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(54) **High purity lithium polyhalogenated boron cluster salts useful in lithium batteries**

Lithium-Salze von polyhalogenierten Bor-Clusters hoher Reinheit und deren Verwendung in Lithium-Batterien

Sels de lithium d'aggrégats polyhalogénés de bore de pureté élevée et leur utilisation dans les piles au lithium

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Description

BACKGROUND OF THE INVENTION

[0001] Lithium secondary batteries, by virtue of the large reduction potential and low molecular weight of elemental lithium, offer a dramatic improvement in power density over existing primary and secondary battery technologies. Here, lithium secondary battery refers to both batteries containing metallic lithium as the negative electrode and batteries which contain a lithium ion host material as the negative electrode, also known as lithium-ion batteries. By secondary battery it is meant a battery that provides for multiple cycles of charging and discharging. The small size and high mobility of lithium cations allow for the possibility of rapid recharging. These advantages make lithium batteries ideal for portable electronic devices, e.g., cell phones and laptop computers. Recently, larger size lithium batteries have been developed and have application for use in the hybrid vehicle market.

[0002] The following patents are representative of lithium batteries and electrochemical cells:

[0003] US 4,201,839 discloses an electrochemical cell based upon alkali metal-containing anodes, solid cathodes, and electrolytes where the electrolytes are closoborane compounds carried in aprotic solvents. Closoboranes employed are of the formula Z_2BnXn and ZCRBmXm wherein Z is an alkali metal, C is carbon, R is a radical selected from the group consisting of organic hydrogen and halogen atoms, B is boron, X is one or more substituents from the group consisting of hydrogen and the halogens, m is an integer from 5 to 11, and n is an integer from 6-12. Specifically disclosed examples of closoborane electrolytes employed in the electrochemical cells include lithium bromooctaborate, lithium chlorodecaborate, lithium chlorododecabate, and lithium iododecaborate.

[0004] US 5,849,432 discloses electrolyte solvents for use in liquid or rubbery polymer electrolyte solutions based upon boron compounds with Lewis acid characteristics, e.g., boron linked to oxygen, halogen atoms, and sulfur. A specific example of an electrolyte solution comprises lithium perchlororate and boron ethylene carbonate.

[0005] US 6,346,351 discloses secondary electrolyte systems for a rechargeable battery of high compatibility towards positive electrode structures based upon a salt and solvent mixture. Lithium tetrafluoroborate and lithium hexafluorophosphate are examples of salts. Examples of solvents include diethyl carbonate, dimethoxyethane, methylformate, and so forth. In the background, there is disclosed known electrolytes for lithium batteries, which include lithium perchlorate, lithium hexafluoroarsenate, lithium trifluoromethylsulfonate, lithium tetrafluoroborate, lithium bromide, and lithium hexafluoroantimonate electrolytes incorporated in solvents.

[0006] US 6,159,640 discloses electrolyte systems for lithium batteries used in electronic equipment such as mobile phones, laptop computers, camcorders, etc based upon fluorinated carbamates. A variety of fluorinated carbamate salts, e.g., trifluoroethyl-N, N-dimethylcarbamate is suggested.

[0007] US 6,537,697 discloses lithium secondary battery using a nonaqueous electrolyte including lithium tetrakis (pentafluorophenyl)borate as an electrolyte salt.

[0008] US 6514,474 discloses the need for removing traces of water and acid from lithium hexafluorophosphate salt to be used in lithium battery applications and a purification process.

[0009] US 4,020,240 discloses an electrolyte salt containing a clovoborate anion when employed in an electrochemical cell comprising an active metal anode and an electrolyte/cathode depolarizer, which cell has the characteristics of high potential and current capabilities at low temperatures and resists anode passivation during long time storage even at elevated temperature.

[0010] US 4,071,664 discloses an electrolyte salt additive which reduces anode passivation during long time storage even at elevated temperature in an non-aqueous electrochemical cell comprising an active metal anode and an electrolyte/cathode depolarizer. Said electrolyte salt additive is included in a minor proportion into the electrolyte and has a clovoborate anion and a metal cation.

[0011] US 2004/072067 discloses a lithium secondary battery comprising an electrode in which an active material layer which includes an active material that electrochemically occludes and releases lithium is formed on a current collector, wherein cracks are formed in the active material layer by occlusion and release of lithium ions and thereafter a solid electrolyte is formed in the cracks in the active material layer. Thereby the current collectability of an electrode is improved and a lithium secondary battery having excellent charge and discharge cycle characteristics is provided.

[0012] EP 1 598 884 discloses a non-aqueous electrolyte secondary battery comprising a positive electrode containing a positive electrode active material, a negative electrode containing a negative electrode active material, and a non-aqueous electrolyte. The invention is characterized in that the positive electrode active material is composed of a lithium transition metal oxide having a layer structure and containing Li and Co and further contains a group IVA element and group IIA element of the periodic table.

[0013] JP 03 285264 discloses a non-aqueous electrolyte battery comprising a lithium salt electrolyte consisting of a fluorinated lithium closoborane compound obtained by reaction of a fluorine-containing Lewis acid with a lithium compound containing boron and chlorine.

[0014] GB 2 083 273 discloses a method for increasing the cycling life of non-aqueous cells containing an active anode metal subject to dendritic plating on charging, a porous cathode, an electrolyte solvent and a dissolved salt which is stable at charging voltages, said salt consisting of a clovoborate salt.

[0015] FR 2 523 770 discloses a solid polymeric electrolyte comprising a least in part a solid solution of one or more closoborane ionic compounds of formula $M_2B_nX_aY_b$ being dissolved within a plastic macromolecular material formed at least in part by one or more polymers or copolymers of monomers including a heteroatom capable of forming donor-acceptor type bonds with the cation of the ionic compound, wherein M is an alkali metal ion or the ammonium ion, X and Y are each independently H, a halogen, CN or hydrocarbyl, n is 8,10 or 12, and a and b are integers, with $a + b = n$.

[0016] As represented above a wide variety of lithium-based electrolytes comprising a lithium salt for lithium batteries are disclosed and, although having use in many electronic applications, they are faced with problems associated with safety, oxidative stability, thermal stability, and so forth. Fluorinated electrolyte salts have had the additional problem that deleterious and toxic HF can be produced on compound breakdown. The following are some of the deficiencies associated with specific electrolyte salts: lithium hexafluorophosphate fails primarily on the basis that it is unstable, generating HF, which leads to electrode corrosion, particularly with $LiMn_2O_4$ cathode materials; lithium perchlorate has relatively low thermal stability leading to explosive mixtures above 100°C; lithium hexafluoroarsenate has a problem of arsenic toxicity; and lithium triflate lead to significant corrosion of aluminum current collectors typically used in lithium ion batteries.

BRIEF SUMMARY OF THE INVENTION

[0017] The present invention relates to a lithium salt comprising:

$$Li_2B_{12}F_xH_{12-x-y}Z_y$$

where x+y is from 3 to 12, and x and y are independently from 0 to 12, and Z comprises at least one of Cl and Br, wherein the total hydroxyl containing impurity level of said salt is less than 500 ppm.

[0018] The present invention further relates to an electrolyte comprising a combination of at least one lithium salt as defined above and at least one solvent.

[0019] The present invention further relates to a battery comprising an anode, a cathode and an electrolyte as defined above.

[0020] The present invention further relates to a method for treating lithium salts to obtain a lithium salt as described above comprising at least one step selected from the group of:

a) dissolving the salt in an aprotic organic solvent to form a solution and passing said solution through an alumina column,

b) dissolving the salt in a solvent to form a solution, and passing said solution through a cation exchange column in Li^+ form,

c) drying the salt at greater than 180 °C under dynamic vacuum or dynamic nitrogen purge,

d) dissolving the salt in an aprotic organic solvent to form a solution and passing said solution through a Li-substituted molecular sieve, and;

recovering lithium salts.

[0021] Some of the advantages associated with the use of the fluorinated lithium dodecaborate salt for forming the lithium-based electrolyte may include:

an ability to use a lithium based salt for an electrolyte solution which has electrochemical, thermal, and hydrolytic stability;
an ability to use a salt with acceptably low levels of impurities harmful to lithium ion cells (e.g., substantially free of water, hydroxyl moieties, metal cations including alkali metals and hydrogen fluoride);
an ability to use a lithium electrolyte solution which can be used at a low lithium based salt concentration, e.g., one-half the concentration of many other lithium-based salts, e.g.,$LiPF_6$; and,
an ability to form low viscosity, low impedance lithium electrolyte solutions which can be recycled.

BRIEF DESCRIPTION OF THE DRAWINGS

[0022] Figure 1 is a Thermogravimetric Analysis in which volatiles are analyzed by IR spectroscopy.

[0023] Figure 2 is a cyclic voltammetry graph illustrating the affect of OH impurities.

DETAILED DESCRIPTION OF THE INVENTION

[0024] The instant invention relates to a lithium secondary battery, an electrolyte containing lithium ions, high purity lithium containing salts and methods for making and using the salts. Two desirable properties for lithium battery electrolyte solutions are: (a) a high conductivity in a non-aqueous ionizing solution, and (b) chemical stability to both heat, hydrolysis and to electrochemical cycling over a wide potential range. Other desired features of lithium electrolyte solutions include: high flash point; low vapor pressure; high boiling point; low viscosity; good miscibility with solvents customarily employed in batteries, especially ethylene carbonate, propylene carbonate and alpha-omega-dialkyl glycol ethers; good electrical conductivity of their solutions over a wide temperature range, and tolerance to initial moisture content.

[0025] The present lithium salt for forming lithium electrolyte solutions is based upon a lithium fluorododecaborate comprising:

$$Li_2B_{12}F_xH_{12-x-y}Z_y$$

where x+y is from 3 to 12, and x and y are independently from 0 to 12, and Z is at least one of Cl and Br, wherein the total hydroxyl containing impurity level of said salt is less than 500 ppm. Specific examples of lithium based dodecaborates comprise at least one member selected from the group consisting of $Li_2B_{12}F_5H_7$, $Li_2B_{12}F_6H_6$, $Li_2B_{12}F_7H_5$, $Li_2B_{12}F_8H_4$, $Li_2B_{12}F_9H_3$, $Li_2B_{12}F_{10}H_2$, $Li_2B_{12}F_{11}H$ and mixtures of salts with varying x such that the average x is equal to or greater than 5, or equal to 9 or 10, or $Li_2B_{12}F_xCl_{12-x}$ and $Li_2B_{12}F_xBr_{12-x}$ where x is 10 or 11, or $Li_2B_{12}FCl_2H_9$, $Li_2B_{12}Cl_3H_9$, $Li_2B_{12}F_2Cl_3H_7$, $Li_2B_{12}Cl_5H_7$ and $Li_2B_{12}FCl_6H_5$; and mixtures thereof.

[0026] The lithium salt employed for forming electrolytes solutions for use in lithium batteries can be formed by fluorinating hydridodecaborates to provide a fluorododecaborate having at least 5, usually at least 8 and typically at least 10 but not more than 12 or more hydrogen atoms replaced with fluorine (average basis). Metathesis using lithium hydroxide can provide the lithium salt. This reaction is normally conducted in a liquid medium. In direct fluorination, fluorine is usually diluted with an inert gas, e.g., nitrogen. Fluorine concentrations from about 10 to about 40 % by volume are commonly employed. If further halogenation is desired, the partially fluorinated hydridoborate can be reacted with the desired halogen, e.g., chlorine or bromine.

[0027] To facilitate formation of the lithium fluorododecaborates as electrolyte salts, direct fluorination of the lithium hydridododecaborate can be conducted in an acidic liquid medium, e.g., an acidic liquid medium or carrier such as neat or anhydrous HF reduced in acidity by the incorporation of a weak base. While any suitable acid can be employed, examples of suitable acids comprise at least one member selected from the group consisting of formic, acetic, trifluoroacetic, dilute sulfuric triflic, and sulfonic acids hydrohalic ($HCl_{(aq)}$, $HBr_{(aq)}$, $HI_{(aq)}$, and $HF_{(aq)}$), and mixtures thereof. The addition of buffering salts, e.g., alkali metal fluorides such as potassium and sodium fluoride, also can reduce the acidity of neat HF in the fluorination reaction. A Hammett acidity, H_o, between $0 > H_o > -11$ is useful as an acidic medium for effecting fluorination.

[0028] Radical scavengers can be used in the fluorination of lithium hydridododecaborates to reduce byproduct formation and improve reaction efficiency. Without wishing to be bound by any theory or explanation, it is believed that radical scavengers can limit the formation of hydrogen peroxide, or HOF which may be generated with fluorine. Radical scavengers can be used to inhibit the side-reaction of fluorine with the solvent, thereby improving fluorination efficiency. Examples of radical scavengers comprise oxygen, nitroaromatics, and mixtures thereof. One method for employing a radical scavenger comprises introducing a relatively small amount of air to the liquid medium.

[0029] Fluorinating hydridododecaborate anion can be conducted under conditions sufficient to maintain liquid phase conditions. Fluorination of the hydridododecaborate anion can be performed at a temperature from about -30 to about 100°C, typically from about 0 to about 20°C. Pressures during fluorination are such as to maintain liquid phase conditions, and typically atmospheric for fluorinating the dodecaborate anion.

[0030] Lithium ion cells can be sensitive to impurities in any of the components. According to the invention the lithium containing salts as well as the electrolyte are substantianlly free of impurities. By "substantially free" it is meant that the lithium salts have a total hydroxyl containing impurity level of less than 500 ppm (e.g., OH and other moieties). These impurities can react with the electrodes themselves, or when present with a hydrolyzable salt such as lithium hexafluorophosphate, lead to HF generation, which, in turn, can corrode electrode materials. As a result, the inventive salts and electrolytes are also substantially free of hydrogen fluoride (HF). Typical OH containing impurities are water and alcohols in the electrolyte salts and solvents.

[0031] In a preferred aspect of the invention, the inventive salts and electrolyte are also substantially free of metal cations including alkali metals (other than lithium). By substantially free of metal cations, it is meant that the salts contain less than 500 ppm of non-lithium alkali or alkaline earth cations. Without wishing to be bound by any theory or explanation, it is believed that the presence of such non-lithium salts, because the reduced solubility of sodium, potassium and cesium salts, can lead to their salting out with subsequent short circuiting of the cell.

[0032] Impurities may be removed from the salt and/or an electrolyte containing the salt by at least one of the following methods:

a) dissolving the salt in an aprotic organic solvent to form a solution and passing said solution through an alumina column,
b) dissolving the salt in a solvent to form a solution, and passing said solution through a cation exchange column in Li^+ form,
c) drying the salt at greater than 180°C under dynamic vacuum or dynamic nitrogen purge,
d) dissolving the salt in an aprotic organic solvent to form a solution and passing said solution through a Li-substituted molecular sieve. These methods can produce salts and electrolytes that are substantially free of OH groups, HF and metal cations.

[0033] Preferably, the recovered salt is substantially free of water, HF, and non-lithium metal cations.

[0034] For removing hydroxyl or -OH impurities where the hydroxyl group is bound directly to the dodecaborate anion of the salt such as $Li_2B_{12}F_{11}(OH)$, a lithium salt containing from about 0.02 mol% -OH substituted dodecaborate anion, or ~ 10ppm hydroxyl group impurity to 10 mol % - OH substituted anion, or ~ 5000 ppm hydroxyl group impurity can be dissolved in at least one aprotic organic solvent. While any suitable aprotic solvent can be employed, examples of suitable solvents comprise at least one member selected from the group consisting of ketones, carbonates esters alcohols and mixtures thereof. The solvent concentration ranges from about 0.1 to about 50 weight %. The solvated salt is eluted through a column containing neutral alumina at room temperature under atmospheric pressure, vacuum or elevated pressure between about -20 and about 80°C. If a hydrophobic ketone solvent is used (e.g., such as 5-methyl-2-hexanone), the purified salt may be extracted from the aprotic organic solvent using water. Residual organic solvent in the aqueous product solution may be removed by extraction with an even less polar organic solvent, e.g., hexanes. Removal of water can provide a purified salt containing less than about 100 ppm and usually less than about 10 ppm bound -hydroxyl group impurity.

[0035] The salt as well as the electrolyte can also be purified by removing metal cation impurities including alkali metal impurities. In one aspect an aqueous solution comprising the lithium fluorododecaborate containing between about 100 ppm and about 10 weight % (100,000 ppm) of sodium or potassium is eluted via a column with cation - exchange resin (e.g., DOWEX 50WX8-200), in its Li^+ form, at a temperature between about 0 and about 80°C, under atmospheric pressure, vacuum or elevated pressure. After removing water from the eluent, the purified salt lithium salt contains less than about 100 ppm of sodium or potassium, as determined by ICP/MS.

[0036] In one aspect of the invention, the amount of water impurity in the lithium salt (e.g., a salt containing > 1000 ppm water and bound -OH), can be reduced to less than about 200 ppm and typically below about 20 ppm by grinding and drying. For example, the salt is ground with a mortar and pestle, and dried in a vacuum oven under a dynamic vacuum of less than about 100 mTorr at a temperature of about 150 to about 200°C for approximately 4 hrs. This step produces a lithium salt product containing between about 200 to about 1,000 ppm water. TGA/IR analysis shows a drying temperature of greater than about 180°C and usually greater than about 220°C is needed for efficient drying. The lithum salt is further ground and loaded into a vessel (e.g., a drying column), which can be heated and allows for a dry, inert gas to a be purged through the lithium salt at sufficient rate to fluidize or cause percolation of the bed of salt. Dry nitrogen is suitable as an inert gas and the vessel is typically heated to between about 230 to about 280°C. After about 3 to about 72 hrs, the lithium salt was analyized (i.e., by Karl-Fischer analysis), and determined to contain between about 1 to about 50 ppm water, and usually about 5 to about 20 ppm water.

[0037] Alternatively, an electrolyte solution that comprises a combination of about 0.1 to about 25 weight % of the lithium salt and any aprotic organic solvent or combination of solvents, and containing from about 20 to about 100 ppm water, may be dried. The solution is stored over dry, lithium substituted molecular sieves for about 1 to about 72 hrs. While any suitable molecular sieves can be used, examples of suitable molecular sieves comprise 3A through 5A and normally lithium cation exchanged versions of these. After this treatment the electrolyte solution typically contains less than about 20ppm water and usually less than about 10 ppm water. When similarly impure (e.g., about >20 to >100 ppm) electrolyte solutions comprising $LiPF_6$ combined with aprotic organic solvents were dried by using molecular sieves, hydrolysis of the PF_6^- anion was observed. Unlike $LiPF_6$, the inventive salt is stable with respect to such molecular sieves.

[0038] In order to obtain an electrolyte for a lithium battery, the inventive lithium containing salt is combined with at least one aprotic solvent. Typically, these aprotic solvents are anhydrous, and anhydrous electrolyte solutions are desirable. While any suitable solvent can be employed, examples of aprotic solvents or carriers for forming the electrolyte systems can comprise at least one member selected from the group consisting of organic carbonates, esters, ketones and nitriles, preferably dimethyl carbonate, ethyl methyl carbonate, diethyl carbonate, methyl propyl carbonate, ethyl propyl carbonate, dipropyl carbonate, bis(trifluoroethyl) carbonate, bis(pentafluoropropyl) carbonate, trifluoroethyl methyl carbonate, pentafluoroethyl methyl carbonate, heptafluoropropyl methyl carbonate, perfluorobutyl methyl carbonate, trifluoroethyl ethyl carbonate, pentafluoroethyl ethyl carbonate, heptafluoropropyl ethyl carbonate, perfluorobutyl ethyl carbonate, fluorinated oligomers, dimethoxyethane, triglyme, dimethylvinylene carbonate, tetraethyleneglycol, dimethyl ether, polyethylene glycols, sulfones, and gamma-butyrolactone; and mixtures thereof.

[0039] In one aspect of the invention, the electrolyte system of the present invention can comprise an aprotic gel polymer carrier/solvent. While any suitable polymer can be employed, examples of suitable gel polymer carrier/solvents comprise at least one member selected from the group consisting of polyethers, polyethylene oxides, polyimides, polyphosphazines, polyacrylonitriles, polysiloxanes, polyether grafted polysiloxanes, derivatives of the foregoing, copolymers of the foregoing, crosslinked and network structures of the foregoing, blends of the foregoing, which are added an appropriate ionic electrolyte salt. Other gel-polymer carrier/solvents can comprise those prepared from polymer matrices derived from polypropylene oxides, polysiloxanes, sulfonated polyimides, perfluorinated membranes (Nafion™ resins), divinyl polyethylene glycols, polyethylene glycol-bis-(methyl acrylates), polyethylene glycol-bis(methyl methacrylates), derivatives of the foregoing, copolymers of the foregoing, crosslinked and network structures of the foregoing; and mixtures thereof.

[0040] A combination or solution comprising at least one aprotic solvent and at least one fluorinated lithium dodecaborate salt employed for forming the lithium based electrolyte for the lithium battery typically will have a concentration of lithium fluorododecaborate of at least about 0.01 to about 1 molar and typically from about 0.1 to about 0.6 molar (e.g., about 0.2 to about 0.5 molar). In some cases, electrolytes formed from lithium based fluoroborates having an increased concentration of halogen atoms other than fluorine may show an increase viscosity relative to the lithium fluorododecaborates having higher fluorine content.

[0041] Other lithium based salts can be used in combination with the lithium based fluorododecaborates, e.g. $LiPF_6$, lithium perchlorate, lithium hexafluoroarsenate, lithium trifluoromethylsulfonate, lithium tetrafluoroborate, lithium bromide, and lithium hexafluoroantimonate, and mixtures thereof. The inventive salts can be used in combination with other salts including, without limitation, hydrolyzable salts such as $LiPF_6$ in any suitable amounts. Typically, the amout of such additional salts ranges from about 0.01 M to about 1.5 M.

[0042] Preferably, the electrolyte is substantially free of water, HF and non-lithium metal cations.

[0043] A lithium battery employing the lithium fluorododecaborate electrolyte can employ any suitable cathode and anode. In forming the lithium battery, the negative electrodes for use in a lithium secondary battery typically can be based upon non-graphitizing carbon, natural or artificial graphite carbon, or tin oxide, silicon, or germanium compounds. Any of the conventional anode compositions may be used in combination with the inventive lithium fluorododecaborate electrolytes.

[0044] The positive electrode for use in lithium secondary batteries typically is based upon a lithium composite oxide with a transition metal such as cobalt, nickel, manganese, among others and mixtures thereof, or a lithium composite oxide, part of whose lithium sites or transition metal sites are replaced with cobalt, nickel, manganese, aluminum, boron, magnesium, iron, copper, among others and mixtures thereof or iron complex compounds such as ferrocyan blue, berlin green, among others and mixtures thereof. Specific examples of lithium composites for use as positive electrodes include $LiNi_{1-x}Co_xO_2$ and lithium manganese spinel, $LiMn_2O_4$.

[0045] The separator for the lithium battery can comprise a microporous polymer film. Examples of polymers for forming films comprise at least one member selected from the group consisting of nylon, cellulose, nitrocellulose, polysulfone, polyacrylonitrile, polyvinylidene fluoride, polypropylene, polyethylene, polybutene, and mixtures thereof. Ceramic separators, such as those based on silicates, can be used.

[0046] The battery is not limited to particular shapes, and can take any appropriate shape such as cylindrical shape, a coin shape, and a square shape. The battery is also not limited to particular capacities, and can have any appropriate capacity for both small appliances and power storage for electric cars.

[0047] The following examples are intended to illustrate various embodiments of the invention and are not intended to restrict the scope thereof or any claims appended hereto. Examples 1-6 illustrate a process for making crude $Li_2B_{12}F_xZ_{12-x}$ salts. Example 7-9 illustrate a method to remove impurities comprising OH groups substituted on the B_{12} cage and alkali metal impurities. Example 10 shows that the last equivalent of water associated with the salt comes off most rapidly above 180°C and preferably above 220°C. Examples 11 and 12 illustrate the difference in efficiency of vacuum drying vs fluidized bed drying of the salt compositions produced in accordance with example 9 (e.g., water levels of 10-20 ppm were obtained). Examples 13 and 14 illustrate molecular sieve drying of electrolyte solutions. Example 15 illustrates the electrochemical impact of traces of water.

Example 1

Preparation of $Li_2B_{12}F_xH_{12-x}$, where x = 10-12

[0048] A colorless slurry containing 2.96 g (11.8 mmol) $K_2B_{12}H_{12}CH_3OH$ in 6 ml formic acid at an average Hammett acidity of H_o = -2 to -4 was fluorinated at 0 to 20°C. When 100% of the desired F_2 (142 mmol) was added as a mixture of $10\%F_2/10\%O_2/80\%N_2$, a colorless solution remained. Further fluorination (3%) at 30°C resulted in precipitation of solid from solution. Solvents were evacuated overnight, leaving 5.1 g of a colorless, friable solid. Analysis of this crude product by ^{19}F NMR revealed primarily $B_{12}F_{10}H_2^{2-}$ (60%), $B_{12}F_{11}H^{2-}$ (35%), and $B_{12}F_{12}^{2-}$ (5%). The crude reaction product was dissolved in water and the pH of the solution adjusted to between 4-6 with triethylamine and triethylamine hydrochloride. The precipitated product was filtered, dried, and resuspended in water. Two equivalents of lithium hydroxide monohydrate were added to the slurry and the resulting triethylamine evacuated. Additional lithium hydroxide was added until the pH of the final solution remained at 9-10 after distillation of all triethylamine. Water was removed by distillation and the final product was vacuum-dried at 200°C for 4-8 hrs. Typical yields of $Li_2B_{12}F_xH_{12-x}$ (x = 10,11,12) were ~ 75%.

Example 2

Preparation of $Li_2B_{12}F_xBr_{12-x}$ ($x \geq 10$, ave. x = 11)

[0049] 3g $Li_2B_{12}F_xH_{12-x}$ ($x \geq 10$) (0. 008 mol) of average composition $Li_2B_{12}F_{11}H$ was dissolved in 160 mL of 1 M $HCl_{(aq)}$. Br_2, 1.4 mL (0.027mol) was added and the mixture refluxed at 100°C for 4 hours. A sample was taken for NMR analysis.

[0050] A portion of the above sample was returned to reflux and chlorine was added over a period of 6 hrs to form the more potent brominating agent BrCl. At the completion of chlorine addition, an aliquot was taken and NMR analysis showed the composition of the aliquot to be identical to the composition of the first aliquot. HCl and water were distilled away and the product was vacuum dried at 150°C. A total of 2.55 g white solid product was isolated. Theoretical for $Li_2B_{12}F_xBr_{12-x}$ ($x \geq 10$, ave. x = 11) is 3.66 g.

Example 3

Preparation of $Li_2B_{12}F_xCl_{12-x}$ (ave. x = 11)

[0051] 20 g $Li_2B_{12}F_{11}H$ mixture dissolved in 160 mL 1 M HCl in a three neck round bottom flask fitted with a reflux condenser and fritted bubbler. The mixture was heated to 100°C and Cl_2 gas was bubbled through at 15 standard cubic centimeter (sccm/min) The effluent, through the condenser, was passed through a solution of KOH and Na_2SO_3. After 16 hours of bubbling Cl_2, the solution was purged with air. The HCl and water were distilled out and the residue was tritrated with ether. Upon ether evaporation and vacuum oven drying of the white solid, 20 g of material of the above formula were recovered (92%). ^{19}F-NMR in D_2O: -260.5, 0.035 F; -262.0, 0.082 F; -263.0, 0.022 F; -264.5, 0.344 F; -265.5, 0.066 F; -267.0, 0.308 F; -268.0, 0.022 F; -269.5, 1.0 F. "B-NMR in D_2O: -16.841; -17.878

Example 4

Preparation of $Li_2B_{12}F_xCl_{12-x}$ (ave. x =3)

[0052] 3.78 g $K_2B_{12}F_3H_9$ mixture was dissolved in 100 mL 1M HCl in a three neck round bottom flask fitted with a reflux condenser and fritted bubbler. The mixture was heated to 100 °C and Cl_2 gas was bubbled through at 15 sccm. The effluent, through the condenser was passed through a solution of KOH and Na_2SO_3. After 8 hours of bubbling Cl_2, the solution was purged with air. There was some precipitate that formed and it was filtered out. The solution was brought to a pH of 9 by the addition of Et_3N which produced a white precipitate. The solution was cooled to 0 °C to maximize precipitation and then filtered on a Buchner funnel and washed with cold water. The solid was dried in a vacuum at 120 °C. 4.62 g of a composition of the above formula was recovered. ^{19}F-NMR in acetone-d_6: -225.2, 0.023 F; -228.5, 0.078 F; -229.5, 0.082 F; -231.2, 0.036 F; -232.8, 0.302 F; -233.2, 0.073 F; -234.3, 0.032 F; -235.5, 0.104 F; -237.6, 0.239 F; -238.4, 0.037 F; -239.8, 0.057 F; -242.0, 0.033 F. ^{11}B-NMR in acetone-d_6: -6 multiplet; -15 multiplet.

Example 5

Preparation of $Li_2B_{12}F_xCl_{12-x}$ (ave. x = 11)

[0053] 3 g $Li_2B_{12}F_{11}H$ mixture dissolved in 110 mL 1 M HCl in a three neck round bottom flask fitted with a reflux condenser and fritted bubbler. 1.4 mL Br_2 was added. The mixture was heated to 100° C for 4 hours. An aliquot was removed for NMR analysis. The mixture was again heated to 100° C and Cl_2 gas was bubbled through at 15 sccm. The effluent, through the condenser was passed through a solution of KOH and Na_2SO_3. After half an hour, the red Br_2 solution was yellowish. After another 6 hours of bubbling Cl_2, the solution was purged with air. An aliquot was taken for

19F NMR and found to be identical to the first sample. HCl and water were distilled out. The residue was vacuum dried at 150 C. 2.55 g of a composition of the above formula were recovered. ^{19}F-NMR in D_2O: -257.8, 0.024 F; -259.0, 0.039 F; -259.5, 0.040 F; -261.0, 0.028 F; -261.5, 0.028 F; -263.0, 0.321 F; -265.2, 0.382 F; -269.2, 1.0 F.

Example 6

Preparation of $Li_2B_{12}F_xCl_{12-x}$ (ave. x = 3)

[0054] 2.48 g $K_2B_{12}F_3H_9$ mixture was dissolved in 100 mL 1M HCl in a round bottom flask fitted with a reflux condenser. The mixture was heated to 100° C. After 8 hours of stirring, the solution was cooled to room temperature and left over the weekend. The excess Br_2 was neutralized with Na_2SO_3 and the solution was brought to a pH of 9 by the addition of Et_3N which produced a white precipitate. The solution was cooled to 0° C to maximize precipitation and then filtered on a Buchner funnel and washed with cold water. The solid was dried in a vacuum at 120° C. ^{19}F-NMR in acetone-d_6: -212.2, 0.030F; -213.6, 0.284 F; -216, 0.100 F; -217.0, 0.100 F; -217.9, 0.100 F; -219.3, 1.0 F; -221.3, 0.201 F; -222.5, 0.311 F; -223.2, 0.100 F; -225.2, 0.100 F; -225.5, 0.639 F; -226.6, 0.149 F; -229, 0.245 F; -232.0, 0.120 F. Metathesis with $LiOH \cdot H_2O$ was carried out as in Example 1. A composition described by the above formula was obtained.

Example 7

Purification of $Li_2B_{12}F_xZ_{12-x}$ from $Li_2B_{12}F_xZ_y(OH)_{12-x-y}$

[0055] In this example 50.5 g of partially fluorinated lithium fluorododecaborate salt having an average composition $Li_2B_{12}F_9H_3$, and also containing ~ 10 mol. % of $Li_2B_{12}F_9H_2(OH)$ (an average composition of hydroxyl-substituted anions), was dissolved in 250 ml of 5-methyl-2-hexanone. The small amount of insoluble material was removed on the centrifuge and the clear solution was eluted via a column containing neutral alumina. The lithium salt was extracted from the eluent with 4x75 ml of water. Aqueous fraction was washed with 3x100 ml of hexanes and water was distilled off. The solid was dried under vacuum at 150 °C to give 38.6 g of white powder, having an average composition $Li_2B_{12}F_9H_3$ and having undetectable by NMR or IR levels of hydroxyl-derivatives of fluoroborate anions (< 1000 ppm). Alumina column was washed with 600 ml of water, water was distilled off and the residue was dried under vacuum at 150 °C to give 5.8 g of tan solid, which was mostly lithium salt with average composition $Li_2B_{12}F_9H_2(OH)$. Thus, using this method lithium fluorododecaborate salts can be purified from the fluorinated hydroxyl derivatives.

qExample 8

Purification of $Li_2B_{12}F_{12}$ from $Li_2B_{12}F_{11}(OH)$

[0056] In this example 100.8 g of crude $Li_2B_{12}F_{12}$, containing ~ 1 mol. % of $Li_2B_{12}F_{11}(OH)$, was dissolved in 400 ml of 5-methyl-2-hexanone. The small amount of insoluble material was removed on the centrifuge and the clear solution was eluted via a column containing neutral alumina. The compound $Li_2B_{12}F_{12}$ was extracted from the eluent with 4x125 ml of water. Aqueous fraction was washed with 3x100 ml of hexanes and water was distilled off. The solid was dried under vacuum at 200 °C to give 87 g of white $Li_2B_{12}F_{12}$, which had non-detectable levels (by NMR or IR) of $Li_2B_{12}F_{11}$ (OH) (note that in a separate experiment, ~ 0.02 mol.% of $Li_2B_{12}F_{11}(OH)$ (~ 200 ppm) were detected in $Li_2B_{12}F_{12}$ by NMR using the difference in ^{19}F NMR spectra of these two compounds). Thus, using this method $Li_2B_{12}F_{12}$ containing < 200 ppm of hydroxyl-derivatives of fluorododecaborate anions (< ~ 10 ppm of hydroxyl group) can be prepared.

Example 9

Purification of $Li_2B_{12}F_{12}$ from Sodium and Potassium.

[0057] An aqueous solution of $Li_2B_{12}F_{12}$ containing ~ 200 ppm of sodium was eluted via a column with cation -exchange resin DOWEX 50WX8-200 in Li^+ form. Water was distilled off from the eluent and the residue was dried under vacuum at 150 °C. The purified salt $Li_2B_{12}F_{12}$ contained ~ 60 ppm of sodium, as determined by ICP.

Example 10

Thermal Gravimetric Analysis(TGA)/IR of $Li_2B_{12}F_{12}$

[0058] TGA/IR analyses were performed on $Li_2B_{12}F_{12}$ by ramping the sample in the TA 2960 SDT by heating from

RT to 800 °C at 10 °C/min. in 100 cc/min. of N_2, H_2O saturated N_2 or air. The evolved gas is passed through a 10 cm IR gas cell. The IR spectrum is collected at 4 cm^{-1} resolution and a gain of 1 on the AVATAR IR. The spectra are collected as a series of spectra at 1-minute intervals. Profiles of the evolved gases were prepared by measuring the absorbance for different compounds at the band maximum in the IR spectra. The quantitative information was derived by multiplying the area under the profile curve by the calibration factor and dividing by the sample weight. The IR profiles shown in Figure 1 show that under N_2 purge most of the water comes off this sample at ~190°C, and it is still being removed at 225°C. Final water removal at or below 180°C will proceed relatively slowly.

Comparitive Example 11

Vacuum Drying of $Li_2B_{12}F_xZ_{12-x}$ Salts

[0059] Approximately 200 g $Li_2B_{12}F_{12}$ salt prepared according to example 1 was ground and dried under a dynamic vacuum of 30 mTorr for 8 hrs at 250°C. The sample was transferred to an argon-filled inert atmosphere dry-box. Moisture analysis of our salt was carried out on an Orion AF7 Coulometeric Karl - Fischer Titrator. Hydranal™ Karl-Fischer reagents and standards from Riedel-de Haen were used. ~ 0.60g $Li_2B_{12}F_{12}$ was dissolved in 3 ml dry acetonitrile and 3-1 mL were taken for water analysis. After this drying procedure water values of ~ 100 ppm on a salt weight basis were obtained. Vacuum drying in this manner typically gave water readings of 100-500 ppm.

Example 12

Drying of $Li_2B_{12}F_xZ_{12-x}$ in a Fluidized Bed

[0060] Approximately 100 g $Li_2B_{12}F_{12}$ salt prepared according to example 1 was ground and dried under a dynamic vacuum of 100 mTorr at 150-200°C for 4 hrs. The sample was further ground and loaded on to a quartz frit in a vertical glass tube. The tube was externally heated to 260°C and dry nitrogen was purged through the salt at a sufficient rate to fluidize the bed of salt. After 12 hrs the sample was cooled and transferred to an argon filled inert atmosphere box for analysis of water content. Karl-Fischer analysis performed as in example 7 showed the salt contained 10-20 ppm water on a salt weight basis.

Example 13

Drying of Electrolyte Solution Comprising a Combination of $Li_2B_{12}F_{12}$ in 1:1 Ethylene carbonate (EC):Diethylene carbonate (DEC)

[0061] Approximately 100 g of a solution comprising ~ 10 g $Li_2B_{12}F_{12}$ salt, prepared according to example 1, combined with ~ 90 g of a 50:50 weight % mixture of EC and DEC was measured to have a water content > 100 ppm. The solution was stored over dry 4A molecular sieves for 4 hrs and then decanted on to fresh, dry 4A molecular sieves for an additonal 8 hrs. After filtration the solution was found to contain between 5-15 ppm water by Karl-Fischer analysis. ^{19}F NMR showed no evidence of hydrolysis of the $B_{12}F_{12}^{2-}$ anion

Comparitive Example 14

Drying of Electrolyte Solution Comprising a Combination of mixtures of $Li_2B_{12}F_{12}$ and $LiPF_6$ in 1:1 Ethylene carbonate (EC):Diethylene carbonate (DEC)

[0062] When an attempt was made to dry a solution comprising a mixture of 9 wt. % $Li_2B_{12}F_{12}$ and 1 wt. % $LiPF_6$ in combination with EC:DEC by the method of example 12, hydrolysis of the PF_6^-anion to $PO_2F_2^-$ and HF was observed by ^{19}F NMR, while no evidence of $B_{12}F_{12}^{2-}$ hydrolysis was observed.

Example 15

Determination of Oxidative and Reductive Stability and Decomposition Temperature of Lithium Electrolyte Solutions for Use in Lithium Secondary Batteries

[0063] To assess the oxidative stability of substituted dodecaborates as battery electrolytes, and the impact of OH containing impurities, cyclic voltammetry (CV) experiments were performed using CH Instruments potentiostat and a conventional three-electrode cell under laboratory atmosphere. Two solutions each containing 0.4 M $Li_2B_{12}F_{12}$ salt were prepared using EC:DEC (3:7) solvents. The salt used in one of the solutions contained > 100 ppm water and the salt used in the second solution contained < 20 ppm water as an impurity and were produced in accordance with Example 12. Cyclic voltammetry was carried out to evaluate the oxidation characteristics of the two salt solutions. The working electrode was Pt (1.6 mm diameter). The reference and the counter electrodes were both lithium foils. The scan rate was 20 mV/s.

[0064] The CV results are represented graphically in Figure 2. Referring now to Figure 2, Figure 2 shows that $Li_2B_{12}F_{12}$ containing only 100-200 ppm water has observable electrochemistry at ~ 3 V vs lithium. Because this is well within the electrochemical window of lithium ion cells water is shown to have a deleterious affect on electrolyte performance (and in turn adversely affect battery performance).

Claims

1. A lithium salt comprising:

$$Li_2B_{12}F_XH_{12\text{-}X\text{-}y}Z_y$$

where x + y is from 3 to 12, and x and y are independently from 0 to 12, and Z comprises at least one of Cl and Br, wherein the total hydroxyl containing impurity level of said salt is less than 500 ppm.

2. The salt of claim 1 wherein the non-lithium alkali or alkaline earth content of said salt is less than 500 ppm.

3. An electrolyte comprising a combination of at least one lithium salt according to claims 1 or 2 and at least one solvent.

4. The electrolyte of Claim 3 wherein said at least one solvent comprises at least one member selected from the group consisting of organic carbonates, esters, ketones and nitriles.

5. The electrolyte of Claim 3 wherein the electrolyte is substantially free of water, HF and non-lithium metal cations.

6. The electrolyte of Claim 3 wherein the solvent comprises at least one member selected from the group consisting of dimethyl carbonate, ethyl methyl carbonate, diethyl carbonate, methyl propyl carbonate, ethyl propyl carbonate, dipropyl carbonate, bis(trifluoroethyl) carbonate, bis(pentafluoropropyl) carbonate, trifluoroethyl methyl carbonate, pentafluoroethyl methyl carbonate, heptafluoropropyl methyl carbonate, perfluorobutyl methyl carbonate, trifluoroethyl ethyl carbonate, pentafluoroethyl ethyl carbonate, heptafluoropropyl ethyl carbonate, perfluorobutyl ethyl carbonate, fluorinated oligomers, dimethoxyethane, triglyme, dimethylvinylene carbonate, tetraethyleneglycol, dimethyl ether, polyethylene glycols, sulfones, and gamma-butyrolactone.

7. The electrolyte of Claim 3 wherein the electrolyte comprises a gel and comprises at least one solvent selected from the group consisting of polyethers, polyethylene oxides, polyimides, polyphosphazines, polyacrylonitriles, polysiloxanes, polyether grafted polysiloxanes, derivatives of the foregoing, copolymers of the foregoing, crosslinked and network structures of the foregoing.

8. The electrolyte of Claim 3 further comprising at least one member selected from the group consisting of $LiPF_6$, lithium perchlorate, lithium hexafluoroarsenate, lithium trifluoromethylsulfonate, lithium tetrafluoroborate, lithium bromide, and lithium hexafluoroantimonate.

9. A battery comprising:

   an anode, a cathode and an electrolyte according to any one of claims 3 to 8.

10. A method for treating lithium salts to obtain a lithium salt according to claim 1 or 2, comprising at least one step selected from the group of:

    a) dissolving the salt in an aprotic organic solvent to form a solution and passing said solution through an alumina column,
    b) dissolving the salt in a solvent to form a solution, and passing said solution through a cation exchange column in Li^+ form,
    c) drying the salt at greater than 180 °C under dynamic vacuum or dynamic nitrogen purge,

d) dissolving the salt in an aprotic organic solvent to form a solution and passing said solution through a Li-substituted molecular sieve,

and recovering lithium salts.

11. The method of Claim 10 wherein the step comprises:

dissolving the salt in a solvent to form a solution, and passing said solution through a cation exchange column in Li^+ form.

12. The method of Claim 10 wherein the step comprises:

drying the salt at a temperature greater than 180 °C under dynamic vacuum or dynamic nitrogen purge.

13. The method of Claim 10 wherein the step comprises:

dissolving the salt in at least one aprotic organic solvent to form a solution and passing said solution through a Li-substituted molecular sieve.

14. The method of Claim 10 wherein the step comprises:

dissolving the salt in an aprotic organic solvent to form a solution and passing said solution through an alumina column.

15. The method of Claim 10 wherein the recovered salt is substantially free of water, HF and non-lithium metal cations.

16. The method of Claim 12 wherein the step comprises drying the salt at a temperature greater than 180 °C under nitrogen purge.

Patentansprüche

1. Lithiumsalz, umfassend:

$$Li_2B_{12}F_XH_{12\text{-}x\text{-}y}Z_y$$

worin x + y gleich 3 bis 12 ist und x und y unabhängig voneinander 0 bis 12 sind und Z Cl und/oder Br umfaßt, wobei die Gesamtmenge an Hydroxyl enthaltenden Verunreinigungen des Salzes weniger als 500 ppm beträgt.

2. Salz nach Anspruch 1, wobei der Gehalt an von Lithium verschiedenem Alkali- oder Erdalkali des Salzes weniger als 500 ppm beträgt.

3. Elektrolyt, umfassend eine Kombination von zumindest einem Lithiumsalz nach Anspruch 1 oder 2 und zumindest ein Lösungsmittel.

4. Elektrolyt nach Anspruch 3, wobei das zumindest eine Lösungsmittel zumindest einen Bestandteil umfaßt, der aus der Gruppe ausgewählt ist, bestehend aus organischen Carbonaten, Estern, Ketonen und Nitrilen.

5. Elektrolyt nach Anspruch 3, wobei der Elektrolyt im wesentlichen frei von Wasser, HF und von Lithium verschiedenen Metallkationen ist.

6. Elektrolyt nach Anspruch 3, wobei das Lösungsmittel zumindest einen Bestandteil umfaßt, der aus der Gruppe ausgewählt ist, bestehend aus Dimethylcarbonat, Ethylmethylcarbonat, Diethylcarbonat, Methylpropylcarbonat, Ethylpropylcarbonat, Dipropylcarbonat, Bis(trifluorethyl)carbonat, Bis(pentafluorpropyl)carbonat, Trifluorethylmethylcarbonat, Pentafluorethylmethylcarbonat, Heptafluorpropylmethylcarbonat, Perfluorbutylmethylcarbonat, Trifluorethylethylcarbonat, Pentafluorethylethylcarbonat, Heptafluorpropylethylcarbonat, Perfluorbutylethylcarbonat, fluorierten Oligomeren, Dimethoxyethan, Triethylenglycoldimethylether, Dimethylvinylencarbonat, Tetraethylenglycol, Dimethylether, Polyethylenglycolen, Sulfonen und γ-Butyrolacton.

7. Elektrolyt nach Anspruch 3, wobei der Elektrolyt ein Gel umfaßt und zumindest ein Lösungsmittel aufweist, das aus der Gruppe ausgewählt ist, bestehend aus Polyethern, Polyethylenoxiden, Polyimiden, Polyphosphazinen, Polyacrylnitrilen, Polysiloxanen, mit Polyether gepfropften Polysiloxanen, Derivaten der vorstehend genannten, Copolymeren der vorstehend genannten, vernetzten Strukturen und Netzwerkstrukturen der vorstehend genannten.

8. Elektrolyt nach Anspruch 3, ferner umfassend zumindest einen Bestandteil, der aus der Gruppe ausgewählt ist, bestehend aus $LiPF_6$, Lithiumperchlorat, Lithiumhexafluorarsenat, Lithiumtrifluormethylsulfonat, Lithiumtetrafluorborat, Lithiumbromid und Lithiumhexafluorantimonat.

9. Batterie, umfassend:

   eine Anode, eine Kathode und einen Elektrolyt nach einem der Ansprüche 3 bis 8.

10. Verfahren zum Behandeln von Lithiumsalzen, so daß ein Lithiumsalz nach Anspruch 1 oder 2 erhalten wird, umfassend zumindest einen Schritt, der aus der folgenden Gruppe ausgewählt ist:

    a) Lösen des Salzes in einem aprotischen organischen Lösungsmittel, so daß eine Lösung entsteht und Leiten dieser Lösung durch eine Aluminiumoxid-Säule;
    b) Lösen des Salzes in einem Lösungsmittel, so daß eine Lösung entsteht, und Leiten dieser Lösung durch eine Kationaustauschsäule in der Li^+-Form;
    c) Trocknen des Salzes bei mehr als 180°C unter einem dynamischen Vakuum oder einer dynamischen Stickstoffspülung;
    d) Lösen des Salzes in einem aprotischen organischen Lösungsmittel, so daß eine Lösung entsteht, und Leiten dieser Lösung durch ein mit Li substituiertes Molekularsieb;

    und Gewinnen von Lithiumsalzen.

11. Verfahren nach Anspruch 10, wobei der Schritt folgendes aufweist:

    Lösen des Salzes in einem Lösungsmittel, so daß eine Lösung entsteht, und Leiten dieser Lösung durch eine Kationenaustauschsäule in der Li^+-Form.

12. Verfahren nach Anspruch 10, wobei der Schritt folgendes aufweist:

    Trocknen des Salzes bei einer Temperatur von mehr als 180°C unter einem dynamischen Vakuum oder einer dynamischen Stickstoffspülung.

13. Verfahren nach Anspruch 10, wobei der Schritt folgendes aufweist:

    Lösen des Salzes in zumindest einem aprotischen organischen Lösungsmittel, so daß eine Lösung entsteht, und Leiten dieser Lösung durch ein mit Li substituiertes Molekularsieb.

14. Verfahren nach Anspruch 10, wobei der Schritt folgendes aufweist:

    Lösen des Salzes in einem aprotischen organischen Lösungsmittel, so daß eine Lösung entsteht, und Leiten dieser Lösung durch eine Aluminiumoxid-Säule.

15. Verfahren nach Anspruch 10, wobei das gewonnene Salz im wesentlichen frei von Wasser, HF und von Lithium verschiedenen Metallkationen ist.

16. Verfahren nach Anspruch 12, wobei der Schritt das Trocknen des Salzes bei einer Temperatur von mehr als 180°C unter einer Stickstoffspülung umfaßt.

Revendications

1. Sel de lithium répondant à la formule suivante :

$Li_2Bi_2F_xH_{12-x-y}Z_y$

Dans laquelle x + y vaut 3 à 12, et x et y valent indépendamment 0 à 12, et Z comprend au moins l'un des éléments Cl et Br, dans lequel le niveau total d'impuretés à teneur en hydroxyle dudit sel est inférieur à 500 ppm.

2. Sel selon la revendication 1, dans lequel la teneur en agents alcalins non de type lithium ou en agents alcalinoterreux dudit sel est inférieure à 500 ppm.

3. Electrolyte comprenant une combinaison d'au moins un sel de lithium selon la revendication 1 ou 2, et au moins un solvant.

4. Electrolyte selon la revendication 3, dans lequel ledit au moins un solvant comprend au moins un membre sélectionné dans le groupe constitué des carbonates, des esters, des cétones et des nitriles organiques.

5. Electrolyte selon la revendication 3, dans lequel l'électrolyte est sensiblement exempt d'eau, de HF et de cations de métal non de type lithium.

6. Electrolyte selon la revendication 3, dans lequel le solvant comprend au moins un membre sélectionné dans le groupe constitué des composés du carbonate de diméthyle, du méthylcarbonate d'éthyle, du carbonate de diéthyle, du propylcarbonate de méthyle, du propylcarbonate d'éthyle, du carbonate de dipropyle, du carbonate de bis(trifluoroéthyle), du carbonate de bis(pentafluoropropyle), du méthylcarbonate de trifluoroéthyle, du méthylcarbonate de pentafluoroéthyle, du méthylcarbonate d'heptafluoropropyle, du méthylcarbonate de perfluorobutyle, de l'éthylcarbonate de trifluoroéthyle, de l'éthylcarbonate de pentafluoroéthyle, de l'éthylcarbonate d'heptafluoropropyle, de l'éthylcarbonate de perfluorobutyle, d'oligomère fluorés, du diméthoxyéthane, du triglyme, du carbonate de diméthylvinylène, du tétraéthylèneglycol, de l'éther de diméthyle, de polyéthylèneglycols, de sulfones et de la gamma-butyrolactone.

7. Electrolyte selon la revendication 3, dans lequel l'électrolyte comprend un gel et comprend au moins un solvant sélectionné dans le groupe constitué des polyéthers, des oxydes de polyéthylène, des polyimides, des polyphosphazines, des polyacrylonitriles, des polysiloxanes, des polysiloxanes greffés par du polyéther, des dérivés des composés précédents, des copolymères des composés précités, des structures réticulées et en réseau des composé précités.

8. Electrolyte selon la revendication 3, comprenant en outre au moins un membre sélectionné dans le groupe constitué du $LiPF_6$, du perchlorate de lithium, de l'hexafluoroarsénate de lithium, du trifluorométhylsulfonate de lithium, du tétrafluoroborate de lithium, du bromure de lithium et de l'hexafluoroantimonate de lithium.

9. Pile comprenant :

une anode, une cathode et un électrolyte selon l'une quelconque des revendications 3 à 8.

10. Procédé pour traiter des sels de lithium dans le but d'obtenir un sel de lithium selon la revendication 1 ou 2, comprenant au moins une étape sélectionnée dans le groupe comprenant les étapes consistant à :

a) dissoudre le sel dans un solvant organique aprotique pour former une solution et faire passer ladite solution à travers une colonne d'alumine,
b) dissoudre le sel dans un solvant pour former une solution et faire passer ladite solution à travers une colonne échangeuse de cations sous forme Li^+,
c) sécher le sel à plus de 180 °C sous un vide dynamique ou sous une purge d'azote dynamique,
d) dissoudre le sel dans un solvant organique aprotique pour former une solution et faire passer ladite solution à travers un tamis moléculaire à substitution Li,

et récupérer les sels de lithium.

11. Procédé selon la revendication 10, dans lequel l'étape consiste à :

dissoudre le sel dans un solvant pour former une solution et faire passer ladite solution à travers une colonne échangeuse de cations sous forme Li^+.

12. Procédé selon la revendication 10 dans lequel l'étape consiste à :

faire sécher le sel à une température supérieure à 180 °C sous un vide dynamique ou sous une purge d'azote dynamique.

13. Procédé selon la revendication 10, dans lequel l'étape consiste à :

dissoudre le sel dans au moins un solvant organique aprotique pour former une solution et faire passer ladite solution à travers un tamis moléculaire à substitution Li.

14. Procédé selon la revendication 10, dans lequel l'étape consiste à :

dissoudre le sel dans un solvant organique aprotique pour former une solution et faire passer ladite solution à travers une colonne d'alumine.

15. Procédé selon la revendication 10, dans lequel le sel récupéré est sensiblement exempt d'eau, de HF et de cations de métal non de type lithium.

16. Procédé selon la revendication 12, dans lequel l'étape consiste à faire sécher le sel à une température supérieure à 180 °C sous une purge d'azote.

Fig. 1 IR Profile Plots for in N_2 for 19914-LiF12 ($Li_2B_{12}F_{12}$)

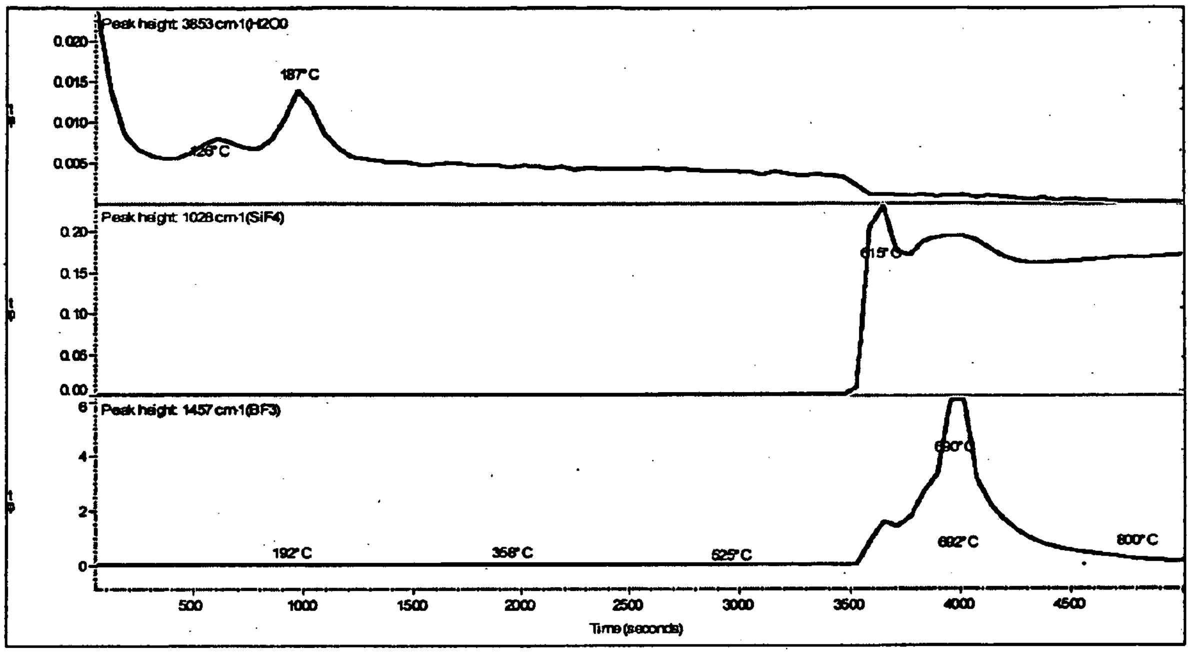
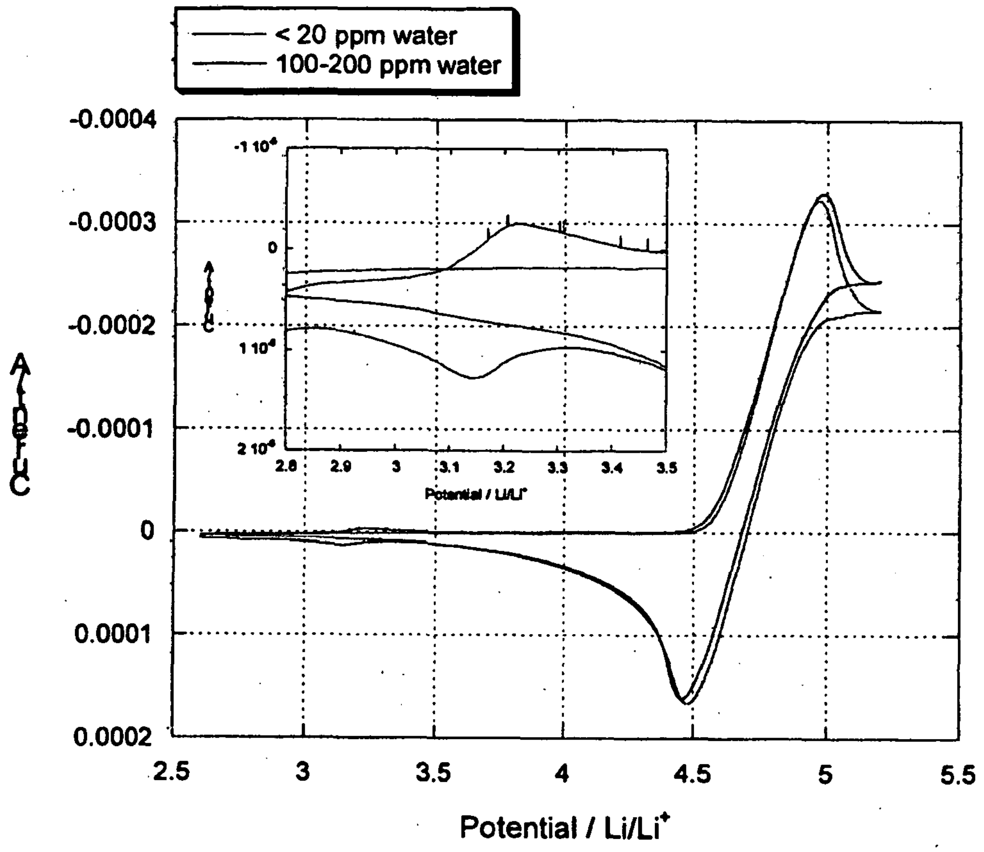


Figure 2 -- Impact of water on electrochemistry of $Li_2B_{12}F_{12}$



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