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(54) **Title:** BATTERY ELECTROLYTE SOLUTIONS CONTAINING AROMATIC PHOSPHITE COMPOUNDS

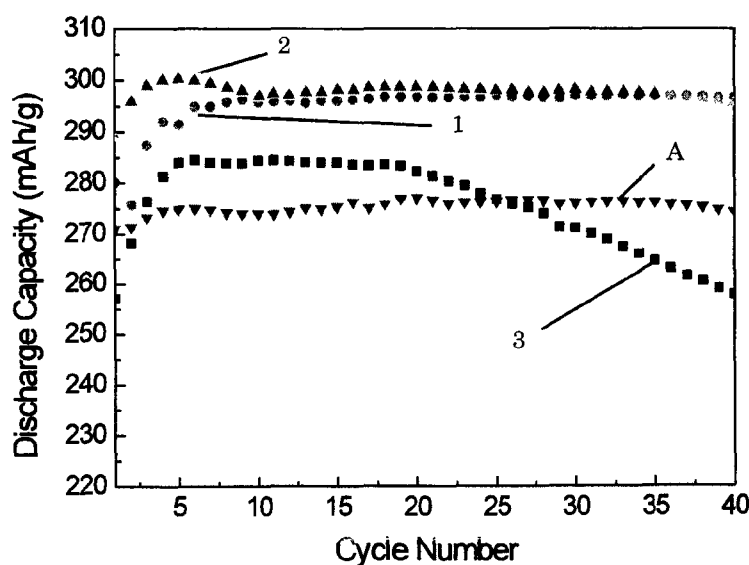


FIGURE 2

(57) **Abstract:** A battery electrolyte solution contains from 0.1 to 10% by weight of tris(alkyl-substituted aryl) phosphite compound. The tris(alkyl-substituted aryl) phosphite compound provides increased thermal stability for the electrolyte, helping to reduce thermal degradation, thermal runaway reactions and the possibility of burning. The tris(alkyl-substituted aryl) phosphite compound has little or no adverse impact on the electrical properties of the battery, and in some cases actually improves battery performance.



BATTERY ELECTROLYTE SOLUTIONS CONTAINING AROMATIC PHOSPHITE
COMPOUNDS

The present invention relates to nonaqueous electrolyte solutions that contain an aromatic phosphite compound.

Lithium batteries are widely used as primary and secondary batteries for vehicles and many types of electronic equipment. These batteries tend to have high energy and power densities and for that reason are favored in many applications. The electrolyte solution in a lithium battery is by necessity a nonaqueous type. The nonaqueous electrolyte solution is generally a high dielectric content solution of a lithium salt in an organic solvent or a mixture of organic solvents. Various linear and cyclic carbonates are commonly used, but certain esters, alkyl ethers, nitriles, sulfones, sulfolanes, sultones and siloxanes may also serve as the solvent. In many cases, the solvent may contain two or more of these materials. Polymer gel electrolyte solutions are also known.

Because they contain high concentrations of organic materials, these electrolyte solutions are sensitive to high temperatures. They may decompose, engage in runaway exothermic reactions or even burn if exposed to the wrong conditions. Lithium batteries have been known to catch fire due to overcharge, overdischarge, short circuit conditions, and mechanical or thermal abuses. Other problems can occur short of burning, including a significant loss of battery life. Therefore, additives have been incorporated into the electrolyte solutions of lithium batteries to help stabilize the electrolyte.

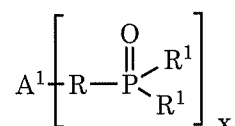
A number of phosphorus compounds have been suggested as flame retardants or "thermal runaway inhibitors" for battery electrolyte solutions. These include various phosphine oxide (O:PR_3), phosphinite (P(OR)R_2), phosphonite ($\text{P(OR}_2\text{)R}$), phosphinate (O:P(OR)R_2), phosphonate ($\text{O:P(OR)}_2\text{R}$), phosphate (O:P(OR)_3) and phosphazene ($\text{(-N=PR}_2\text{)}_n$) compounds.

These phosphorus compounds have not been altogether satisfactory. Some must be added in very large amounts to be effective. Others interact with the nonaqueous solvent, the lithium salt or other additives in the electrolyte solution, or with the anode or cathode material. Still others have an adverse impact on the performance of the battery. It would be desirable to provide an additive for a nonaqueous battery electrolyte solution, which provides good stabilization at reasonable levels, does not

adversely interact with other components in the electrolyte solution or with the anode or cathode, and which has little or no adverse impact on battery performance.

Phosphite compounds also have been evaluated. These phosphite compounds include, for example, trimethyl phosphite (*see, e.g.*, Yao et al., "Comparative Study of trimethylphosphite and trimethylphosphate as electrolyte additives in lithium ion batteries", *J. Power Sources* (2005), 144(1), 170-175) and tris (2,2,2-trifluoroethyl)phosphite (*see, e.g.*, Zhang et al., "Tris(2,2,2-trifluoroethyl)phosphite as a cosolvent for nonflammable electrolyte in Li-ion batteries", *J. Power Sources* 2003, 113(1) 166). USP 6,939,647 describes other trialkyl phosphites as additives for lithium ion battery electrolyte solutions. US Published Patent Application No. 2007/0048622 mentions a number of phosphite compounds as possible battery electrolyte additives, although it reports experimental data for only a specific dioxaphospholane (a cyclic phosphite). This specific dioxaphospholane (4-methyl-2-(2,2,3,3-tetrafluoropropoxy)1,3,2-dioxaphospholane) has minimal effect on the flame resistance of the battery electrolyte solution, even when used in quantities as much as 30% of the electrolyte solution.

WO 2010/074838 describes battery electrolyte solutions that contain aromatic phosphate compounds having the structure



wherein A^1 is a radical that contains one or more aromatic rings; each R is independently an alkylene diradical which may contain 1, 2 or 3 carbon atoms and which is bonded directly to a carbon atom of an aromatic ring of the A^1 group; each R^1 is independently hydrogen, halogen, OH, a hydrocarbyl group having up to 12 carbon atoms or an alkoxyl group having up to 12 carbon atoms; or two R^1 groups attached to the same phosphorus atom may together form a ring structure that includes the phosphorus atom; and x is an integer of at least 2.

This invention is in one aspect a battery electrolyte solution comprising at least one lithium salt and a nonaqueous solvent in which the lithium salt is soluble, wherein from 0.01 to 10% of the weight of the battery electrolyte solution is at least one tris(alkyl-substituted aryl) phosphite compound.

This invention is also an electrical battery comprising an anode, a cathode, a separator disposed between the anode and cathode, and a nonaqueous battery electrolyte solution in contact with the anode and cathode, wherein the battery electrolyte solution comprises at least one lithium salt, a nonaqueous solvent in which the lithium salt is soluble, and wherein from about 0.01 to 10% by weight of the weight of the battery electrolyte solution is at least one tris(alkyl-substituted aryl) phosphite compound.

The tris(alkyl-substituted aryl) phosphite compound provides good thermal stabilization to the battery electrolyte solution. The battery electrolyte solution is resistant to thermal degradation, is less likely to engage in thermal runaway reactions and is resistant to combustion. When used in small but effective amounts, the tris(alkyl-substituted aryl) phosphite compounds have minimal adverse impact on the performance of the battery and in some cases has been seen to actually increase discharge capacity.

Figure 1 illustrates differential scanning calorimetry curves for one comparative battery electrolyte solution and three battery electrolyte solutions in accordance with the invention.

Figure 2 is a graph of 0.1C discharge curves for three anode half-cells in accordance with the invention and one comparative anode half-cell.

Figure 3 is a graph of discharge curves for three cathode half-cells in accordance with the invention and one comparative anode half-cell.

Figure 4 is a graph of discharge curves for three cathode half-cells in accordance with the invention and one comparative anode half-cell.

Figure 5 is a graph of 0.1C discharge curves for three batteries in accordance with the invention and one comparative battery.

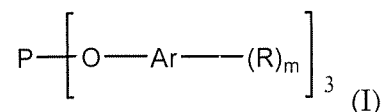
Figure 6A is a differential scanning calorimetry (DSC) curve of a comparative battery electrolyte solution (Comparative Sample C).

Figure 6B is a DSC curve of a battery electrolyte solution of the invention (Example 7).

Figure 7A is a DSC curve of a fully charged MCMB electrode in a comparative battery electrolyte solution (Comparative Sample C).

Figure 7B is a DSC curve of a fully charged MCMB electrode in a battery electrolyte solution of the invention (Example 7).

The tris(alkyl-substituted aryl) phosphite compound can be represented by the structure

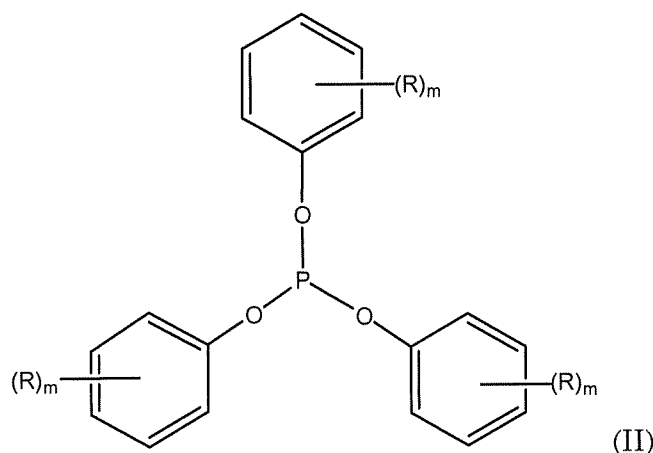


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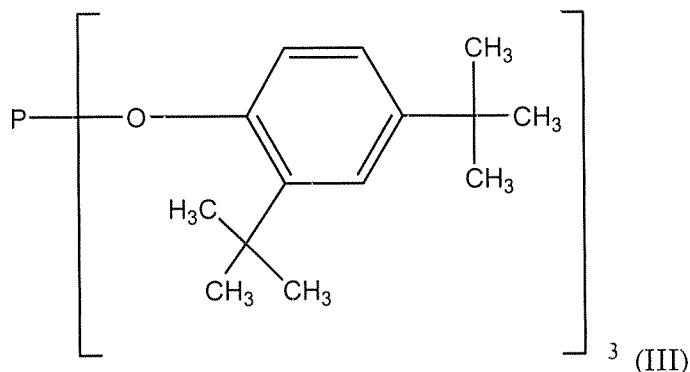
wherein each Ar independently represents an aryl group, each R independently represents an alkyl group, and each m is at least one.

The Ar groups each may be phenyl, naphthyl, or other fused ring structure. The R groups each may be linear, branched and/or cyclic, and may contain further substituents such as halogen, aryl, and the like. The R groups each preferably have up to 20 carbon atoms, more preferably up to 8 carbon atoms and still more preferably up to 4 carbons. The R groups preferably are bonded to the respective Ar groups through tertiary carbon atoms. Each R is most preferably t-butyl. Each m is preferably from 1 to 4, more preferably from 1 to 2 and more preferably 2.

A preferred class of phosphite compounds, in which the Ar groups are phenyl, have the structure II, in which R and m are as defined before:



A particularly preferred phosphite compound is tris(di-tert-butylphenyl)phosphite, which has the structure:



Mixtures of two or more tris(alkyl-substituted aryl) phosphites can be present in the battery electrolyte solution. Other thermal stabilizers also may be present, in addition to the tris(alkyl-substituted aryl) phosphite compound.

5 The tris(alkyl-substituted aryl) phosphite compound(s) may constitute from about 0.01 to as much as 10% of the total weight of the battery electrolyte solution. A preferred upper amount is up to 5% of the total weight of the battery electrolyte solution, and a more preferred upper amount is up to 2% or, still more preferably, up to 1% of the total weight of the battery electrolyte solution. A preferred lower amount is at least
10 0.1%, more preferably 0.25%, of the total electrolyte solution weight.

The other main components of the battery electrolyte solution are a lithium salt and a nonaqueous solvent for the lithium salt.

The lithium salt may be any that is suitable for battery use, including inorganic lithium salts such as LiAsF_6 , LiPF_6 , $\text{LiB}(\text{C}_2\text{O}_4)_2$, LiBF_4 , $\text{LiBF}_2\text{C}_2\text{O}_4$, LiClO_4 , LiBrO_4 and
15 LiIO_4 and organic lithium salts such as $\text{LiB}(\text{C}_6\text{H}_5)_4$, LiCH_3SO_3 , $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$ and LiCF_3SO_3 . LiPF_6 , LiClO_4 , LiBF_4 , LiAsF_6 , LiCF_3SO_3 and $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ are preferred types, and LiPF_6 is an especially preferred lithium salt.

The lithium salt is suitably present in a concentration of at least 0.5 moles/liter of electrolyte solution, preferably at least 0.75 moles/liter, up to 3 moles/liter and more
20 preferably up to 1.5 moles/liter.

The nonaqueous solvent may include, for example, one or more linear alkyl carbonates, cyclic carbonates, cyclic esters, linear esters, cyclic ethers, alkyl ethers, nitriles, sulfones, sulfolanes, siloxanes and sultones. Mixtures of any two or more of the foregoing types can be used. Cyclic esters, linear alkyl carbonates, and cyclic carbonates
25 are preferred types of nonaqueous solvents.

Suitable linear alkyl carbonates include dimethyl carbonate, diethyl carbonate, methyl ethyl carbonate and the like. Cyclic carbonates that are suitable include ethylene

carbonate, propylene carbonate, butylene carbonate and the like. Suitable cyclic esters include, for example, γ -butyrolactone and γ -valerolactone. Cyclic ethers include tetrahydrofuran, 2-methyltetrahydrofuran, tetrahydropyran and the like. Alkyl ethers include dimethoxyethane, diethoxyethane and the like. Nitriles include mononitriles such as acetonitrile and propionitrile, dinitriles such as glutaronitrile, and their derivatives. Sulfones include symmetric sulfones such as dimethyl sulfone, diethyl sulfone and the like, asymmetric sulfones such as ethyl methyl sulfone, propyl methyl sulfone and the like, and their derivatives. Sulfolanes include tetramethylene sulfolane and the like.

Some preferred solvent mixtures include a cyclic carbonate/linear alkyl carbonate mixture at a volume ratio of from 15:85 to 40:60; a cyclic carbonate/cyclic ester mixture at a volume ratio of from 20:80 to 60:40; a cyclic carbonate/cyclic ester/linear alkyl carbonate mixture at volume ratios of 20:48:50-78:2-20; and a cyclic ester/linear alkyl carbonate mixture at a volume ratio of from 70:30 to 98:2.

Solvent mixtures of particular interest are mixtures of ethylene carbonate and propylene carbonate at a volume ratio of from 15:85 to 40:60; mixtures of ethylene carbonate and dimethyl carbonate or ethylene carbonate and diethyl carbonate at a volume ratio of from 15:85 to 40:60; mixtures of ethylene carbonate, diethyl carbonate and dimethyl carbonate at a volume ratio of from 20:60:2-78:2-78; mixtures of ethylene carbonate, propylene carbonate and dimethyl carbonate at a volume ratio of 20:48:50-78:2-20, and mixtures of propylene carbonate and dimethyl carbonate at a volume ratio of from 15:85 to 40:60.

Various other additives may be present in the battery electrolyte solution, in addition to the components already mentioned. These may include, for example, additives which promote the formation of a solid electrolyte interface at the surface of a graphite electrode; various cathode protection agents; lithium salt stabilizers; lithium deposition improving agents; ionic solvation enhancers; corrosion inhibitors; wetting agents; flame retardants; and viscosity reducing agents. Many additives of these types are described by Zhang in "A review on electrolyte additives for lithium-ion batteries", *J. Power Sources* 162 (2006) 1379-1394.

Agents which promote solid electrolyte interface (SEI) formation include various polymerizable ethylenically unsaturated compounds, various sulfur compounds, as well as other materials. Suitable cathode protection agents include materials such as N,N-diethylaminotrimethylsilane and $\text{LiB}(\text{C}_2\text{O}_4)_2$. Lithium salt stabilizers include LiF ,

tris(2,2,2-trifluoroethyl)phosphite, 1-methyl-2-pyrrolidinone, fluorinated carbamate and hexamethylphosphoramide. Examples of lithium deposition improving agents include sulfur dioxide, polysulfides, carbon dioxide, surfactants such as tetraalkylammonium chlorides, lithium and tetraethylammonium salts of perfluorooctanesulfonate, various
5 perfluoropolyethers and the like. Crown ethers can be suitable ionic solvation enhancers, as are various borate, boron and borole compounds. $\text{LiB}(\text{C}_2\text{O}_4)_2$ and $\text{LiF}_2\text{C}_2\text{O}_4$ are examples of aluminum corrosion inhibitors. Cyclohexane, trialkyl phosphates and certain carboxylic acid esters are useful as wetting agents and viscosity reducers. Some materials, such as $\text{LiB}(\text{C}_2\text{O}_4)_2$, may perform multiple functions in the electrolyte solution.

10 The various other additives may together constitute up to 20%, preferably up to 10%, of the total weight of the battery electrolyte solution.

The battery electrolyte solution is conveniently prepared by dissolving or dispersing the lithium salt, the tris(alkyl-substituted aryl) phosphite and any other additives as may be used into the nonaqueous solvent. The order of mixing is in general
15 not critical. The water content of the resulting battery electrolyte solution should be as low as possible. A water content of 50 ppm or less is desired and a more preferred water content is 30 ppm or less. The various components can be individually dried before forming the electrolyte solution, and/or the formulated electrolyte solution can be dried to remove residual water. The drying method selected should not degrade or decompose
20 the various components of the electrolyte solution, nor promote undesired reactions between them. Thermal methods can be used, as can drying agents such as molecular sieves.

A battery containing the battery electrolyte solution of the invention can be of any useful construction. A typical battery construction includes an anode and cathode,
25 with a separator and the electrolyte solution interposed between the anode and cathode so that ions can migrate through the electrolyte solution between the anode and the cathode. The assembly is generally packaged into a case. The shape of the battery is not limited. The battery may be a cylindrical type containing spirally-wound sheet electrodes and separators. The battery may be a cylindrical type having an inside-out
30 structure that includes a combination of pellet electrodes and a separator. The battery may be a plate type containing electrodes and a separator that have been superimposed.

Suitable anode materials include, for example, carbonaceous materials such as natural or artificial graphite, carbonized pitch, carbon fibers, graphitized mesophase microspheres, furnace black, acetylene black and various other graphitized materials.

The carbonaceous materials may be bound together using a binder such as a poly(vinylidene fluoride), polytetrafluoroethylene, a styrene-butadiene copolymer, an isoprene rubber, a poly(vinyl acetate), a poly(ethyl methacrylate), polyethylene or nitrocellulose. Suitable carbonaceous anodes and methods for constructing same are described, for example, in U. S. Patent No. 7,169,511.

Other suitable anode materials include lithium metal, lithium alloys and other lithium compounds such as a lithium titanate anode.

Suitable cathode materials include inorganic compounds such as transition metal oxides, transition metal/lithium composite oxides, lithium/transition metal composite phosphates, transition metal sulfides, metal oxides, and transition metal silicates. Examples of transition metal oxides include MnO , V_2O_5 , V_6O_{13} and TiO_2 . Transition metal/lithium composite oxides include lithium/cobalt composite oxides whose basic composition is approximately LiCoO_2 , lithium/nickel composite oxides whose basic composition is approximately LiNiO_2 , lithium/manganese composite oxides whose basic composition is approximately LiMn_2O_4 or LiMnO_2 and lithium/nickel/manganese/cobalt oxide electrodes whose basic composition is $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ or $\text{Li}(\text{Li}_a\text{Ni}_x\text{Mn}_y\text{Co}_z)\text{O}_2$, where x, y, z and a are such as to provide an electrostatically neutral compound. In each of these cases, part of the cobalt, nickel or manganese can be replaced with one or two metals such as Al, Ti, V, Cr, Fe, Co, Ni, Cu, Zn, Mg, Ga or Zr. Lithium/transition metal composite phosphates include lithium iron phosphate, lithium manganese phosphate, lithium cobalt phosphate, lithium iron manganese phosphate and the like. Examples of useful metal oxides include SnO_2 and SiO_2 . Examples of useful metal silicates include lithium iron orthosilicate.

The electrodes are each generally in electrical contact with or formed onto a current collector. A suitable current collector for the anode is made of a metal or metal alloy such as copper, a copper alloy, nickel, a nickel alloy, stainless steel and the like. Suitable current collectors for the cathode include those made of aluminum, titanium, tantalum, alloys of two or more of these and the like.

The separator is interposed between the anode and cathode to prevent the anode and cathode from coming into contact with each other and short-circuiting. The separator is conveniently constructed from a nonconductive material. It should not be reactive with or soluble in the electrolyte solution or any of the components of the electrolyte solution under operating conditions. Polymeric separators are generally suitable. Examples of suitable polymers for forming the separator include polyethylene,

polypropylene, polybutene-1, poly-3-methylpentene, ethylene-propylene copolymers, polytetrafluoroethylene, polystyrene, polymethylmethacrylate, polydimethylsiloxane, polyethersulfones and the like.

5 The electrolyte solution must be able to permeate through the separator. For this reason, the separator is generally porous, being in the form of a porous sheet, nonwoven or woven fabric or the like. The porosity of the separator is generally 20% or higher, up to as high as 90%. A preferred porosity is from 30 to 75%. The pores are generally no larger than 0.5 microns, and are preferably up to 0.05 microns in their longest dimension. The separator is typically at least one micron thick, and may be up
10 to 50 microns thick. A preferred thickness is from 5 to 30 microns.

The battery is preferably a secondary (rechargeable) lithium battery. In such a battery, the discharge reaction includes a dissolution or delithiation of lithium ions from the anode into the electrolyte solution and concurrent incorporation of lithium ions into the cathode. The charging reaction, conversely, includes an incorporation of lithium
15 ions into the anode from the electrolyte solution. Upon charging, lithium ions are reduced on the anode side, at the same time, lithium ions in the cathode material dissolve into the electrolyte solution.

The presence of the tris(alkyl-substituted aryl) phosphite compound described herein improves battery safety and battery life by stabilizing the electrolyte solution
20 against thermal degradation and runaway reactions, and/or otherwise reducing the ability of the electrolyte solution to catch on fire. Thermal degradation and runaway reactions can occur due to several circumstances, including (1) mechanical damage to the battery, which may cause short-circuiting within the battery structure; (2) thermal abuse of the battery, which is mainly due to storing and/or operating the battery under
25 high temperature conditions; and (3) electrical conditions such as overcharging or the creation of electrical shorts.

Overcharge situations can cause lithium to form a dendritic structure. The dendritic structure can extend through the electrolyte solution and through the separator between the cathode and the anode, causing a short circuit. The short circuit
30 can allow a very large current to flow through the electrolyte solution over a very short time period, releasing heat that can cause degradation of the electrolyte solution or even runaway reactions to occur. The runaway reactions can even cause the electrolyte solution to catch fire in the absence of a flame retardant or thermal runaway inhibitor.

Even if the electrolyte solution does not catch on fire, the heat released by the runaway reactions can severely shorten the battery life.

The presence of the tris(alkyl-substituted aryl) phosphite compound, even in very small quantities, has been found to provide excellent resistance to thermal degradation and runaway reactions.

When present in small but effective amounts, the tris(alkyl-substituted aryl) phosphite compound has little or no adverse affect on battery performance. Discharge capacities are often equal to or even exceed those of otherwise like batteries that lack the tris(alkyl-substituted aryl) phosphite. In addition, batteries in accordance with the invention have been seen to retain their discharge capacities better than when no tris(alkyl-substituted aryl) phosphite is present in the electrolyte solution.

Cycling stability can be evaluated by running the battery through a fixed number of charge/discharge cycles, at a given charge/discharge rate, and measuring the capacity of the battery at the start and at the end of the evaluation. Capacity tends to fall as the battery continues to be charged and discharged, when the battery electrolyte solution is a simple solution of lithium salt in a carbonate or mixed carbonate solvent. However, when the battery electrolyte solution contains a small amount of the tris(alkyl-substituted aryl) phosphite, this loss of discharge capacity upon cycling is often greatly reduced.

The battery of the invention can be used in industrial applications such as electric vehicles, hybrid electric vehicles, plug-in hybrid electric vehicles, aerospace, e-bikes, etc. The battery of the invention is also useful for operating a large number of electrical and electronic devices, such as computers, cameras, video cameras, cell phones, PDAs, MP3 and other music players, televisions, toys, video game players, household appliances, power tools, medical devices such as pacemakers and defibrillators, among many others.

The following examples are provided to illustrate the invention, but are not intended to limit the scope thereof. All parts and percentages are by weight unless otherwise indicated.

Examples 1-3 and Comparative Battery Electrolyte Solution A

A. Battery electrolyte solutions. Four battery electrolyte solutions are prepared. Each battery electrolyte solution is a 1M solution of LiPF₆ in a 1:1:1 (V/V/V) mixture of ethylene carbonate, diethyl carbonate and dimethyl carbonate. Comparative Battery

Electrolyte Solution A contains no other additives. Battery Electrolyte Solutions 1-3 contain, respectively, 0.25, 0.5 and 1.0 weight percent of tris(2,4-di-tert-butylphenyl) phosphite.

5 B. Thermal stability testing of battery electrolyte solutions. The thermal stability of each of these battery electrolyte solutions is evaluated by differential scanning calorimetry (DSC) over the temperature range of 20°C to 300°C, using a Universal V4/5A TA Instruments device operated at a heating rate of 10°C/minute. Results of this testing are as shown in Figure 1, with reference numerals A, 1, 2 and 3 indicating the results for Comparative Battery Electrolyte Solution A and Battery Electrolyte
10 Solutions 1-3, respectively.

Each of the battery electrolyte solutions exhibits two endothermic peaks that are indicative of thermal degradation. As can be seen in Figure 1, the onset temperature for each of these peaks increases with the addition of tris(2,4-di-tert-butylphenyl)phosphite in amounts ranging from 0.25 to 1 weight percent. The onset temperature for the first
15 endothermic peak increases from about 37°C to about 51°C as the phosphite concentration is increased from zero to 1%; that for the higher endothermic peak increases from about 164°C to about 199°C. The higher onset temperatures indicate greater thermal stability in the examples of the invention, compared with the control. In addition, the higher temperature peaks become smaller as more of the phosphite
20 compound is added into the electrolyte solution, indicating that less heat is generated during the exothermic events.

C. Anode half-cell performance testing

Separate model CR 2025 coin cells with a Mesocarbon Microbead (MCMB) anode (85% mesocarbon microbeads, 10% conductive carbon and 5% polytetrafluoroethene) and
25 a metallic lithium sheet cathode are prepared with each of Examples 1-3 and Comparative Sample B as the electrolyte solution. The discharge capacity and coulomb efficiency of these cells is evaluated by galvanostatic cycling at a C/10 rate, using cutoff potentials of 0.01V vs. Li/Li⁺ for charge and 1.5 V vs. Li/Li⁺ for discharge.

The results of the discharge capacity testing are shown graphically in Figure 2.
30 The discharge capacity of the half-cell containing Comparative Battery Electrolyte Solution A is indicated by reference numeral A. The discharge capacity for this cell peaks at about 285 mAh/g after about 5 charge/discharge cycles, and then gradually decays to below 260 mAh/g after 40 cycles.

Discharge capacities for the half-cells containing Battery Electrolyte Solutions 1, 2 and 3 are indicated by reference numerals 1-3, respectively. The cells containing Solutions 1 and 2 are seen to have discharge capacities of about 300 mAh/g, and to retain these capacities over the entire test of 40 charge/discharge cycles. The cell containing Battery Electrolyte Solution 3 (1% of the phosphite compound) has a peak discharge capacity of about 275 mAh/g, which is slightly lower than that of the cell containing Comparative Battery Electrolyte Solution A, but, unlike the control, this cell retains essentially its entire peak discharge capacity over the entire test of 40 charge/discharge cycles.

The coulomb efficiency of each of the cells is close to 100% over the entire test of 40 charge/discharge cycles.

Examples 4-6 and Comparative Sample B

A. Battery electrolyte solutions:

Four battery electrolyte solutions are prepared. Each battery electrolyte solution is a 1M solution of LiPF_6 in a 1:1 (V/V) mixture of ethylene carbonate and diethyl carbonate. Comparative Battery Electrolyte Solution B contains no other additives. Battery Electrolyte Solutions 4-6 contain, respectively, 0.25, 0.5 and 1.0 weight percent of tris(2,4-di-tert-butylphenyl) phosphite.

B. Cathode half-cell performance testing with $\text{Li}_{0.5}\text{CoO}_2$ electrode

Separate model CR 2025 coin cells with a $\text{Li}_{0.5}\text{CoO}_2$ cathode (ALE company) and a metallic lithium sheet anode are prepared with each of Battery Electrolyte Solutions 4-6 and Comparative Battery Electrolyte Solution B as the electrolyte solution. The discharge capacity of these cells is evaluated by galvanostatic cycling, using cutoff potentials of 4.2V vs. Li/Li^+ for charge and 3.0 V vs. Li/Li^+ for discharge. Cycling is performed a C/10 for three cycles, C/2 for 5 cycles, 1C for five cycles, 5C for five cycles, 8C for five cycles, 10C for 5 cycles, C/2 for 5 cycles and C/10 for 5 cycles, for a total of 38 charge/discharge cycles.

The results of the discharge capacity testing are shown graphically in Figure 3. The discharge capacity of the half-cell containing Comparative Battery Electrolyte Solution B is indicated by reference numeral B; those for the half-cells containing Battery Electrolyte Solutions 4-6 are indicated by reference numerals 4-6, respectively. As can be seen from Figure 3, the presence of the phosphite compound has no significant

adverse effect on discharge capacity during the course of this evaluation. At the 0.5% additive level (Example 5), a positive effect on discharge capacity is seen at most cycling rates.

C. Cathode half-cell performance testing with $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC) electrode

Separate model CR 2025 coin cells with a $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ cathode (Kokam Company) against a metallic lithium sheet anode are prepared with each of Examples 4-6 and Comparative Sample B as the electrolyte solution. The discharge capacity of these cells is evaluated in the manner described in part D above.

The results of the discharge capacity testing are shown graphically in Figure 4. The discharge capacity of the half-cell containing Comparative Battery Electrolyte Solution B is indicated by reference numeral B; those for the half-cells containing Battery Electrolyte Solutions 4-6 are indicated by reference numerals 4-6, respectively. As can be seen from Figure 4, the presence of the phosphite compound has no significant adverse effect on discharge capacity during the course of this evaluation.

D. Full cell performance testing

Separate model CR 2025 coin cells with a graphite anode and $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ cathode (Kokam Company) are prepared with each of Examples 4-6 and Comparative Sample B as the electrolyte solution. The discharge capacity and Coulomb efficiency of these cells is evaluated by galvanostatically cycling at a C/10 rate, using cutoff potentials of 4.2V vs. Li/Li⁺ for charge and 3.0 V vs. Li/Li⁺ for discharge.

The results of the discharge capacity testing are shown graphically in Figure 5. The discharge capacity of the cell containing Comparative Battery Electrolyte Solution B is indicated by reference numeral B; those for the cells containing Battery Electrolyte Solutions 4-6 are indicated by reference numerals 4-6, respectively. As can be seen from Figure 5, the presence of the phosphite compound has no significant adverse effect on discharge capacity during the course of this evaluation. At the 0.5% additive level (Example 5), an increase in discharge capacity is seen after initial cycles, as shown more clearly in the inset.

Example 7 and Comparative Sample C

The thermal stability of a fully charged $\text{Li}_{0.5}\text{CoO}_2$ cathode (90% $\text{Li}_{0.5}\text{CoO}_2$ 5% conductive carbon and 5% polyvinylidene fluoride binder) in a 1M LiPF_6 solution in a 1:1 by volume mixture of ethylene carbonate and diethyl carbonate (Comparative Sample C) is evaluated by DSC in the manner described in the previous example. The experiment

is repeated, this time using a battery electrolyte solution that in addition contains 0.5% by weight of tris(2,4-di-tert-butylphenyl) phosphite (Example 7). The DSC scans for Comparative Sample C and Example 7 are shown in Figures 6A and 6B, respectively.

Comparative Sample C exhibits three endothermic peaks (indicated as A, B and C in Figure 6A) in the temperature range from 20 to 350°C, the lowest of these having onset temperatures of about 203°C. Peak endotherms are seen at about 222°C, 258°C and 269°C; total endothermic heat is 368 J/g.

Example 7 exhibits only two endothermic peaks (indicated as A and B in Figure 6B). The first of these has an onset temperature of about 227°C. Peak endotherms are seen at 234°C and 263°C, and total endothermic heat is only 134 J/g. The higher onset temperature, higher peak temperatures and lower total endothermic heat all indicate that the presence of the phosphite compound substantially increases the thermal stability of the fully charged cathode in the electrolyte solution.

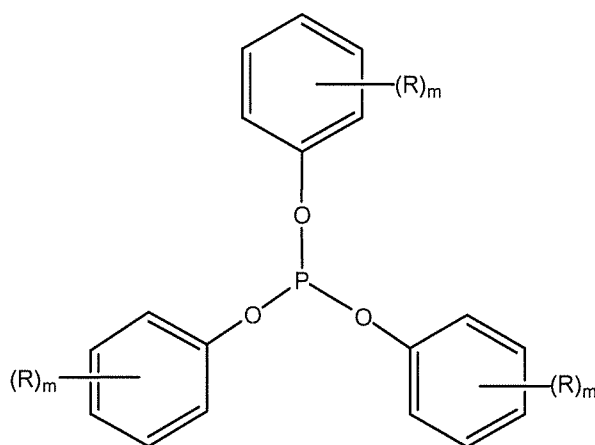
The thermal stability of a fully charged MCMB electrode (85% mesocarbon microbeads, 10% conductive carbon and 5% polytetrafluoroethene) is evaluated in the same manner, in each of the same two battery electrolyte solutions (Comparative Sample C and Example 7). The DSC scans for Comparative Sample C and Example 7 are shown in Figures 7A and 7B, respectively. When this electrode is evaluated in Comparative Sample C, three endothermic peaks (indicated as A, B and C in Figure 7A) are seen, with the lowest of these having an onset temperature of 124°C. The three peaks have peak temperatures of about 133°C, 210°C and 310°C; total endothermic heat is 381 J/g.

When the electrode is evaluated in Battery Electrode Solution Example 7, the onset temperature and peak endotherms for the first two peaks (indicated as A and B in Figure 7B) are similar. However, the third peak endotherm (indicated as C in Figure 7B) is increased to 327°C and the total endothermic heat is only 240 J/g, which represents a 37% decrease in endothermic heat. Again, a significant increase in thermal stability is seen when the phosphite compound is present in the electrolyte solution.

WHAT IS CLAIMED IS:

1. A battery electrolyte solution comprising at least one lithium salt and a nonaqueous solvent in which the lithium salt is soluble, wherein from 0.01 to 10% of the weight of the battery electrolyte solution is at least one tris(alkyl-substituted aryl) phosphite compound.

2. The battery electrolyte solution of claim 1, wherein the tris(alkyl-substituted aryl)phosphite compound includes at least one compound having the structure



wherein each R independently represents an alkyl group, and each m is at least one.

3. The battery electrolyte solution of claim 2, wherein the R groups each have up to 8 carbon atoms.

4. The battery electrolyte solution of claim 3, wherein the R groups are bonded to the respective aryl groups through tertiary carbon atoms.

5. The battery electrolyte solution of claim 4, wherein the R groups each have up to 4 carbon atoms.

6. The battery electrolyte solution of claim 4, wherein the tris(alkyl-substituted aryl) phosphite is tris(2,4-di-tert-butylaryl)phosphite.

7. The battery electrolyte solution of any of claims 1-6 wherein the solvent includes at least one material selected from linear alkyl carbonates, cyclic carbonates, esters, alkyl ethers, nitriles, sulfones, sulfolanes, siloxanes and sultones.

5 8. The battery electrolyte solution of claim 7 wherein the solvent includes at least one linear alkyl carbonate, at least one cyclic carbonate, or a mixture thereof.

9. The battery electrolyte solution of any of claims 1-8 wherein the lithium salt is at least one of LiPF_6 , LiClO_4 , LiBF_4 , LiAsF_6 , LiCF_3SO_3 and $\text{Li}[(\text{CF}_3\text{SO}_3)_2\text{N}]$.

10 10. The battery electrolyte solution of any of claims 1-9 which further comprises at least one other additive selected from a solid electrolyte interface formation promoter, a cathode protection agent, a lithium salt stabilizer, a lithium deposition improving agent, an ionic solvation enhancer, a corrosion inhibitor, a wetting agent and
15 a viscosity reducing agent.

11. An electrical battery comprising an anode, a cathode, a separator disposed between the anode and cathode, and an electrolyte solution in contact with the anode and cathode, wherein the electrolyte solution is a battery electrolyte solution of any of
20 claims 1 to 10.

12. The electrical battery of claim 1 which is a secondary battery.

13. The electrical battery of claim 11 or 12, which is a lithium ion, lithium
25 sulfur, lithium metal or lithium polymer battery.

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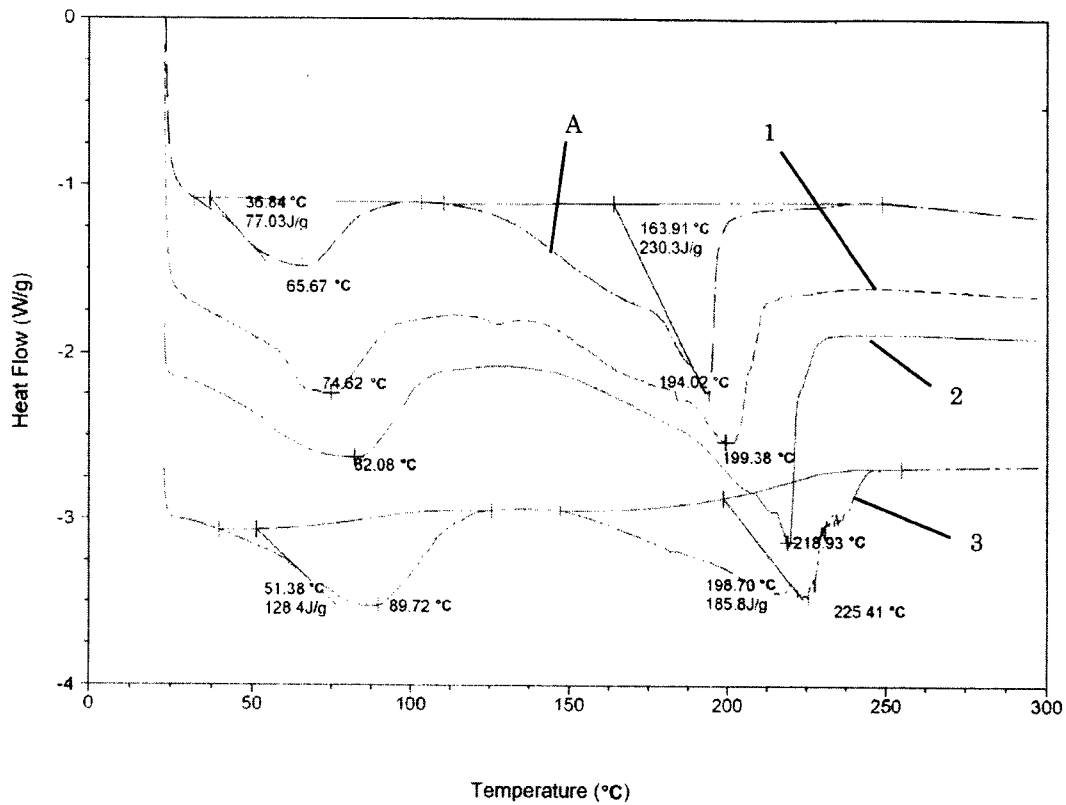


FIGURE 1

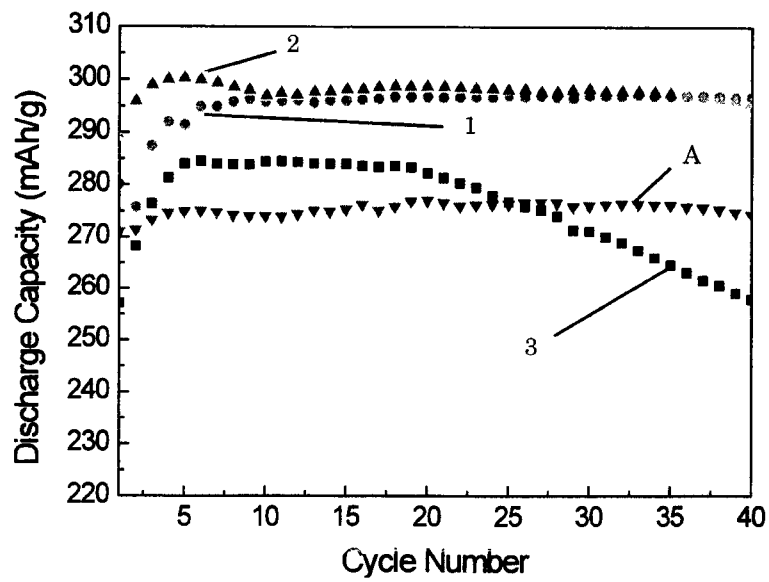


FIGURE 2

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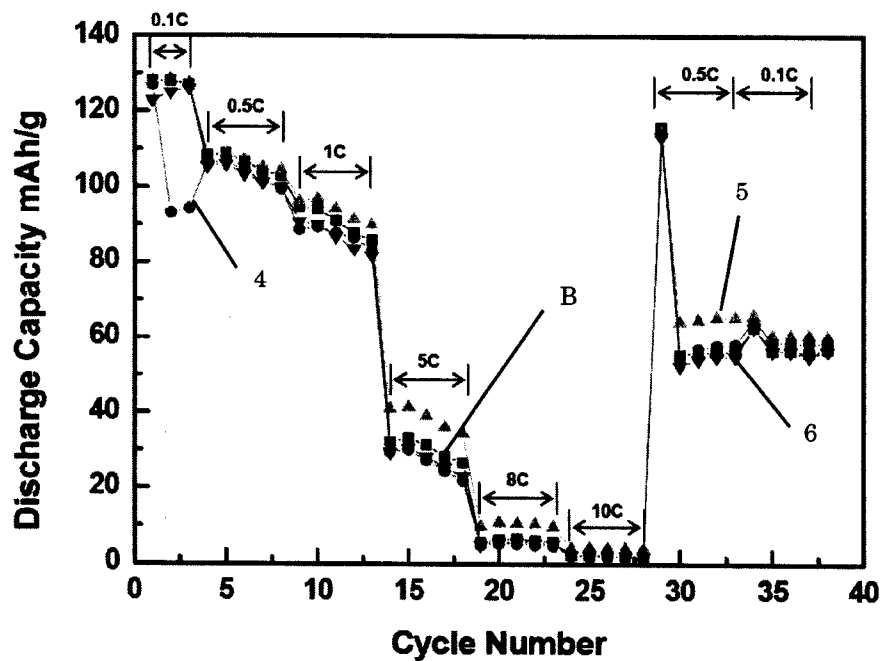


FIGURE 3

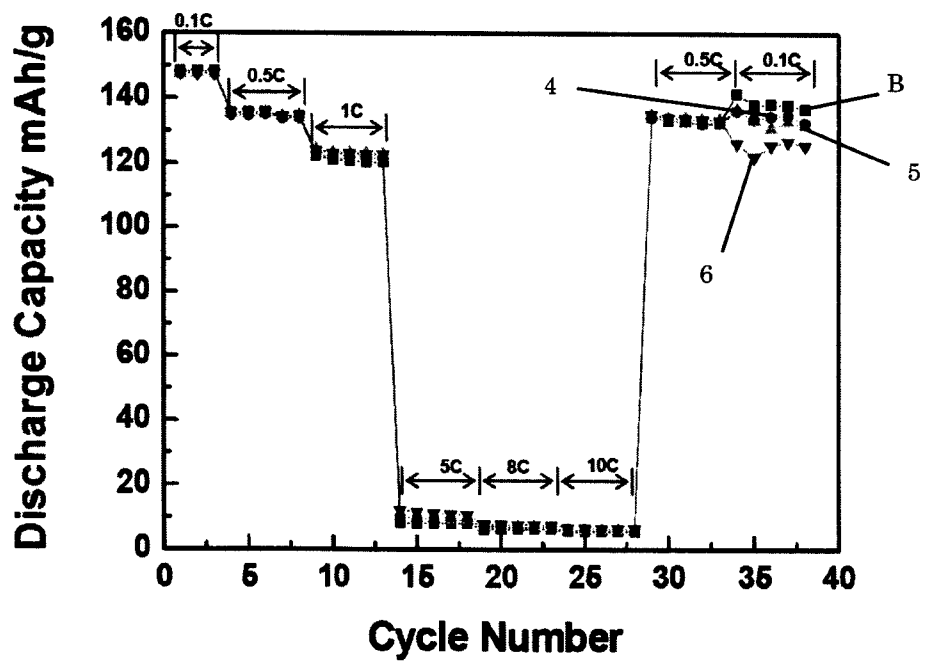


FIGURE 4

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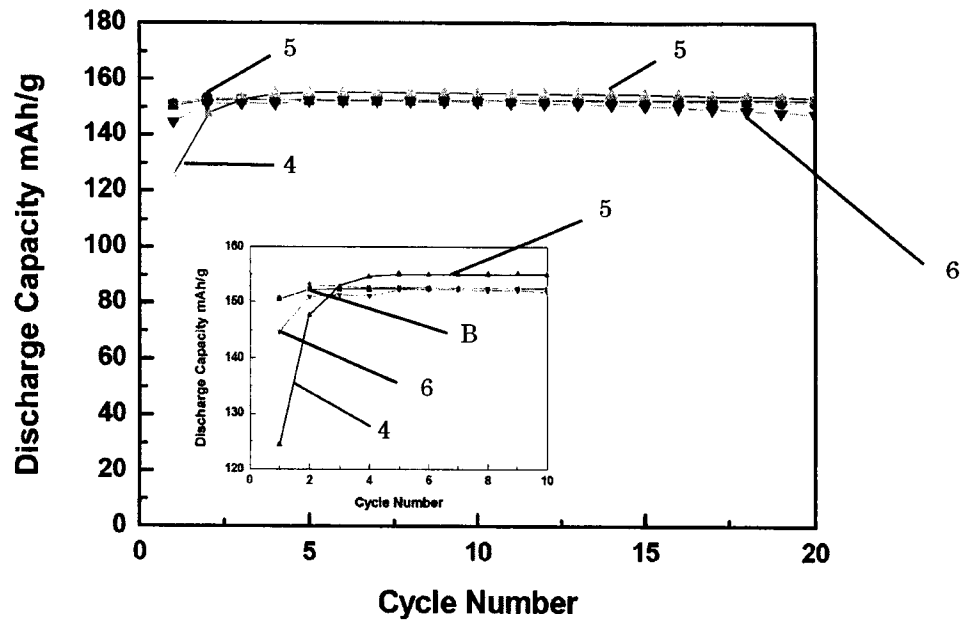


FIGURE 5

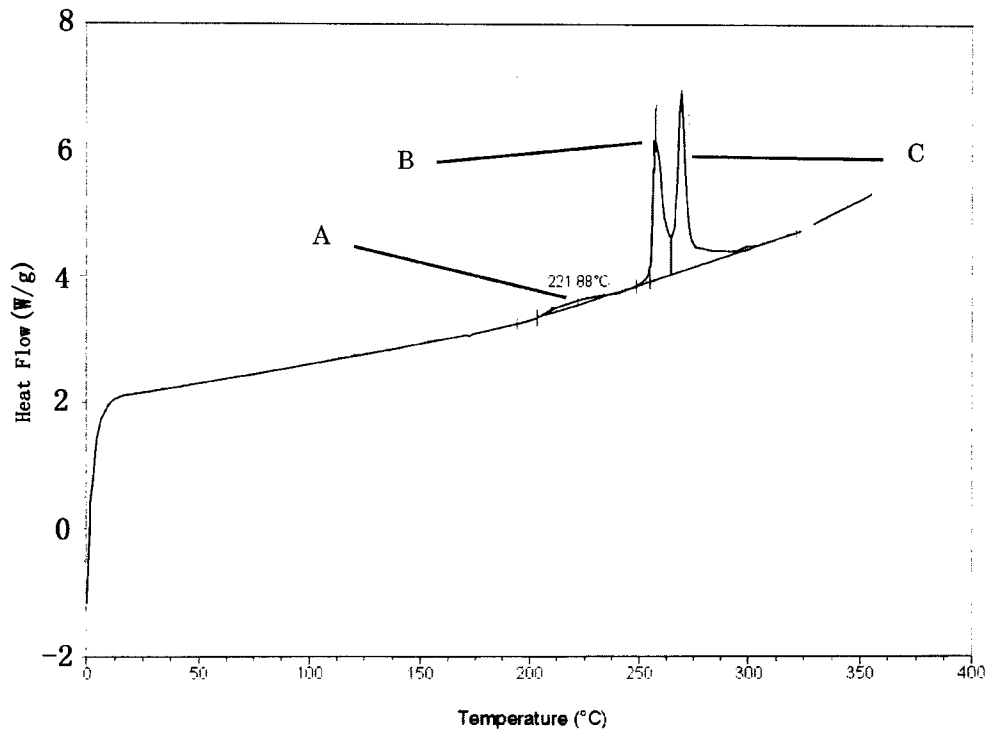


FIGURE 6A

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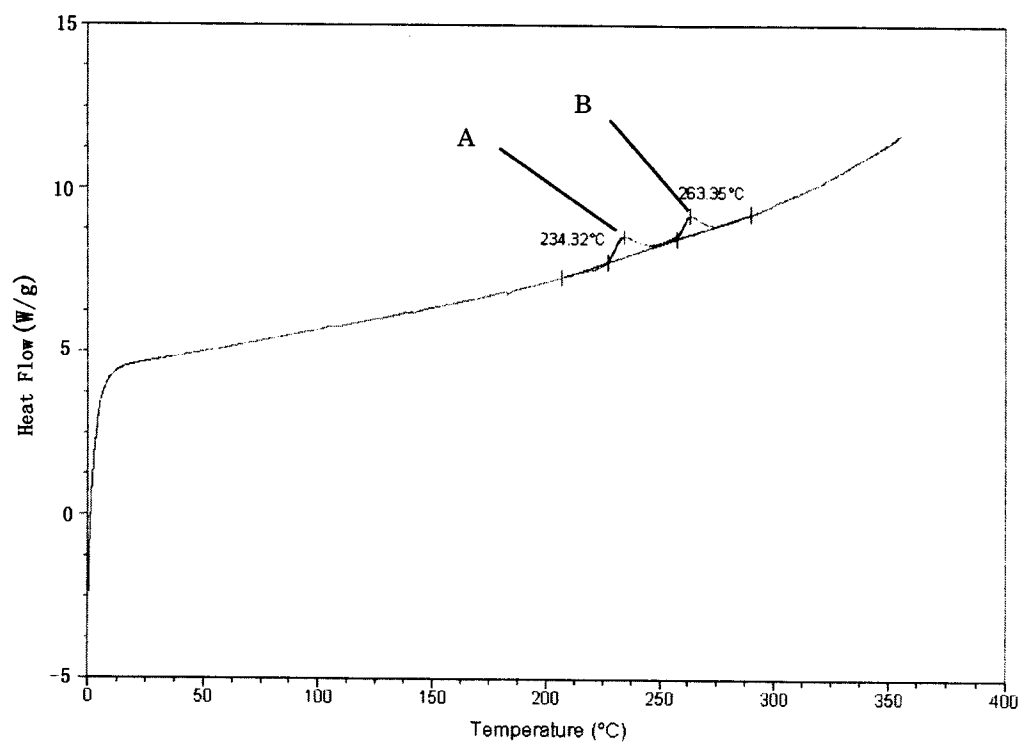


FIGURE 6B

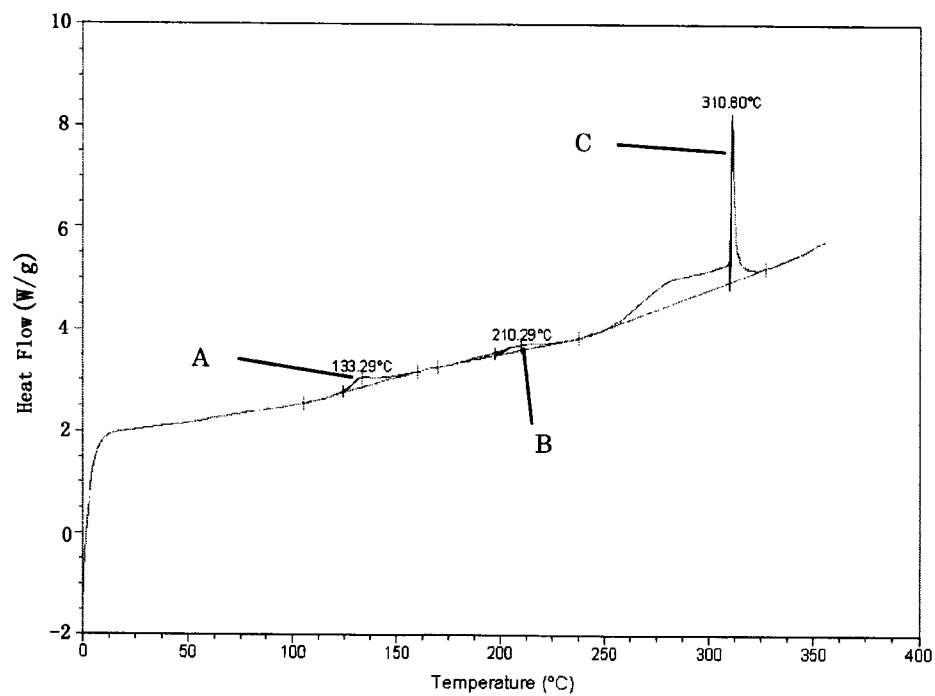


FIGURE 7A

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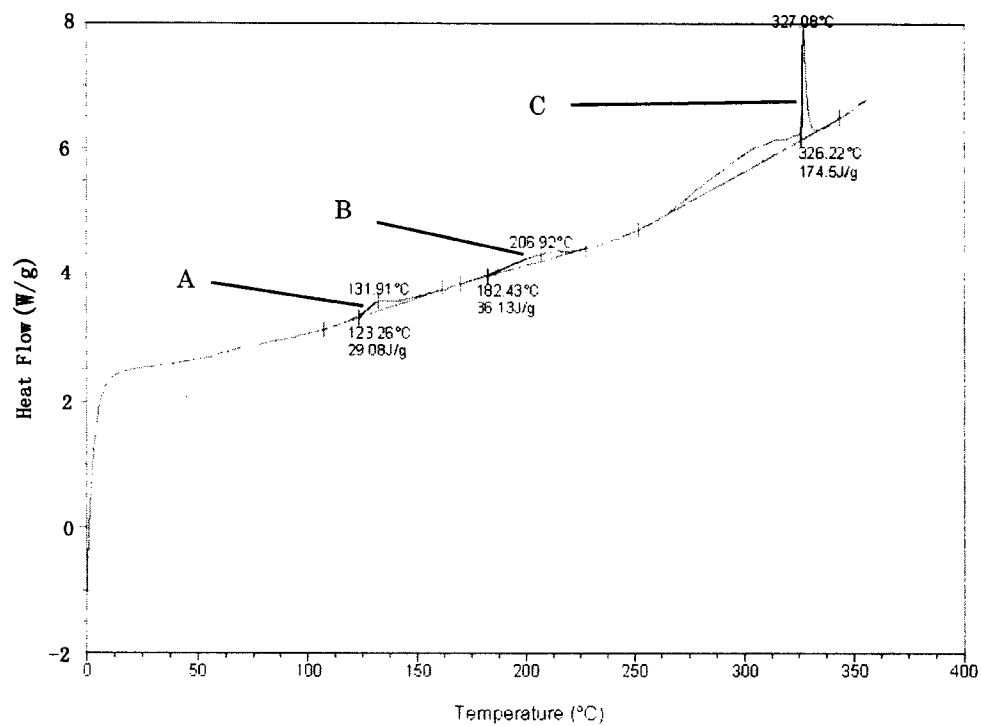


FIGURE 7B

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2011/075941

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: H01M6/-, H01M10/-

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNPAT, WPI, EPODOC, CNKI, CA: phosphite, butylphenyl, dow global technologies llc, battery, electrolyte, 31570-04-4

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO2007109435A2 (FERRO CORPORATION et al.), 27 Sep. 2007 (27.09.2007) Examples 1-6, paragraphs [0013]-[0015],[0017],[0020],[0025] and [0040]	1-13
A	US20070048622A1 (SAMSUNG SDI. CO. LTD. et al.), 01 Mar. 2007 (01.03.2007) Examples 1-5, claim 1	1-13

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance

“E” earlier application or patent but published on or after the international filing date

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“O” document referring to an oral disclosure, use, exhibition or other means

“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&”document member of the same patent family

Date of the actual completion of the international search
15 Feb. 2012 (15.02.2012)Date of mailing of the international search report
15 Mar. 2012 (15.03.2012)Name and mailing address of the ISA/CN
The State Intellectual Property Office, the P.R.China
6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China
100088
Facsimile No. 86-10-62019451

Authorized officer

LI, Zhe

Telephone No. (86-10)82245331

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2011/075941

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
WO2007109435A2	27.09.2007	US2007224515A1	27.09.2007
		WO2007109435A3	10.07.2008
		EP1997183A2	03.12.2008
		KR20080105087A	03.12.2008
		CN101405912A	08.04.2009
		US7638243B2	29.12.2009
US20070048622A1	01.03.2007	KR20070023450A	28.02.2007
		KR100803193B1	14.02.2008

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2011/075941

Continuation of: A. CLASSIFICATION OF SUBJECT MATTER

H01M10/0567 (2010.01) i

H01M10/052 (2010.01) i