(54) Title: DISSOCIATING AGENTS, FORMULATIONS AND METHODS PROVIDING ENHANCED SOLUBILITY OF FLUORIDES

(57) Abstract: The present invention provides compositions, formulations and methods providing for the effective dissolution of inorganic fluorides in solvents via incorporation of a dissociating agent component. Dissociating agents of the present invention participate in chemical reactions in solution, such as complex formation, acid-base reactions, and adduct formation reactions, that result in enhancement in the dissolution of inorganic fluorides in a range of solvent environments. Dissociating agents comprising Lewis acids, Lewis bases, anion receptors, cation receptors or combinations thereof are provided that significantly increase the extent of dissolution of a range of inorganic fluorides, particularly inorganic fluorides, such as LiF, that are highly insoluble in many solvents in the absence of the dissociating agents of the present invention.
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).  Published: — without international search report and to be republished upon receipt of that report.
DISASSOCIATING AGENTS, FORMULATIONS AND METHODS PROVIDING ENHANCED SOLUBILITY OF FLUORIDES

CROSS-REFERENCE TO RELATED APPLICATIONS

[001] This application claims the benefit of priority to U.S. Patent Application No. 60/837,174, filed August 11, 2006 and to U.S. Application 11/681,493 filed March 2, 2007, both of which are incorporated herein by reference in their entireties to the extent not inconsistent with the present description.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[002] Not applicable.

BACKGROUND OF INVENTION

[003] Advances in electrochemical storage and conversion devices have significantly expanded the capabilities of these systems in a variety of fields including portable electronics, aerospace technologies, communications and biomedical instrumentation. State of the art electrochemical storage and conversion devices are specifically engineered to have designs and performance attributes supporting specific target application requirements and operating environments. Such advanced electrochemical storage systems include high energy density batteries exhibiting low self discharge rates and high discharge reliability for implanted medical devices; inexpensive light weight rechargeable batteries for portable electronics, and high capacity batteries capable of providing high discharge rates over short time intervals for military and aerospace applications.

[004] Widespread implementation of this diverse suite of advanced electrochemical storage and conversion systems continues to motivate research directed to expanding the functionality of these systems to enable the next generation of high performance device applications. Growth in the demand for high power portable electronic products, for example, has created enormous interest in developing safe, light weight primary and secondary batteries with higher energy densities. The demand for miniaturization in the field of consumer electronics and instrumentation also continues to stimulate research...
into novel design strategies for reducing the sizes, masses and form factors of high performance batteries. Further, developments in the fields of electric vehicles and aerospace engineering has also created a significant need for highly reliable batteries exhibiting high energy densities and high power densities for a range of useful operating environments.

[005] Many advances in electrochemical storage and conversion technology are directly attributable to discovery and integration of new materials for battery components. Lithium battery technology, for example, continues to rapidly develop, at least in part, due to the discovery of novel electrode and electrolyte materials for these systems. From the pioneering identification of intercalation host materials for positive and negative electrodes to the development of high performance non-aqueous electrolytes, the discovery and optimization of novel materials for lithium battery systems have revolutionized their design and performance capabilities. As a result of these advances, lithium based battery technology is currently preferred for certain commercially significant applications including primary and secondary electrochemical cells for portable electronic systems.

[006] Advances in materials strategies and cell designs for lithium battery technology have realized primary and secondary electrochemical cells capable of providing useful device performance including: (i) large energy densities (e.g., ≈150 Wh kg⁻¹), (ii) high cell voltages (e.g. up to about 3.6 V), (iii) substantially constant (e.g., flat) discharge profiles, (iv) long shelf-life (e.g., up to 10 years), (v) good cycling characteristics, and (vi) compatibility with a range of operating temperatures (e.g., -20 to 60 degrees Celsius). As a result of these beneficial characteristics, primary and secondary lithium batteries are widely employed as power sources for many portable electronic devices, such as cellular telephones and portable computers, and for other important device applications in the fields of biomedical engineering, sensing, military communications, and lighting.

[007] Primary lithium battery systems typically utilize a lithium metal negative electrode for generating lithium ions. During discharge, lithium ions are transported from the negative electrode through a liquid phase or solid phase electrolyte and undergo intercalation reaction at a positive electrode comprising an intercalation host material. Dual intercalation lithium ion secondary batteries have also been developed, wherein lithium metal is replaced with a second lithium ion intercalation host material providing the negative electrode. In lithium ion secondary cells, simultaneous lithium ion
insertion and de-insertion reactions allow lithium ions to migrate between the positive and negative intercalation electrodes during discharge and charging cycles. Incorporation of a lithium ion intercalation host material for the negative electrode has the significant advantage of avoiding the use of metallic lithium which is susceptible to safety problems upon recharging attributable to the highly reactive nature and non-epitaxial deposition properties of lithium. Useful intercalation host materials for electrodes in lithium cells include carbonaceous materials (e.g., graphite, cokes, subfluorinated carbons etc.), metal oxides, metal sulfides, metal nitrides, metal selenides and metal phosphides. U.S. Patents Nos. 6,852,446, 6,306,540, 6,489,055, and "Lithium Batteries Science and Technology" edited by Gholam-Abbas Nazri and Gianfranceo Pistoia, Kluer Academic Publishers, 2004, are directed to lithium and lithium ion battery systems which are hereby incorporated by reference in their entireties.

[008] Electrolytes for lithium electrochemical cells are limited to nonaqueous materials given the extremely reactive nature of lithium with water. Several classes of nonaqueous electrolytes have been successfully implemented for lithium electrochemical cells including: (i) solutions of lithium salts dissolved in organic or inorganic solvents, (ii) ionically conducting polymers, (iii) ionic liquids and (iv) fused lithium salts. Nonaqueous electrolyte solutions comprising lithium salts dissolved in polar organic solvents are currently the most widely adopted electrolytes for primary and secondary lithium cells. Useful solvents for these electrolytes include polar solvents that facilitate dissociation of lithium salts into their ionic components. Polar solvents exhibiting useful properties for lithium cell electrolytes include linear and cyclic esters (e.g., methyl formate, ethylene carbonate, dimethyl carbonate and propylene carbonate), linear and cyclic ethers (e.g., dimethoxiethane, and dioxolane) acetonitrile, and γ-butyrolactone. Lithium salts in these electrolyte systems are typically salts comprising lithium and complex anions that have relatively low lattice energies so as to facilitate their dissociation in polar organic solvents. Lithium salts that have been successfully incorporated in electrolytes for these systems include LiClO₄, LiBF₄, LiAsF₆, LiSbF₆, LiAlCl₄ and LiPF₆ provided at concentrations ranging from 0.01 M to 1M.

[009] Successful implementation of polar organic solvent based electrolyte systems for primary or secondary lithium batteries involves a number of considerations involving their chemical and physical properties. First, the electrolyte must be capable of forming a stable passivation layer on the surfaces of the electrode that does not result in a
significant voltage delay at the onset of discharge and is capable of rapid reformation upon high current discharge. Second, the electrolyte must be chemically stable with respect to electrolytic degradation for relevant electrode material and discharge conditions. Third, the electrolyte must exhibit a useful ionic conductivity. State of the art electrolytes for these systems, for example, exhibit ionic conductivities at 25 degrees Celsius greater than or equal to about 0.005 S cm\(^{-1}\). Other physical properties of electrolytes useful for providing enhanced performance in electrochemical cells include thermal stability, low viscosity, low melting point, and high boiling point.

[010] The power output of many state of the art lithium cells is currently limited by the conductivity of electrolytes which determines, in part, the internal resistance of these systems. Accordingly, substantial research is currently directed toward developing electrolytes for primary and secondary lithium cells providing large ionic conductivities for accessing higher device performance. A number of strategies have been developed for increasing the ionic conductivities of polar organic solvent based electrolyte systems for primary or secondary lithium batteries. Many of these strategies involve providing additives to the electrolyte to enhance dissolution of a lithium salt while at the same time maintaining chemical and electrochemical stability under discharge and charging conditions.

[011] Anion receptors are a class of compounds that have been recently developed as additives to increase the ionic conductivity of nonaqueous electrolyte solutions (See, e.g., U.S. Pat. Nos. 6,022,643, 6,120,941, and 6,352,798). Anion receptors enhance the ionic disassociation of lithium salts in low dielectric solvents by incorporating non-hydrogen bonded electrophilic groups that participate in complex formation reactions with anions of the lithium salt provided to the electrolyte. Some anion receptor additives have been demonstrated to enhance the dissolution of specific lithium salts in a manner resulting in an increase in solubility by several orders of magnitude. Anion receptor additives encompass a wide range of compounds including fluorinated boron-based anion receptors, such as boranes, boronates and borates having electron withdrawing ligands, polyammonium compounds, guanidiniums, calixarene compounds, and aza-ether compounds. Successful integration of anion receptors in lithium batteries, however, depends on a number of key factors. First, the anion receptor must be stable with respect to electrolyte decomposition under useful discharge and charging conditions. Second, anion receptors should be capable of releasing (or de-complexing) complexed anions so as not to hinder intercalation reactions at the electrodes. Third,
the anion receptor itself preferably should not participate in intercalation with the intercalation host material, and if it does participate in such intercalation reactions it should not result in mechanically induced degradation of the electrodes.

[012] Additives have also been developed to impart other useful chemical and physical characteristics to polar organic solvent based electrolytes for lithium cells. U.S. Patent No. 6,306,540 (Hiroi et al.), for example, provides additives for improving the stability of nonaqueous electrolytes by minimizing gas formation decomposition reactions involving lithium salts and their dissociation products. This reference discloses electrolyte compositions having a LiF additive provided to a solution of LiPF₆ in a nonaqueous organic solvent. At least partial dissolution of the LiF additive generates fluoride ions in the nonaqueous electrolyte which is reported to suppress gas forming decomposition reactions involving PF₆⁻ anions. The reference notes, however, that very little fluoride ion is generated in the electrolyte due to the inherently low solubility of LiF in the nonaqueous organic solvents evaluated. The reference reports, for example, that due to the poor solubility of LiF in the electrolytic solution it was difficult to dissolve 0.2% by weight of LiF (~ 0.077 M) at room temperature.

[013] As will be clear from the foregoing, there exists a need in the art for nonaqueous electrolytes exhibiting chemical and physical properties useful for electrochemical conversion and storage systems. Nonaqueous electrolytes are needed that exhibit large ionic conductivities and good stability for use in primary and secondary lithium electrochemical cells. Specifically, a need exists for additives for enhancing the solubility and stability of lithium salts in nonaqueous electrolytes for primary and secondary lithium electrochemical cells.

[014] Further, there exists generally a need in the art for methods providing for enhanced solubility and/or dissolution of fluorides, including inorganic fluorides that typically exhibit very low solubilities in many solvent environments. Processes and compositions providing enhanced solubility of fluorides are needed to allow new chemistries to take place in the solution phase, including aqueous and nonaqueous phases. A broad range of potential applications exists for methods and compositions for enhancing the solubility of fluorides including surface fluorination, and organic and inorganic fluorination using soft chemistry methods. One example of a class of such reactions involves surface fluorination for the purpose of enhancing corrosion
resistance. Sources of solution phase fluoride ions are particularly needed that do involve the use of, or formation of, highly corrosive HF in solution and/or gas phases.

[015] Table 1 provides a summary of solubility data for a range of inorganic fluorides in water. As shown in Table 1, many solid state inorganic fluorides (MFₙ), for example CdF₂, CoF₂, FeF₃, MnF₂, NaF, NiF₂, ZnF₂, ZrF₄, AlF₃, BaF₂, CaF₂, CuF₂, FeF₂, InF₃, LiF, MgF₂, PbF₂, SrF₂, UF₄, VF₃·3H₂O, BiF₃, CeF₃, CrF₂/3CrF₃, GaF₃, LaF₃, NdF₃, and ThF₄, are poorly soluble in water and many organic solvents. Other fluorides, such as CsF, RbF, KF, SbF₃ and AgF, readily dissolve into water at the ambient temperatures. When hydrolysis is not a problem, insoluble element fluorides can be prepared as water precipitates by halide metathesis or by the reaction of aqueous hydrofluoric acid with the appropriate element oxide, hydroxide, carbonate or with the element itself. As discussed above, however, the use of hydrofluoric acid has significant drawbacks given its highly corrosive and toxic nature.

[016] Accordingly, the dissolution of insoluble fluorides is currently a great challenge in chemical science and technology. Among other advantages, it can provide fluorine rich solutions for new chemical synthesis through solution reactions or for appropriate physical properties of dissolved fluohnhated species. Specifically, methods and compositions providing enhanced solubility of fluorides may provide an important tool for accessing solution phase fluoride compositions useful for solution phase and surface phase synthetic pathways. As discussed above, methods and compositions providing enhanced solubility of fluorides would also enable new electrolyte solutions for many applications, including electrosynthesis, electrodeposition, and electropassivation, and in electrochemical energy storage and conversion systems such as primary and secondary batteries, electrochemical double-layer capacitors and fuel cells.
Table 1: Summary Of Solubility Data For A Range Of Inorganic Fluorides

<table>
<thead>
<tr>
<th>Fluoride Solubility</th>
<th>Fluoride</th>
<th>Solubility in Water (g/100mL)</th>
<th>Solubility in Water (mL/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VVS-Very Very S.</td>
<td>AgF</td>
<td>172</td>
<td>13.1</td>
</tr>
<tr>
<td>VVS</td>
<td>CaF</td>
<td>675</td>
<td>27.7</td>
</tr>
<tr>
<td>VVS</td>
<td>FeF</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>VVS</td>
<td>RbF</td>
<td>300</td>
<td>28.8</td>
</tr>
<tr>
<td>VVS</td>
<td>SrF3</td>
<td>492</td>
<td>27.5</td>
</tr>
<tr>
<td>VVS</td>
<td>TiF</td>
<td>246</td>
<td>11.5</td>
</tr>
<tr>
<td>VS (Very S.)</td>
<td>BaF2</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>VS</td>
<td>KF</td>
<td>102</td>
<td>17.9</td>
</tr>
<tr>
<td>VS</td>
<td>NH4F</td>
<td>63.3</td>
<td>22.2</td>
</tr>
<tr>
<td>VS</td>
<td>SmF3</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>VS</td>
<td>TaF6</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>VS</td>
<td>WF4</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>LS (Low S.)</td>
<td>CaF2</td>
<td>4.26</td>
<td>0.29</td>
</tr>
<tr>
<td>LS</td>
<td>CaF3</td>
<td>1.4</td>
<td>0.14</td>
</tr>
<tr>
<td>LS</td>
<td>FeF3</td>
<td>0.52</td>
<td>0.02</td>
</tr>
<tr>
<td>LS</td>
<td>MnF2</td>
<td>1.12</td>
<td>0.01</td>
</tr>
<tr>
<td>LS</td>
<td>NaF</td>
<td>1.13</td>
<td>0.09</td>
</tr>
<tr>
<td>LS</td>
<td>NiF2</td>
<td>2.36</td>
<td>0.26</td>
</tr>
<tr>
<td>LS</td>
<td>ZnF2</td>
<td>1.58</td>
<td>0.15</td>
</tr>
<tr>
<td>LS</td>
<td>ZrF4</td>
<td>4.5</td>
<td>0.09</td>
</tr>
</tbody>
</table>
SUMMARY OF THE INVENTION

The present invention provides compositions, formulations and methods providing for the effective dissolution of inorganic fluorides (i.e., an inorganic salt containing one or more fluoride groups) in solvents via incorporation of a dissociating agent component. Dissociating agents of the present invention participate in chemical reactions in solution, such as complex formation, acid-base reactions and adduct formation reactions, that result in enhancement in the dissolution of inorganic fluorides in a range of solvent environments. Dissociating agents comprising Lewis acids, Lewis bases, anion receptors, cation receptors or combinations thereof are provided that significantly increase the extent of dissolution of a range of inorganic fluorides, particularly inorganic fluorides, such as LiF, that are highly insoluble in many solvents in the absence of the dissociating agents of present invention. The compositions, formulations and methods of the present invention are versatile and, thus, are useful for making solutions containing dissolved inorganic fluorides, including aqueous solutions, nonaqueous organic solutions and nonaqueous inorganic solutions. Dissociating
agents, formulations and methods of the present invention are useful for producing
fluoride ion rich solutions having selected chemical, electronic and physical properties. For example, the present invention provides compositions useful for providing solution phase reagents for chemical synthesis applications. Further, the present invention provides compositions useful for in electrochemical conversion and storage systems, electrosynthesis, electrodeposition (electroplating), electropassivation, electro-etching, and electrochemical detection and analysis, such as enhanced F\(^{-}\) ions sensors and specific electrodes applications. The methods and compositions of the present are also useful for sensing systems, including electrochemical sensing systems such as fluoride ion specific electrodes.

[021] The present invention also provides a new class of nonaqueous electrolytes for electrochemical devices, particularly for primary and secondary lithium electrochemical cells. Electrolyte formulations of this embodiment provide for effective dissolution of lithium salts having inherently low solubilities in many nonaqueous organic solvents. This aspect of the present invention provides electrolyte compositions having chemical and physical properties, such as high ionic conductivities, good chemical and electrochemical stability and useful fluoride ion containing solution phase compositions, that are otherwise inaccessible in these systems. Dissociating agents comprising Lewis acids, Lewis bases, anion receptors, cation receptors or combinations thereof are provided in electrolyte formulations of the present invention that significantly increase the extent of dissolution and solubility of lithium salts, such as LiF, in polar nonaqueous organic solvents such as polar carbonates and γ-butyrolactone. The present nonaqueous electrolyte compositions and dissociating agents are chemically stable in contact with metallic lithium and also exhibit high voltage stabilities over a useful range of discharge and charging potentials. Nonaqueous electrolytes of the present invention enable primary and secondary electrochemical cells, including primary and secondary lithium batteries, exhibiting advanced performance characteristics relative to conventional systems, including large discharge rates and power output capabilities.

[022] In an aspect, the present invention provides a solution having a dissociating agent for enhancing dissolution of one or more inorganic fluorides provided to a solvent or combination of solvents. A solution of this aspect of the present invention is a multi-component formulation comprising: (i) one or more solvents; (ii) a dissociating agent provided to the one or more solvents; and (iii) one or more inorganic fluorides dissolved in the one or more solvents having the dissociating agent. Useful dissociating agents in
This aspect of the present invention include Lewis acids, Lewis bases, anion receptors, cation receptors and combinations of these. This aspect of the present invention further provides methods of dissolving an inorganic fluoride in a solvent or combination of solvents comprising the steps of providing a dissociating agent to the solvent(s) and dissolving the inorganic fluoride into the solvent(s) containing the dissociating agent.

[023] Incorporation of a dissociating agent component in solutions of this aspect of the present invention increases the extent of dissolution of the inorganic fluoride in the solvent(s) by participating in chemical reactions in solution, including complex formation, acid-base reactions and adduct formation reactions, that affect the solubility equilibrium conditions in a manner to provide for dissolution of inorganic fluoride(s). In an embodiment, for example, the dissociating agent and inorganic fluoride are provided in amounts sufficient to generate a concentration of inorganic fluoride dissolved in the one or more solvents greater than or equal to 0.15 M. For some applications, the dissociating agent and inorganic fluoride are provided in amounts sufficient to generate a concentration of the inorganic fluoride dissolved in the one or more solvents selected over the range of 0.15 M to 3M, and preferably for particular applications selected over the range of 0.5 M to 1M. Dissociating agents preferred for some applications exhibit a significant enhancement of the dissolution of the inorganic fluoride on a mole-to-mole basis. In an embodiment, for example, the molar ratio of inorganic fluoride dissolved in the one or more solvents to dissociating agent dissolved in the one or more solvents:

[024] \[ \text{Molar Ratio} = \frac{[\text{Inorganic Fluoride}]}{[\text{Dissociating Agent}]} \]

[025] is greater than or equal to 0.1, and preferably for some applications selected over the range of 0.1 to 10.

[026] The present formulations, dissociating agents and methods are applicable to a broad range of inorganic fluorides, particularly those exhibiting low solubilities in pure solvent or solvent combinations. Classes of inorganic fluorides useful in the present solutions, formulations and methods include alkali metal fluorides, alkaline earth metal fluorides, transition metal fluorides and ammonium fluorides. The present invention provides solutions of dissolved fluorides having the formula:
(F1) (F2)

wherein M is a metal selected from the group consisting of Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, Sn Pb, and Sb, and n is the oxidation state of M; and wherein B is a polyatomic cation selected from the group consisting of NH$_4^+$ (i.e., ammonium ion) and N(R-|R$_2$R$_3$R$_4$)$_i^+$ (quaternary ammonium), wherein R-i, R$_2$, R$_3$, and R$_4$ are each selected independently from the group consisting of a H atom, an alkyl group, an acetyl group and an aromatic (phenyl) group, and wherein y is the charge state of B. In an embodiment, for example, a solution of the present invention comprises an inorganic fluoride component selected from the group consisting of CdF$_2$, CoF$_2$, FeF$_3$, MnF$_2$, NaF, NiF$_2$, ZnF$_2$, ZrF$_4$, AlF$_3$, BaF$_2$, CaF$_2$, CuF$_2$, FeF$_2$, InF$_3$, LiF, MgF$_2$, PbF$_2$, SrF$_2$, UF$_4$, VF$_3$-3H$_2$O, BiF$_3$, CeF$_3$, CrF$_2$/CrF$_3$, GaF$_3$, LaF$_3$, NdF$_3$, ThF$_4$, AgF, CsF, RbF, SbF$_3$, TlF, BeF$_2$, KF, NH$_4$F, SnF$_2$, TaF$_5$, VF$_4$, BF$_3$, BrF, BrF$_3$, BrF$_5$, CoF$_3$, GeF$_2$/GeF$_4$, Hg$_2$F$_2$/HgF$_2$, NbF$_5$, OsF$_6$, PF$_3$/PF$_5$, RhF$_3$, SF$_4$/SF$_6$, SnF$_4$, TeF$_4$, UF$_6$, VF$_5$, and WF$_6$. In an embodiment, for example, a solution of the present invention comprises an inorganic fluoride component selected from the group consisting of: CdF$_2$, CoF$_2$, FeF$_3$, MnF$_2$, NaF, NiF$_2$, ZnF$_2$, ZrF$_4$, AlF$_3$, BaF$_2$, CaF$_2$, CuF$_2$, FeF$_2$, InF$_3$, LiF, MgF$_2$, PbF$_2$, SrF$_2$, UF$_4$, VF$_3$-3H$_2$O, BiF$_3$, CeF$_3$, CrF$_2$/CrF$_3$, GaF$_3$, LaF$_3$, NdF$_3$, and ThF$_4$.

In another aspect, the present invention provides a solution containing one or more dissociating agents having chemical properties specifically tailored for dissolving a LiF salt in a solvent or combination of solvents. In an embodiment, a solution of this aspect comprises: (i) one or more solvents; (ii) a dissociating agent provided to the one or more solvents, the dissociating agent comprising one or more compounds selected from the group consisting of a Lewis acid, a Lewis base; and a crown ether; and (iii) LiF dissolved in the one or more solvents having the dissociating agent, wherein the concentration of LiF dissolved in said one or more solvents is greater than or equal to 0.15 M. Specific embodiments of this aspect of the present invention provide for the dissolution of LiF so as to generate a concentration of dissolved LiF in the solvent(s) selected over the range of 0.15 M to 3M, preferably for some applications selected over the range of 0.5 M to 1M. This aspect of the present invention further provides methods of dissolving LiF in a solvent or combination of solvents comprising the steps of providing a dissociating agent comprising a Lewis acid, a Lewis base, a crown ether or
combination of these to the solvent(s) and dissolving the LiF into the solvent(s) 
containing the dissociating agent.

[031] Selection of the composition and concentration of the dissociating agent 
determines, at least in part, the composition, chemical properties and/or physical 
properties of the solutions and formulations of this aspect of the present invention. For 
example, the composition and concentration of dissociating agents in solutions and 
methods of the present invention are important parameters for achieving a desired 
extent of dissolution of an inorganic fluoride such as LiF. Useful dissociating agents in 
some embodiments include Lewis acids, Lewis bases, anion receptors, cation receptors, 
complexing agents, adduct formation agents and combinations of these compounds. In 
some embodiments, the dissociating agent is provided in the one or more solvents at a 
concentration selected over the range of 0.01 M to 10 M, and preferably for some 
applications selected over the range of 0.1 M to 5 M, and more preferably for some 
applications selected over the range of 0.5 M to 1.5 M. Other properties of dissociating 
agents useful for some embodiments include chemical stability (for example in the 
presence of lithium metal), electrochemical stability under discharge or charge 
conditions in an electrochemical cell, low viscosity impact when provided to solution, 
thermal stability and an enhancement in ionic conductivity when provided to solution. In 
some embodiments for lithium battery applications, dissociating reagents do not 
significantly undergo intercalation reactions at the electrodes.

[032] Lewis acids and Lewis bases are a particularly useful class of dissociating 
agents in the present solutions, formulations and methods. As used herein, the term 
"Lewis acid" refers to a substance which, in solution, is able to generate a cation or 
combine with an anion, and/or a molecule which can accept a pair of electrons and form 
a coordinate covalent bond, and the term "Lewis base" refers to a substance which, in 
solution, is able to generate an anion or combine with a cation, and/or a molecule or ion 
that can form a coordinate covalent bond by donating a pair of electrons. Useful Lewis 
base or Lewis acid dissociating agents provided to solutions of the present invention 
include, but are not limited to, inorganic fluorides, inorganic chlorides, inorganic 
carbonates, and inorganic oxides. In an embodiment, for example, the dissociating 
agent is one or more Lewis base selected from the group consisting of AlCl₄⁻, ClO₄⁻, 
SnCl₆²⁻, BF₄⁻, PF₆⁻, and AsF₆⁻. In an embodiment, for example, the dissociating agent is 
one or more Lewis acid selected from the group consisting of BF₃, PF₅, SbF₅, AsF₅, 
AlCl₃, SnCl₄, FeCl₃, NbCl₅, TiCl₄, and ZnCl₂.
In an embodiment, a dissociating agent comprising one or more Lewis acid
and/or Lewis base is provided at a concentration in the solution selected over the range of 0.1 M to 10 M, a preferably for some applications selected over the range of 0.5 M to
3 M. Lewis acids and bases may be provided to solutions of the present invention via
providing a precursor compound to the solution. In the context of the description the
term "precursor compound" refers to a substance that generates a Lewis acid, Lewis
base or both in solution when provided to a solvent or combination of solvents. In an
embodiment, for example, the dissociating agent is provided by dissolving a precursor
compound in the one or more solvents to generate a Lewis base, a Lewis acid or a
combination of a Lewis acid and a Lewis base, wherein the precursor compound
comprises an alkali metal salt, alkaline earth metal salt; a transition metal salt, a rare
earth metal salt, or an ammonium salt having the formula:

AX:

(F3);

wherein A is selected from the group consisting of a metal, a metal cation and
an ammonium group; and wherein X is selected from the group consisting of a
fluorinated anion, a perchlorate group, an imide group, a carbide group, a carbonate
group, an oxide group and a chloride group. Lithium salts are precursors useful for
generating Lewis acids and/or Lewis bases in some solutions and methods of the
present invention. Precursor compounds useful in the present solutions, formulations
and methods include, but are not limited to, LiPF₆, LiBF₄, LiAsF₆, LiClO₄, LiSnCl₅,
LiAlCl₄, LiFeCl₄, LiNbCl₆, LiTiCl₅, LiZnCl₃, NaPF₆, NaBF₄, NaAsF₆, NaClO₄, NaSnCl₅,
NaAlCl₄, NaFeCl₄, NaNbCl₆, NaTiCl₅, NaZnCl₃, KPF₆, KBF₄, KAsF₆, KCIO₄, KSnCl₅,
KAICl₄, KFeCl₄, KNbCl₆, KTiCl₅, KZnCl₃, NH₄PF₆, NH₄BF₄, NH₄AsF₆, NH₄ClO₄,
NH₄SnCl₅, NH₄AlCl₄, NH₄FeCl₄, NH₄NbCl₆, NH₄TiCl₅, NH₄ZnCl₃, N(CH₃)₄ClO₄,
N(CH₃)₄SnCl₅, N(CH₃)₄AlCl₄, N(CH₃)₄FeCl₄, N(CH₃)₄NbCl₆, N(CH₃)₄TiCl₅, N(CH₃)₄ZnCl₃,
N(C₂H₅)₄ClO₄, N(C₂H₅)₄SnCl₅, N(C₂H₅)₄AlCl₄, N(C₂H₅)₄FeCl₄, N(C₂H₅)₄NbCl₆, N(C₂H₅)₄TiCl₅, and N(C₂H₅)₄ZnCl₃.

Cation receptors are another particularly useful class of dissociating agents in
the present solutions, formulations and methods. As used herein, the term "cation
receptor" refers to a molecule or ion which can bind or otherwise take up a cation in
solution. Some solutions of the present invention comprise one or more cation
receptors selected from the group consisting of a crown ether, a Lewis base, and a
cation complexing agent. In an embodiment, a dissociating agent comprising one or more cation receptor is provided at a concentration in the solution selected over the range of 0.1 M to 10M, a preferably for some applications selected over the range of 0.3M to 5M.

[038] Crown ethers are a class of cation receptor exhibiting chemical and physical properties beneficial for enhancing the dissolution of inorganic fluorides, including LiF. These compounds are useful for complexing with metal ions in solution. Crown ether cation receptors useful in the present invention include, but are not limited to, Benzo-15-crown-5, 15-Crown-5, 18-Crown-6, Cyclohexyl-15-crown-5, Dibenzo-18-crown-6, Dicyclohexyl-δ-crown-6, Di-t-butyldibenzo-18-crown-6, 4,4r(5r)-Di-t-tert-butyl dibenzo-24-crown-8, 4-Aminobenzo-15-Crown-5, Benzo-15-Crown-5, Benzo-1,8-crown-6, 4-tert-Butylbenzo-15-crown-5, 4-tert-Butylcyclohexan-1-5-crown-5, 18-Crown-6, Cyclohexano-15-crown-5, Di-2,3-naphtho-30-crown-1 0, 4,4r(5r)-Di-t-tert-butyl dibenzo-18-crown-6, 4'-r(5')-Di-t-tert-butyl dicyclohexano-18-crown-6, 4,4r(5')-Di-t-tert-butyl dicyclohexano-24-crown-8, 4,10-Diaza-15-crown-5, Dibenzo-18-crown-6, Dibenzo-21-crown-7, Dibenzo-24-crown-8, Dibenzo-30-crown-1 0, Dicyclohexano-18-crown-6, Dicyclohexano-21-crown-7, Dicyclohexano-24-crown-8, 2,6-Diketo-18-crown-6, 2,3-Naphtho-15-crown-5, 4'-Nitrobenzo-15-crown-5, Tetraaza-12-crown-4 tetrahydrochloride, Tetraaza-12-crown-4 tetrahydrogen sulfate, 1,4,10,13-Tetraoxa-7,16-diazacyclooctadecane, 12-crown-4, 15-crown-5, and 21-crown-7. In an embodiment, a crown ether dissociating agent is provided to the solvent at a concentration in the solution selected over the range of 0.1 M to 10M, a preferably for some applications selected over the range of 0.5M to 3M.

[039] Anion receptors are another particularly useful class of dissociating agents in the present solutions, formulations and methods. As used herein, the term anion receptor refers to a molecule or ion which can bind or otherwise take up an anion in solution. Anion receptors useful in the present solutions, formulations and methods include, but are not limited to fluoro nated and semifluorinated borate compounds, fluorinated and semifluorinated boronate compounds, fluorinated and semifluorinated boranes, phenyl boron compounds, aza-ether boron compounds, Lewis acids, cyclic polyammonium compounds, guanidinium compounds, calixarene compounds, aza-ether compounds, quaternary ammonium compounds, amines, imidazolinium based receptors, mercury metallacycle compounds, silicon containing cages, and macrocycles. In an embodiment, a dissociating agent comprising one or more anion
receptor is provided at a concentration in the solution selected over the range of 0.1 M to 10M, a preferably for some applications selected over the range of 0.5M to 3M.


[041] Solutions, formulations, and methods of the present invention are compatible with a range of solvents, including water, nonaqueous organic solvents and nonaqueous inorganic solvents. In some embodiments useful for providing electrolytes for electrochemical cells, such as lithium electrochemical cells, the solvent(s) comprises one or more polar nonaqueous solvents, such as linear and cyclic esters, linear and cyclic ethers and polar carbonates. Electrolytes of the present invention may comprise a single nonaqueous solvent or a combination of nonaqueous solvents provided in relative proportions useful for a given electrochemical device or application. The composition of nonaqueous solvents in some embodiments of the present invention is
selected to provide electrolyte formulations having desired physical, electronic and chemical properties, such as ionic conductivities, viscosities, melting points, freezing points and stability with respect to electrolytic decomposition and/or reaction with lithium metal. Useful solvents in the present invention include, but are not limited to, one or more of γ-butyrolactone, propylene carbonate, dimethyl carbonate, ethylene carbonate, acetonitrile, 1,2, -dimethoxy ethane, N,N-dimethyl formamide, dimethyl sulfoxide, 1,3-diolane, methyl formate, nitromethane, phosphoroxichloride, thionylchloride, sulfurylchloride, diethyl ether, diethoxy ethane, 1,3-dioxolane, tetrahydrofuran, 2-methyl-THF, diethyl carbonate, ethyl methyl carbonate, methylacetate and 1,3-tratahydrofurane.

[042] In another aspect, solutions and formulations of the present invention provide electrolyte compositions useful for electrochemical storage and conversion applications. In these embodiments, inorganic fluoride, dissociating agent and solvent components are selected to provide solution properties useful for a target electrochemical device application. In some embodiments of this aspect, for example, the composition of solution components of an electrolyte are selected to establish useful chemical and physical properties, such as large ionic conductivities, and enhanced solubility for solutions containing inorganic fluorides that are relatively insoluble in pure nonaqueous organic solvents. The present invention includes electrolytes, including nonaqueous electrolytes, exhibiting a high degree of chemical and electrochemical stability. In an embodiment, for example, an electrolyte of the present invention has a high voltage stability window over 5V vs. Li⁺/Li. In another embodiment, electrolyte formulations of the present invention are stable with respect to contact with Li metal under discharge or charging conditions. A electrolyte of the present invention has an ionic conductivity at 25 degrees Celsius greater than or equal to 10⁻⁴ S cm⁻¹, preferably for some applications greater than or equal to 10⁻³ S cm⁻¹, and more preferably for some applications greater than or equal to 5 x 10⁻³ S cm⁻¹. A nonaqueous electrolyte of the present invention has a viscosity at 25 degrees Celsius less than or equal to 5 cP, more preferably for some applications less than or equal to 3 cP.

[043] Although the present invention encompasses electrolytes comprising a broad range of inorganic fluorides, a preferred class of electrolytes for lithium electrochemical cells comprises LiF and a dissociating agent provided in one or more nonaqueous organic solvents. In this aspect, the present invention provides electrolyte formulations having an inorganic fluoride component comprising LiF salt and a dissociating agent
capable of significantly enhancing the dissociation and solubility of LiF in organic solvent(s). Embodiments of this aspect are particularly useful for electrolytes of electrochemical cells because F is the most electronegative element and Li is the most electropositive element. Therefore, electrolytes of the present invention comprising LiF are particularly attractive for providing electrochemical cells having enhanced cell voltages and specific capacities relative to conventional lithium electrochemical cells. Dissociating agents of the present invention are capable of increasing the conductivity of LiF in a selected nonaqueous organic solvent or combination of nonaqueous organic solvents, at 25°C, to a value equal to or greater than 10^{-4} \text{ S cm}^{-1}, preferably equal to or greater 5 \times 10^{-4} \text{ S cm}^{-1}, and more preferably equal to or greater 10^{-3} \text{ S cm}^{-1}. In an embodiment, dissociating agents of the present invention increase the solubility of LiF in a selected nonaqueous organic solvent (or combination of solvents) from a low value (e.g., on the order of micromolar) to 0.1 \text{ M} or greater, preferably 0.5 \text{ M} or greater, and preferably 1 \text{ M} or greater. In an embodiment, LiF solubility at a temperature of about 25°C in an electrolyte of the present invention is increased by addition of a dissociating agent to a value greater than about 0.1 \text{ M}, including between about 0.1 \text{ M} to 5 \text{ M}, and between about 1 \text{ M} to 2 \text{ M}.

The present invention includes electrochemical devices comprising the present electrolytes, such as nonaqueous electrolytes, including, but not limited to, primary electrochemical cells, secondary electrochemical cells, capacitors, supercapacitors and fuel cells. In addition, the solutions, dissociating agents and methods of the present invention are also useful for sensing systems, including electrochemical sensing systems. Solutions and dissociating agents of the present invention, for example, are useful for reducing interference and enhancing the selectivity of fluoride ion specific electrodes. In an embodiment, the present invention provides an electrochemical cell comprising: (i) a positive electrode; (ii) a negative electrode; and (iii) an electrolyte of the present invention provided between the positive electrode and the negative electrode. As will be appreciated by those having skill in the art of electrochemistry, electrolytes useful in electrochemical devices of the present invention include those provided throughout the present description. In an embodiment, an electrolyte of an electrochemical device of the present invention comprises (i) one or more solvents; (ii) a dissociating agent provided to the one or more solvents; and (iii) an inorganic fluoride dissolved in the one or more solvents having the dissociating agent; wherein the dissociating agent and inorganic fluoride are provided in amounts sufficient to generate...
a concentration of inorganic fluoride dissolved in the one or more solvents greater than or equal to 0.15 M.

[045] As will be appreciate by those of skill in the art a wide range of electrode materials and configurations can be used in electrochemical devices of the present invention, including metallic and semiconducting materials. Use of nanostructured and/or intercalating electrodes is useful for some applications. In an embodiment, the negative electrode comprises lithium metal, a carbonaceous material, such as graphite, coke, multiwalled carbon nanotubes, multi-layered carbon nanofibers, multi-layered carbon nanoparticles, carbon nanowhiskers and carbon nanorods having lithium storage capability or a lithium metal alloy. In an embodiment, the positive electrode comprises a carbonaceous material, such as graphite, coke, multiwalled carbon nanotubes, multi-layered carbon nanofibers, multi-layered carbon nanoparticles, carbon nanowhiskers and carbon nanorods having fluoride ion storage capability. In an embodiment, positive electrode comprises a carbonaceous material comprises a subfluorinated carbonaceous material having an average stoichiometry $\text{CF}_x$, wherein x is the average atomic ratio of fluorine atoms to carbon atoms and is selected from the range of about 0.3 to about 1.0; the subfluorinated carbonaceous material being a multiphase material having an unfluorinated carbon component. In an embodiment, positive electrode comprises a fluorinated element such a transition metal or a rare earth metal having reversible fluoride ion storage capability.

[046] Solutions, dissociating agents and methods of the present invention providing enhanced solubility of fluorides have significant applications in addition to their use as electrolytes in electrochemical devices and systems. The compositions and methods of the present invention are beneficial for accessing solution phase compositions and properties (e.g., chemical, physical and/or electrochemical) useful for enabling a broad class of surface phase and solution synthetic pathways and other processes. Fluoride containing solutions of the present invention, for example, may provide solution phase reagents for important synthetic chemistries, including organic and inorganic fluorination, for example by soft chemistry methods, and surface fluorination reactions. Fluoride containing solutions of the present invention may also be useful for accessing solution properties (e.g., ionic conductivities, ionic strength, etc.) critical for accessing important solution phase processes, including electrosynthesis, electrodeposition, and electropassivation.
[047] In another aspect, the present invention provides a method for dissolving an inorganic fluoride in one or more solvents comprising the steps of: (i) providing the one or more solvents; (ii) providing a dissociating agent to the one or more solvents; and (iii) dissolving the inorganic fluoride in the one or more solvents having the dissociating agent; wherein the dissociating agent and inorganic fluoride are provided in amounts sufficient to generate a concentration of inorganic fluoride dissolved in the one or more solvents greater than or equal to 0.15 M, thereby dissolving the inorganic fluoride into the one or more solvents.

[048] In another aspect, the present invention provides a method for dissolving LiF in one or more solvents, comprising the steps of: (i) providing the one or more solvents; (ii) providing a dissociating agent to the one or more solvents, the dissociating agent comprising one or more compound selected from the group consisting of a Lewis acid, a Lewis base; and a crown ether; and dissolving LiF in the one or more solvents having the dissociating agent, wherein the concentration of LiF dissolved in said one or more solvents is greater than or equal to 0.15 M, and optionally greater than or equal to 0.5M.

[049] In another aspect, the present invention provides a method of making an electrolyte for an electrochemical device, the method comprising the steps of: (i) providing one or more solvents; (ii) providing a dissociating agent to the one or more solvents; and (iii) dissolving an inorganic fluoride in the one or more solvents having the dissociating agent; wherein the dissociating agent and inorganic fluoride are provided in amounts sufficient to generate a concentration of inorganic fluoride dissolved in the one or more solvents greater than or equal to 0.15 M, thereby making the electrolyte for the electrochemical device.

[050] In another aspect, the present invention provides a method of making an electrolyte for an electrochemical device, the method comprising the steps of: (i) providing one or more solvents; (ii) providing a dissociating agent to the one or more solvents, the dissociating agent comprising one or more compounds selected from the group consisting of a Lewis acid, a Lewis base; and a crown ether; and (iii) dissolving LiF in the one or more solvents having the dissociating agent, thereby making the electrolyte for the electrochemical device.

[051] In another aspect, the present invention provides a solution having LiF dissolved in one or more solvents, said solution comprising: (i) said one or more
solvents; and (ii) LiF dissolved in said one or more solvents; wherein the concentration of LiF dissolved in said one or more solvents is greater than or equal to 0.15 M.

[052] Without wishing to be bound by any particular theory, there can be discussion herein of beliefs or understandings of underlying principles relating to the invention. It is recognized that regardless of the ultimate correctness of any mechanistic explanation or hypothesis, an embodiment of the invention can nonetheless be operative and useful.

BRIEF DESCRIPTION OF THE DRAWINGS

[053] Figure 1. Comparative (normalized) discharge profile of Li/electrolyte/graphite-based electrode cells with LiF-containing and LiF-free electrolytes consisting of 1M LiPF$_6$ solution in EC-DMC.

[054] Figure 2. Shows the cyclic voltammogram obtained with the LiF containing electrolyte cell between 2.1 and 4.8V under 15mV/mn sweeping rate. It shows oxidation and reduction peaks corresponding to negatively charged species intercalation and de-intercalation into graphite.

[055] Figure 3. Comparative (normalized) discharge profile of Li/electrolyte/graphite fluoride (CF$_{0.53}$)-based electrode cells with LiF-containing and LiF-free electrolytes consisting of 1M LiPF$_6$ solution in EC-DMC.

[056] Figure 4 depicts the current provided by the cell containing LiPF$_6$ during a charge/discharge cycle.

[057] Figure 5 depicts the current provided by the cell containing LiF and 12-crown-4 during a charge/discharge cycle.

DETAILED DESCRIPTION OF THE INVENTION

[058] Referring to the drawings, like numerals indicate like elements and the same number appearing in more than one drawing refers to the same element. In general the terms and phrases used herein have their art-recognized meaning, which can be found by reference to standard texts, journal references and contexts known to those skilled in the art. The following definitions are provided to clarify their specific use in the context of the invention.
"Standard electrode potential" (E°) refers to the electrode potential when concentrations of solutes are 1M, the gas pressures are 1 atm and the temperature is 25 degrees Celsius. As used herein standard electrode potentials are measured relative to a standard hydrogen electrode.

"Intercalation" refers to the process wherein an ion inserts into a host material to generate an intercalation compound via a host/guest solid state redox reaction involving electrochemical charge transfer processes coupled with insertion of mobile guest ions, such as fluoride ions. Major structural features of the host material are preserved after insertion of the guest ions via intercalation. In some host materials, intercalation refers to a process wherein guest ions are taken up with interlayer gaps (e.g., galleries) of a layered host material. Examples of intercalation compounds include fluoride ion intercalation compounds wherein fluoride ions are inserted into a host material, such as a layered fluoride host material or carbon host material. Host materials useful for forming intercalation compounds for electrodes of the present invention include, but are not limited to, CFₓ, FeFx, MnFx, NiFx, CoFx, LiCₓ, LiₓSi, and LiₓGe.

The term "electrochemical cell" refers to devices and/or device components that convert chemical energy into electrical energy or electrical energy into chemical energy. Electrochemical cells have two or more electrodes (e.g., positive and negative electrodes) and an electrolyte, wherein electrode reactions occurring at the electrode surfaces result in charge transfer processes. Electrochemical cells include, but are not limited to, primary batteries, secondary batteries and electrolysis systems. General cell and/or battery construction is known in the art, see e.g., U.S. Pat. Nos. 6,489,055, 4,052,539, 6,306,540, Seel and Dahn J. Electrochem. Soc. 147(3) 892-898 (2000).

The term "capacity" is a characteristic of an electrochemical cell that refers to the total amount of electrical charge an electrochemical cell, such as a battery, is able to hold. Capacity is typically expressed in units of ampere-hours. The term "specific capacity" refers to the capacity output of an electrochemical cell, such as a battery, per unit weight. Specific capacity is typically expressed in units of ampere-hours kg⁻¹.

The term "discharge rate" refers to the current at which an electrochemical cell is discharged. Discharge current can be expressed in units of ampere-hours. Alternatively, discharge current can be normalized to the rated capacity of the electrochemical cell, and expressed as C/(X t), wherein C is the capacity of the
electrochemical cell, \( X \) is a variable and \( t \) is a specified unit of time, as used herein, equal to 1 hour.

[064] "Current density" refers to the current flowing per unit electrode area.

[065] The term "open circuit voltage" refers to the difference in potential between terminals (i.e. electrodes) of an electrochemical cell when the circuit is open (i.e. no load conditions). Under certain conditions the open circuit voltage can be used to estimate the composition of an electrochemical cell. The present methods and system utilize measurements of open circuit voltage for thermochemically stabilized conditions of an electrochemical cell to determine thermodynamic parameters, materials properties and electrochemical properties of electrodes, electrochemical cells and electrochemical systems.

[066] The expression "state of charge" is a characteristic of an electrochemical cell or component thereof (e.g. electrode - cathode and/or anode) referring to its available capacity, such as a battery, expressed as a percentage of its rated capacity.

[067] Electrode refers to an electrical conductor where ions and electrons are exchanged with electrolyte and an outer circuit. "Positive electrode" and "cathode" are used synonymously in the present description and refer to the electrode having the higher electrode potential in an electrochemical cell (i.e. higher than the negative electrode). "Negative electrode" and "anode" are used synonymously in the present description and refer to the electrode having the lower electrode potential in an electrochemical cell (i.e. lower than the positive electrode). Cathodic reduction refers to a gain of electron(s) of a chemical species, and anodic oxidation refers to the loss of electron(s) of a chemical species. Positive electrodes and negative electrodes of the present electrochemical cell may further comprise a conductive diluent, such as acetylene black, carbon black, powdered graphite, coke, carbon fiber, and metallic powder, and/or may further comprises a binder, such as a polymer binder. Useful binders for positive electrodes in some embodiments comprise a fluoropolymer such as polyvinylidene fluoride (PVDF). Positive and negative electrodes of the present invention may be provided in a range of useful configurations and form factors as known in the art of electrochemistry and battery science, including thin electrode designs, such as thin film electrode configurations. Electrodes are manufactured as disclosed herein and as known in the art, including as disclosed in, for example, U.S. Pat. Nos. 4,052,539, 6,306,540, 6,852,446. For some embodiments, the electrode is typically
fabricated by depositing a slurry of the electrode material, an electrically conductive inert material, the binder, and a liquid carrier on the electrode current collector, and then evaporating the carrier to leave a coherent mass in electrical contact with the current collector.

"Electrode potential" refers to a voltage, usually measured against a reference electrode, due to the presence within or in contact with the electrode of chemical species at different oxidation (valence) states.

"Electrolyte" refers to an ionic conductor which can be in the solid state, the liquid state (most common) or more rarely a gas (e.g., plasma). In the context of an electrochemical cell, the electrolyte provides ionic conductivity between two or more electrodes of an electrochemical cell.

"Cation" refers to a positively charged ion, and "anion" refers to a negatively charged ion.

"Lewis acid" refers to a substance which, in solution, is able to generate a cation or combine with an anion, and/or a molecule which can accept a pair of electrons and form a coordinate covalent bond. Useful classes of Lewis acids include, but are not limited to, inorganic fluorides, inorganic chlorides, inorganic carbonates, and inorganic oxides. Examples of inorganic fluoride Lewis acids are BF$_3$, PF$_5$, SbF$_5$, and AsF$_5$. Examples of inorganic chloride Lewis acids are AlCl$_3$, SnCl$_4$, FeCl$_3$, NbCl$_5$, TiCl$_4$, and ZnCl$_2$.

"Lewis base" refers to a substance which, in solution, is able to generate an anion or combine with a cation, and/or a molecule or ion that can form a coordinate covalent bond by donating a pair of electrons. Useful classes of Lewis bases include, but are not limited to, inorganic fluorides, inorganic chlorides, inorganic carbonates, and inorganic oxides. Examples of inorganic chloride Lewis bases are AlCl$_4^-$, ClO$_4^-$, and SnCl$_6^{2-}$. Examples of inorganic fluoride Lewis bases are BF$_4^-$, PF$_6^-$, and AsF$_6^-$.

"Lewis acid precursor" or "precursor" and "Lewis base precursor" or "precursor" refers to a substance which is able to generate Lewis acids and/or Lewis bases when introduced into a solvent and/or solution. Examples of Lewis acid/base precursors are LiPF$_6$, LiBF$_4$, LiAsF$_6$, LiClO$_4$, LiSnCl$_5$, LiAlCl$_4$, LiFeCl$_4$, LiNbCl$_6$, LiTiCl$_5$, LiZnCl$_3$, NaPF$_6$, NaBF$_4$, NaAsF$_6$, NaClO$_4$, NaSnCl$_5$, NaAlCl$_4$, NaFeCl$_4$, NaNbCl$_6$, NaTiCl$_5$, NaNZnCl$_3$, KPF$_6$, KBF$_4$, KAsF$_6$, KClO$_4$, KSnCl$_5$, KAlCl$_4$, KFeCl$_4$, KNbCl$_6$, KTiCl$_5$, KZnCl$_3$, NH$_4$PF$_6$. 

Page 23 of 44
NH₄BF₄, NH₄AsF₆, NH₄ClO₄, NH₄SnCl₅, NH₄AlCl₄, NH₄FeCl₄, NH₄NbCl₆, NH₄TiCl₅, and NH₄ZnCl₂ and others.

"Cation receptor" refers to a molecule or ion which can bind or otherwise take up a cation. Useful classes of cation receptors include, but are not limited to, crown ethers, Lewis bases, and other cation complexing agents. Examples of crown ether cation receptors include, but are not limited to, Benzo-1 5-crown-5, 15-Crown-5, 18-Crown-6, Cyclohexyl-1 5-crown-5, Dibenzo-1 8-crown-6, Dicyclohexyl-1 5-crown-6, Di-t-butyldibenzo-1 8-crown-6, 4,4r(5r)-Di-t-butyldibenzo-24-crown-8, 4-Aminobenzo-1 5-Crown-5, Benzo-1 5-Crown-5, Benzo-1 8-crown-6, 4-tert-Butylbenzo-1 5-crown-5, 4-tert-Butylcyclohexano-1 5-crown-5, 18-Crown-6, Cyclohexano-1 5-crown-5, Di-2,3-naphtho-30-crown-1 0, 4,4'(5')-Di-t-butyldibenzo1 8-crown-6, 4'-(5')-Di-tert-butyldicyclohexano-18-crown-6, 4,4'(5')-Di-tert-butyldicyclohexano-24-crown-8, 4,1 0-Diaza-1 5-crown-5, Dibenzo-1 8-crown-6, Dibenzo-21 -crown-7, Dibenzo-24-crown-8, Dibenzo-30-crown-1 0, Dicyclohexano-1 8-crown-6, Dicyclohexano-21 -crown-7,Dicyclohexano-24-crown-8, 2,6-Diketo-1 8-crown-6, 2,3-Naphtho-1 5-crown-5, 4'-Nitrobenzo-1 5-crown-5, Tetraaza-12-crown-4 tetrahydrochloride, Tetraaza-12-crown-4 tetrahydrogen sulfate, 1,4,1 0,1 3-Tetraoxa-7,1 6-diazacyclooctadecane, 12-crown-4, 15-crown-5, and 21-crown-7.

"Dissociating agent" and "dissociation agent" are used synonymously and refer to a compound added to a solution, solvent, and/or electrolyte to increase the solubility and/or dissolution of a salt. Dissociating agents of the present invention are useful for increasing the dissolution of inorganic fluorides, particularly inorganic fluorides, generally regarded to be relatively insoluble, such as LiF.

The present invention provides methods for generating solutions containing large concentrations of dissolved fluoride salts which are generally regarded as insoluble. In another aspect, the present invention provides solutions, solvents, and electrolytes containing large concentrations of dissolved fluoride salts which are generally regarded as insoluble. In an embodiment, compounds are provided to the solutions, solvents, and electrolytes which facilitate dissolution of the fluoride salts. These compounds can be regarded as dissolution, dissolving, dissociating, or dissociation agents, since they provide a means for dissolving normally insoluble compounds. In an embodiment, the fluoride salts are present as solutes in solution at concentrations much larger than that which occurs at a natural equilibrium in a solution that does not contain the dissociating agents. In an embodiment, the fluoride salts are a minor solute component. In another embodiment, the fluoride salts are the most abundant solute present in the solution, solvent, or electrolyte.
The present invention provides additives and methods for dissolving element fluorides \((MF_n)\) such as LiF. In an embodiment, for example, organic solutions of lithium salts \((LiX)\), such as \(LiPF_6\), \(LiBF_4\), \(LiAsF_6\) and \(LiClO_4\), in carbonate or gamma butyrolactone \((\gamma\text{-BL})\) based liquid solvents dissolve a significant amount LiF, whereas, the same solvents without the presence of the LiX salt do not appreciably dissolve LiF. The present methods apply to a variety of other insoluble fluorides \((MF_n)\) thus providing a large range of 'complex-type' solutions of \(MF_n + AX\), \(A=\text{alkali metal or NH}_4\), and \(X=\text{fluorinated anion, perchlorate, imide, carbide}\). Compositions of the present invention also provide a new family of electrolytes for lithium batteries applications containing LiF dissolved at significant solubilities in nonaqueous organic solvents.

**Example 1: Electrolytes and Dissociating Agents for Electrochemical Cells**

To demonstrate the chemical properties and utility of the present additives, compositions, formulations and methods, electrolytes of the present invention were prepared and integrated into lithium electrochemical cells. The electrolytes evaluated comprise LiF and an appropriate dissociating agent dissolved in a selected nonaqueous organic solvent or combination of nonaqueous organic solvents. The electronic performance of the electrochemical cells was evaluated to demonstrate the beneficial chemical and physical properties of electrolytes of the present invention.

1. **Preparation of the mother solutions**: 1 M solutions of \(LiPF_6\) in EC-DMC and of \(LiBF_4\) in \(\gamma\text{-BL}\) and of \(LiAsF_6\) and of \(LiClO_4\) in PC were prepared in a dry box filled with argon. \((EC=\text{ethylene carbonate, DMC=dimethyl carbonate and PC=propylene carbonate})\). These solutions are called 'mother solutions' throughout this description.

2. **Dissolving LiF in mother solutions**: In a dry box filled with argon, a sample of 5 milliliters \((5\times 10^{-3} \text{ mole of LiX})\) was taken from each of the above described mother solutions and 65 milligrams \((2.5\times 10^{-3} \text{ mole})\) of LiF was added to it. The solution was stirred magnetically until full dissolution of LiF occurred, i.e., the solution becomes clear. The molar ratio LiF/LiX in these solutions is 0.5, with an absolute LiF concentration of 0.5 M.

3. **Electrochemical tests**: Coin cells were created in a dry box, consisting of a metallic lithium disc (negative pole), a polypropylene microporous separator wet with 'electrolyte', and a composite electrode (positive pole). Two types of composite cathode electrodes were used: a graphite based electrode and a graphite fluoride based
electrode. The 'electrolyte' is either the LiPF$_6$ in EC-DMC mother solution or the LiF dissolved in LiPF$_6$ in EC-DMC mother solution.

[083] 3a) graphite based cells: The cells were first discharged under a constant current of 10 mA/g-graphite to 250 mV. The 250 mV vs. Li$^+/Li$ Potential was chosen between that of the first passivation (solid electrolyte interphase: SEI formation usually at >500 mV vs. Li$^+/Li$) and that of the lithium intercalation (usually at <200 mV vs. Li7U). The cells were then charged to 5V vs. Li$^+/Li$ under the same 10 mA/g-graphite rate. A constant 5V was then applied for several hours to further charge. The cells were then allowed to rest for several hours and were then discharged to 3V under the same 10 mA/g-graphite rate. Following this, the cells were cycled between 3V and 5V several times under the same procedure described above.

[084] Linear voltammetry under a 15mV/min sweeping rate was also performed on the cell with LiF containing electrolyte in the 2.1 -4.8V voltage window.

[085] 3b) graphite fluoride based cells: The CF$_x$ material tested here is CF$_0$ obtained from graphite. The cells were discharged to different depths of discharge (DOD=10, 20, 30,...100%) under constant current (C/20 rate: i.e., 32.1 mA/g-CF$_0$). The cells were then charged to 4.8V and to 5.0V and allowed to rest for several hours the same constant voltage was applied (4.8 or 5.0V) for several hours to further charge. After this, the cells were discharged to 3V and then recharged to 4.8 V or 5.0 V following the same procedure described above.

[086] 4. Results:

4a) Graphite based electrodes: Figure 1 provides a comparative (normalized) discharge profile of Li/electrolyte/graphite-based electrode cells with LiF-containing and LiF-free electrolytes consisting of 1M LiPF$_6$ solution in EC-DMC. Figure 1 shows the voltage versus discharge/charge ratio of the graphite based cells using mother solution electrolyte (no LiF) and LiF dissolved in mother electrolyte (LiF) with charge voltage up to 4.8V. These results indicate that the LiF containing electrolyte has a higher discharge voltage and relative capacity than the non LiF containing electrolyte.

[087] Figure 2 shows a cyclic voltammogram obtained with the Li/0.5M LiF+1 M LiPF$_6$ in EC-DMC/graphite cell, obtained between 2.1 and 4.8 V under a 15mV/min sweeping rate. Visible in Figure 2 are oxidation and reduction peaks corresponding to the intercalation and de-intercalation of the negatively charged species into graphite. These
positive current (oxidation) peaks and negative current peaks (reduction) peaks correspond to reversible charging and discharging of the cell. The peaks may be associated with negatively charged species (or anions) intercalation and de-intercalation, respectively.

[088] 4b) Graphite fluoride based electrodes: Figure 3 provides a comparative (normalized) discharge profile of Li/electrolyte/graphite fluoride (CF$_{0.53}$)-based electrode cells with LiF-containing and LiF-free electrolytes consisting of 1M LiPF$_6$ solution in EC-DMC. Figure 3 shows the voltage versus discharge/charge capacity ratio of the graphite fluoride (CF$_{0.53}$) based cells using mother solution electrolyte (no LiF) and LiF dissolved in mother electrolyte (LiF) with charge voltage up to 4.8V. These results indicate that the LiF containing electrolyte has a higher discharge voltage and relative capacity than the non-LiF containing electrolyte.

[089] 5. Conclusions: New electrolyte solutions based on element fluoride LiF were successfully prepared. The solutions are light transparent and stable under an argon atmosphere. Dissolution of LiF was achieved in different organic liquid media comprised of polar solvents chosen among carbonates such as EC, DMC, PC or y-butyrolactone and containing a dissolved lithium salt such as LiPF$_6$, LiBF$_4$, LiAsF$_6$ and LiClO$_4$. Electrolyte solutions with LiF have a high voltage stability window over 5V vs. Li$^+$/Li. They are also stable in contact with metallic lithium. LiF containing electrolyte solutions show enhanced electrochemical performances of electrode materials for batteries applications such as those based on pure graphite or graphite fluoride positive electrodes. Dissolution of many insoluble element fluorides can be achieved using the same principle of ‘mother solution’ electrolytes.

Example 2: Comparison of fluorinated carbon electrode lithium half-cells with and without LiF

[090] Two fluorinated carbon electrode (CF$_{0.125}$) lithium half cells were prepared. One cell contained an electrolyte of 1M LiPF$_6$ in propylene carbonate (PC); the other cell contained an electrolyte of 1M LiF and 1M 12-crown-4 in PC. The crown ether acts as a cation receptor to allow LiF to dissolve in the PC. The cells were cycled between about 3.2V and 5.5V at a rate of 1 mV/s.
Figure 4 depicts the current provided by the cell containing LiPF$_6$ during a charge/discharge cycle and shows no clear oxidation or reduction peaks. This cell has a much higher charge capacity than discharge, indicating a large irreversibility.

Figure 5 depicts the current provided by the cell containing LiF during a charge/discharge cycle and shows oxidation peaks at about 3.6V and 4.15V and a reduction peak at about 4 V. This cell has similar charge and discharge capacities, indicating good reversibility.

These results indicate that the presence of dissolved LiF makes fluohnated carbon a suitable cathode for high voltage, high cycleability, rechargeable, fluoride ion batteries, since F$^-$ is able to reversibly intercalate into a fluorinated carbon cathode.

Example 3: Fluoride Solutions having Dissociating Agents

Table 2 provides a summary of experimental conditions useful for making fluorides solutions of the present invention from a variety of fluoride salts, including NH$_4$F, NaF, KF, MgF$_2$ and AlF$_3$. 
## Table 2: Example Fluoride Solutions

<table>
<thead>
<tr>
<th>Fluoride</th>
<th>PC or ECDMC</th>
<th>Crown ether</th>
<th>Anion receptor</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄F</td>
<td>Dissolved in PC. Not in ECDM. NH₄F was dried in vacuum at 100°C overnight. 0.165g NH₄F was dissolved in PC and stirred overnight at about 40°C.</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>NaF</td>
<td>Dissolved 0.21g NaF was added into 1.1g 15-crown-5 (1:1 molar ratio). The mixture was stirred at room temperature for 20 minutes. Add 4ml PC to reach 5ml in total volume. Stirring solution overnight at about 40°C.</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>kF</td>
<td>Dissolved 0.20g HF and 1.32g 19-crown-6 were added into 5ml PC. The solution was stirred overnight at about 40°C.</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>MgF₂</td>
<td>Dissolved Yellow color solution (0.1g Tris(pentafluorophenyl)borate was dissolved in 5ml PC. 0.35g MgF₂ was mixed with the solution and stirred overnight at about 40°C.</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>AFS</td>
<td>X</td>
<td></td>
<td>β</td>
</tr>
</tbody>
</table>

### Statements Regarding Incorporation by Reference and Variations

All references throughout this application, for example patent documents including issued or granted patents or equivalents; patent application publications; and non-patent literature documents or other source material; are hereby incorporated by reference herein in their entireties, as though individually incorporated by reference, to the extent each reference is at least partially not inconsistent with the disclosure in this application (for example, a reference that is partially inconsistent is incorporated by reference except for the partially inconsistent portion of the reference).

The terms and expressions which have been employed herein are used as terms of description and not of limitation, and there is no intention in the use of such
terms and expressions of excluding any equivalents of the features shown and
described or portions thereof, but it is recognized that various modifications are possible
within the scope of the invention claimed. Thus, it should be understood that although
the present invention has been specifically disclosed by preferred embodiments,
5 exemplary embodiments and optional features, modification and variation of the
concepts herein disclosed may be resorted to by those skilled in the art, and that such
modifications and variations are considered to be within the scope of this invention as
defined by the appended claims. The specific embodiments provided herein are
examples of useful embodiments of the present invention and it will be apparent to one
skilled in the art that the present invention may be carried out using a large number of
variations of the devices, device components, methods steps set forth in the present
description. As will be obvious to one of skill in the art, methods and devices useful for
the present methods can include a large number of optional composition and processing
elements and steps.

[0100] When a group of substituents is disclosed herein, it is understood that all
15 individual members of that group and all subgroups, including any isomers,
enantiomers, and diastereomers of the group members, are disclosed separately.
When a Markush group or other grouping is used herein, all individual members of the
group and all combinations and subcombinations possible of the group are intended to
be individually included in the disclosure. When a compound is described herein such
that a particular isomer, enantiomer or diastereomer of the compound is not specified,
for example, in a formula or in a chemical name, that description is intended to include
each isomers and enantiomer of the compound described individual or in any
combination. Additionally, unless otherwise specified, all isotopic variants of
20 compounds disclosed herein are intended to be encompassed by the disclosure. For
example, it will be understood that any one or more hydrogens in a molecule disclosed
can be replaced with deuterium or tritium. Isotopic variants of a molecule are generally
useful as standards in assays for the molecule and in chemical and biological research
related to the molecule or its use. Methods for making such isotopic variants are known
in the art. Specific names of compounds are intended to be exemplary, as it is known
that one of ordinary skill in the art can name the same compounds differently.

[0101] Many of the molecules disclosed herein contain one or more ionizable groups
25 [groups from which a proton can be removed (e.g., -COOH) or added (e.g., amines) or
which can be quaternized (e.g., amines)]. All possible ionic forms of such molecules
and salts thereof are intended to be included individually in the disclosure herein. With
regard to salts of the compounds herein, one of ordinary skill in the art can select from
among a wide variety of available countehons those that are appropriate for preparation
of salts of this invention for a given application. In specific applications, the selection of
a given anion or cation for preparation of a salt may result in increased or decreased
solubility of that salt.

[0102] Every formulation or combination of components described or exemplified
herein can be used to practice the invention, unless otherwise stated.

[0103] Whenever a range is given in the specification, for example, a temperature
range, a time range, or a composition or concentration range, all intermediate ranges
and subranges, as well as all individual values included in the ranges given are intended
to be included in the disclosure. It will be understood that any subranges or individual
values in a range or subrange that are included in the description herein can be
excluded from the claims herein.

[0104] All patents and publications mentioned in the specification are indicative of the
levels of skill of those skilled in the art to which the invention pertains. References cited
herein are incorporated by reference herein in their entirety to indicate the state of the
art as of their publication or filing date and it is intended that this information can be
employed herein, if needed, to exclude specific embodiments that are in the prior art.
For example, when composition of matter are claimed, it should be understood that
compounds known and available in the art prior to Applicant's invention, including
compounds for which an enabling disclosure is provided in the references cited herein,
are not intended to be included in the composition of matter claims herein.

[0105] As used herein, "comprising" is synonymous with "including," "containing," or
"characterized by," and is inclusive or open-ended and does not exclude additional,
unrecited elements or method steps. As used herein, "consisting of excludes any
element, step, or ingredient not specified in the claim element. As used herein,
"consisting essentially of does not exclude materials or steps that do not materially
affect the basic and novel characteristics of the claim. In each instance herein any of
the terms "comprising", "consisting essentially of and "consisting of may be replaced
with either of the other two terms. The invention illustratively described herein suitably
may be practiced in the absence of any element or elements, limitation or limitations
which is not specifically disclosed herein.
One of ordinary skill in the art will appreciate that starting materials, biological materials, reagents, synthetic methods, purification methods, analytical methods, assay methods, and biological methods other than those specifically exemplified can be employed in the practice of the invention without resort to undue experimentation. All art-known functional equivalents, of any such materials and methods are intended to be included in this invention. The terms and expressions which have been employed are used as terms of description and not of limitation, and there is no intention that in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the concepts herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention as defined by the appended claims.
We claim:

1. A solution having an inorganic fluoride dissolved in one or more solvents, said solution comprising:

   said one or more solvents;
   a dissociating agent provided to said one or more solvents; and
   said inorganic fluoride dissolved in said one or more solvents having said dissociating agent;

   wherein said dissociating agent and inorganic fluoride are provided in amounts sufficient to generate a concentration of inorganic fluoride dissolved in said one or more solvents greater than or equal to 0.15 M.

2. The solution of claim 1 wherein said dissociating agent and inorganic fluoride are provided in amounts sufficient to generate a concentration of said inorganic fluoride dissolved in said one or more solvents selected over the range of 0.15 M to 3M.

3. The solution of claim 1 wherein said dissociating agent and inorganic fluoride are provided in amounts sufficient to generate a concentration of said inorganic fluoride dissolved in said one or more solvents selected over the range of 0.5 M to 1M.

4. The solution of claim 1 wherein the molar ratio of inorganic fluoride dissolved in said one or more solvents to dissociating agent dissolved in said one or more solvents is greater than or equal to 0.1.

5. The solution of claim 1 wherein the molar ratio of inorganic fluoride dissolved in said one or more solvents to dissociating agent dissolved in said one or more solvents is selected over the range of 0.1 to 10.
6. The solution of claim 1 wherein said inorganic fluoride has the formula:

\[
\text{MF}_n \quad \text{or} \quad \text{BF}_y ;
\]

\[(F1) \quad (F2)\]

wherein M is a metal selected from the group consisting of Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, Sn Pb, and Sb, and n is the oxidation state of M; and wherein B is a polyatomic cation selected from the group consisting of \(\text{NH}_4^+\) and \(\text{N(R-R}_2\text{R}_4\text{)}^+\), wherein \(R_i, R_2, R_3\), and \(R_4\) are each selected independently from the group consisting of a H atom, an alkyl group, an acetyl group and an aromatic (phenyl) group.

7. The solution of claim 1 wherein said inorganic fluoride is selected from the group consisting of \(\text{CdF}_2, \text{CoF}_2, \text{FeF}_3, \text{MnF}_2, \text{NaF}, \text{NiF}_2, \text{ZnF}_2, \text{ZrF}_4, \text{AlF}_3, \text{BaF}_2, \text{CaF}_2, \text{CuF}_2, \text{FeF}_2, \text{InF}_3, \text{LiF}, \text{MgF}_2, \text{PbF}_2, \text{SrF}_2, \text{UF}_4, \text{VF}_3, 3\text{H}_2\text{O}, \text{BiF}_3, \text{CeF}_3, \text{CrF}_2/\text{CrF}_3, \text{GaF}_3, \text{LaF}_3, \text{NdF}_3, \text{ThF}_4, \text{AgF}, \text{CsF}, \text{RbF}, \text{SbF}_3, \text{TIF}, \text{BeF}_2, \text{KF}, \text{NH}_4\text{F}, \text{SnF}_2, \text{TaF}_5, \text{VF}_4, \text{BF}_3, \text{BrF}, \text{BrF}_3, \text{BrF}_5, \text{CoF}_3, \text{GeF}_2/\text{GeF}_4, \text{Hg}_2\text{F}_2/\text{HgF}_2, \text{NbF}_5, \text{OsF}_6, \text{PF}_3/\text{PF}_5, \text{RhF}_3, \text{SF}_4/\text{SF}_6, \text{SnF}_4, \text{TeF}_4, \text{UF}_6, \text{VF}_5, \text{and} \text{WF}_6\).

8. The solution of claim 1 wherein said dissociating agent is provided in said one or more solvents at a concentration selected over the range of 0.1 M to 10 M.

9. The solution of claim 1 wherein said dissociating agent is one or more compounds selected from the group consisting of a Lewis acid, a Lewis base, an anion receptor, and a cation receptor.

10. The solution of claim 9 wherein said dissociating agent is one or more Lewis bases or Lewis acids selected from the group consisting of an inorganic fluoride, an inorganic chloride, an inorganic carbonate, and an inorganic oxide.

11. The solution of claim 9 wherein said dissociating agent is one or more Lewis bases selected from the group consisting of \(\text{AlCl}_4^-, \text{ClO}_4^-, \text{SnCl}_6^{2-}, \text{BF}_4^-\), \(\text{PF}_6^-\), and \(\text{AsF}_6^-\).
12. The solution of claim 9 wherein said dissociating agent is one or more Lewis acids selected from the group consisting of BF₃, PF₅, SbF₅, AsF₅, AlCl₃, SnCl₄, FeCl₃, NbCl₅, TiCl₄, and ZnCl₂.

13. The solution of claim 9 wherein said dissociating agent is provided by dissolving a precursor compound in said one or more solvents to generate a Lewis base, a Lewis acid or a Lewis acid and a Lewis base, said precursor compound comprising an alkali metal salt, alkaline earth metal salt; a transition metal salt or an ammonium salt having the formula:

\[
AX:\quad \text{(F3)}
\]

wherein \( A \) is selected from the group consisting of a metal, a metal cation and an ammonium group; and wherein \( X \) is selected from the group consisting of a fluonated anion, a perchlorate group, an imide group, a carbide group, a carbonate group, an oxide group and a chloride group.

14. The solution of claim 13 wherein said precursor compound is one or more lithium salt.

15. The solution of claim 13 wherein said precursor compound is one or more salt selected from the group consisting of LiPF₆, LiBF₄, LiAsF₆, LiClO₄, LiSnCl₅, LiAlCl₄, LiFeCl₄, LiNbCl₆, LiTiCl₅, LiZnCl₃, NaPF₆, NaBF₄, NaAsF₆, NaClO₄, NaSnCl₅, NaAlCl₄, NaFeCl₄, NaNbCl₆, NaTiCl₅, NaN₃, KPF₆, KBF₄, KAsF₆, KClO₄, KSnCl₅, KAICl₄, KFeCl₄, KNbCl₆, KTiCl₅, KZnCl₃, NH₄PF₆, NH₄BF₄, NH₄AsF₆, NH₄ClO₄, NH₄SnCl₅, NH₄AlCl₄, NH₄FeCl₄, NH₄NbCl₆, NH₄TiCl₅, NH₄ZnCl₃, N(CH₃)₄ClO₄, N(CH₃)₄SnCl₅, N(CH₃)₄AlCl₄, N(CH₃)₄FeCl₄, N(CH₃)₄NbCl₆, N(CH₃)₄TiCl₅, N(CH₃)₄ZnCl₅, N(CH₃)₄AlCl₄, N(CH₃)₄FeCl₄, N(CH₃)₄NbCl₆, N(CH₃)₄TiCl₅, and N(CH₃)₄ZnCl₅.

16. The solution of claim 1 wherein said dissociating agent comprises one or more anion receptors.

17. The solution of claim 1 wherein said dissociating agent comprises one or more cation receptors.
18. The solution of claim 17 wherein said cation receptor is one or more compound selected from the group consisting of a crown ether, a Lewis base, and a cation complexing agent.


20. The solution of claim 1 wherein said one or more solvents is selected from the group consisting of water, a nonaqueous organic solvent and a nonaqueous inorganic solvent.

21. The solution of claim 1 wherein said one or more solvents comprise one or more polar nonaqueous solvents.

22. The solution of claim 1 wherein said one or more solvents comprise one or more solvents selected from the group consisting of γ-butyrolactone, propylene carbonate, dimethyl carbonate, ethylene carbonate, acetonithile, 1,2, -dimethoxyethane, N,N-dimethyl formamide, dimethyl sulfoxide, 1,3-diolane, methyl formate, nitromethane, phosphoroxichloride, thionylchloride, sulfurylchloride, diethyl ether, diethoxy ethane, 1,3 -dioxolane, tetrahydrofuran, 2-methyl-THF, diethyl carbonate, ethyl methyl carbonate, methylacetate and tratahydrofurane.
23. The solution of claim 1 wherein said one or more solvents comprise one or more polar carbonates.

24. An electrolyte comprising the solution of claim 1.

25. An electrochemical device comprising the solution of claim 1.

26. A method for dissolving an inorganic fluoride in one or more solvents, said method comprising the steps of:

   providing said one or more solvents;

   providing a dissociating agent to said one or more solvents; and

   dissolving said inorganic fluoride in said one or more solvents having said dissociating agent;

wherein said dissociating agent and inorganic fluoride are provided in amounts sufficient to generate a concentration of inorganic fluoride dissolved in said one or more solvents greater than or equal to 0.15 M, thereby dissolving said inorganic fluoride into said one or more solvents.

27. A solution comprising LiF dissolved in one or more solvents, said solution comprising:

   said one or more solvents;

   a dissociating agent provided to said one or more solvents, said dissociating agent comprising one or more compound selected from the group consisting of a Lewis acid, a Lewis base; and a crown ether; and

   said LiF dissolved in said one or more solvents having said dissociating agent, wherein the concentration of LiF dissolved in said one or more solvents is greater than or equal to 0.15 M.
28. The solution of claim 27 wherein said dissociating agent and LiF are provided in amounts sufficient to generate a concentration of LiF dissolved in said one or more solvents selected over the range of 0.15 M to 3M.

29. The solution of claim 27 wherein said dissociating agent and LiF are provided in amounts sufficient to generate a concentration of LiF dissolved in said one or more solvents selected over the range of 0.5 M to 1M.

30. The solution of claim 27 wherein said dissociating agent is provided in said one or more solvents at a concentration selected over the range of 0.1 M to 10 M.

31. The solution of claim 27 wherein said dissociating agent is one or more Lewis base or Lewis acid selected from the group consisting of an inorganic fluoride, an inorganic chloride, an inorganic carbonate, and an inorganic oxide.

32. The solution of claim 27 wherein said dissociating agent is one or more Lewis base selected from the group consisting of $\text{AlCl}_4^-$, $\text{ClO}_4^-$, $\text{SnCl}_6^{2-}$, $\text{BF}_4^-$, $\text{PF}_6^-$, and $\text{AsF}_6^-$.

33. The solution of claim 27 wherein said dissociating agent is one or more Lewis acid selected from the group consisting of $\text{BF}_3$, $\text{PF}_5$, $\text{SbF}_5$, $\text{AsF}_5$, $\text{AlCl}_3$, $\text{SnCl}_4$, $\text{FeCl}_3$, $\text{NbCl}_5$, $\text{TiCl}_4$, and $\text{ZnCl}_2$.

34. The solution of claim 27 wherein said dissociating agent is provided by dissolving a precursor compound in said one or more solvents to generate a Lewis base, a Lewis acid or a Lewis acid and a Lewis base, said precursor compound comprising an alkali metal salt, alkaline earth metal salt; a transition metal salt or an ammonium salt having the formula:

$$AX:$$

(F3)

wherein A is selected from the group consisting of a metal, a metal cation and an ammonium group; and wherein X is selected from the group consisting of a fluohnated anion, a perchlorate group, an imide group, a carbide group, a carbonate group, an oxide group and a chloride group.
35. The solution of claim 34 wherein said precursor compound is one or more lithium salt.

36. The solution of claim 34 wherein said precursor compound is one or more lithium salt selected from the group consisting of LiPF$_6$, LiBF$_4$, LiAsF$_6$, LiClO$_4$, LiSnCl$_5$, LiAlCl$_4$, LiFeCl$_4$, LiNbCl$_6$, LiTiCl$_5$, LiZnCl$_3$, NaPF$_6$, NaBF$_4$, NaAsF$_6$, NaClO$_4$, NaSnCl$_5$, NaAlCl$_4$, NaFeCl$_4$, NaNbCl$_6$, NaTiCl$_5$, NaZnCl$_3$, KPF$_6$, KBF$_4$, KAsF$_6$, KClO$_4$, KSnCl$_5$, KAlCl$_4$, KFeCl$_4$, KNaCl$_6$, KTiCl$_5$, KZnCl$_3$, NH$_4$PF$_6$, NH$_4$BF$_4$, NH$_4$AsF$_6$, NH$_4$ClO$_4$, NH$_4$SnCl$_5$, NH$_4$AlCl$_4$, NH$_4$FeCl$_4$, NH$_4$NbCl$_6$, NH$_4$TiCl$_5$, NH$_2$ZnCl$_3$, N(CH$_3$)$_4$ClO$_4$, N(CH$_3$)$_4$SnCl$_5$, N(CH$_3$)$_4$AlCl$_4$, N(CH$_3$)$_4$FeCl$_4$, N(CH$_3$)$_4$NbCl$_6$, N(CH$_3$)$_4$TiCl$_5$, N(CH$_3$)$_4$ZnCl$_3$, N(C$_2$H$_4$)$_4$ClO$_4$, N(C$_2$H$_4$)$_4$SnCl$_5$, N(C$_2$H$_4$)$_4$AlCl$_4$, N(C$_2$H$_4$)$_4$FeCl$_4$, N(C$_2$H$_4$)$_4$NbCl$_6$, N(C$_2$H$_4$)$_4$TiCl$_5$, and N(C$_2$H$_4$)$_4$ZnCl$_3$.


38. The solution of claim 27 wherein said one or more solvents is selected from the group consisting of water, a nonaqueous organic solvent and a nonaqueous inorganic solvent.

39. The solution of claim 27 wherein said one or more solvents comprise one or more polar nonaqueous solvents.
40. The solution of claim 27 wherein said one or more solvents comprise one or more solvents selected from the group consisting of γ-butyrolactone, propylene carbonate, dimethyl carbonate, ethylene carbonate, acetonitrile, 1,2, -dimethoxy ethane, N,N-dimethyl formamide, dimethyl sulfoxide, 1,3-diolane, methyl formate, nitromethane, phosphoroxichloride, thionylchloride, sulfurylchloride, diethyl ether, diethoxy ethane, 1,3 -dioxolane, tetrahydrofuran, 2-methyl-THF, diethyl carbonate, ethyl methyl carbonate, methylacetate and tratahydrosurane.

41. The solution of claim 27 wherein said one or more solvents comprise one or more polar carbonates.

42. An electrolyte comprising the solution of claim 27.

43. An electrochemical device comprising the solution of claim 27.

44. A method for dissolving LiF in one or more solvents, said method comprising the steps of:

   providing said one or more solvents;

   providing a dissociating agent to said one or more solvents, said dissociating agent comprising one or more compound selected from the group consisting of a Lewis acid, a Lewis base; and a crown ether; and

   dissolving LiF in said one or more solvents having said dissociating agent, wherein the concentration of LiF dissolved in said one or more solvents is greater than or equal to 0.15 M.

45. An electrolyte for an electrochemical device, said electrolyte comprising:

   one or more solvents;

   a dissociating agent provided to said one or more solvents; and
an inorganic fluoride dissolved in said one or more solvents having said
dissociating agent;

wherein said dissociating agent and inorganic fluoride are provided in amounts
sufficient to generate a concentration of inorganic fluoride dissolved in said one or
more solvents greater than or equal to 0.15 M.

46. An electrochemical cell comprising: a positive electrode; a negative electrode; and
the electrolyte of claim 45; said electrolyte provided between said positive
electrode and said negative electrode.

47. An electrolyte for an electrochemical device, said electrolyte comprising:
one or more solvents;
a dissociating agent provided to said one or more solvents, said dissociating agent
comprising one or more compound selected from the group consisting of a Lewis
acid, a Lewis base; and a crown ether; and

LiF dissolved in said one or more solvents having said dissociating agent, wherein
the concentration of LiF dissolved in said one or more solvents is greater than or
equal to 0.15 M.

48. An electrochemical cell comprising: a positive electrode; a negative electrode; and
the electrolyte of claim 47; said electrolyte provided between said positive
electrode and said negative electrode.

49. A method of making an electrolyte for an electrochemical device, said method
comprising the steps of:
providing one or more solvents;

providing a dissociating agent to said one or more solvents; and
dissolving an inorganic fluoride in said one or more solvents having said
dissociating agent;
wherein said dissociating agent and inorganic fluoride are provided in amounts sufficient to generate a concentration of inorganic fluoride dissolved in said one or more solvents greater than or equal to 0.15 M, thereby making said electrolyte for said electrochemical device.

50. A method of making an electrolyte for an electrochemical device, said method comprising the steps of:
providing one or more solvents;

providing a dissociating agent to said one or more solvents, said dissociating agent comprising one or more compound selected from the group consisting of a Lewis acid, a Lewis base; and a crown ether.

dissolving LiF in said one or more solvents having said dissociating agent, wherein the concentration of LiF dissolved in said one or more solvents is greater than or equal to 0.15 M, thereby making said electrolyte for said electrochemical device.

51. A solution having LiF dissolved in one or more solvents, said solution comprising:
said one or more solvents; and

LiF dissolved in said one or more solvents; wherein the concentration of LiF dissolved in said one or more solvents is greater than or equal to 0.15 M.
Li/0.5M LiF+1M LiPF$_6$ in EC-DMC/graphite

Voltage sweeping rate = 15 mV/mn

Figure 2
Figure 3
No LiF

Figure 4
With LiF

Figure 5