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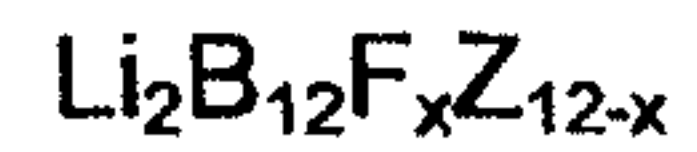
(54) Titre : ANIONS DE CLUSTER DE BORE POLYFLUORE POUR ELECTROLYTES AU LITHIUM
(54) Title: POLYFLUORINATED BORON CLUSTER ANIONS FOR LITHIUM ELECTROLYTES

(57) **Abrégé/Abstract:**

The present invention relates to an improvement in lithium secondary batteries comprised of a negative electrode, a positive electrode, a separator, and a lithium-based electrolyte carried in an aprotic solvent and to the electrolyte compositions. The improvement resides in the use of a lithium salt of the formula: $\text{Li}_2\text{B}_{12}\text{F}_x\text{Z}_{12-x}$ wherein x greater than or equal to 4 and Z represents H, Cl, and Br.

ABSTRACT OF THE DISCLOSURE

The present invention relates to an improvement in lithium secondary batteries comprised of a negative electrode, a positive electrode, a separator, and a lithium-based electrolyte carried in an aprotic solvent and to the electrolyte compositions. The improvement resides in the use of a lithium salt of the formula:



wherein x greater than or equal to 4 and Z represents H, Cl, and Br.

POLYFLUORINATED BORON CLUSTER ANIONS FOR LITHIUM
ELECTROLYTES

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 $Z_2B_nX_n$ and $ZCRB_mX_m$ 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 chlorododecaborate, 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 perchlorate and boron ethylene carbonate.

5 **[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.

10 **[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.

15 **[0007]** US 6,537,697 discloses lithium secondary battery using a nonaqueous electrolyte including lithium tetrakis(pentafluorophenyl)borate as an electrolyte salt.

20 **[0008]** 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 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
25 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

30 **[0009]** The present invention relates in one embodiment to lithium secondary batteries comprising a negative electrode, a positive electrode and a lithium based electrolyte salt of the formula: $\text{Li}_2\text{B}_{12}\text{F}_x\text{Z}_{12-x}$ wherein x is greater than or equal to 4, or 5, preferably at least 8, or at least 10 but not more than 12 or 11 and Z represents H, Cl, and Br. Preferably, when x is less than 12, Z is H, Br or Cl.

[0010] In another embodiment of the present invention there is provided a battery comprising: a lithium salt of the formula: $\text{Li}_2\text{B}_{12}\text{F}_x\text{Z}_{12-x}$ where x averages at least 4 but not more than 12 and Z is H, Cl, or Br. Preferably, x is equal to or greater than 5; in another aspect x can be equal to or greater than 8; in a still further aspect x is less than 12. Desirably, Z is Cl or Br.

[0011] In a desirable embodiment, the above lithium salt can comprises a solvent; desirably, the concentration of the lithium salt in the solvent is from 0.01 to 1 molar.

[0012] Preferably, the solvent is one selected from the group consisting of ethylene carbonate, dimethyl carbonate, ethyl methyl carbonate, diethyl carbonate, methyl propyl carbonate, methyl trifluoroethyl carbonate, dimethoxyethane, diglyme, and triglyme, propylene carbonate, trifluoropropylene carbonate, chloroethylene carbonate, vinylene carbonate, butylene carbonate, dimethylvinylene carbonate, and aprotic gel polymers.

[0013] In another embodiment of the present invention there is provided a lithium based fluorododecaborate selected from the group represented by the formula: $\text{Li}_2\text{B}_{12}\text{F}_x\text{Z}_{12-x}$ wherein x is at least 4 on an average basis but not more than 12; Preferred embodiments include those where x is at least 5, more desirably at least 8, and preferably at least 8 and less than 12; another embodiment is where x is 10 or 11. In the above formula Z is Cl, H or Br, or preferably Z is Cl or Br.

[0014] In another embodiment of the present invention there is provided a lithium electrolyte comprising a lithium salt and a solvent for use in a chemical cell, the lithium salt comprising: $\text{Li}_2\text{B}_{12}\text{F}_x\text{Z}_{12-x}$ wherein x is at least 4 but not more than 12; desirably x is at least 10 and Z is H, Cl, or Br. It is preferable the solvent be selected from the group consisting of ethylene carbonate, dimethyl carbonate, ethyl methyl carbonate, diethyl carbonate, methyl propyl carbonate, methyl trifluoroethyl carbonate, dimethoxyethane, diglyme, and triglyme, propylene carbonate, trifluoropropylene carbonate, chloroethylene carbonate, vinylene carbonate, butylene carbonate, dimethylvinylene carbonate, and an aprotic gel polymer, or polymer matrix.

[0015] Desirably, in the precedeing embodiment the solvent is selected from the group consisting of ethylene carbonate, propylene carbonate, dimethyl carbonate

and diethyl carbonate, x is 10 or 11 and Z is Cl or Br. In another embodiment the above lithium compound may have x being at least 4 and less than 12.

[0016] Some of the advantages associated with the use of the fluorinated lithium borohydride salt for forming the lithium-based electrolyte may include:

5 an ability to use a lithium based salt for an electrolyte solution which has electrochemical, thermal, and hydrolytic stability;

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,

10 an ability to form low viscosity, low impedance lithium electrolyte solutions which can be recycled.

DETAILED DESCRIPTION OF THE INVENTION

[0017] A lithium secondary battery, capable of multiple cycles of charging and discharging, is dependent on an electrolyte conducting solution carrying lithium ions. The two major requirements 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 particularly 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.

[0018] The present lithium secondary battery is characterized in that the lithium based electrolyte salt for forming lithium electrolyte solutions is based upon a lithium fluorododecaborate of the formula: $\text{Li}_2\text{B}_{12}\text{F}_x\text{Z}_{12-x}$ where x is greater than or equal to 4 or 5 (average basis), preferably at least 8, and most preferably at least 10 but not more than 12, or 11, and Z represents H, Cl, and Br. Specific examples of lithium based fluorinated dodecaborates include: $\text{Li}_2\text{B}_{12}\text{F}_5\text{H}_7$, $\text{Li}_2\text{B}_{12}\text{F}_6\text{H}_6$, $\text{Li}_2\text{B}_{12}\text{F}_7\text{H}_5$, $\text{Li}_2\text{B}_{12}\text{F}_8\text{H}_4$, $\text{Li}_2\text{B}_{12}\text{F}_9\text{H}_3$, $\text{Li}_2\text{B}_{12}\text{F}_{10}\text{H}_2$, $\text{Li}_2\text{B}_{12}\text{F}_{11}\text{H}$ 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 $\text{Li}_2\text{B}_{12}\text{F}_x\text{Cl}_{12-x}$ and $\text{Li}_2\text{B}_{12}\text{F}_x\text{Br}_{12-x}$ where x is 10 or 11.

[0019] The lithium salt employed for forming electrolytes solutions for use in lithium batteries can be formed by fluorinating hydridodecaborates initially to provide a fluorododecaborate having at least 5, preferably at least 8 and most preferably at least 10 but not more than 12 or more hydrogen atoms replaced with fluorine
5 (average basis). Lithium-ion metathesis gives the lithium salt. This reaction is carried out in a liquid medium. In direct fluorination, fluorine is diluted with an inert gas, e.g., nitrogen. Fluorine concentrations from 10 to 40 % by volume are commonly employed. If further halogenation is desired, the partially fluorinated hydridoborate is reacted with the desired halogen, e.g., chlorine or bromine.

10 **[0020]** Unlike the formation of lithium bromoborates and chloroborates, the formation of the highly fluorinated lithium fluorododecaborates, e.g., those having at least 10 fluorine atoms is extremely difficult. Complete fluorination of the lithium hydridoborate can be effected, but because of the reactive nature of fluorine, there is associated attack of the hydridoborate, which leads to yield loss.

15 **[0021]** To facilitate formation of the lithium fluoroborates as electrolyte salts, direct fluorination of the lithium hydridoborate is carried out 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 an acid. Examples of acids include formic, acetic, trifluoroacetic, dilute sulfuric triflic, and sulfonic acids hydrohalic ($\text{HCl}_{(\text{aq})}$,
20 $\text{HBr}_{(\text{aq})}$, $\text{HI}_{(\text{aq})}$, and $\text{HF}_{(\text{aq})}$). 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_0 , between $0 > H_0 > -11$ is preferred as an acidic medium for effecting fluorination.

[0022] Radical scavengers can be used in the fluorination of lithium
25 hydridododecaborates to reduce byproduct formation and improve reaction efficiency. In aqueous solutions, radical scavengers appear to limit the formation of hydrogen peroxide, or HOF which may be generated with fluorine. Radical scavengers are used to adjust acidity, and inhibit the side-reaction of fluorine with the solvent, thereby improving fluorination efficiency. Examples of radical
30 scavengers include oxygen, and nitroaromatics. A simple method for introducing a radical scavenger is to introduce a small amount of air to the liquid medium.

[0023] Fluorination of the hydridoborate anion can be carried out over a temperature range sufficient to maintain liquid phase conditions. For effecting the

fluorination of the dodecaborate anion the temperature generally ranges from -30 to 100°C, typically from 0 to 20°C. Pressures during fluorination are such as to maintain liquid phase conditions, typically atmospheric for the fluorination of the dodecaborate anion.

5 **[0024]** In the formulation of an electrolyte solution for a lithium battery, the lithium salt is carried in an aprotic solvent. Typically, these aprotic solvents are anhydrous, and anhydrous electrolyte solutions are preferred. Examples of aprotic solvents or carriers for forming the electrolyte systems include dimethyl carbonate, ethyl methyl carbonate, diethyl carbonate, methyl propyl carbonate, ethyl propyl
10 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, etc., fluorinated oligomers, dimethoxyethane,
15 triglyme, dimethylvinylene carbonate, tetraethyleneglycol, dimethyl ether, polyethylene glycols, sulfones, and gamma-butyrolactone.

[0025] In another embodiment, the electrolyte system of the present invention can comprise an aprotic gel polymer carrier/solvent. Suitable gel polymer carrier/solvents include polyethers, polyethylene oxides, polyimides,
20 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, and the like, to which is added an appropriate ionic electrolyte salt. Other gel-polymer carrier/solvents include those prepared from polymer matrices derived from polypropylene oxides,
25 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.

[0026] The solution of aprotic solvent and fluorinated lithium dodecaborate salt employed for forming the lithium based electrolyte for the lithium battery typically will
30 have a concentration of lithium fluorododecaborate of at least 0.01 or 0.05 to 1 molar and preferably from 0.1 to 0.6 molar or from 0.2 to 0.5 molar. Higher concentrations tend to become too viscous and, the bulk conductivity characteristics

are adversely affected. Also, solutions formed from lithium based fluoroborates having an increased concentration of halogen atoms other than fluorine show an increase viscosity to the lithium fluoroborates having higher fluorine content.

5 **[0027]** Other lithium based salts can be used in combination with the lithium based fluoroborates, e.g. LiPF_6 , lithium perchlorate, lithium hexafluoroarsenate, lithium trifluoromethylsulfonate, lithium tetrafluoroborate, lithium bromide, and lithium hexafluoroantimonate as desired. The salts of this invention can be used in combination with other salts in any amounts. If such salts are used, they may be added in any (or small) amounts to the lithium fluoroborate based electrolyte here or
10 the lithium based fluoroborates may be added to the batteries employing other based lithium salt in any (or small) amounts.

[0028] The lithium battery employing the lithium fluorododecaborate electrolyte can be any using a cathode and a negative anode. In forming the lithium battery, the negative electrodes for use in a lithium secondary battery typically can be based
15 generally upon non-graphitizing carbon, natural or artificial graphite carbon, or tin oxide, silicon, or germanium compound. Any of the conventional anode compositions may be used in combination with the lithium fluorododecaborate electrolytes here.

[0029] The positive electrode for use in lithium secondary batteries typically can
20 be based upon a lithium composite oxide with a transition metal such as cobalt, nickel, manganese, etc., or a lithium composite oxide, part of whose lithium sites or transition metal sites is replaced with cobalt, nickel, manganese, aluminum, boron, magnesium, iron, copper, etc. or iron complex compounds such as ferrocyan blue, berlin green, etc.. Specific examples of lithium composites for use as positive
25 electrodes include $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ and lithium manganese spinel, LiMn_2O_4 . The former composite presents significant safety concerns due to the very high oxidizing potential of Ni(IV). The latter composite is significantly less oxidizing than the Ni(IV) lithium battery and leads to far better redox kinetics and much higher power densities than the nickel cobaltate cathode.

30 **[0030]** The separator for the lithium battery often is a microporous polymer film. Examples of polymers for forming films include: nylon, cellulose, nitrocellulose, polysulfone, polyacrylonitrile, polyvinylidene fluoride, polypropylene, polyethylene,

polybutene, etc. Recently ceramic separators, based on silicates, have also been used.

[0031] 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.
 5 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.

[0032] The following examples are intended to illustrate various embodiments of the invention and are not intended to restrict the scope thereof.

Example 1

10 Preparation of $\text{Li}_2\text{B}_{12}\text{F}_x\text{H}_{12-x}$, where $x = 10-12$

[0033] A colorless slurry containing 2.96 g (11.8 mmol) $\text{K}_2\text{B}_{12}\text{H}_{12}\cdot\text{CH}_3\text{OH}$ in 6 ml formic acid at an average Hammett acidity of $H_0 = -2$ 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
 15 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 $\text{B}_{12}\text{F}_{10}\text{H}_2^{2-}$ (60%), $\text{B}_{12}\text{F}_{11}\text{H}^{2-}$ (35%), and $\text{B}_{12}\text{F}_{12}^{2-}$ (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
 20 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.
 25 Typical yields of $\text{Li}_2\text{B}_{12}\text{F}_x\text{H}_{12-x}$ ($x = 10, 11, 12$) were ~ 75%.

Example 2

Preparation of $\text{Li}_2\text{B}_{12}\text{F}_x\text{Br}_{12-x}$ ($x \geq 10$, ave. $x = 11$)

[0034] 3g $\text{Li}_2\text{B}_{12}\text{F}_x\text{H}_{12-x}$ ($x \geq 10$) (0.008 mol) of average composition $\text{Li}_2\text{B}_{12}\text{F}_{11}\text{H}$ was dissolved in 160 mL of 1 M $\text{HCl}_{(\text{aq})}$. Br_2 , 1.4 mL (0.027mol) was added and the
 30 mixture refluxed at 100°C for 4 hours. A sample was taken for NMR analysis.

[0035] 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 $\text{Li}_2\text{B}_{12}\text{F}_x\text{Br}_{12-x}$ ($x \geq 10$, ave. $x = 11$) is 3.66 g.

Example 3

Preparation of $\text{Li}_2\text{B}_{12}\text{F}_x\text{Cl}_{12-x}$ (ave. $x = 11$)

[0036] 20 g $\text{Li}_2\text{B}_{12}\text{F}_{11}\text{H}$ 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 triturated 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. ^{11}B -NMR in D_2O : -16.841; -17.878

Example 4

Preparation of $\text{Li}_2\text{B}_{12}\text{F}_x\text{Cl}_{12-x}$ (ave. $x = 3$)

[0037] 3.78 g $\text{K}_2\text{B}_{12}\text{F}_3\text{H}_9$ 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 $\text{Li}_2\text{B}_{12}\text{F}_x\text{Cl}_{12-x}$ (ave. $x = 11$)

5 **[0038]** 3 g $\text{Li}_2\text{B}_{12}\text{F}_{11}\text{H}$ 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
10 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 ^{19}F 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,
15 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 $\text{Li}_2\text{B}_{12}\text{F}_x\text{Cl}_{12-x}$ (ave. $x = 3$)

[0039] 2.48 g $\text{K}_2\text{B}_{12}\text{F}_3\text{H}_9$ mixture was dissolved in 100 mL 1M HCl in a round
20 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
25 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 $\text{LiOH}\cdot\text{H}_2\text{O}$ was carried out as in Example 1. A composition
30 described by the above formula was obtained.

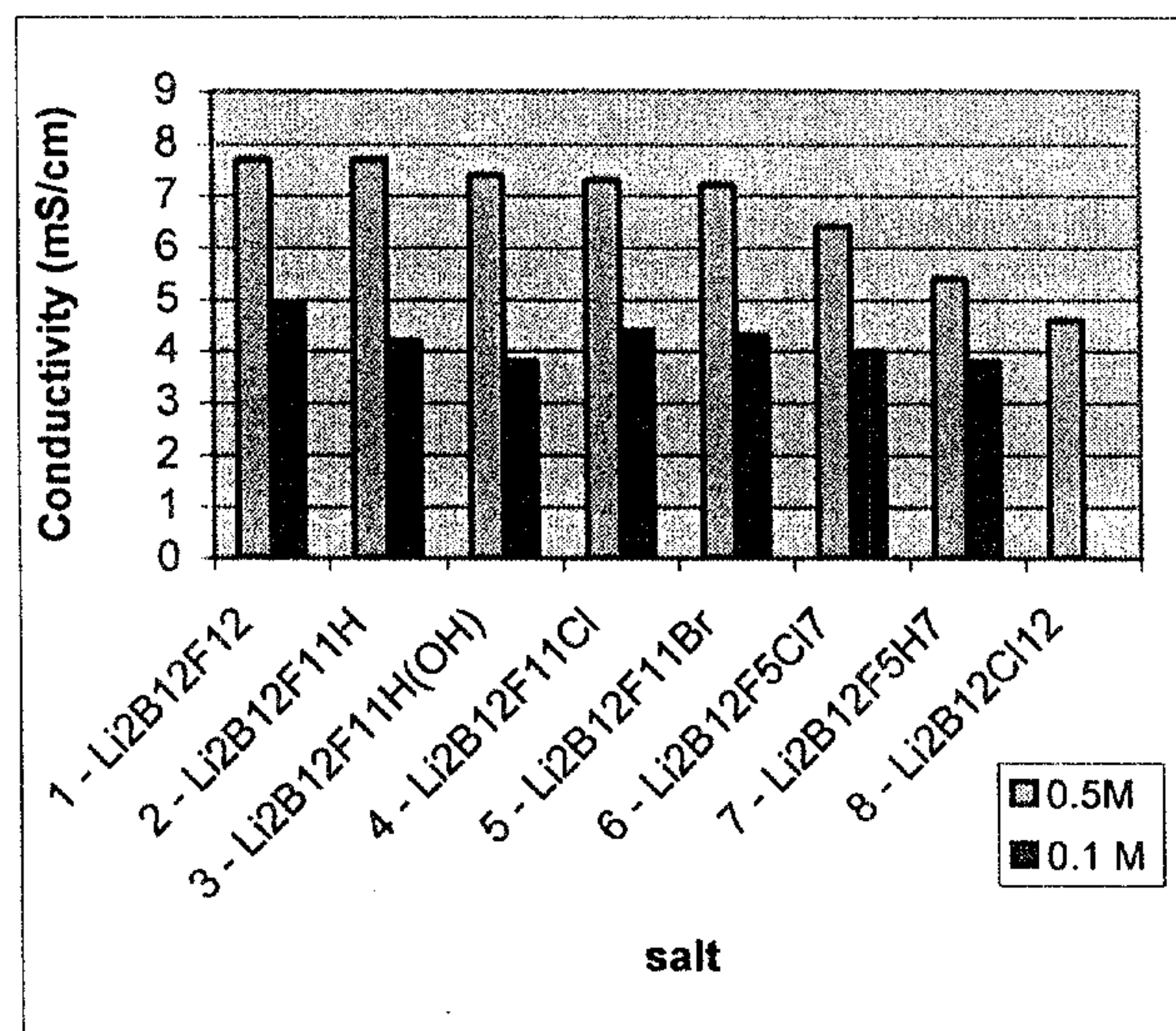
Example 7

Conductivity of Lithium Electrolyte Solutions for Use in Lithium Secondary Batteries

5 [0040] The conductivities of solutions of the $\text{Li}_2\text{B}_{12}\text{F}_x\text{Z}_{12-x}$ salts and pure $\text{Li}_2\text{B}_{12}\text{Cl}_{12}$ dissolved in a 50/50 wt.% ethylene carbonate (EC)/dimethyl carbonate (DMC) were determined using a Radiometer CDM210 conductivity meter and 2 pole CDC741T conductivity cell with build-in temperature sensor. The conductivity cell was calibrated using KCl solutions.

[0041] The conductivities, are shown in Graph 1

Graph 1



10

[0042] Graph 1 shows that 0.5 M electrolyte solutions of salts of the anions having 5 or more fluorine atoms have excellent bulk conductivity. Surprisingly, the

15 [0043] salt, $\text{Li}_2\text{B}_{12}\text{Cl}_{12}$, (Comparative sample 8) had the poorest conductivity of all the salts tested. At the 0.1 molar concentration, the conductivities were significantly poorer showing that commercial, large scale batteries would require higher salt concentrations.

20 [0044] Viewing the results in greater detail, it is unexpected that at comparable concentrations, $\text{Li}_2\text{B}_{12}\text{Cl}_{12}$ (Comparative sample 8) has a conductivity of only ~ 0.6X that of the conductivity of $\text{Li}_2\text{B}_{12}\text{F}_{12}$ (sample 1), even though $\text{B}_{12}\text{Cl}_{12}^{2-}$ is expected to be more weakly coordinating. Even more surprising is the fact that a 0.1M solution of $\text{Li}_2\text{B}_{12}\text{F}_{12}$ (sample 1) is more conducting than $\text{Li}_2\text{B}_{12}\text{Cl}_{12}$ (sample 8) at 5X the

concentration. This effectively means that on a weight basis it takes ~ 10 times as much $\text{Li}_2\text{B}_{12}\text{Cl}_{12}$ as $\text{Li}_2\text{B}_{12}\text{F}_{12}$ in an EC/DMC mixture to achieve the same ionic conductivity.

5 [0045] Not revealed from Graph 1 is the relationship of the viscosity of the solutions to the bulk conductivity of the electrolyte. Under the test conditions, all of the fluorinated dodecaborates exhibited a viscosity similar to water, i.e., the solutions were pourable. On the other hand, as the concentration of halogen atoms other than fluorine increased in the lithium fluoroborate, the viscosity of the resulting solutions formed from the lithium based fluoroborate increased substantially. The 10 bulk conductivity of the resulting solution also decreased dramatically. For example, the salt, $\text{Li}_2\text{B}_{12}\text{Cl}_{12}$, at a 0.5 M level was too viscous and too low in bulk conductivity to be of commercial value.

15 [0046] In summary, the fully chlorinated lithium salt ($\text{Li}_2\text{B}_{12}\text{Cl}_{12}$) when evaluated as an electrolyte salt for a lithium battery has a conductivity at useful concentrations in typical aprotic electrolytes which is relatively low (4.6mS/cm at 0.5M in 50/50 EC/DMC). On the other hand, and quite unexpectedly, $\text{Li}_2\text{B}_{12}\text{F}_{12}$ and the mixtures of salts $\text{Li}_2\text{B}_{12}\text{F}_x(\text{H}, \text{Cl}, \text{Br})_{12-x}$ give rise to 0.5M solutions in EC/DMC of substantially greater conductivity than the fully chlorinated derivative (7.2-7.7mS/cm). This result is surprising in view of the fact that the smaller $\text{B}_{12}\text{F}_x(\text{H}, \text{Cl}, \text{Br})_{12-x}^{2-}$ anions were not 20 expected to be as weakly coordinating as the $\text{B}_{12}\text{Cl}_{12}^{2-}$ anions.

Example 8

Evaluation of Lithium-Based Electrolyte In Lithium Battery

25 [0047] In this example, a 2032 button cell battery configuration was used employing a lithium foil (- electrode)||0.4-0.5M $\text{Li}_2\text{B}_{12}\text{F}_{12}$ in EC/DMC|| $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (+ electrode). The cell was pulse charged and discharged using an Arbin Instruments BT4 series potentiostat to assess the area specific impedance (ASI) of the cell. Using this configuration, it was demonstrated that a 0.5 molar (M) solution of $\text{Li}_2\text{B}_{12}\text{F}_{12}$ in EC/DMC (3:7) allows equivalent or even slightly greater capacities than optimized electrolyte solutions employing 1.2 M LiPF_6 in the same 30 cell configuration. More importantly in comparative tests it was seen that reducing the $\text{Li}_2\text{B}_{12}\text{F}_{12}$ concentration from 1 M to 0.5M reduces the ASI from $100\Omega\cdot\text{cm}^2$ to $40\Omega\cdot\text{cm}^2$ in this unoptimized solvent system. The highest electrolyte solution conductivity for $\text{Li}_2\text{B}_{12}\text{F}_{12}$ was observed at 0.4 M, and the conductivity at 0.3M was

only slightly less than that at 0.5M. This suggested that it is possible to reduce concentration perhaps to a level of 0.3M or even 0.2 M and achieve the desired ASI without making any significant changes in solvent formulation. In fact it has been found that at a concentration of 0.4M in EC/DMC(3:7) the ASI remains at $\sim 40\Omega\cdot\text{cm}^2$.

5

Example 9

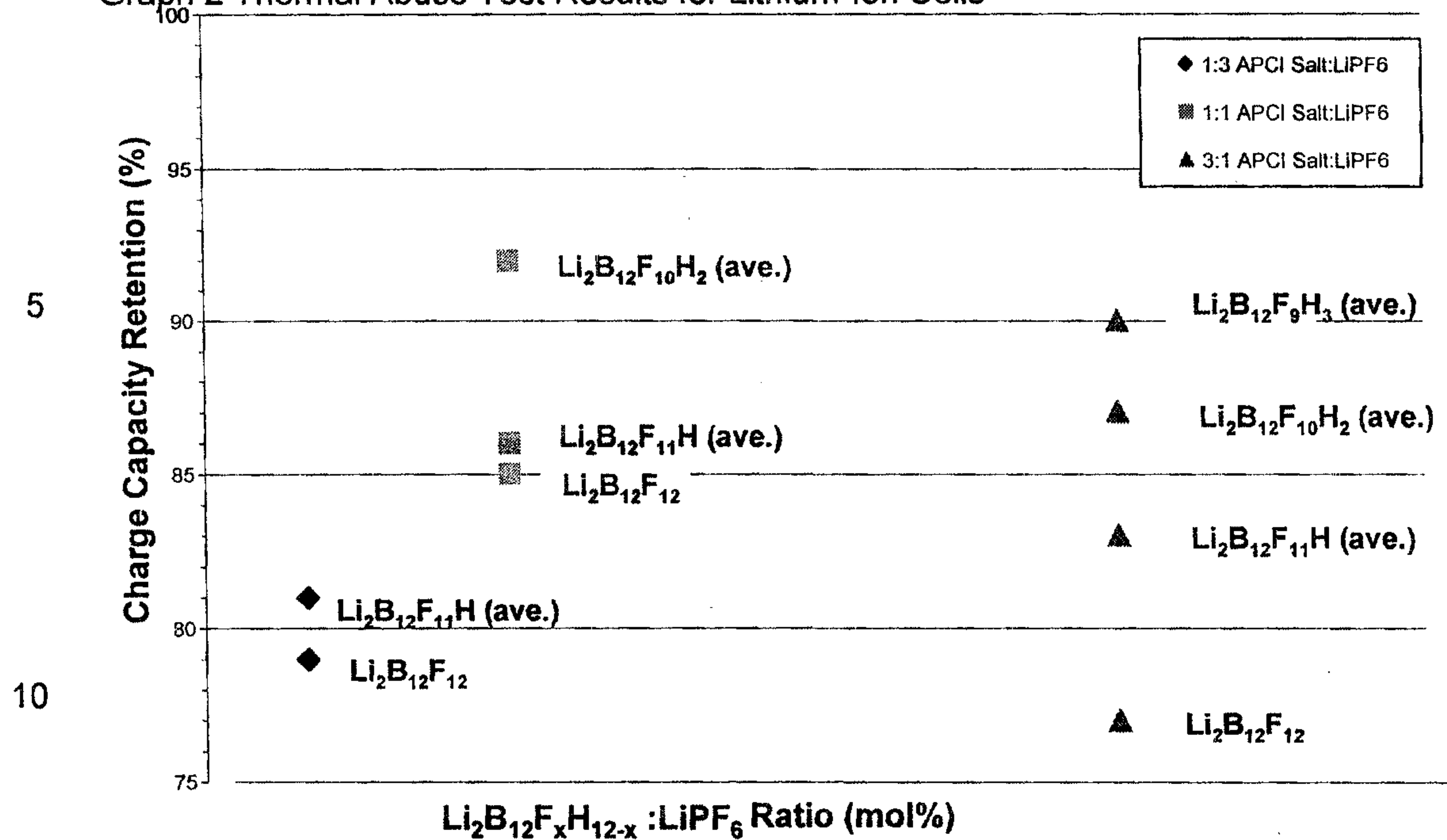
Thermal Abuse Testing of Fully Charged Lithium-Ion Cells

[0048] Lithium-ion cells were fabricated and tested as in the previous example using a graphite rather than a lithium metal negative electrode according to the following configuration:

10 Graphite(- electrode)|| $\text{Li}_2\text{B}_{12}\text{F}_x\text{H}_{12-x}/\text{LiPF}_6$ in EC/DEC|| $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (+ electrode)

A number of different fluorododecaborate compositions were used (average x ranging from 9 to 12) and 3 different ratios of fluorododecaborate salt to hexafluorophosphate salt were used. Cells containing these solutions were tested according to the following profile. Using an Arbin Instruments potentiostat, the cells were charged and discharged
 15 through two 0.1 mAh (C/20 rate) formation cycles. The cells were then charged at 0.7 mAh (C/3 rate) to 4.1 V to determine pre-bake charge capacity. The open circuit potential of the cells was monitored for 2 hours as a quality control test. Only cells which remained at or above $\sim 4\text{V}$ were used in the subsequent stages of this test. These cells were stored at 85°C for 72 hours in their fully charged state. The cells were then
 20 discharged at 0.7 mAh (C/3 rate) to 3 V, and charged at the same rate back to 4.1 V to determine post heat treatment charge capacity. The ratio of post- to pre-heat treatment charge capacity was determined giving the % charge capacity retention. Such a test is a good accelerated measure of calendar and cycle-life stability. The higher the ratio of post- to pre-bake charge capacity the better the overall stability of the cell system.
 25 Results of these tests are shown in Graph 2.

Graph 2 Thermal Abuse Test Results for Lithium-Ion Cells



[0049] The data show that for all 3 dodecaborate:LiPF₆ ratios partially fluorinated (average x less than 12) mixtures of Li₂B₁₂F_xH_{12-x} perform better than the fully fluorinated Li₂B₁₂F₁₂ in terms of charge capacity retention and hence stability.

[0050] ¹⁹F NMR analyses of electrolyte solution from the least stable Li₂B₁₂F₁₂ containing cells revealed that significant amounts of Li₂B₁₂F₁₂ had been cleanly reduced to Li₂B₁₂F₁₁H with only minor amounts of further reduction to Li₂B₁₂F₁₀H₂. Since this reduction must remove active lithium capacity from the cell, it suggests that the greater capacity losses for cells containing largely Li₂B₁₂F₁₂ may be due to the reductive instability of that salt in fully charged lithium ion cells.

[0051] However, in similar thermal abuse tests using propylene carbonate as solvent no reduction of Li₂B₁₂F₁₂ is observed suggesting that Li₂B₁₂F₁₂ will have suitable reductive stability for some lithium-ion cell configurations.

25 Example 10

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

[0052] To assess the oxidative stability of substituted dodecaborates as possible electrolytes, cyclic voltammetry (CV) experiments were performed using CH Instruments potentiostat and a conventional three-electrode cell under

laboratory atmosphere. The working electrode was a platinum disc electrode (2 mm) and potentials were referenced to a Ag/Ag⁺ reference electrode (silver wire immersed into 0.01 M AgNO₃ in 0.1 M acetonitrile [(*n*-Bu)₄N][BF₄] in a glass tube fitted with a Vycor tip). The reference electrode was calibrated to be 0.32 V versus
5 the normal hydrogen electrode (NHE) using a ferrocene standard (E_{1/2}(FeCp₂/FeCp₂⁺) = 0.08 V under described conditions). The electrolyte solutions were 0.01 M solutions of [(*n*-Bu)₄N][A] (A = anion of interest) in 0.1 M acetonitrile solution of [(*n*-Bu)₄N][BF₄].

[0053] The relative reductive stability was calculated as the electron affinity (EA) using Density Functional Theory (DFT) computational methods. All DFT
10 calculations were performed with the DMol software package. The electron affinities (EA) are the energies required to push an electron from "infinity" on to the doubly charged anion in the gas phase and a higher positive electron affinity (here calculated in eV) is associated with greater stability toward reduction.

[0054] The decomposition temperature was determined by DSC measurements
15 on a TA Instruments DC2910 Differential Scanning Calorimeter.

Table 1. Oxidation, Decomposition Temp. (Stability) And Conductivity Of Lithium Electrolytes.

Compound	Molecular wt.	Conductivity (mS/cm) ^a	Decomp. Temp. (°C)	Oxidation Potential E _{1/2} (V) vs. NHE; {~vs Li}; (reversible ?)
Li ₂ B ₁₂ Cl ₁₂	569.5	4.6 (0.5M)	>400	> 2.2 {> 5.3}; ?
Li ₂ B ₁₂ F ₁₂	371.6	7.7 (0.5M) 6.0 (0.25M) 4.9(0.1M)	465	1.87{4.9}; (yes)
Li ₂ B ₁₂ F _x H _{12-x} (x≥10) Average x = 11	353.6	7.7 (0.5M) 4.2 (0.1M)	465	1.73 {4.7}; (yes)
Li ₂ B ₁₂ F _x Cl _{12-x} (x≥10) Average x = 11	388.1	7.3(0.5M) 4.4 (0.1M)	---	1.98 {5.1}; (yes)
Li ₂ B ₁₂ F _x Br _{12-x} (x≥10) Average x = 11	432.5	7.2 (0.5) 4.3 (0.1)	---	---
Li ₂ B ₁₂ F _x H _{12-x} (x≥10) Average x = 11 Contains 5% Li ₂ B ₁₂ F _x (OH) _{12-x} (x=10,11) B ₁₂ F ₁₀ (OH) ₂ ²⁻	~ 353.6	7.4 (0.5) 4.0 (0.1) ---	465 ---	1.28 {4.2}; (yes)
Li ₂ B ₁₂ F ₅ H ₇			>400	1.6 {4.6}; (yes)
Li ₂ B ₁₂ F ₃ H ₉			>400	1.5 {4.5}; (no)
B ₁₀ Cl ₁₀ ²⁻ *				1.35; (yes)

* B₁₀Cl₁₀²⁻ is a literature value

Table 2. Calculated electron affinities for halogenated dodecaborate salts

Molecule	EA (eV)
B ₁₂ Cl ₁₂ (2-)	5.04
B ₁₂ F ₁₂ (2-)	6.24
B ₁₂ H ₁₂ (2-)	10.4
B ₁₂ F ₁₁ Cl(2-)	5.79
B ₁₂ F ₁₀ Cl ₂ (2-)	5.92
B ₁₂ F ₁₁ (OH)(2-)	6.32
B ₁₂ F ₁₀ (OH) ₂ (2-)	6.40
B ₁₂ F ₁₀ (OCF ₃) ₂ (2-)	5.52
B ₁₂ F ₁₁ H(2-)	6.66
B ₁₂ F ₁₀ H ₂ (2-)	7.09
B ₁₂ F ₉ H ₃ (2-)	7.57
B ₁₂ F ₈ H ₄ (2-)	7.99

[0055] Table 1 shows that the oxidative stabilities of the pure $\text{Li}_2\text{B}_{12}\text{Cl}_{12}$ (Comparative Sample), $\text{Li}_2\text{B}_{12}\text{F}_{12}$ and other salts of the invention are sufficiently high to evaluate them as potential lithium battery electrolytes. From Table 1, it is interesting and unexpected that the oxidative stabilities of the $\text{B}_{12}\text{Cl}_{12}^{2-}$ anion and the $\text{Li}_2\text{B}_{12}\text{F}_x\text{Cl}_{12-x}$ ($x \geq 10$) salt mixture were higher than that of the fully fluorinated anion $\text{B}_{12}\text{F}_{12}^{2-}$. Thus, the mixed salt compositions, $\text{Li}_2\text{B}_{12}\text{F}_x\text{Cl}_{12-x}$ ($x \geq 10$) are observed to provide a unique combination of a high conductivity with even better oxidative stability than $\text{Li}_2\text{B}_{12}\text{F}_{12}$, possibly rendering them useful for both high power and high voltage battery applications. Although not intending to be bound by speculation, the decrease in oxidative stability of the fully fluorinated anion $\text{B}_{12}\text{F}_{12}^{2-}$ may be due to a π -back donation from fluorine atom to boron cluster. That analysis suggests that the $\text{B}_{12}\text{Cl}_{12}^{2-}$ anion may actually be a more weakly coordinating anion than $\text{B}_{12}\text{F}_{12}^{2-}$.

[0056] Table 1 also shows that the decomposition temperature of the of the fully fluorinated anion $\text{B}_{12}\text{F}_{12}^{2-}$ and of the fully fluorinated/halogenated anion, $\text{B}_{12}\text{F}_x\text{Z}_{12-x}^{2-}$, are at least 400°C and thus resistant to decomposition under normal battery conditions for operation. With respect to oxidative stability, lithium battery electrolytes are required to have high electrochemical oxidative stability. For high voltage lithium ion batteries, electrolyte oxidation at greater than 4.2 V vs. lithium metal (1.2 V vs NHE) is required. Because, the measured $E_{1/2}$ is usually 0.2 to 0.4 V higher than the actual onset of oxidation, electrolyte stability to at least a measured $E_{1/2}$ of 1.4 to 1.6 V vs. NHE is desired. As can be seen from the data in Table 1, this stability is readily met for those lithium dodecaborate salts containing more than 3 fluorine atoms.

[0057] From the data in Table 1, it is also clear that while fluorinated lithium dodecaborates with as few as 3 fluorine atoms, may possess suitable oxidative stability for certain lithium ion applications, the fact that its first oxidation is irreversible, suggests that $\text{Li}_2\text{B}_{12}\text{F}_3\text{H}_9$ would slowly, but steadily be depleted on successive charging and discharging of a 4.2 V lithium ion battery. The $\text{Li}_2\text{B}_{12}\text{F}_4\text{H}_8$ has better oxidative stability and it is likely that its first oxidation is sufficiently reversible that this salt would have reasonable stability on repeated charge/discharge cycling.

[0058] Table 2 shows the calculated electron affinities of several substituted dodecaborate salts. The results mirror the oxidative stabilities. While the data in

Table 1 indicate that it is harder to oxidize $B_{12}Cl_{12}^{2-}$ than $B_{12}F_{12}^{2-}$, it is significantly easier to reduce $B_{12}Cl_{12}^{2-}$ than $B_{12}F_{12}^{2-}$. Similarly, just as chlorine atom substitution increases the oxidation potential of these salts while hydrogen atom substitution reduces these potentials, the opposite is true of the electron affinity values.

5 Substitution of fluorine atoms with chlorine makes the $B_{12}F_xZ_{12-x}^{2-}$ easier to reduce while substitution of fluorine atoms with hydrogen make these salts harder to reduce, that is, $B_{12}F_{11}H^{2-}$ is harder to reduce than is $B_{12}F_{12}^{2-}$. Substitution with bis-trifluoromethoxy groups ($-OCF_3$) is similar in effect to chlorine substitution. Replacing F with OH marginally increases the EA, by an amount that is probably
10 within the uncertainty of the method.

[0059] Based on these calculations and the thermal abuse cell stability results of example 9, it now appears that highly chlorinated dodecaborate salts, including $B_{12}Cl_{12}^{2-}$, because of their ease of reduction, relative to $B_{12}F_{12}^{2-}$, will have very poor stability in lithium ion cells.

15 **[0060]** Surprisingly, it also appears that the partially fluorinated lithium fluorododecaborate salts, $Li_2B_{12}F_xH_{12-x}$ (where $4 \leq x \leq 12$ or where $4 \leq x \leq 11$) have the optimal combination of oxidative and reductive stability for commercial lithium ion cells.

CLAIMS:

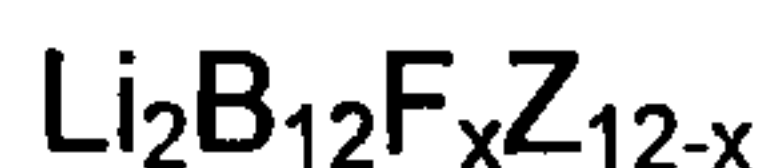
1. A lithium secondary battery comprising:

a positive electrode,

a negative electrode,

an organic solvent comprising at least one carbonate,

a lithium salt of the formula:



where x is greater than or equal to 8 and less than or equal to 12 and Z is H, Cl or Br; and

at least one member selected from the group consisting of LiPF_6 , lithium perchlorate, lithium hexafluoroarsenate, lithium tetrafluoroborate and lithium hexafluoroantimonate.

2. The battery of claim 1 wherein x is 12.

3. The battery of claim 1 wherein x is less than 12 and Z is Cl or Br.

4. The battery of claim 1 wherein the lithium salt is selected from the group consisting of $\text{Li}_2\text{B}_{12}\text{F}_8\text{H}_4$, $\text{Li}_2\text{B}_{12}\text{F}_9\text{H}_3$, $\text{Li}_2\text{B}_{12}\text{F}_{10}\text{H}_2$ and $\text{Li}_2\text{B}_{12}\text{F}_{11}\text{H}$.

5. The battery of claim 2 wherein the concentration of said lithium salt in said solvent is from 0.01 to 1 molar.

6. The battery of claim 1 wherein said lithium salt is selected from the group consisting of $\text{Li}_2\text{B}_{12}\text{F}_x\text{Cl}_{12-x}$ and $\text{Li}_2\text{B}_{12}\text{F}_x\text{Br}_{12-x}$ where x is 10 or 11.

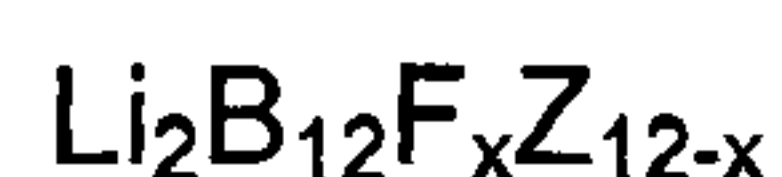
7. The battery of any one of claims 1 to 6 wherein said solvent is selected from the group consisting of ethylene carbonate, dimethyl carbonate, ethyl methyl carbonate, diethyl carbonate, methyl propyl carbonate, methyl trifluoroethyl carbonate, dimethoxyethane, diglyme, triglyme, propylene carbonate, trifluoropropylene carbonate,

chloroethylene carbonate, vinylene carbonate, butylene carbonate, dimethylvinylene carbonate and aprotic gel polymers.

8. The battery of claim 1 wherein x is 10 and at least one Z is Cl.
9. The battery of claim 7 wherein x is 10 or 11 and Z is Cl or Br.
10. The battery of any one of claims 1 to 9 wherein the positive electrode comprises at least one oxide.
11. The battery of any one of claims 1 to 10 wherein the negative electrode comprises at least one member selected from the group consisting of carbon, tin oxide, silicon and germanium compounds.
12. The battery of any one of claims 1 to 11 wherein the battery retains at least 75% of its charge capacity after being maintained at a temperature of 85°C for 72 hours.
13. An electrolyte for a lithium secondary battery comprising a first lithium salt, and at least one carbonate solvent, said first lithium salt comprising:

$$\text{Li}_2\text{B}_{12}\text{F}_x\text{Z}_{12-x}$$
 wherein x is at least 10 but not more than 12 and Z is H, Cl or Br, and at least one other lithium based salt.
14. The lithium electrolyte of claim 13 wherein x is at least 11.
15. The lithium electrolyte of claim 13 or 14 wherein the solvent is selected from the group consisting of ethylene carbonate, dimethyl carbonate, ethyl methyl carbonate, diethyl carbonate, methyl propyl carbonate, methyl trifluoroethyl carbonate, dimethoxyethane, diglyme, triglyme, propylene carbonate, trifluoropropylene carbonate, chloroethylene carbonate, vinylene carbonate, butylene carbonate, dimethylvinylene carbonate, an aprotic gel polymer and polymer matrix.

16. The lithium electrolyte of claim 13 or 14 wherein the solvent is selected from the group consisting of ethylene carbonate, propylene carbonate, dimethyl carbonate and diethyl carbonate.
17. The lithium electrolyte of claim 13 wherein x is 10 or 11 and Z is Cl or Br.
18. The lithium electrolyte of claim 13 wherein x is 12.
19. The lithium electrolyte of claim 13 wherein said first lithium salt is selected from the group consisting of $\text{Li}_2\text{B}_{12}\text{F}_{10}\text{H}_2$, and $\text{Li}_2\text{B}_{12}\text{F}_{11}\text{H}$.
20. The lithium electrolyte of any one of claims 13 to 19 wherein said at least one other lithium based salt comprises at least one member selected from the group consisting of LiPF_6 , lithium perchlorate, lithium hexafluoroarsenate, lithium tetrafluoroborate and lithium hexafluoroantimonate.
21. The lithium electrolyte of claim 20 wherein said at least one member comprises LiPF_6 .
22. The electrolyte of any one of claims 13 to 21 wherein said electrolyte has a conductivity of greater than about 4 mS/cm.
23. The electrolyte of claim 15 wherein the solvent comprises vinylene carbonate.
24. A lithium secondary battery comprising:
 a positive electrode comprising at least one oxide,
 a negative electrode,
 an organic solvent comprising at least one carbonate,
 a first lithium salt of the formula:



where x is greater than or equal to 10 and less than or equal to 12 and Z is H, Cl or Br; and
at least one other lithium based salt.

25. The battery of claim 24 wherein the positive electrode comprises a lithium composite oxide.

26. The battery of claim 25 wherein the lithium composite oxide comprises lithium manganese spinel.

27. The battery of claim 24, 25 or 26 wherein the negative electrode comprises carbon.