

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
30 March 2006 (30.03.2006)

PCT

(10) International Publication Number
WO 2006/032207 A1

(51) International Patent Classification⁷: **H01M 10/40**,
6/16

(21) International Application Number:
PCT/CN2005/001530

(22) International Filing Date:
22 September 2005 (22.09.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
200410051676.X
24 September 2004 (24.09.2004) CN

(71) Applicant (for all designated States except US): **BYD COMPANY LIMITED** [CN/CN]; Yan An Road, Kuichong, Longgang, Shenzhen, Guangdong 518119 (CN).

(72) Inventors: **TAN, Weihua**; Yan An Road, Kuichong, Longgang, Shenzhen, Guangdong 518119 (CN). **DONG, Junqing**; Yan An Road, Kuichong, Longgang, Shenzhen, Guangdong 518119 (CN). **LIU, Zhaosheng**; Yan An Road, Kuichong, Longgang, Shenzhen, Guangdong 518119 (CN).

(74) Agent: **RUNPING & PARTNERS**; Suite 509, Yingu Mansion, No. 9 Beisihuanxilu, Haidian District, Beijing 100080 (CN).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: ELECTROLYTES FOR LITHIUM ION BATTERIES

(57) Abstract: The present invention discloses non-aqueous electrolytes for lithium ion batteries. Said electrolytes comprise of lithium salts and a non-aqueous organic solvent. The non-aqueous organic solvent comprises of compounds having the formate derivative or formamide derivative. The chemical formulas for these compounds are HCOOR_1 and HCONR_2R_3 , where R_1 , R_2 , R_3 are alkyls having 1 to 4 carbon atoms. The weight percentage of the compounds having the formate derivative or formamide derivative is between 5wt% and 70wt% of the total weight of the non-aqueous organic solvent. Lithium ion batteries using said electrolytes exhibit improved discharge properties at low temperatures. These batteries are especially suitable for use as power batteries with large capacities.



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Electrolytes for Lithium Ion Batteries

Cross Reference

[1] This application claims priority from a Chinese patent application entitled "Non-Aqueous Electrolytes and Their Lithium Ion Secondary Batteries" filed on September 24, 2004, having a Chinese Application No. 200410051676.X. This Chinese application is incorporated here by reference.

Field of Invention

[2] This invention relates to lithium secondary batteries, and in particular, non-aqueous electrolytes of lithium ion secondary batteries.

Background

[3] In recent years, lithium ion rechargeable batteries have been widely used in portable electronics and communications equipment such as cameras, mobile phones, and laptop computers. With increased research, the properties of these batteries are improving rapidly. Lithium ion rechargeable batteries with a small capacity are generally used at temperatures greater than -10°C . As such, the discharge problems that these batteries exhibit at low temperatures are not as apparent.

[4] However, with the rapid development of electric bicycles and automobiles, lithium ion rechargeable batteries with large capacities have become the preferred choice of energy sources for power equipment, as these batteries have a high discharge voltage, high energy density and long cycle life. The operating temperatures for these equipments are often lower than -10°C . At low temperatures, lithium ion rechargeable batteries with large capacities have significant discharge problems that include a low rate of utilization of the active materials, low specific energy, and poor cycling properties.

[5] The discharge properties of these batteries using non-aqueous electrolyte at low temperatures can be improved, not only by changing the active material of the positive and negative electrodes, but also by changing the composition of the non-aqueous electrolyte. When the ambient temperature is relatively low, the ion conductivity of the electrolyte decreases. In addition, its viscosity increases, causing its electrical conductivity to decrease. As a result, the discharge properties of the battery at low temperatures can deteriorate. Increasing the dielectric constant of the electrolyte and enhancing the conductivity of the solvent with the electrolyte solute ions can improve these discharge properties.

[6] Usually, the non-aqueous electrolytes of lithium ion secondary batteries are comprised of solvents with chain organic esters such as dimethyl carbonate, diethyl carbonate, methyl ethyl carbonate etc., or solvents with ring organic esters such as ethylene

carbonate, propylene carbonate, vinylene carbonate, γ -butyrolactone. The solutes in the electrolyte are comprised of lithium salts such as lithium perchlorate, lithium hexaaluminate, lithium hexafluorophosphate, lithium tetrafluoroborate, dissolved in the electrolyte. The concentration of the electrolyte solute is usually at 1mol/l.

- 5 [7] Patent CN1278953A noted that batteries achieve better low temperature characteristics and long term stability when compounds with the S—O bond are added to the organic solvent of the electrolyte. However, when this method is used in the electrolyte for large capacity lithium ion rechargeable power batteries with a discharge capacity that is greater than 10Ah at normal temperatures, the discharge capacity
10 conservation rate at low temperatures and the cycling properties of the batteries are still poor, such that these batteries are unable to meet the demands of the power equipment.
[8] Due to the limitations of the prior art, it is therefore desirable to have novel non-aqueous electrolytes that can enhance the low temperature discharge properties of large capacity lithium ion rechargeable batteries.

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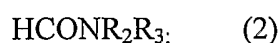
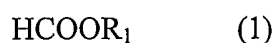
Summary of Invention

- [9] An object of this invention is to provide electrolytes that improve the discharge properties of large capacity lithium ion batteries at low temperatures.
[10] Briefly, the present invention relates to new compositions for non-aqueous
20 electrolyte of lithium ion batteries. Said electrolytes are comprised of lithium salts with a non-aqueous organic solvent. The non-aqueous organic solvent is comprised of compounds having the formate derivative or formamide derivative. The chemical formulas for these compounds are HCOOR_1 and HCONR_2R_3 , where R_1 , R_2 , R_3 are alkyls having 1 to 4 carbon atoms. The amount of said compound having the formate derivative or formamide
25 derivative is between 5wt% and 70wt% of the total weight of the non-aqueous organic solvent.
[11] An advantage of this invention is that large capacity lithium ion batteries having electrolytes that are embodiments of this invention have improved discharge properties at low temperatures.

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Detailed Description of the Preferred Embodiments

- [12] Embodiments of non-aqueous electrolytes for lithium ion rechargeable batteries of the present invention may be comprised of a lithium salt, an electrolyte solute, and a non-aqueous organic solvent. Said non-aqueous organic solvent is comprised of at least a
35 compound having a formate derivative or a compound having a formamide derivative. In preferred embodiments, the compounds are represented by the following formulas:



[13] where R_1 , R_2 , R_3 are alkyls. Preferably, R_1 , R_2 , and R_3 are alkyls that have 1 to 4 carbon atoms.

[14] Preferred embodiments of said non-aqueous organic solvent may be comprised of at least one compound containing a formate or formamide selected from the following: methyl formate, isopropyl formate, butyl formate, dimethyl formamide, dipropyl formamide.

[15] This invention adds two groups of compounds to the non-aqueous electrolytes of the lithium ion rechargeable batteries, compounds having formates and compounds having formamide. Electrolyte solutes such as LiPF_6 , LiAsF_6 , LiClO_4 can easily dissolve in this electrolyte.

[16] In addition, the molecules in these compounds contain oxygen and nitrogen atoms that strongly attract electrons. When the number of attached carbons is low, the electrons associated with the hydrogen of the formate and formamide derivatives are strongly attracted to the carbonyl. This results in the strong polarity of molecules having the formate or the formamide derivative and causes the dielectric constant of the electrolyte to increase.

[17] In addition, when the number of carbon atoms attached to the compounds with the formate derivative and formamide derivative is low, strong hydrogen bonds can be formed between molecules. The viscosity of the solvents formed by this type of molecular structure may decrease. Methyl formate and dimethyl formamide are such examples.

[18] As the number of carbon atoms attached to the compounds with the formate derivative and formamide derivative increases, the polarity of the compounds may decrease gradually and the ability to form hydrogen bonds will also decrease gradually. As a result, the dielectric constant is decreased and the viscosity of molecules is increased. Therefore, the preferred number of carbon atoms in the alkyls contained in the compound represented by formulas (1) and (2) is between 1 and 4.

[19] To form the non-aqueous electrolyte, appropriate quantity of ring acid esters, chain acid esters, or their mixtures should be added to form a mixture of solvents. By doing so, a passivated-film can be formed at the surface of the carbon atoms. In addition, the dielectric constant of the solvent and the dissociation of electrolyte solute can be increased. Also, the viscosity of the electrolyte can be adjusted such that the electrolyte has high conductivity and stability, even at low temperatures, i.e., at temperatures between -10°C and -40°C .

[20] Therefore, in preferred embodiments, said non-aqueous organic solvent is also comprised of at least one chain acid ester selected from the following: methyl carbonate, dimethyl carbonate, ethyl carbonate, diethyl carbonate, methyl ethyl carbonate, ethyl propyl carbonate, diphenyl carbonate, ethyl acetate, methyl acetate, methyl propionate, ethyl propionate, dimethoxy ethane, diethoxy ethane, chain organic esters with fluorine, chain organic esters with sulfate, and chain organic esters with unsaturated bonds.

[21] In preferred embodiments, said non-aqueous organic solvent also contains at least one ring acid ester selected from the following: ethylene carbonate, propylene carbonate, vinylene carbonate, γ -butyrolactone, sultone, ring organic ester with fluorine, ring organic ester with sulfate, and ring organic ester with unsaturated bond.

5 [22] The optimal quantity of compounds represented by formulas (1) and (2) in the solvent of the non-aqueous electrolyte is related to the types of ring carbonate and chain carbonate that they are mixed with, the types and quantity of electrolyte solutes, and the types and quantity of additives. Too much of either of the above compounds can cause the reduction of the quantity of active materials of negative electrode and the peeling of the
10 carbon layer. On the other hand, if there were too little of the latter, the objective of increasing the high current conductivity rate cannot be achieved. In preferred embodiments, the weight percent of said compounds having the formate derivative or formamide derivative is between 5wt% and 70wt% of the total weight of the non-aqueous organic solvent.

15 [23] In embodiments, the lithium salt is at least one chemical selected from the following: lithium perchlorate, lithium hexaaluminate, lithium hexafluorophosphate, lithium tetrafluoroborate, lithium halide, lithium fluorocarbon fluoro oxide phosphate, and lithium fluorocarbon sulfonate.

[24] The concentration of electrolyte solute has two opposing effects on the electrolyte
20 solution. When the concentration is increased, the electrolyte solute in the solvent that can contribute to dissociation is also increased. This can result in the increase of the electrical conductivity. However, increasing the concentration can also increase the solvent viscosity and cause the decrease in the moving velocity of lithium ions. This results in the decrease in the electrical conductivity. Therefore, there is an optimal value for the
25 concentration of the electrolyte solute. Under normal temperatures conditions, that is, for temperatures between 10°C and 30°C, this concentration is typically around 1mol/l. At low temperatures, the effects are similar. However, when temperature drops, the viscosity of solvents increases greatly and significantly affect the conductivity. Therefore, the concentration of electrolyte solute should be reduced slightly and the optimal concentration
30 should be lower than that at normal temperatures. The specific optimal value for the optimal concentration varies depending on the type and composition of the solvent, and the type of electrolyte solute. For electrolyte using EC/DEC, EC/DMC as solvents, and LiPF₆ as solute, the optimal concentration of electrolyte solute is usually lower than 1mol/l. However, the concentration also cannot be too low as this will decrease the conductivity of
35 the electrolyte. Taking into consideration that the battery may operate at both the normal and low temperature ranges, in preferred embodiments, the concentration of the electrolyte solute, i.e., the lithium salt in the solvent, is between 0.8mol/l and 1.0mol/l.

[25] One method to reduce the reaction between the solvent compounds and the embedded lithium is the addition of ring carbonates. Another effective method is to form a passivated-film on the surface of the carbon atoms that is in contact with the electrolyte. To achieve this effect, additives are added such that, during the initial reaction of the battery, they react with the lithium that are embedded in the negative electrode to form a dense solid protective passivated-film. In some embodiments, CO₂, CO, and N₂O can be used as additives. Using CO₂ as an additive is more effective as the principle composition of the passivated-film formed is LiCO₃. The film is thin and dense and can prevent the continued reaction between the solvent and lithium, as well as the cross diffusion of the solvent molecules. In preferred embodiments, between 0.05wt% and 1.0wt% of the total weight of the electrolyte of the additive carbon dioxide gas is added into non-aqueous electrolyte.

[26] To fabricate the lithium ion rechargeable batteries using the electrolyte that are said embodiments of this invention, oxides of transition metal lithium are used as the active material for the positive electrodes. They include one or more material represented by the following formulas: Li_xNi_{1-y}Co_yO₂, where $0.9 \leq x \leq 1.1$, and $0 \leq y \leq 1.0$; Li_xMn_{2-y}B_yO₂ where $0.9 \leq x \leq 1.1$, and $0 \leq y \leq 1.0$ and B is a transition metal. Examples of the active materials include LiCoO₂, LiNiCoO₂, and LiMnO₄.

[27] The active materials of the negative electrode of said lithium ion rechargeable batteries are carbon group materials that can embed and detach lithium ions. Preferably, the active materials for the negative electrode to be used with electrolytes that are embodiments of this invention are at least one material selected from the following: natural graphite, artificial graphite, middle phase carbon micro-granule, middle phase carbon fiber.

[28] The electrolyte solutes used in the embodiments are metal lithium salts such as LiPF₆ dissolved in organic solvents. After the batteries are fabricated, the lithium ions from the active material of positive electrodes can pass in and out of the granules of carbon to charge and discharge the battery.

[29] The following embodiments and comparison examples further describe this invention in detail. For each electrolyte that is an embodiment or a comparison example, a battery comprising of said electrolyte is fabricated such that the properties of that battery can be tested and compared with other batteries made from other embodiments and comparison examples.

[30] The positive electrodes of the batteries that use the following embodiments and comparison examples are fabricated by the method comprising of:

35 mixing 91wt% of LiCoO₂ powder, 6wt% of graphite flakes as conducting agent and 3wt% of PVDF as binding agent;
 dispersing the mixture into N-methyl pyrrolidone as solvent to form a paste; and

uniformly coating both sides of a 20 μm belt-shaped aluminum foil of positive electrode current collector with the paste mixture;

drying with heat; and

pressing at a pressure of between 0.5 Mpa and 2 Mpa to obtain the belt-shaped positive electrode slice with thickness of 150 μm and length 2070mm.

[31] The negative electrodes of the batteries that use the following embodiments and comparison examples are fabricated by the method comprising of:

mixing 90wt% of artificial graphite and 10wt% of PTFE as binding agent;

dispersing the mixture into de-ionized water as solvent to form a paste;

uniformly coating both sides of a 15 μm belt-shaped copper foil of negative electrode current collector with the paste mixture;

drying with heat; and

pressing at pressure between 0.5 Mpa and 2 Mpa to obtain the belt-shaped negative electrode slice with thickness of 140 μm and length 2150mm.

[32] The batteries that use the following embodiments and comparison examples are fabricated and assembled by the method comprising of:

winding and stacking the positive electrode slice, separation membrane, negative electrode slice by layers one by one,

inserting into round angle quadric shell of dimension 18X70X125mm;

injecting the electrolyte in the following embodiments and comparison examples into the battery to obtain the lithium ion rechargeable battery with the non-aqueous electrolyte of that embodiment or comparison example.

[33] The batteries that are fabricated are tested to obtain their characteristics at normal temperatures and low temperatures. To test each battery at normal temperature, the battery is charged to 4.20V at a temperature 25°C using 1 C current. The cut-off charging current is 150mA. The battery is then discharged to 2.75V using 1C current. The discharging capacity at normal temperatures C_N is obtained. Similarly the discharge capacity at low temperature C_L is obtained by repeating the above stated procedure at -25°C. That is, at -25°C, the battery is charged using 1C current of -25°C to 4.2V. The cut-off charging current is 150mA. The battery is then discharged to 2.75V using 1C current. The discharging capacity at low temperatures C_L is then obtained. The discharging ratio at low/normal temperatures, k, is defined as $k = C_L / C_N \times 100\%$.

Embodiment 1

[34] The electrolyte in this embodiment is fabricated as follows:

mixing methyl formate, a compound that contains the formate derivative as represented by formula (1); with ethyl carbonate(EC), diethyl carbonate (DEC) in the weight ratio of 5: 25: 70;

adding the electrolyte solute LiPF_6 with concentration of 0.9mol/l; and
at the same time, adding CO_2 at 0.2wt% of total weight of electrolyte.

Embodiment 2

- 5 [35] The composition of the solvent in the electrolyte in this embodiment is changed to methyl formate: EC: DEC = 45: 15: 40. Everything else remains the same as in Embodiment 1.

Embodiment 3

- 10 [36] The composition of the solvent in the electrolyte in this embodiment is changed to methyl formate: isopropyl formate: EC: DEC = 60: 10: 15:15. Everything else remains the same as in Embodiment 1.

Embodiment 4

- 15 [37] The composition of the solvent in the electrolyte of this embodiment is changed to dimethyl formamide: EC: DEC = 30: 15:55 and the concentration of electrolyte solute is changed to 0.8mol/l. Everything else remains the same as in Embodiment 1.

Embodiment 5

- 20 [38] The composition of the solvent in the electrolyte in this embodiment is changed to dimethyl formamide: dipropyl formamide: EC: DEC = 15: 5: 40: 40 and the concentration of electrolyte solute is changed to 0.7mol/l. The additive, CO_2 , additive is not added. Everything else remains the same as in Embodiment 1.

Embodiment 6

- 25 [39] The composition of the solvent in the electrolyte in this embodiment is changed to methyl formate: butyl formate: dipropyl formamide: EC: DEC = 15: 10: 15: 30: 30. Everything else remains the same as in Embodiment 1.

Comparison Example 1

- 30 [40] The electrolyte in this comparison example is fabricated as follows:
mixing ethyl carbonate (EC), diethyl carbonate (DEC) and dimethyl carbonate(DMC)
in the weight ratio of 15: 15: 70;
adding the electrolyte solute LiPF_6 with concentration of 1.0 mol/l; and
35 not adding the additive CO_2 .
[41] Everything else remains the same as in Embodiment 1.

Comparison Example 2

[42] The electrolyte in this comparison example is fabricated as follows:

5 mixing propenoic carbonate (PC), diethyl carbonate (DEC) and dimethyl carbonate(DMC) in the weight ratio of 30: 25: 45;
adding the electrolyte solute LiPF_6 with concentration of 1.0 mol/l; and
not adding the additive CO_2 .

[43] Everything else remains the same as in Embodiment 1.

10 [44] The results of the testing of the discharge properties of the batteries fabricated using the electrolytes from the above embodiments and comparison examples are shown in Table 1 and Table 2.

[45] Comparing the electrical properties of the batteries fabricated with electrolytes in the above described embodiments and comparison examples shows that, at normal temperatures, there is little difference in the discharge capacities of batteries between
15 electrolytes containing compounds with formate derivative or formamide derivative and traditional electrolytes that do not contain either of these two derivatives. However, at temperatures below -25°C , there is a significant difference in the discharge capacities. In addition, for the solvents containing the same formate derivative or formamide derivative, when different alkyls are attached, the low temperature properties exhibit large differences.
20 Generally speaking, the less the number of carbon atoms that are contained in the alkyl, the better the characteristics of the batteries are at low temperatures. The larger discharging ratio in Embodiment 2 and Embodiment 6 illustrates this effect.

[46] Alkyls are the electron provider group. When carbon atoms increase, the polarity of the compounds that contain the formate derivative or formamide derivative decreases
25 gradually. As a result, the power to form hydrogen bonds between molecules or within the molecules decreases gradually; and the melting point of the compounds increases. At the same time, the dielectric constant of the molecules also decreases. As a result, the properties of the electrolyte formed at low temperatures deteriorate gradually. This may be the reason for the deterioration of the properties of the electrolyte at low temperatures
30 when the number of carbon atoms attached to the alkyl is increased.

[47] A comparison between Embodiment 5 and the other embodiments shows that adding the additive CO_2 can improve the properties of electrolyte at normal temperatures and especially at low temperatures. This is due to the fact that CO_2 can facilitate or accelerate the formation of the passivated-film.

35 [48] A comparison between Embodiment 1, Embodiment 2 and Embodiment 4 shows that, by appropriately reducing the concentration of electrolyte solute, the properties of the electrolyte at low temperatures can be improved. This increases the discharge ratio without significantly affecting the capacity of the battery at normal temperatures.

- However, Embodiment 5 shows that too low a concentration of electrolyte will cause a significant decrease in the discharge capacity of a battery at normal temperatures, and, the decrease of the discharge ratio at low/normal temperatures. This effect is primarily caused by the decrease of the conductivity of the electrolyte. Therefore, in order for a battery to have better overall properties, the optimal molar concentration of the electrolyte solute should be between 0.8mol/l and 1.0mol/l.

TABLE 1

	Composition of Solvent; Concentration of Electrolyte Solute	Additive CO ₂	Capacity at Normal Temper- atures C _N (Ah)	Capacity at Low Temper- atures C _L (Ah)	Discharge Ratio K(%)
Embodi- ment 1	methyl formate: EC : DEC=5: 25: 70; LiPF ₆ =0.9 mol/l	Yes	12.10	6.32	52.23
Embodi- ment 2	methyl formate: EC: DEC= 45: 15: 40; LiPF ₆ =0.9 mol/l	Yes	12.50	8.50	68.00
Embodi- ment 3	methyl formate: isopropyl formate: EC : DEC=60: 10: 15: 15; LiPF ₆ =0.9 mol/l	Yes	12.30	6.65	54.06
Embodi- ment 4	dimethyl formamide: EC : DEC =30: 15: 55; LiPF ₆ =0.8 mol/l	Yes	12.10	7.15	59.09
Embodi- ment 5	dimethyl formamide: dipropyl formamide: EC : DEC =15: 5: 40: 40; LiPF ₆ =0.7 mol/l	No	11.13	5.38	48.34
Embodi- ment 6	methyl formate: butyl formate: dipropyl formamide: EC : DEC=10: 20: 15: 15: 40; LiPF ₆ =0.9 mol/l	Yes	12.28	7.90	64.33

TABLE 2

	Composition of Solvent (Weight Ratio)			Additive CO ₂	Capacity at Normal Temperature C _N (Ah)	Capacity at Low Temperature C _L (Ah)	Dis-charge Ratio k (%)
	EC/PC	DEC	DMC				
Comparison Example 1	EC 15	15	70	No	12.44	5.30	42.60
Comparison Example 2	PC 30	25	45	No	11.25	4.16	36.97

[49] While the present invention has been described with reference to certain preferred
embodiments, it is to be understood that the present invention is not limited to such
5 specific embodiments. Rather, it is the inventor's contention that the invention be
understood and construed in its broadest meaning as reflected by the following claims.
Thus, these claims are to be understood as incorporating not only the preferred
embodiments described herein but all those other and further alterations and modifications
10 as would be apparent to those of ordinary skilled in the art.

Claims

[50]—We Claim:

- 5 1. An electrolyte comprising:
a lithium salt;
a non-aqueous organic solvent wherein said non-aqueous solvent comprises of at
least one compound selected from the group consisting of: a compound having a formate
derivative and a compound having a formamide derivative.
- 10 2. The electrolyte of claim 1 wherein said compound having a formate derivative is
represented by the formula HCOOR_1 .
3. The electrolyte of claim 1 wherein said compound having a formamide derivative is
15 represented by the formula HCONR_2R_3 .
4. The electrolyte of claim 2 wherein said R_1 is an alkyl.
5. The electrolyte of claim 2 wherein said R_1 is selected from the group consisting of
20 alkyl having 1 to 4 carbons atoms.
6. The electrolyte of claim 3 wherein said R_2 and R_3 are alkyls.
7. The electrolyte of claim 3 wherein said R_2 and R_3 are selected from the group
25 consisting of alkyl having 1 to 4 carbon atoms.
8. The electrolyte of claim 7 wherein said compound having a formate derivative is
represented by the formula HCOOR_1 and said R_1 is selected from the group consisting of
alkyl having 1 to 4 carbons atoms.
- 30 9. The electrolyte of claim 1 wherein said non-aqueous organic solvent comprises of at
least one compound selected from the group consisting of: methyl formate, isopropyl
formate, butyl formate, dimethyl formamide, dipropyl formamide.

10. The electrolyte of claim 8 wherein said non-aqueous organic solvent comprises of at least one chain acid ester selected from the group consisting of: methyl carbonate, dimethyl carbonate, ethyl carbonate, diethyl carbonate, methyl ethyl carbonate, ethyl propyl carbonate, diphenyl carbonate, ethyl acetate, methyl acetate, methyl propionate, ethyl propionate,
5 dimethoxy ethane, diethoxy ethane, chain organic esters with fluorine, chain acid esters with sulfate, and chain acid esters with unsaturated bond.
11. The electrolyte of claim 8, wherein said non-aqueous organic solvent comprises of at least one ring acid ester selected from the group consisting of: ethylene carbonate, propylene
10 carbonate, vinylene carbonate, γ -butyrolactone, sultone, ring organic esters with fluorine, ring organic esters with sulfate, and ring organic esters with unsaturated bond.
12. The electrolyte of claim 8 wherein the weight of said compound having a formate derivative and said compound having a formamide derivative is between 5wt% and 70wt%
15 of the total weight of said non-aqueous organic solvent.
13. The electrolyte of claim 8 wherein said lithium salt is at least one lithium compound selected from the group consisting of: lithium perchlorate, lithium hexaaluminate, lithium hexafluorophosphate, lithium tetrafluoroborate, lithium halide, lithium fluorocarbon fluoro
20 oxide phosphate and lithium fluorocarbon sulfonate.
14. The electrolyte of claim 8 wherein the concentration of said lithium salt in said nonaqueous organic solvent is between 0.8 mol/l and 1.0 mol/l.
- 25 15. The electrolyte of claim 8 wherein said electrolyte also comprises of an additive selected from the group consisting of: CO₂, CO, and N₂O and wherein the weight of said additive is between 0.05wt% and 1.0wt% of the weight of the electrolyte.
16. The electrolyte of claim 10 wherein said non-aqueous organic solvent comprises of
30 at least one ring acid ester selected from the group consisting of: ethylene carbonate, propylene carbonate, vinylene carbonate, γ -butyrolactone, sultone, ring organic esters with fluorine, ring organic esters with sulfate, and ring organic esters with unsaturated bond.

17. The electrolyte of claim 13 wherein the concentration of said lithium salt in said nonaqueous organic solvent is between 0.8 mol/l and 1.0 mol/l.
18. The electrolyte of claim 16 wherein
5 said lithium salt is at least one lithium compound selected from the group consisting of: lithium perchlorate, lithium hexaaluminate, lithium hexafluorophosphate, lithium tetrafluoroborate, lithium halide, lithium fluorocarbon fluoro oxide phosphate and lithium fluorocarbon sulfonate;
the concentration of said lithium salt in said nonaqueous organic solvent is between
10 0.8 mol/l and 1.0 mol/l; and
the weight of said compound having a formate derivative and said compound having a formamide derivative is between 5wt% and 70wt% of the total weight of said non-aqueous organic solvent.
- 15 19. An electrolyte, comprising:
a lithium salt;
a non-aqueous organic solvent wherein said non-aqueous solvent comprises of at least one compound selected from the group consisting of: compound having a formate represented by the formula HCOOR_1 compound having a formamide derivative
20 represented by the formula HCONR_2R_3 ; and
an additive selected from the group consisting of: CO_2 , CO , and N_2O ; and wherein
said R_1 is selected from the group consisting of alkyl having 1 to 4 carbons atoms;
said R_2 and R_3 are selected from the group consisting of alkyl having 1 to 4
25 carbon atoms;
said non-aqueous organic solvent comprises of at least one chain acid ester selected from the group consisting of: methyl carbonate, dimethyl carbonate, ethyl carbonate, diethyl carbonate, methyl ethyl carbonate, ethyl propyl carbonate, diphenyl carbonate, ethyl acetate, methyl acetate, methyl propionate, ethyl propionate,
30 dimethoxy ethane, diethoxy ethane, chain organic esters with fluorine, chain acid esters with sulfate, and chain acid esters with unsaturated bond;
said non-aqueous organic solvent comprises of at least one ring acid ester selected from the group consisting of: ethylene carbonate, propylene carbonate,

vinylene carbonate, γ -butyrolactone, sultone, ring organic esters with fluorine, ring organic esters with sulfate, and ring organic esters with unsaturated bond;

the weight of said compound having a formate derivative and said compound having a formamide derivative is between 5wt% and 70wt% of the total weight of said non-aqueous organic solvent;

said lithium salt is at least one lithium compound selected from the group consisting of: lithium perchlorate, lithium hexaaluminate, lithium hexafluorophosphate, lithium tetrafluoroborate, lithium halide, lithium fluorocarbon fluoro oxide phosphate and lithium fluorocarbon sulfonate;

the concentration of said lithium salt in said nonaqueous organic solvent is between 0.8 mol/l and 1.0 mol/l; and

the weight of said additive is between 0.05wt% and 1.0wt% of the weight of the electrolyte.

20. A lithium ion battery, comprising:

a positive electrode;

a negative electrode,

a separation membrane, and

an electrolyte wherein

said electrolyte comprises of a lithium salt; a non-aqueous organic solvent comprises of at least one compound selected from the group consisting of: compound having a formate represented by the formula HCOOR_1 compound having a formamide derivative represented by the formula HCONR_2R_3 ; and an additive selected from the group consisting of: CO_2 , CO , and N_2O ;

said R_1 is selected from the group consisting of alkyl having 1 to 4 carbons atoms;

said R_2 and R_3 are selected from the group consisting of alkyl having 1 to 4 carbon atoms;

said non-aqueous organic solvent comprises of at least one chain acid ester selected from the group consisting of: methyl carbonate, dimethyl carbonate, ethyl carbonate, diethyl carbonate, methyl ethyl carbonate, ethyl propyl carbonate, diphenyl carbonate, ethyl acetate, methyl acetate, methyl propionate, ethyl propionate,

dimethoxy ethane, diethoxy ethane, chain organic esters with fluorine, chain acid esters with sulfate, and chain acid esters with unsaturated bond;

said non-aqueous organic solvent comprises of at least one ring acid ester selected from the group consisting of: ethylene carbonate, propylene carbonate,
5 vinylene carbonate, γ -butyrolactone, sultone, ring organic esters with fluorine, ring organic esters with sulfate, and ring organic esters with unsaturated bond;

the weight of said compound having a formate derivative and said compound having a formamide derivative is between 5wt% and 70wt% of the total weight of said non-aqueous organic solvent;

10 said lithium salt is at least one lithium compound selected from the group consisting of: lithium perchlorate, lithium hexaaluminate, lithium hexafluorophosphate, lithium tetrafluoroborate, lithium halide, lithium fluorocarbon fluoro oxide phosphate and lithium fluorocarbon sulfonate;

the concentration of said lithium salt in said nonaqueous organic solvent is
15 between 0.8 mol/l and 1.0 mol/l; and

the weight of said additive is between 0.05wt% and 1.0wt% of the weight of the electrolyte.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2005/001530

A. CLASSIFICATION OF SUBJECT MATTER

IPC⁷ H01M10/40, H01M6/16

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)

IPC⁷ H01M10/40, H01M6/16, H01M10/36, H01M6/14

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

CNPAT

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

WPI, EPODOC, PAJ, CNPAT: FROMATE, FORMAMIDE, NONAQUEOUS, ORGANIC, ELECTROLYTE, LITHIUM

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP48015249B, 14 May 1973 (14.05.1973), column 2 line 30- column 3 line 6	1-11, 13-14, 16-17
Y		12, 18
A		15, 19-20
X	JP2001-357875A, 26 Dec. 2001 (26.12.2001), paragraph [0022]	1, 3, 6, 7, 9
Y		12, 18
X	JP8-339825A, 24 Dec.1996 (24.12.1996), claim 1	1-2, 4-5, 9
X	US5747194A, 05. May 1998 (05.05.1998), claims 6&11	1-2, 4-5, 9

☒ 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

“L” document which may throw doubts on priority claim (S) or which is cited to establish the publication date of another citation or other special reason (as specified)

“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

25 Nov. 2005 (25.11.2005)

Date of mailing of the international search report

08 · DEC 2005 (08 · 12 · 2005)

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

WANG, Fang

Telephone No. (86-10) 62085032



INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2005/001530

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CA971219A, 15. Jul.1975 (15.07.1975), claims 1&2	1、 3、 6、 7、 9
X	GB1278978A, 21 Jun.1972 (21.06.1972), claims 6-8	1、 3、 6、 7、 9
X	GB1325055A, 01.Aug.1973, (01.08. 1973), claims 9-11	1-11、 13-14、 16-17

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2005/001530

Patent document Cited in search report	Publication date	Patent family member(s)	Publication date
JP48015249B	14.05.1973	NONE	
JP2001-357875A	26.12.2001	NONE	
JP8-339825A	24.12.1996	NONE	
US5747194A	05.05.1998	CA2163182 C	07. 03.2000
		WO9505684 A1	23. 02.1995
		AU7454894 A	14. 03.1995
		US5506078 A	09. 04.1996
		US5629112 A	13. 05.1997
		CA2163182 A	18. 05.1997
CA971219A	15.07.1975	GB1349768 A	10. 04.1974
		CH578260 A	30. 07.1976
GB1278978A	21.06.1972	JP50015048B B	02. 06.1975
		FR2024849 A5	04. 09.1970
		DE1957169 A1	22. 10.1970
		CA925159 A1	24. 04.1973
GB1325055A	01.08.1973	US3804672 A	16. 04.1972
		US3808052 A	30. 04.1974
		CA951377 A	16. 07.1974
		JP50031925B B	16. 10.1975