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$$(RO)_x\text{-}Si\text{-}[(CH_2)y\text{-}CN]_{(4-x)} \qquad (I)$$

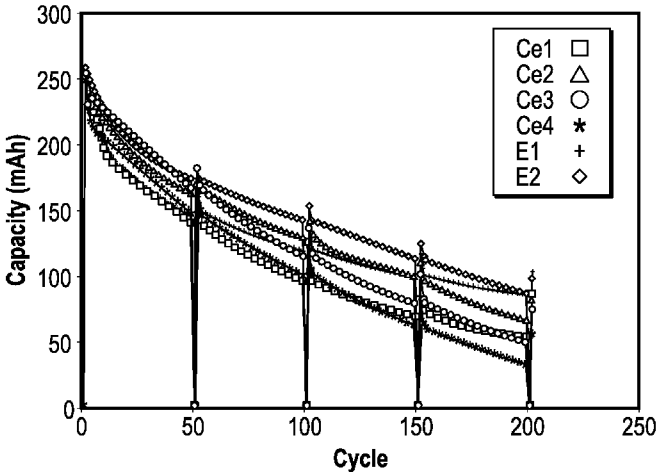

FIG. 2

(57) Abstract: An electrolyte solution includes a solvent; an electrolyte salt; and a cyano silane having formula (I): In formula (I), R is a linear, branched, or cyclic alkylene group having from 1 to 5 carbon atoms, and optionally includes one or more catenary heteroatoms; x is 1-3; and y is 1-5.

[Continued on next page]

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ELECTROLYTE SOLUTIONS AND ELECTROCHEMICAL CELLS CONTAINING SAME

Field

The present disclosure relates to electrolyte solutions for electrochemical cells.

Background

Various electrolyte compositions have been introduced for use in electrochemical cells. Such compositions are described, for example, in JP 2013/097908; U.S. Pat. Pub. 2011/021489; U.S. Pat. Pub. 2012/0021279; JP 2010/044883; and JP 2009/218005.

Summary

In some embodiments, an electrolyte solution is provided. The electrolyte solution includes a solvent; an electrolyte salt; and a cyano silane having formula (I):

$$(RO)_x\text{-Si-}[(CH_2)y\text{-CN}]_{(4-x)} \qquad (I)$$

In formula (I), R is a linear, branched, or cyclic alkylene group having from 1 to 5 carbon atoms, and optionally includes one or more catenary heteroatoms; x is 1-3; and y is 1-5.

The above summary is not intended to describe each disclosed embodiment of every implementation of the present disclosure. The brief description of the drawings and the detailed description which follows more particularly exemplify illustrative embodiments.

Brief Description of the Drawings

Figure 1A shows ^{19}F NMR spectra of an electrolyte composition of a comparative example after 20 hours storage at 80°C.

Figure 1B shows ^{19}F NMR spectra of an electrolyte composition of the present disclosure after 20 hours storage at 80°C.

Figure 1C shows ^{19}F NMR spectra of an electrolyte composition of the present disclosure after 20 hours storage at 80°C.

Figure 2 shows discharge capacity during long-term cycling at 4.3V and 45°C of lithium ion cells containing Si alloy anodes and electrolytes of the present invention.

Detailed Description

There continues to be a need to develop materials for the production of next generation lithium-ion electrochemical cells that exhibit improved safety, improved energy or power density, and lower cost of manufacture. An important component of these development efforts is the development of new electrolyte additives. Generally, electrolyte additives that: 1) are capable of improving the high temperature performance and stability (e.g. > 45 °C or 55°C) of lithium-ion cells, 2) provide electrolyte stability at high voltages (e.g. > 4.2V) for increased energy density, and 3) enable new high capacity electrode materials (e.g., silicon alloy anodes), may be desired.

Further regarding high capacity anode materials, it is believed that a high loading of fluorethylene carbonate (FEC) in the electrolyte solution (e.g., greater than 10 or 20 wt. % based on the total weight of the electrolyte solution) plays an important part in achieving industry acceptable cycle life in electrochemical cells having such anode materials. However, high loadings of FEC has been associated with undesirable gassing which is believed to be induced by FEC decomposition at elevated temperatures. Consequently, electrolyte additives capable of reducing gassing without sacrificing cycle life, particularly in electrochemical cell systems that incorporate high capacity anode materials and high loadings of FEC in the electrolyte solution, are desirable.

As used herein, "catenated heteroatom" means an atom other than carbon (for example, oxygen, nitrogen, or sulfur) that is bonded to at least two carbon atoms in a carbon chain (linear or branched or within a ring) so as to form a carbon-heteroatom-carbon linkage.

As used herein, the singular forms "a", "an", and "the" include plural referents unless the content clearly dictates otherwise. As used in this specification and the appended embodiments, the term "or" is generally employed in its sense including "and/or" unless the content clearly dictates otherwise.

As used herein, the recitation of numerical ranges by endpoints includes all numbers subsumed within that range (e.g. 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.8, 4, and 5).

Unless otherwise indicated, all numbers expressing quantities or ingredients, measurement of properties and so forth used in the specification and embodiments are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the foregoing specification and attached listing of embodiments can vary depending upon the desired properties sought to be obtained by those skilled in the art utilizing the teachings of the present disclosure. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claimed embodiments, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

Generally, the present disclosure, in some embodiments, relates to a class of cyano silane compounds that act as performance enhancing additives to the electrolytes of electrochemical cells (e.g., lithium ion electrochemical cells). For example, electrochemical cells having electrolytes that include the cyano silanes of the present disclosure, relative to known electrolytes including known additives, may reduce capacity fade, cell swelling, and impedance rise at elevated temperatures or under high voltage cycling/storage. Furthermore, the unexpected efficacy of the present cyano silanes at low loadings and their low manufacturing cost can lead to a reduction in overall electrolyte additive cost per electrochemical cell. Indeed, reduction in material costs is an important factor in the adoption of lithium-ion battery technology in new applications (e.g., electric vehicles, renewable energy storage).

In some embodiments, the present disclosure relates to electrolyte solutions for electrochemical cells. The electrolyte solutions may include a solvent, one or more electrolyte salts, and one or more cyano silanes having formula (I):

$$(RO)_x\text{-Si-}[(CH_2)_y\text{-CN}]_{(4-x)} \qquad (I)$$

where R is a linear, branched, or cyclic alkylene group having from 1 to 8, 2 to 5, or 2 to 3 carbon atoms, and optionally includes one or more catenary heteroatoms; x is 1-3, 2-3, or 3; and y is 0-5, 1-5, 2-4, or 2-3. In some embodiments the cyano silanes may be selected from $(CH_3CH_2O)_3Si(CH_2)_2CN$ and $(CH_3CH_2O)_3Si(CH_2)_3CN$.

To minimize volatility and associated problems with evaporative losses, pressure buildup in cells, and human exposure during manufacturing, industry practice suggests electrolyte components having boiling points of greater than 80°C or greater than 100°C. In this regard, surprisingly, it was discovered that the cyano silanes of the present disclosure have the boiling points indicated in Table 1. As can be seen from Table 1, when y is 2-4, the boiling point of the cyano silane is greater than 80°C, and when y is 1 or 5 the boiling point of the cyano silane is less than 80°C.

Table 1. Boiling Points of Cyano Silanes

$(RO)_x$-Si-$[(CH_2)y$-$CN]_{(4-x)}$	Boiling point (°C)
y = 1, x=3	58
y = 2, x=3	224
y = 3, x=3	100
y = 4, x=3	83
y = 5, x=3	58

Thus, in order to minimize volatility within the cyano silanes of the present disclosure, variable y of formula (I) may be 2-4 or 2-3.

In some embodiments, the cyano silanes of formula (I) may be present in the electrolyte solution in an amount of between 0.01 and 40 wt.%, 0.01 and 20 wt.%, 0.1 and 15 wt.%, 0.1 and 10 wt.%, 0.5 and 10 wt.%, or 0.5 and 5 wt.%, based on the total weight of the electrolyte solution.

In various embodiments, the electrolyte solutions of the present disclosure may include fluoroethylene carbonate (FEC) as a component (e.g., solvent component, additive component). The FEC may be present as, for example, either or both of monofluoro ethylene carbonate and difluoro ethylene carbonate. As previously discussed, the presence of FEC, while desirable for achieving adequate cycle life, has been associated with undesirable gassing. In this regard, it has been discovered that the cyano silanes of the present disclosure can significantly reduce or eliminate undesirable gassing, without sacrificing cycle life. In some embodiments, FEC may be present in the electrolyte

solutions of the present disclosure in an amount of 1-60 wt. %, 5-50 wt. %, 10-40 wt. %, 10-30 wt. %, or 20-30 wt. %, based on the total weight of the electrolyte solution.

In various embodiments, the electrolyte solutions may include one or more solvents. In some embodiments, the solvent may include one or more organic carbonates. Examples of suitable solvents include ethylene carbonate, diethyl carbonate, dimethyl carbonate, ethyl methyl carbonate, vinylene carbonate, propylene carbonate, tetrahydrofuran (THF), acetonitrile, gamma butyrolactone, sulfolane, ethyl acetate, or combinations thereof. In some embodiments, organic polymer containing electrolyte solvents, which can include solid polymer electrolytes or gel polymer electrolytes, may also be employed. Organic polymers may include polyethylene oxide, polypropylene oxide, ethylene oxide/propylene oxide copolymers, polyacrylonitrile, polyvinylidene fluoride, vinylidene fluoride-hexafluoropropylene copolymers, and poly-[bis((methoxyethoxy)ethoxy)phosphazene] (MEEP), or combinations thereof. The solvents may be present in the electrolyte solution in an amount of between 15 and 98 wt.%, 25 and 95 wt.%, 50 and 90 wt.%, or 70 and 90 wt.%, based on the total weight of the electrolyte solution.

In some embodiments, the electrolyte solution may include one or more electrolyte salts. In some embodiments, the electrolyte salts may include lithium salts and, optionally, other salts such as sodium salts (e.g., $NaPF_6$). Suitable lithium salts may include $LiPF_6$, $LiBF_4$, $LiClO_4$, lithium bis(oxalato)borate, $LiN(SO_2CF_3)_2$, $LiN(SO_2C_2F_5)_2$, $LiAsF_6$, $LiC(SO_2CF_3)_3$, $LiN(SO_2F)_2$, $LiN(SO_2F)(SO_2CF_3)$, $LiN(SO_2F)(SO_2C_4F_9)$, or combinations thereof. In some embodiments, the lithium salts may include $LiPF_6$, lithium bis(oxalato)borate, $LiN(SO_2CF_3)_2$, or combinations thereof. In some embodiments, the lithium salts may include $LiPF_6$ and either or both of lithium bis(oxalato)borate and $LiN(SO_2CF_3)_2$. The electrolyte salts may be present in the electrolyte solution in an amount of between 2 and 85 wt%, 5 and 75 wt%, 10 and 50 wt%, or 10 and 30 wt%, based on the total weight of the electrolyte solution.

In some embodiments, the electrolyte solutions of the present disclosure may also include one or more electrolyte additives such as any one of or any combination of, for example, vinylene carbonate (VC), propane-1,3- sultone (PS), prop-1-ene-1,3-sultone (PES), succinonitrile (SN), 1,5,2,4-dioxadithiane-2,2,4,4-tetraoxide (MMDS), lithium bis(oxalate)borate (LiBOB), lithium difluoro(oxalato)borate (LiDFOB),

tris(trimethylsilyl)phosphite (TTSPi), ethylene sulfite (ES), 1,3,2-dioxathiolan-2,2-oxide (DTD), vinyl ethylene carbonate(VEC), trimethylene sulfite (TMS), tri-allyl-phosphate (TAP), methyl phenyl carbonate (MPC), diphenyl carbonate (DPC), ethyl phenyl carbonate (EPC), and tris(trimethylsilyl)phosphate (TTSP). The additional electrolyte additives may be present, individually or in combination, in an amount of between 0.1 and 5 wt%, 0.5 and 5 wt%, 1 and 5 wt%, or 1 and 3 wt%, based on the total weight of the electrolyte solution.

The electrolyte solutions of the present disclosure, which include the cyano silane additives discussed above, provide clear benefits to lithium ion cell performance, particularly in cells using an electrolyte solution having FEC present in an amount of at least 10 or 20 wt. % based on the total weight of the electrolyte, and an active anode material that includes a silicon alloy. Specifically, the electrolyte solutions can significantly improve cycle life at elevated temperature (> 45°C or 55°C) and high voltage (> 4.3 V), reduce cell swelling and voltage drop on thermal storage at 60 °C and 80 °C, and decrease cell resistance at high temperature.

In some embodiments, the present disclosure is further directed to electrochemical cells that include the above-described electrolyte solutions. In addition to the electrolyte solution, the electrochemical cells may include at least one positive electrode, at least one negative electrode, and a separator.

In some embodiments, the positive electrode may include a current collector having disposed thereon a positive electrode composition. The current collector for the positive electrode may be formed of a conductive material such as a metal. According to some embodiments, the current collector includes aluminum or an aluminum alloy. According to some embodiments, the thickness of the current collector is 5 μm to 75 μm. It should also be noted that while the positive current collector may be described as being a thin foil material, the positive current collector may have any of a variety of other configurations according to various exemplary embodiments. For example, the positive current collector may be a grid such as a mesh grid, an expanded metal grid, a photochemically etched grid, or the like.

In some embodiments, the positive electrode composition may include an active material. The active material may include a lithium metal oxide or lithium metal phosphate. In an exemplary embodiment, the active material may include lithium transition metal oxide intercalation compounds such as $LiCoO_2$, $LiCo_{0.2}Ni_{0.8}O_2$, $LiMn_2O_4$, $LiFePO_4$, $LiNiO_2$, or lithium mixed metal oxides of manganese, nickel, and cobalt in any proportion. Blends of these materials can also be used in positive electrode compositions. Other exemplary cathode materials are disclosed in U.S. Patent No. 6,680,145 (Obrovac et al.) and include transition metal grains in combination with lithium-containing grains. Suitable transition metal grains include, for example, iron, cobalt, chromium, nickel, vanadium, manganese, copper, zinc, zirconium, molybdenum, niobium, or combinations thereof with a grain size no greater than about 50 nanometers. Suitable lithium-containing grains can be selected from lithium oxides, lithium sulfides, lithium halides (e.g., chlorides, bromides, iodides, or fluorides), or combinations thereof. The positive electrode composition may further include additives such as binders (e.g., polymeric binders (e.g., polyvinylidene fluoride)), conductive diluents (e.g., carbon), fillers, adhesion promoters, thickening agents for coating viscosity modification such as carboxymethylcellulose, or other additives known by those skilled in the art.

The positive electrode composition can be provided on only one side of the positive current collector or it may be provided or coated on both sides of the current collector. The thickness of the positive electrode composition may be 0.1 μm to 3 mm, 10 μm to 300 μm, or 20 μm to 90 μm.

In various embodiments, the negative electrode may include a current collector and a negative electrode composition disposed on the current collector. The current collector of the negative electrode may be formed of a conductive material such as a metal. According to some embodiments, the current collector includes copper or a copper alloy, titanium or a titanium alloy, nickel or a nickel alloy, or aluminum or an aluminum alloy. According to some embodiments, the thickness of the current collector may be 5 μm to 75 μm. It should also be noted that while the current collector of the negative electrode may be described as being a thin foil material, the current collector may have any of a variety of other configurations according to various exemplary embodiments. For example, the current collector of the negative electrode may be a grid such as a mesh grid, an expanded metal grid, a photochemically etched grid, or the like.

In some embodiments, the negative electrode composition may include an active material (e.g., a material that is capable of intercalating or alloying with lithium.) The active material may include lithium metal, carbonaceous materials, or metal alloys (e.g., silicon alloy composition or lithium alloy compositions). Suitable carbonaceous materials can include synthetic graphites such as mesocarbon microbeads (MCMB) (available from China Steel, Taiwan, China) , SLP30 (available from TimCal Ltd., Bodio Switzerland), natural graphites and hard carbons. Suitable alloys may include electrochemically active components such as silicon, tin, aluminum, gallium, indium, lead, bismuth, and zinc and may also include electrochemically inactive components such as iron, cobalt, transition metal silicides and transition metal aluminides.

In some embodiments, the active material of the negative electrode may include a silicon alloy. For example, the active material of the negative electrode may include a silicon alloy that includes silicon, one or more transition metals, and carbon. In yet another example, the active material of the negative electrode may include a silicon alloy material having the formula II:

$$Si_wM^1_xC_y \qquad (II)$$

where w, x, y, and z represent atomic % values and $w + x + y + z = 100$; M^1 is one or more transition metals; and $w > 0$, $x > 0$, $y \geq 0$. In some embodiments M^1 may include one or more of Mg, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, B or Ti, B, Mg, V, Fe, Mn, Co, Ni, Cu. In some embodiments, M^1 may include iron. In some embodiments w may be between 50% and 90%, 65% and 85%, 70% and 80%, or 72% and 77%; x may be between 5% and 20%, 12% and 20%, or 14% and 18%; y may be between 2% and 15%, 5% and 12%, or 8% and 12%. In some embodiments, the silicon alloy material may be described as one or more active phases and one or more inactive phases.

In some embodiments, the negative electrode composition may further include additives such as binders (e.g., polymeric binders (e.g., polyvinylidene fluoride or styrene butadiene rubber (SBR)), conductive diluents (e.g., carbon black and/or carbon nanotubes), fillers, adhesion promoters, thickening agents for coating viscosity modification such as carboxymethylcellulose, or other additives known by those skilled in the art.

In various embodiments, the negative electrode composition can be provided on only one side of the negative current collector or it may be provided or coated on both sides of the current collector. The thickness of the negative electrode composition may be 0.1 μm to 3 mm, 10 μm to 300 μm, or 20 μm to 90 μm.

In some embodiments, the electrochemical cells of the present disclosure may include a separator (e.g., a polymeric microporous separator which may or may not be coated with a layer of inorganic particles such as Al_2O_3) provided intermediate or between the positive electrode and the negative electrode. The electrodes may be provided as relatively flat or planar plates or may be wrapped or wound in a spiral or other configuration (e.g., an oval configuration). For example, the electrodes may be wrapped around a relatively rectangular mandrel such that they form an oval wound coil for insertion into a relatively prismatic battery case. According to other exemplary embodiments, the battery may be provided as a button cell battery, a thin film solid state battery, or as another lithium ion battery configuration.

According to some embodiments, the separator can be a polymeric material such as a polypropylene/polyethylene copolymer or another polyolefin multilayer laminate that includes micropores formed therein to allow electrolyte and lithium ions to flow from one side of the separator to the other. The thickness of the separator may be between approximately 10 micrometers (μm) and 50 μm according to an exemplary embodiment. The average pore size of the separator may be between approximately 0.02 μm and 0.1 μm.

In some embodiments, the present disclosure is further directed to electronic devices that include the above-described electrochemical cells. For example, the disclosed electrochemical cells can be used in a variety of devices including, without limitation, portable computers, tablet displays, personal digital assistants, mobile telephones, motorized devices (e.g., personal or household appliances and vehicles), power tools, illumination devices, and heating devices.

In some embodiments, the present disclosure relates to methods of making the cyano silanes of formula (I). The methods may include titrating a stoichiometric amount of alkenylnitrile of the formula $CH_2=CH(CH_2)_yCN$, into a solution of an alkoxidesilane of the formula $(RO)_xSiH$ at 393-453 K in a high-boiling organic solvent, e.g.

tetraethoxysilane that does not react with the substrates. The resulting cyano silane of formula (I) may then be isolated using conventional techniques prior to formulation into a battery electrolyte.

The present disclosure further relates to methods of making the above-described electrolyte solutions. The method may include combining one or more of the above described solvent(s), one or more of the above-described electrolyte salts, and one or more of the above described cyano silanes having formula (I). The method may further include combining these components in the relative amounts discussed above.

The present disclosure further relates to methods of making an electrochemical cell. In various embodiments, the method may include providing the above-described negative electrode, providing the above-described positive electrode, and incorporating the negative electrode and the positive electrode into a battery comprising the above-described electrolyte solution.

Listing of Embodiments

1. An electrolyte solution comprising:

a solvent;

an electrolyte salt; and

a cyano silane having formula (I):

$$(RO)_x\text{-}Si\text{-}[(CH_2)y\text{-}CN]_{(4-x)} \qquad (I)$$

where R is a linear, branched, or cyclic alkylene group having from 1 to 5 carbon atoms, and optionally includes one or more catenary heteroatoms; x is 1-3; and y is 1-5.

2. The electrolyte solution of embodiment 1, wherein the cyano silane is present in the electrolyte solution in an amount of between 0.1 and 10 wt.%, based on the total weight of the electrolyte solution.

3. The electrolyte solution according to any one of embodiments 1-2, wherein the electrolyte solution comprises FEC in an amount of between 5 and 50 wt. %, based on the total weight of the electrolyte solution.

4. The electrolyte solution according to any one of embodiments 1-3, wherein the cyano silane has a boiling point of greater than 80°C.

5. The electrolyte solution according to any one of embodiments 1-4, wherein the cyano silane is $(CH_3CH_2O)_3Si(CH_2)_2CN$ or $(CH_3CH_2O)_3Si(CH_2)_3CN$.

6. The electrolyte solution according to any one of embodiments 1-5, wherein the electrolyte salt comprises a lithium salt.

7. The electrolyte solution according to embodiment 6, wherein the electrolyte salt comprises $LiPF_6$, $LiBF_4$, $LiClO_4$, lithium bis(oxalato)borate, $LiN(SO_2CF_3)_2$, $LiN(SO_2C_2F_5)_2$, $LiAsF_6$, $LiC(SO_2CF_3)_3$, $LiN(SO_2F)_2$, $LiN(SO_2F)(SO_2CF_3)$, or $LiN(SO_2F)(SO_2C_4F_9)$.

8. The electrolyte solution according to any one of embodiments 6-7, wherein the electrolyte salt is present in the solution in an amount of between 5 and 75 wt.%, based on the total weight of the electrolyte solution.

9. An electrochemical cell comprising:
a positive electrode;
a negative electrode; and
the electrolyte solution according to any one of embodiments 1-8.

10. The electrochemical cell according to embodiment 9, wherein the negative electrode comprises silicon.

11. The electrochemical cell according to embodiment 10, wherein the negative electrode comprises a silicon alloy.

12. The electrochemical cell according to embodiment 11, wherein the silicon alloy comprises silicon, a transition metal, and carbon.

13. The electrochemical cell according to any one of embodiments 9-12, wherein the positive electrode comprises an active material, the active material comprising a lithium metal oxide or a lithium metal phosphate.

14. A method of making an electrolyte solution, the method comprising:

combining a solvent, an electrolyte salt, and the electrolyte solution according to any one of embodiments 1-8.

15. A method of forming an electrochemical cell comprising:

providing a positive electrode;

providing a negative electrode;

providing the electrolyte solution according to any one of embodiments 1-8; and

incorporating the positive electrode, negative electrode, and electrolyte into a cell to form an electrochemical cell.

Examples

Objects and advantages of this disclosure are further illustrated by the following examples. Unless otherwise indicated, all parts and percentages are by weight.

Preparation of Electrolyte

1 M $LiPF_6$ EC/EMC (3:7 wt.% ratio, BASF, Germany) was used as the base electrolyte for the illustrative and comparative examples. To this electrolyte, various electrolyte additives, as listed below in Table 2, were added either singly or in combination with other additives. Additive components were added at specified weight percentages in the electrolyte.

Electrochemical Cell Preparation

Dry pouch cells (240 mAh) were obtained without electrolyte from Li-Fun Technology Corporation (Xinma Industry Zone, China). The positive electrode composition was $LiCoO_2$:Carbon Black:PVDF Binder (96.2%:1.8%:2.0%, Li-Fun Technology Corporation). The negative electrode was Si alloy (C7-4A36, 3M Company, USA):Si alloy (MAGE, Hitachi Chemical, Japan):conductive carbon (KS6L, Timcal, Japan):SBR (X3, Zeon Corporation, Japan):CMC (2200, Daicel FineChem Ltd., Japan) in a ratio of

15%:72.3%:10%:1.5%:1.2%. The positive electrode coating had a thickness of 93 μm. The negative electrode coating had thickness of 44 μm, a loading of 6.6 mg/cm^2 and was calendered to 30% porosity. The positive electrode dimensions were 187 mm x 26 mm and the negative electrode dimensions were 191 mm x 28 mm.

Both electrodes were coated on both sides, except for small regions on one side at the end of the foils. All pouch cells were vacuum sealed without electrolyte by the manufacturer in China. Before electrolyte filling, the cells were cut just below the heat seal and dried at 80°C under vacuum for at least 14 h to remove any residual water in a dry room with a dew point of -40 °C. While still in the dry room, the cells were filled with electrolyte and vacuum sealed. All pouches were filled with 0.65 mL of electrolyte. After filling, cells were vacuum-sealed with a vacuum sealer (MSK-115A, MTI Corp. USA). First, cells were charged to 2V then let to rest open circuit for 12h, then charged to 2V again then left to rest for 12h. The cells were then charged at 10 mA (C/20) up to 3.8 V, taken to the dry room, cut open to release gas generated and then vacuum sealed again. The cells were then charged at 10 mA (C/20) up to 4.35 V and discharged to 3.0 V at 10 mA (C/20).

Electrochemical Testing - Cycling at 45°C

The Li ion pouch cells were cycled with a Maccor 4000 Series cycler (available from Maccor Inc, Tulsa, OK) in a temperature controlled oven at 45 ± 0.1 °C. After the formation cycle described above the cells were charged a 100 mA (C/2) up to 4.3 V and held at 4.3 V until the current dropped to 10 mA (C/20), left to rest open circuit for 15 minutes, then discharged at 100 mA (C/2) until the voltage reached 3.0 V, and then left to rest open circuit for 15 minutes. This cycling was repeated and every 50 cycles a slow cycle was performed which consisted in charging at 10 mA (C/20) up to 4.3 V, resting 15 minutes, discharging at 10 mA down to 3.0 V and resting 15 minutes. This cycling procedure was performed for at least 200 cycles.

Electrochemical Testing - Storage

The cycling/storage procedure used in these tests is described as follows. Cells were first charged to 4.35V and discharged to 3.0 V five times. Then the cells were charged to 4.35 at a current of C/20 (11 mA) and then held at 4.35 V until the measured current

decreased to C/20. A Maccor series 4000 cycler was used for the preparation of the cells prior to storage. After the pre-cycling process, cells were carefully moved to the storage system which monitored their open circuit voltage every 1 hour. Storage experiments were made at 60 ± 0.1°C for a total storage time of 300 hours and 80 ± 0.1°C for a total storage time of 4 hours. The voltage drop, impedance, and cell volume were measured before and after storage.

Measurement of Voltage Drop on Storage

The open circuit voltage of Li-ion pouch cells was monitored and measured before, during, and after storage at 60°C for 300 hours. The voltage drop (ΔV) is described in Equation 1.

$$\Delta V = (\text{Voltage before storage}) - (\text{Voltage after storage}) \quad \text{Eq. 1}$$

DC Impedance measurement

Direct current resistance (DCR) measurements were conducted before and after storage and/or cycle. Cells were charged or discharged to 3.80 V. A charge current at C/20 was applied to lithium ion cells for 1 second duration. After 5 minutes rest, the same discharge current at C/20 was applied to cells for 1 second. The charge end voltage and discharge end voltage is monitored and measured during the DCR measurement. The DCR of cells can be calculated according the following equation:

$$\text{DCR} = \frac{(\text{Voltage after charge} - \text{Voltage after discharge})}{(\text{Charge current} - \text{Discharge current})} \quad \text{Eq. 2}$$

The impedance rise (ohms) recorded in Table 6 was calculated according to the following equation:

$$\Delta R = \text{Impedance after storage (or cycle)} - \text{Impedance before storage (or cycle)} \quad \text{Eq. 3}$$

Determination of Gas Evolution

Ex-situ (static) gas measurements were used to measure gas evolution during storage. The measurements were made using Archimedes' principle with cells suspended

from a balance while submerged in liquid. The changes in the weight of the cell suspended in fluid, before and after testing are directly related to the change in cell volume due to the impact on buoyant force. The change in mass of a cell, Δm, suspended in a fluid of density, ρ, is related to the change in cell volume, Δv, by

$$\Delta v = -\Delta m/\rho \quad \text{Eq. 4}$$

Ex-situ measurements were made by suspending pouch cells from a fine wire "hook" attached under a Shimadzu balance (AUW200D, Shimadzu, Japan). The pouch cells were immersed in a beaker of de-ionized "nanopure" water (18.2 MΩ·cm) at 20 ± 1°C during measurement.

Comparative Examples CE1-CE5 and Examples 1-7

Table 2 shows additives that were added to the formulated electrolyte stock solution containing 0.83 M $LiPF_6$ in EC:EMC:FEC at a ratio of 2.4:5.6:2 by weight. These electrolytes were then used in the lithium ion pouch cells containing the LCO cathode and Si alloy anode.

Table 2. Electrolyte Formulations

Examples	**Additive and Loading** (wt% additive in formulated electrolyte)
CE 1	None
CE 2	5% Succinitrile (SN)
CE 3	5% Ethyltriethoxysilane
CE 4	5% Propyltrimethoxysilane
Example 1	5% (2-Cyanoethyl)triethoxysilane
Example 2	5% (3-Cyanopropyl)triethoxysilane
Example 3	0.5% (2-Cyanoethyl)triethoxysilane
Example 4	1% (2-Cyanoethyl)triethoxysilane
Example 5	3% (2-Cyanoethyl)triethoxysilane
Example 6	7% (2-Cyanoethyl)triethoxysilane
Example 7	10% (2-Cyanoethyl)triethoxysilane

Thermal stability of $LiPF_6$-based electrolyte containing high content of FEC

^1H and ^{19}F NMR spectroscopy was utilized to determine the effects of (2-Cyanoethyl)triethoxysilane (CS2) and (3-Cyanopropyl)triethoxysilane (CS3) on the

hydrolytic stability of $LiPF_6$ and HF generation when high concentrations of FEC exist in $LiPF_6$-containing electrolytes. First, 5.0 wt% CS2 or CS3 was charged to the base electrolyte formulation, 1M $LiPF_6$ EC:EMC (3:7 by volume) + 20% FEC. Then, after 20 hours storage at 80°C in glass vials, each solution was transferred into a sealed NMR tube. The NMR samples were analyzed on a Bruker 500MHz NMR spectrometer. Figure 1A shows ^{19}F NMR spectrum of the baseline electrolyte (Comparative Example 1) after 20 hours storage at 80°C. Figure 1B shows ^{19}F NMR spectrum of the baseline electrolyte + 5.0 wt% CS2 (Example 1) after 20 hours storage at 80°C. Figure 1C shows ^{19}F NMR spectrum of the baseline electrolyte + 5.0 wt% CS3 (Example 2) after 20 hours storage at 80°C. The HF was identified as a doublet appearing at -156 ppm in the ^{19}F NMR spectrum of the baseline electrolyte (splitting due to H-F coupling). Fluorophosphoric acid OPF_2OH was also identified as a doublet at -88 ppm in the ^{19}F NMR spectrum of the baseline electrolyte. Interestingly, for the electrolyte containing 5.0 wt% CS2 and CS3 additive, HF and OPF_2OH signals were not observed, which indicates that CS2 and CS3 inhibits the generation of HF.

Table 3 compares HF generation of electrolytes containing CS2 and CS3 compared to ethyltriethoxysilane (EES). 5.0 wt% CS2 and 5.0 wt% EES additive was added to the baseline electrolytes containing 20% FEC, respectively. After storage for 20 hours at 80°C, the electrolytes were characterized by ^{19}F NMR spectroscopy. Table 3 shows the HF/FEC mol ratio of the baseline electrolyte (CE1), and the electrolytes containing the 5.0 wt% EES (CE3), 5.0 wt% CS2 additives (Example 1), and 5.0 wt% CS3 additives (Example 2), respectively after storage at 80°C for 20 hours. The results indicate that cyano silanes suppress HF generation, whereas EES does not. Since CS2 can prevent FEC decomposition and the corresponding HF generation that results, it is apparent that 5.0 wt % CS2 and CS3 significantly improves the thermal stability of $LiPF_6$-containing electrolytes with addition of high concentration of FEC.

Table 3. HF Generation after Storage at for 20 Hours at 80°C

Electrolyte	Moles HF(LiF) per Mole FEC
CE1	0.0339
CE3	0.0670
Example 1	0.0034
Example 2	0.0022

Electrochemical Cells Storage Test

Lithium ion pouch cells containing the LCO cathode and Si alloy anode were stored at 4.35V and at 60°C, as described above. The voltage drop, impedance rise, and gas evolution results are summarized in Table 4. The data clearly indicates that electrolyte containing cyano silane compound of the invention as electrolyte additives reduce voltage drop, impedance rise and gas generation of cells containing silicon alloy anode and high concentration of FEC upon storage at high temperature and high voltage.

Table 4. LCO /Si alloy Cell Performance Metrics upon Storage at 60°C and 4.35V

Electrolyte	Voltage drop (V)	DCR Impedance (Ohm)	Δ Gas volume (mL)
CE1	0.80	1.6	1.9
CE2	0.53	1.3	1.7
CE3	0.18	1.8	1.6
CE4	0.17	1.6	1.3
Example 1	0.18	1.3	0.9
Example 2	0.17	1.4	0.6

Lithium ion pouch cells containing the LCO cathode and Si alloy anode were stored at 4.35V and at 80°C, as described above. The gas evolution results are summarized in Table 5. The data clearly indicates that electrolyte containing cyano silane compounds of the invention as electrolyte additives reduce gas generation of cells containing silicon alloy anode and high concentration of FEC upon storage at high temperature and high voltage.

Table 5. LCO/Si alloy Gas Evolution upon Storage at 80°C and 4.35V

Electrolyte	Δ Gas volume (mL)
CE1	1.80
CE2	1.20
CE3	1.20
CE4	1.30
Example 1	0.40

Example 2	0.40
Example 3	1.02
Example 4	0.76
Example 5	0.55
Example 6	0.18
Example 7	0.30

Electrochemical cells cycling test

LCO||Si alloy cells were cycled between 3.0 and 4.3 V at 45°C. The performance of the cells is quantified by the capacity retention and DCR after 200 cycles. Table 6 lists the performance of the cells and shows that the additives have resulted in improved cycling and reduced resistance.

Table 6. LCO/Si alloy Cell Performance Metrics upon Cycling at 45°C

	Cycle 1 Discharge Capacity (mAh)	**Cycle 200 Discharge Capacity (mAh)**	**Retention (Cycle 200 / Cycle 1)**	**Cycle 1 DCR Impedance (Ohm)**	**Cycle 200 DCR Impedance (Ohm)**	**ΔR Impedance rise (Ohm) (Cy 200-Cy 1)**
CE1	254	52	20.5%	0.14	1.59	1.45
CE2	254	66	26.0%	0.16	1.24	1.08
CE3	253	49	19.4%	0.17	1.14	0.97
CE4	249	32	12.9%	0.20	1.16	0.96
Example 1	255	85	33.3%	0.16	0.85	0.69
Example 2	257	86	33.5%	0.17	0.81	0.64

Figure 2 shows the discharge capacity versus cycle number of LCO||Si alloy pouch cells containing 20% FEC and different additives under extremely aggressive cycling conditions. The cells were cycled without clamps, so generated gas would promote loss of stack pressure. After 200 cycles, all of these cells retained less than 50% of their initial capacity but Examples 1 and 2 performed best. Cells with additives disclosed in this invention showed promising long-term cycling results at high voltage (4.3V) and high temperature (45°C) vs. CE 1, CE 2, CE 3 and CE 4.

The cyano silane additives in the invention therefore provide significant benefits in combination with Si alloy materials, including increased capacity retention and reduced

impedance. Furthermore, additional benefits are obtained in combination with monofluoro ethylene carbonate (FEC), including improved hydrolytic stability and suppression of gas evolution.

Various modifications and alterations to this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention. It should be understood that this invention is not intended to be unduly limited by the illustrative embodiments and examples set forth herein and that such examples and embodiments are presented by way of example only with the scope of the invention intended to be limited only by the claims set forth herein as follows. All references cited in this disclosure are herein incorporated by reference in their entirety.

What is claimed is:

1. An electrolyte solution comprising:

a solvent;

an electrolyte salt; and

a cyano silane having formula (I):

$$(RO)_x\text{-}Si\text{-}[(CH_2)y\text{-}CN]_{(4-x)} \qquad (I)$$

where R is a linear, branched, or cyclic alkylene group having from 1 to 5 carbon atoms, and optionally includes one or more catenary heteroatoms; x is 1-3; and y is 1-5.

2. The electrolyte solution of claim 1, wherein the cyano silane is present in the electrolyte solution in an amount of between 0.1 and 10 wt.%, based on the total weight of the electrolyte solution.

3. The electrolyte solution according to claim 1, wherein the electrolyte solution comprises FEC in an amount of between 5 and 50 wt. %, based on the total weight of the electrolyte solution.

4. The electrolyte solution according to claim 1, wherein the cyano silane has a boiling point of greater than 80°C.

5. The electrolyte solution according to claim 1, wherein the cyano silane is $(CH_3CH_2O)_3Si(CH_2)_2CN$ or $(CH_3CH_2O)_3Si(CH_2)_3CN$.

6. The electrolyte solution according to claim 1, wherein the electrolyte salt comprises a lithium salt.

7. The electrolyte solution according to claim 6, wherein the electrolyte salt comprises $LiPF_6$, $LiBF_4$, $LiClO_4$, lithium bis(oxalato)borate, $LiN(SO_2CF_3)_2$, $LiN(SO_2C_2F_5)_2$, $LiAsF_6$, $LiC(SO_2CF_3)_3$, $LiN(SO_2F)_2$, $LiN(SO_2F)(SO_2CF_3)$, or $LiN(SO_2F)(SO_2C_4F_9)$.

8. The electrolyte solution according to claim 6, wherein the electrolyte salt is present in the solution in an amount of between 5 and 75 wt.%, based on the total weight of the electrolyte solution.

9. An electrochemical cell comprising:
a positive electrode;
a negative electrode; and
the electrolyte solution according to claim 1.

10. The electrochemical cell according to claim 9, wherein the negative electrode comprises silicon.

11. The electrochemical cell according to claim 10, wherein the negative electrode comprises a silicon alloy.

12. The electrochemical cell according to claim 11, wherein the silicon alloy comprises silicon, a transition metal, and carbon.

13. The electrochemical cell according to claim 9, wherein the positive electrode comprises an active material, the active material comprising a lithium metal oxide or a lithium metal phosphate.

14. A method of making an electrolyte solution, the method comprising:
combining a solvent, an electrolyte salt, and the electrolyte solution according to claim 1.

15. A method of forming an electrochemical cell comprising:
providing a positive electrode;
providing a negative electrode;
providing the electrolyte solution according to claim 1; and
incorporating the positive electrode, negative electrode, and electrolyte into a cell to form an electrochemical cell.

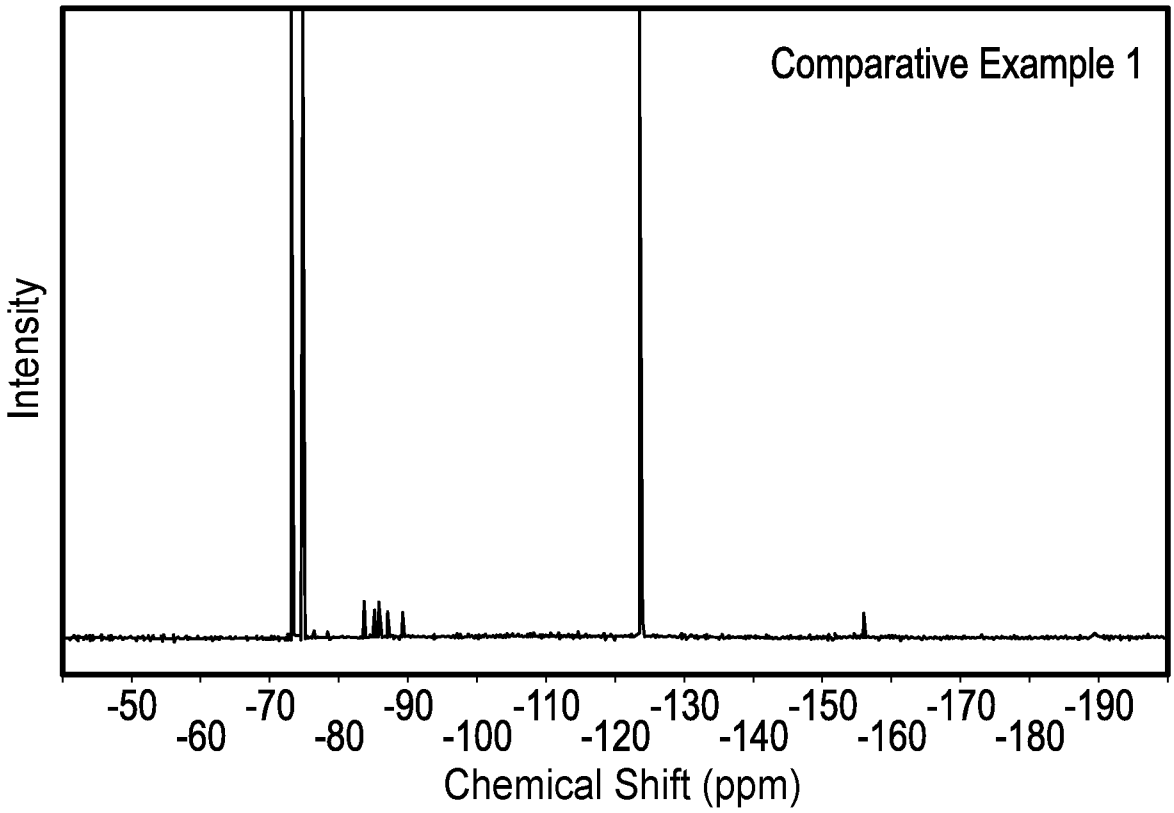
Comparative Example 1
Intensity
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
Chemical Shift (ppm)

FIG. 1A

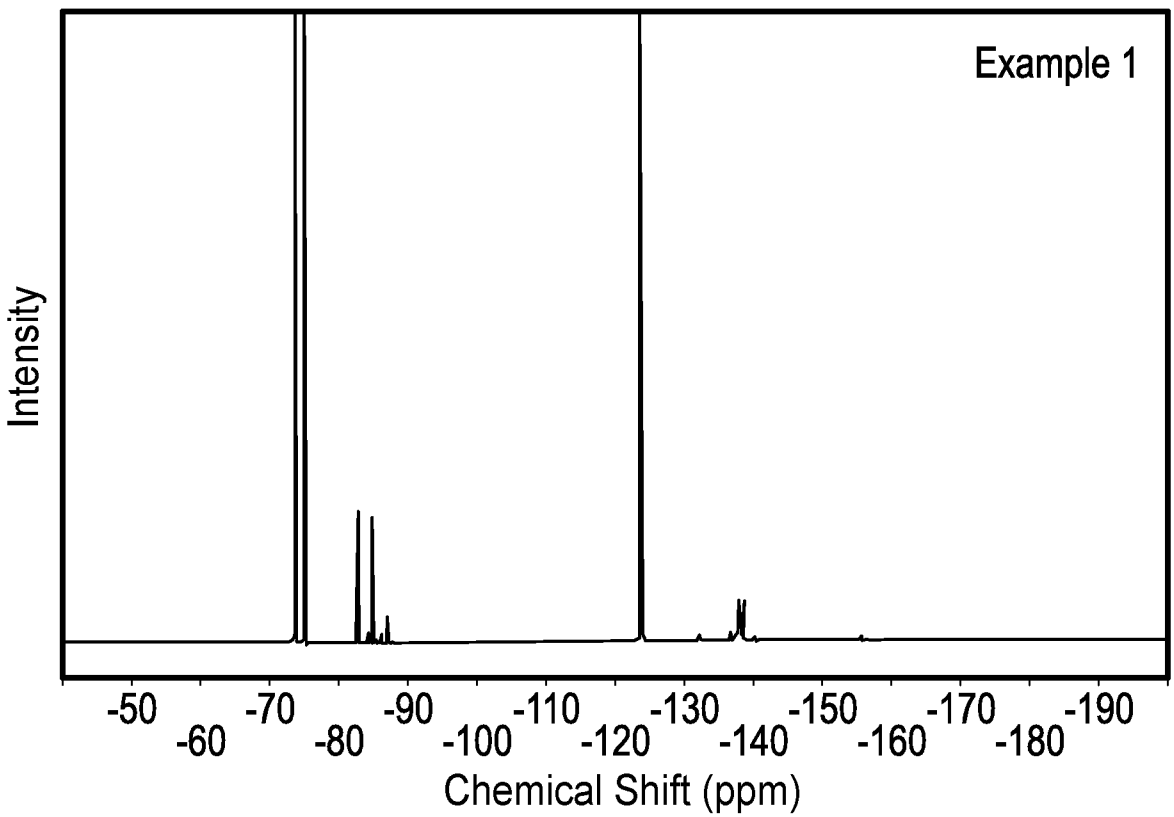
Example 1
Intensity
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
Chemical Shift (ppm)

FIG. 1B

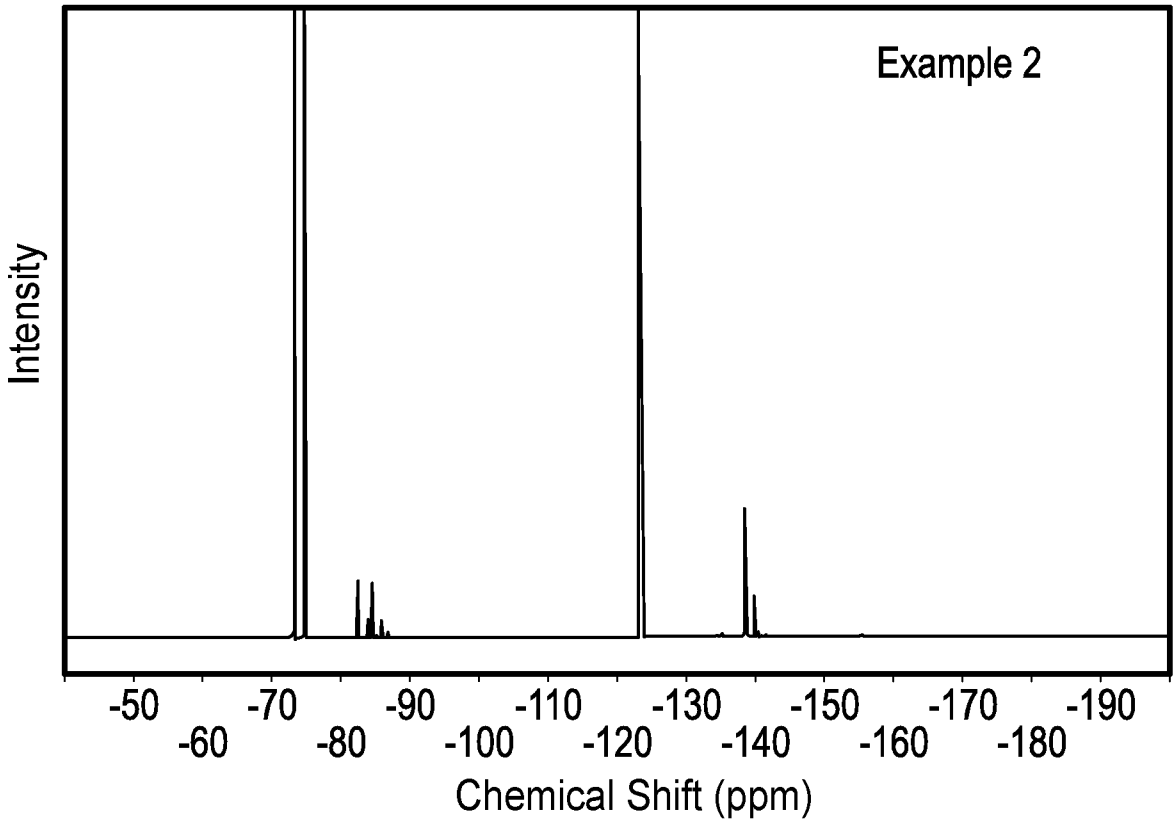
Example 2
Intensity
-50
-70
-90
-110
-130
-150
-170
-190
-60
-80
-100
-120
-140
-160
-180
Chemical Shift (ppm)

FIG. 1C

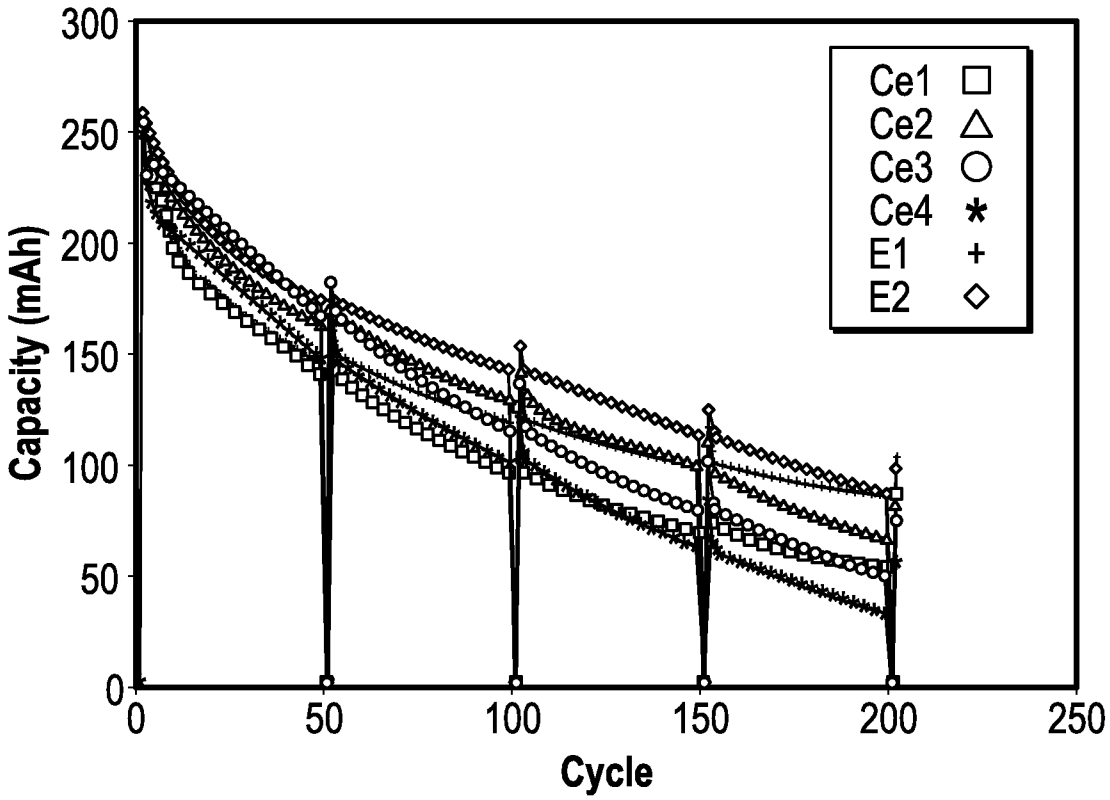
Ce1
Ce2
Ce3
Ce4
E1
E2
Capacity (mAh)
300
250
200
150
100
50
0
0
50
100
150
200
250
Cycle

FIG. 2