8 wt.% DME and 18.9 wt.% THF.

[0089] More generally, the range of solvent compositions that can solve the -40°C “sudden death” problem include DIOX at 25-70 wt.%; DME at 0-67 wt.% and THF at 10-80 wt.%. These values were extracted from a series of experiments, documented in Figure 8.

[0090] Binary DIOX-THF systems, either entirely free from or in very limited amounts of DME (which is Teratogenic), are also possible. Since there is no sudden death issue for Li imide salt in DIOX:DME blends, DIOX:THF solvent systems using Li imide and THF in the range of 10-95 wt.%, with a more preferred range of 35-85 wt.% and most preferred range of 45-75 wt.% are possible. The balance of such systems would be DIOX. Further supporting data is documented in Figure 9.

[0091] Features of the invention and its advantages will be further appreciated by those practicing the invention, particularly with reference to the Examples, Figures, Tables and other information provided herein and any patent references above necessary to better understand the invention are incorporated herein to that extent. In the same manner, it will be understood by those who practice the invention and those skilled in the art that various modifications and improvements may be made to the invention without departing from the spirit of the disclosed concepts. The scope of protection afforded is to be determined by the claims and by the breadth of interpretation allowed by law.

CLAIMS

I claim:

1. An electrochemical cell comprising:
 - a cylindrical container having an open end;
 - a top cover sealing the open end;
 - a jellyroll electrode assembly disposed inside of the container, the electrode assembly comprising: an anode consisting essentially of lithium or a lithium-based alloy; a cathode consisting of a mix comprising a conductor, a binder and at least 80 wt.% of iron disulfide coated onto a solid foil current collector; and a separator disposed between the anode and the cathode; and
 - an electrolyte having a solvent blend consisting essentially of 10-95 wt.% of tetrahydrofuran and 5-90 wt.% of 1,3-dioxolane and a solute selected from the group consisting of: lithium imide, lithium iodide and combinations thereof.
2. The electrochemical cell of claim 1, wherein the solvent blend consists essentially of 35-85 wt.% tetrahydrofuran and 15-65 wt.% 1,3-dioxolane.
3. The electrochemical cell of claim 1, wherein the solvent blend consists essentially of 45-75 wt.% tetrahydrofuran and 25-55 wt.% 1,3-dioxolane.
4. An FR6 or an FR03 battery comprising:
 - a cylindrical container having an open end;
 - a top cover sealing the open end;
 - a jellyroll electrode assembly disposed inside of the container, the electrode assembly comprising: an anode consisting essentially of lithium or a lithium-based alloy; a cathode consisting of a mix comprising a conductor, a binder and at least 80 wt.% of iron disulfide coated onto a solid foil current collector; and a separator disposed between the anode and the cathode; and
 - an electrolyte consisting essentially of a solute dissolved in tetrahydrofuran, 1,3-dioxolane and 1,2-dimethoxyethane.

5. The battery of claim 4, wherein the solute is selected from the group consisting of: lithium imide, lithium iodide and combinations thereof.
6. The battery of claim 5, wherein the electrolyte consists essentially of only 1,3-dioxolane and 1,2-dimethoxyethane and the solute consists essentially of lithium imide.
7. The battery of claim 5, wherein the electrolyte has at least 30 wt.% of tetrahydrofuran.
8. The battery of claim 7, wherein the electrolyte does not include 1,2-dimethoxyethane.
9. The battery of claim 7, wherein the electrolyte also has at least 40 wt.% of 1,3-dioxolane and at least 20 wt.% of 1,2-dimethoxyethane.
10. An electrochemical cell comprising:
 - a cylindrical container having an open end;
 - a top cover sealing the open end;
 - a jellyroll electrode assembly disposed inside of the container, the electrode assembly comprising: an anode consisting essentially of lithium or a lithium-based alloy; a cathode consisting of a mix comprising a conductor, a binder and at least 80 wt.% of iron disulfide coated onto a solid foil current collector; and a separator disposed between the anode and the cathode; and
 - an electrolyte having a solvent blend consisting essentially of 10-95 wt.% of tetrahydrofuran-based solvent, 5-90 wt.% of 1,3-dioxolane and 0-40 wt.% of 1,2-dimethoxyethane and a solute selected from the group consisting of: lithium imide, lithium iodide and combinations thereof.
11. The electrochemical cell of claim 10, wherein the tetrahydrofuran-based solvent is selected from the group consisting of: tetrahydrofuran, 2-methyl tetrahydrofuran and combinations thereof.

12. The electrochemical cell of claim 11, wherein the electrolyte does not include 1,2-dimethoxyethane.
13. The electrochemical cell of claim 11, wherein the electrolyte has at least 30 wt.% tetrahydrofuran.
14. The electrochemical cell of claim 13, wherein the electrolyte includes 2-methyl tetrahydrofuran and has more 2-methyl tetrahydrofuran, on a weight percentage basis, than tetrahydrofuran.
15. The electrochemical cell of claim 11, wherein the electrolyte has at least 40 wt.% of 1,3-dioxolane and at least 20 wt.% of 1,2-dimethoxyethane.