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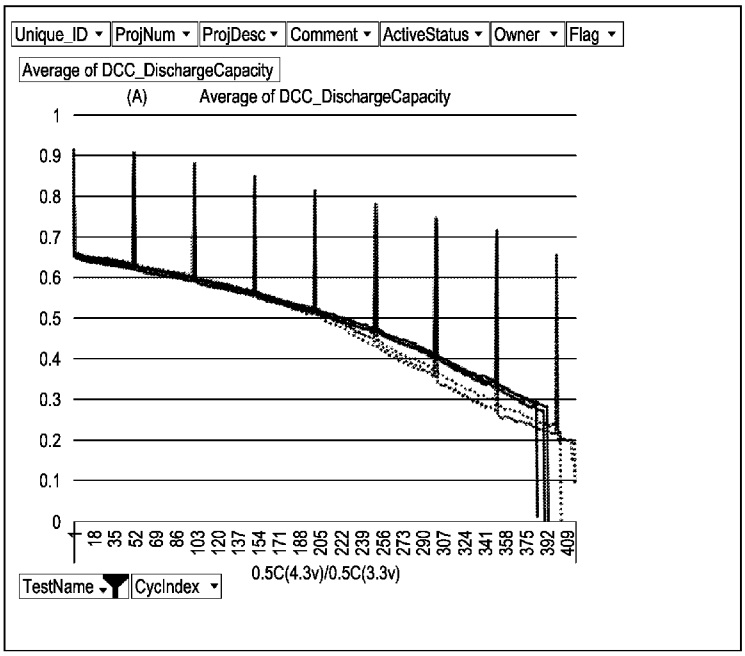
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(54) Title: SILICON-BASED ENERGY STORAGE DEVICES WITH CYCLIC CARBONATE CONTAINING ELECTROLYTE ADDITIVES

FIG. 3A



(57) Abstract: Electrolytes and electrolyte additives for use in energy storage devices, comprising cyclic carbonate compounds.

[Continued on next page]

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SILICON-BASED ENERGY STORAGE DEVICES WITH CYCLIC CARBONATE CONTAINING ELECTROLYTE ADDITIVES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application No. 62/596,034, filed December 7, 2017. The entirety of the above referenced application is hereby incorporated by reference.

BACKGROUND

Field

[0002] The present application relates generally to electrolytes for energy storage devices. In particular, the present application relates to electrolytes and additives for use in lithium-ion energy storage devices with silicon-based anode materials.

Description of the Related Art

[0003] As the demands for both zero-emission electric vehicles and grid-based energy storage systems increase, lower costs and improvements in energy density, power density, and safety of lithium (Li)-ion batteries are highly desirable. Enabling the high energy density and safety of Li-ion batteries requires the development of high-capacity, and high-voltage cathodes, high-capacity anodes and accordingly functional electrolytes with high voltage stability, interfacial compatibility with electrodes and safety.

[0004] A lithium-ion battery typically includes a separator and/or electrolyte between an anode and a cathode. In one class of batteries, the separator, cathode and anode materials are individually formed into sheets or films. Sheets of the cathode, separator and anode are subsequently stacked or rolled with the separator separating the cathode and anode (e.g., electrodes) to form the battery. Typical electrodes include electro-chemically active material layers on electrically conductive metals (e.g., aluminum and copper). Films can be rolled or cut into pieces which are then layered into stacks. The stacks are of alternating electro-chemically active materials with the separator between them.

[0005] Si is one of the most promising anode materials for Li-ion batteries due to its high specific gravimetric and volumetric capacity (3579 mAh/g and 2194 mAh/cm^3 vs.

372 mAh/g and 719 mAh/cm^3 for graphite), and low lithiation potential (< 0.4 V vs. Li/Li$^+$). Among the various cathodes presently available, layered lithium transition-metal oxides such as Ni-rich $Li[Ni_xCo_yMn(Al)_{1-x-y}]O_2$ (NCM or NCA) are the most promising ones due to their high theoretical capacity (~ 280 mAh/g) and relatively high average operating potential (3.6 V vs Li/Li$^+$). In addition to Ni-rich NCM or NCA cathode, $LiCoO_2$ (LCO) is also a very attractive cathode material because of its relatively high theoretical specific capacity of 274 mAh g^{-1}, high theoretical volumetric capacity of 1363 mAh cm^{-3}, low self-discharge, high discharge voltage, and good cycling performance. Coupling Si anodes with high-voltage Ni-rich NCM (or NCA) or LCO cathodes can deliver more energy than conventional Li-ion batteries with graphite-based anodes, due to the high capacity of these new electrodes. However, both Si-based anodes and high-voltage Ni rich NCM (or NCA) or LCO cathodes face formidable technological challenges, and long-term cycling stability with high-Si anodes paired with NCM or NCA cathodes has yet to be achieved.

[0006] For anodes, silicon-based materials can provide significant improvement in energy density. However, the large volumetric expansion (>300%) during the Li alloying/dealloying processes can lead to disintegration of the active material and the loss of electrical conduction paths, thereby reducing the cycling life of the battery. In addition, an unstable solid electrolyte interphase (SEI) layer can develop on the surface of the cycled anodes, and leads to an endless exposure of Si particle surfaces to the liquid electrolyte. This results in an irreversible capacity loss at each cycle due to the reduction at the low potential where the liquid electrolyte reacts with the exposed surface of the Si anode. In addition, oxidative instability of the conventional non-aqueous electrolyte takes place at voltages beyond 4.5 V, which can lead to accelerated decay of cycling performance. Because of the generally inferior cycle life of Si compared to graphite, only a small amount of Si or Si alloy is used in conventional anode materials.

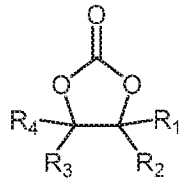
[0007] The NCM (or NCA) or LCO cathode usually suffers from an inferior stability and a low capacity retention at a high cut-off potential. The reasons can be ascribed to the unstable surface layer's gradual exfoliation, the continuous electrolyte decomposition, and the transition metal ion dissolution into electrolyte solution. The major limitations for LCO cathode are high cost, low thermal stability, and fast capacity fade at high current rates or during deep cycling. LCO cathodes are expensive because of the high cost of Co. Low

thermal stability refers to exothermic release of oxygen when a lithium metal oxide cathode is heated. In order to make good use of Si anode//NCM or NCA cathode-, and Si anode//LCO cathode-based Li-ion battery systems, the aforementioned barriers need to be overcome.

[0008] One strategy for overcoming these barriers includes exploring new electrolyte additives in order to make good use of Si anode//NCM or NCA cathode-, and Si anode//LCO cathode-based full cells. The next generation of electrolyte additives to be developed should be able to form a uniform, stable SEI layer on the surface of Si anodes. This layer should have low impedance and be electronically insulating, but ionically conductive to Li-ion. Additionally, the SEI layer formed by the additive should have excellent elasticity and mechanical strength to overcome the problem of expansion and shrinkage of the Si anode volume. On the cathode side, the ideal additives should be oxidized preferentially to the solvent molecule in the bare electrolyte, resulting in a protective cathode electrolyte interphase (CEI) film formed on the surface of the Ni-rich NCM (or NCA) and LCO cathodes. At the same time, it should help alleviate the dissolution phenomenon of transition metal ions and decrease surface resistance on cathode side. In addition, they could help improve the physical properties of the electrolyte such as ionic conductivity, viscosity, and wettability.

SUMMARY

[0009] In some aspects, energy storage devices are provided. In some embodiments, the energy storage device includes a first electrode and a second electrode, wherein at least one of the first electrode and the second electrode is a Si-based electrode. In some embodiments, the energy storage device includes a separator between the first electrode and the second electrode. In some embodiments, the energy storage device includes an electrolyte. In some embodiments, the energy storage device includes at least one electrolyte additive comprising a compound of Formula (A):



(A);

[0010] In some embodiments, R_1 is selected from the group consisting of a C1-C8 alkyl substituted by F, an alkoxy-alkyl substituted by F, and alkenyloxy-alkyl. In some embodiments, each R_2, R_3, and R_4 is independently an –H or a C1-C8 alkyl substituted by F. In some embodiments, R_1 is C1-C10 alkyl substituted by F or $-CH_2-OR_5$. In some embodiments, R_5 is a C1-C10 alkyl substituted by F or a C1-C6 alkenyl. In some embodiments, each R_2, R_3, and R_4 is independently an –H or $–CF_3$.

[0011] In some embodiments, the second electrode is a Si-dominant electrode. In some embodiments, the second electrode comprises a self-supporting composite material film. In some embodiments, the composite material film comprises greater than 0 % and less than about 90 % by weight of silicon particles, and greater than 0 % and less than about 90 % by weight of one or more types of carbon phases, wherein at least one of the one or more types of carbon phases is a substantially continuous phase that holds the composite material film together such that the silicon particles are distributed throughout the composite material film.

[0012] In some embodiments, the electrolyte further comprises fluoroethylene carbonate (FEC). In some embodiments, the electrolyte is substantially free of non-fluorine containing cyclic carbonate.

[0013] In some embodiments, the electrolyte additive is selected from the group consisting of 4-(Trifluoromethyl)-1,3-dioxolan-2-one (TFPC), 4,4-Bis(trifluoromethyl)-1,3-dioxolan-2-one (including cis, trans and racemate forms), 4,5-Bis(Trifluoromethyl)-1,3-dioxolan-2-one, 1,1,2-Tris(trifluoromethyl)ethylene carbonate, Tetrakis(trifluoromethyl)ethylene carbonate, 4-(Fluoromethyl)-1,3-dioxolan-2-one, 3,3-Difluoropropylene carbonate, 4-(2,2,3,3,4,4,4-Heptafluorobutyl)-1,3-dioxolan-2-one, 4-(2,2,3,3,4,4,5,5,5-Nonafluoropentyl)-1,3-dioxolan-2-one, 4-(2,2,3,3,4,4,5,5,6,6,7,7,7-Tridecafluoroheptyl)-1,3-dioxolan-2-one, 4-[(2,2,2-Trifluoroethoxy)methyl]-1,3-dioxolan-2-one, 4-[(2,2,3,3,3-Pentafluoropropoxy)methyl]-1,3-dioxolan-2-one, 4-[(2,2,3,3,4,4,4-Heptafluorobutoxy)methyl]-1,3-dioxolan-2-one, 3-[(2,2,3,3-Tetrafluoropropoxy)methyl]-1,3-dioxolan-2-one, 4-[(2,2,3,4,4,4-Hexafluorobutoxy)methyl]-1,3-dioxolan-2-one, 4-[(2,2-Difluoroethoxy)methyl]-1,3-dioxolan-2-one, 4-[(Hexafluoroisopropoxy)methyl]-1,3-dioxolan-2-one, 4-[(1H,1H-Perfluorohexoxy)methyl]-1,3-dioxolan-2-one, 4-[(1H,1H,9H-Perfluorononoxy)methyl]-1,3-dioxolan-2-one, 4-[(1H,1H,7H-Perfluoroheptoxy)methyl]-1,3-

dioxolan-2-one, 4-[(1H,1H,2H,2H-Perfluorohexoxy)methyl]-1,3-dioxolan-2-one, and 4-[(4,4,5,5,5-Pentafluoropentoxy)methyl]-1,3-dioxolan-2-one.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] Figure 1 depicts a cross-sectional schematic diagram of an example of a lithium-ion battery 300 implemented as a pouch cell.

[0015] Figure 2 depicts an Arbin pulse function.

[0016] Figures 3A and 3B show the capacity (A) and capacity retention (B) of an embodiment of Si-dominant anode//$LiCoO_2$ cathode full cells, respectively.

[0017] Figures 4A and 4B show the average impedance before (A) and after (B) cycling of an embodiment of Si-dominant anode//$LiCoO_2$ cathode full cells, respectively.

[0018] Figures 5A and 5B show the average resistance before (A) and after (B) cycling of an embodiment of Si-dominant anode//$LiCoO_2$ cathode full cells, respectively.

[0019] Figures 6A and 6B show the average resistance after 10s charge (A) and discharge (B) of an embodiment of Si-dominant anode//$LiCoO_2$ cathode full cells, respectively.

[0020] Figures 7A and 7B show the average resistance after 30s charge (A) and discharge (B) of an embodiment of Si-dominant anode//$LiCoO_2$ cathode full cells, respectively.

DETAILED DESCRIPTION

Definitions

[0021] The term "alkyl" refers to a straight or branched, saturated, aliphatic radical having the number of carbon atoms indicated. The alkyl moiety may be branched or straight chain. For example, C1-C6 alkyl includes, but is not limited to, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, pentyl, isopentyl, hexyl, etc. Other alkyl groups include, but are not limited to heptyl, octyl, nonyl, decyl, etc. Alkyl can include any number of carbons, such as 1-2, 1-3, 1-4, 1-5, 1-6, 1-7, 1-8, 1-9, 1-10, 1-11, 1-12 2-3, 2-4, 2-5, 2-6, 3-4, 3-5, 3-6, 4-5, 4-6 and 5-6. The alkyl group is typically monovalent, but can be divalent, such as when the alkyl group links two moieties together.

[0022] The term "fluoro-alkyl" refers to an alkyl group where one, some, or all hydrogen atoms have been replaced by fluorine.

[0023] The term "alkylene" refers to an alkyl group, as defined above, linking at least two other groups, *i.e.*, a divalent hydrocarbon radical. The two moieties linked to the alkylene can be linked to the same atom or different atoms of the alkylene. For instance, a straight chain alkylene can be the bivalent radical of $-(CH_2)_n-$, where n is 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10. Alkylene groups include, but are not limited to, methylene, ethylene, propylene, isopropylene, butylene, isobutylene, sec-butylene, pentylene and hexylene.

[0024] The term "alkoxy" refers to alkyl group having an oxygen atom that either connects the alkoxy group to the point of attachment or is linked to two carbons of the alkoxy group. Alkoxy groups include, for example, methoxy, ethoxy, propoxy, iso-propoxy, butoxy, 2-butoxy, iso-butoxy, sec-butoxy, tert-butoxy, pentoxy, hexoxy, etc. The alkoxy groups can be further substituted with a variety of substituents described within. For example, the alkoxy groups can be substituted with halogens to form a "halo-alkoxy" group, or substituted with fluorine to form a "fluoro-alkoxy" group.

[0025] The term "alkenyl" refers to either a straight chain or branched hydrocarbon of 2 to 6 carbon atoms, having at least one double bond. Examples of alkenyl groups include, but are not limited to, vinyl, propenyl, isopropenyl, 1-butenyl, 2-butenyl, isobutenyl, butadienyl, 1-pentenyl, 2-pentenyl, isopentenyl, 1,3-pentadienyl, 1,4-pentadienyl, 1-hexenyl, 2-hexenyl, 3-hexenyl, 1,3-hexadienyl, 1,4-hexadienyl, 1,5-hexadienyl, 2,4-hexadienyl, or 1,3,5-hexatrienyl. Alkenyl groups can also have from 2 to 3, 2 to 4, 2 to 5, 3 to 4, 3 to 5, 3 to 6, 4 to 5, 4 to 6 and 5 to 6 carbons. The alkenyl group is typically monovalent, but can be divalent, such as when the alkenyl group links two moieties together.

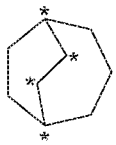
[0026] The term "alkenylene" refers to an alkenyl group, as defined above, linking at least two other groups, *i.e.*, a divalent hydrocarbon radical. The two moieties linked to the alkenylene can be linked to the same atom or different atoms of the alkenylene. Alkenylene groups include, but are not limited to, ethenylene, propenylene, isopropenylene, butenylene, isobutenylene, sec-butenylene, pentenylene and hexenylene.

[0027] The term "alkynyl" refers to either a straight chain or branched hydrocarbon of 2 to 6 carbon atoms, having at least one triple bond. Examples of alkynyl groups include, but are not limited to, acetylenyl, propynyl, 1-butynyl, 2-butynyl, isobutynyl,

sec-butynyl, butadiynyl, 1-pentynyl, 2-pentynyl, isopentynyl, 1,3-pentadiynyl, 1,4-pentadiynyl, 1-hexynyl, 2-hexynyl, 3-hexynyl, 1,3-hexadiynyl, 1,4-hexadiynyl, 1,5-hexadiynyl, 2,4-hexadiynyl, or 1,3,5-hexatriynyl. Alkynyl groups can also have from 2 to 3, 2 to 4, 2 to 5, 3 to 4, 3 to 5, 3 to 6, 4 to 5, 4 to 6 and 5 to 6 carbons. The alkynyl group is typically monovalent, but can be divalent, such as when the alkynyl group links two moieties together.

[0028] The term "alkynylene" refers to an alkynyl group, as defined above, linking at least two other groups, *i.e.*, a divalent hydrocarbon radical. The two moieties linked to the alkynylene can be linked to the same atom or different atoms of the alkynylene. Alkynylene groups include, but are not limited to, ethynylene, propynylene, butynylene, sec-butynylene, pentynylene and hexynylene.

[0029] The term "cycloalkyl" refers to a saturated or partially unsaturated, monocyclic, fused bicyclic, bridged polycyclic, or spiro ring assembly containing from 3 to 12, from 3 to 10, or from 3 to 7 ring atoms, or the number of atoms indicated. Monocyclic rings include, for example, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, and cyclooctyl. Bicyclic and polycyclic rings include, for example, norbornane, decahydronaphthalene and adamantane. For example, C3-C8 cycloalkyl includes cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclooctyl, and norbornane. As used herein, the term "fused" refers to two rings which have two atoms and one bond in common. For example, in the following structure, rings A and B are fused 

. As used herein, the term "bridged polycyclic" refers to compounds wherein the cycloalkyl contains a linkage of one or more atoms connecting non-adjacent atoms. The following structures  and  are examples of "bridged" rings. As used herein, the term "spiro" refers to two rings which have one atom in common and the two rings are not linked by a bridge. Examples of fused cycloalkyl groups are decahydronaphthalenyl, dodecahydro-1H-phenalenyl and tetradecahydroanthracenyl; examples of bridged cycloalkyl groups are bicyclo[1.1.1]pentyl, adamantanyl, and

norbornanyl; and examples of spiro cycloalkyl groups include spiro[3.3]heptane and spiro[4.5]decane.

[0030] The term "cycloalkylene" refers to a cycloalkyl group, as defined above, linking at least two other groups, *i.e.*, a divalent hydrocarbon radical. The two moieties linked to the cycloalkylene can be linked to the same atom or different atoms of the cycloalkylene. Cycloalkylene groups include, but are not limited to, cyclopropylene, cyclobutylene, cyclopentylene, cyclohexylene, and cyclooctylene.

[0031] The term "aryl" refers to a monocyclic or fused bicyclic, tricyclic or greater, aromatic ring assembly containing 6 to 16 ring carbon atoms. For example, aryl may be phenyl, benzyl or naphthyl, preferably phenyl. Aryl groups can be mono-, di- or tri-substituted by one, two or three radicals. Preferred as aryl is naphthyl, phenyl or phenyl mono- or disubstituted by alkoxy, phenyl, halogen, alkyl or trifluoromethyl, especially phenyl or phenyl-mono- or disubstituted by alkoxy, halogen or trifluoromethyl, and in particular phenyl.

[0032] The term "arylene" refers to an aryl group, as defined above, linking at least two other groups. The two moieties linked to the arylene are linked to different atoms of the arylene. Arylene groups include, but are not limited to, phenylene.

[0033] The term "heteroaryl" refers to a monocyclic or fused bicyclic or tricyclic aromatic ring assembly containing 5 to 16 ring atoms, where from 1 to 4 of the ring atoms are a heteroatom each N, O or S. For example, heteroaryl includes pyridyl, indolyl, indazolyl, quinoxalinyl, quinolinyl, isoquinolinyl, benzothienyl, benzofuranyl, furanyl, pyrrolyl, thiazolyl, benzothiazolyl, oxazolyl, isoxazolyl, triazolyl, tetrazolyl, pyrazolyl, imidazolyl, thienyl, or any other radicals substituted, especially mono- or di-substituted, by e.g. alkyl, nitro or halogen. Pyridyl represents 2-, 3- or 4-pyridyl, advantageously 2- or 3-pyridyl. Thienyl represents 2- or 3-thienyl. Quinolinyl represents preferably 2-, 3- or 4-quinolinyl. Isoquinolinyl represents preferably 1-, 3- or 4-isoquinolinyl. Benzopyranyl, benzothiopyranyl represents preferably 3-benzopyranyl or 3-benzothiopyranyl, respectively. Thiazolyl represents preferably 2- or 4-thiazolyl, and most preferred 4-thiazolyl. Triazolyl is preferably 1-, 2- or 5-(1,2,4-triazolyl). Tetrazolyl is preferably 5-tetrazolyl.

[0034] Preferably, heteroaryl is pyridyl, indolyl, quinolinyl, pyrrolyl, thiazolyl, isoxazolyl, triazolyl, tetrazolyl, pyrazolyl, imidazolyl, thienyl, furanyl, benzothiazolyl,

benzofuranyl, isoquinolinyl, benzothienyl, oxazolyl, indazolyl, or any of the radicals substituted, especially mono- or di-substituted.

[0035] The term "heteroalkyl" refers to an alkyl group having from 1 to 3 heteroatoms such as N, O and S. The heteroatoms can also be oxidized, such as, but not limited to, -S(O)- and -$S(O)_2$-. For example, heteroalkyl can include ethers, thioethers, alkyl-amines and alkyl-thiols.

[0036] The term "heteroalkylene" refers to a heteroalkyl group, as defined above, linking at least two other groups. The two moieties linked to the heteroalkylene can be linked to the same atom or different atoms of the heteroalkylene.

[0037] The term "heterocycloalkyl" refers to a ring system having from 3 ring members to about 20 ring members and from 1 to about 5 heteroatoms such as N, O and S. The heteroatoms can also be oxidized, such as, but not limited to, -S(O)- and -$S(O)_2$-. For example, heterocycle includes, but is not limited to, tetrahydrofuranyl, tetrahydrothiophenyl, morpholino, pyrrolidinyl, pyrrolinyl, imidazolidinyl, imidazolinyl, pyrazolidinyl, pyrazolinyl, piperazinyl, piperidinyl, indolinyl, quinuclidinyl and 1,4-dioxa-8-aza-spiro[4.5]dec-8-yl.

[0038] The term "heterocycloalkylene" refers to a heterocyclalkyl group, as defined above, linking at least two other groups. The two moieties linked to the heterocycloalkylene can be linked to the same atom or different atoms of the heterocycloalkylene.

[0039] The term "optionally substituted" is used herein to indicate a moiety that can be unsubstituted or substituted by one or more substituent. When a moiety term is used without specifically indicating as substituted, the moiety is unsubstituted.

Description

[0040] To overcome the current obstacles associated with developing high-energy full-cells with Si-based anodes, the next generation of oxidation-stable electrolytes or electrolyte additives are developed. The electrolyte or electrolyte additives can form a stable, electronically insulating but ionically conducting SEI layer on the surface of Si anodes. Additionally, these electrolytes or additives may also help modify cathode surfaces, forming stable CEI layers. These could enable the electrochemical stability of Li-ion

batteries when cycled at higher voltages and help with calendar life of the batteries. In addition, to alleviate battery safety concerns, these additives may impart an increased thermal stability to the organic components of the electrolyte, drive a rise in the flash point of the electrolyte formulations, increase the flame-retardant effectiveness and enhance thermal stability of SEI or CEI layers on the surface of electrodes.

[0041] In the present disclosure, the use of chemical compounds comprising cyclic carbonate electrolyte additives for energy storage devices with Si-dominant anodes are described. Due to their unique chemical structures and functional groups, cyclic carbonate containing electrolyte additives may bring the following benefits: (i) stabilize solid/electrolyte interface film to reduce electrolyte reactions (oxidation on the NCM, NCA, or LCO cathode and reduction on the Si anode), prevent Si anode volume expansion, and protect transition metal ion dissolution from NCM or NCA cathode and stabilize the subsequent structure changes; and avoid the exothermic reaction between the released oxygen for LCO and organic electrolyte and enhance the thermal stability of LCO cathode; and (ii) reduce the flammability and enhance the thermal stability of organic electrolytes and increase the safety of electrolyte solutions. Due to their versatility in reaction chemistry and overall stability in electrochemical environments, as well as have excellent flame resistance or fire retardant properties, involving cyclic carbonate containing electrolyte additives into electrolyte solutions may help improve both overall electrochemical performance and safety of Si anode-based Li-ion batteries.

[0042] Typical carbon anode electrodes include a current collector such as a copper sheet. Carbon is deposited onto the collector along with an inactive binder material. Carbon is often used because it has excellent electrochemical properties and is also electrically conductive. If the current collector layer (e.g., copper layer) was removed, the carbon would likely be unable to mechanically support itself. Therefore, conventional electrodes require a support structure such as the collector to be able to function as an electrode. The electrode (e.g., anode or cathode) compositions described in this application can produce electrodes that are self-supported. The need for a metal foil current collector is eliminated or minimized because conductive carbonized polymer is used for current collection in the anode structure as well as for mechanical support. In typical applications for the mobile industry, a metal current collector is typically added to ensure sufficient rate

performance. The carbonized polymer can form a substantially continuous conductive carbon phase in the entire electrode as opposed to particulate carbon suspended in a non-conductive binder in one class of conventional lithium-ion battery electrodes. Advantages of a carbon composite blend that utilizes a carbonized polymer can include, for example, 1) higher capacity, 2) enhanced overcharge/discharge protection, 3) lower irreversible capacity due to the elimination (or minimization) of metal foil current collectors, and 4) potential cost savings due to simpler manufacturing.

[0043] Anode electrodes currently used in the rechargeable lithium-ion cells typically have a specific capacity of approximately 200 milliamp hours per gram (including the metal foil current collector, conductive additives, and binder material). Graphite, the active material used in most lithium ion battery anodes, has a theoretical energy density of 372 milliamp hours per gram (mAh/g). In comparison, silicon has a high theoretical capacity of 4200 mAh/g. In order to increase volumetric and gravimetric energy density of lithium-ion batteries, silicon may be used as the active material for the cathode or anode. Several types of silicon materials, e.g., silicon nanopowders, silicon nanofibers, porous silicon, and ball-milled silicon, have also been reported as viable candidates as active materials for the negative or positive electrodes. Small particle sizes (for example, sizes in the nanometer range) generally can increase cycle life performance. They also can display very high initial irreversible capacity. However, small particle sizes also can result in very low volumetric energy density (for example, for the overall cell stack) due to the difficulty of packing the active material. Larger particle sizes, (for example, sizes in the micron range) generally can result in higher density anode material. However, the expansion of the silicon active material can result in poor cycle life due to particle cracking. For example, silicon can swell in excess of 300% upon lithium insertion. Because of this expansion, anodes including silicon should be allowed to expand while maintaining electrical contact between the silicon particles.

[0044] Cathode electrodes described herein may include metal oxide cathode materials, such as Lithium Cobalt Oxide ($LiCoO_2$) (LCO), Ni-rich oxides, high voltage cathode materials, lithium-rich oxides, nickel-rich layered oxides, lithium-rich layered oxides, high-voltage spinel oxides, and high-voltage polyanionic compounds. Ni-rich oxides and/or high voltage cathode materials may include NCM and NCA. One example of NCM material includes $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM-622). Lithium rich oxides may include

$xLi_2MnO_3 \cdot (1-x)LiNi_aCo_bMn_cO_2$. Nickel-rich layered oxides may include $LiNi_{1+x}M_{1-x}O_2$ (where M = Co, Mn or Al). Lithium rich layered oxides may include $LiNi_{1+x}M_{1-x}O_2$ (where M = Co, Mn or Ni). High-voltage spinel oxides may include $LiNi_{0.5}Mn_{1.5}O_4$. High-voltage polyanionic compounds may include phosphates, sulfates, silicates, etc.

[0045] As described herein and in U.S. Patent App. No. 13/008,800 and 13/601,976, entitled "Composite Materials for Electrochemical Storage" and "Silicon Particles for Battery Electrodes," respectively, certain embodiments utilize a method of creating monolithic, self-supported anodes using a carbonized polymer. Because the polymer is converted into an electrically conductive and electrochemically active matrix, the resulting electrode is conductive enough that, in some embodiments, a metal foil or mesh current collector can be omitted or minimized. The converted polymer also acts as an expansion buffer for silicon particles during cycling so that a high cycle life can be achieved. In certain embodiments, the resulting electrode is an electrode that is comprised substantially of active material. In further embodiments, the resulting electrode is substantially active material. The electrodes can have a high energy density of between about 500 mAh/g to about 1200 mAh/g that can be due to, for example, 1) the use of silicon, 2) elimination or substantial reduction of metal current collectors, and 3) being comprised entirely or substantially entirely of active material.

[0046] As described herein and in U.S. Patent App. No. 14/800380, entitled "Electrolyte Compositions for Batteries," the entirety of which is hereby incorporated by reference, composite materials can be used as an anode in most conventional Li-ion batteries; they may also be used as the cathode in some electrochemical couples with additional additives. The composite materials can also be used in either secondary batteries (e.g., rechargeable) or primary batteries (e.g., non-rechargeable). In some embodiments, the composite materials can be used in batteries implemented as a pouch cell, as described in further details herein. In certain embodiments, the composite materials are self-supported structures. In further embodiments, the composite materials are self-supported monolithic structures. For example, a collector may be included in the electrode comprised of the composite material. In certain embodiments, the composite material can be used to form carbon structures discussed in U.S. Patent App. No. 12/838,368 entitled "Carbon Electrode Structures for Batteries," the entirety of which is hereby incorporated by reference.

Furthermore, the composite materials described herein can be, for example, silicon composite materials, carbon composite materials, and/or silicon-carbon composite materials.

[0047] In some embodiments, a largest dimension of the silicon particles can be less than about 40 μm, less than about 1 μm, between about 10 nm and about 40 μm, between about 10 nm and about 1 μm, less than about 500 nm, less than about 100 nm, and about 100 nm. All, substantially all, or at least some of the silicon particles may comprise the largest dimension described above. For example, an average or median largest dimension of the silicon particles can be less than about 40 μm, less than about 1 μm, between about 10 nm and about 40 μm, between about 10 nm and about 1 μm, less than about 500 nm, less than about 100 nm, and about 100 nm. The amount of silicon in the composite material can be greater than zero percent by weight of the mixture and composite material. In certain embodiments, the mixture comprises an amount of silicon, the amount being within a range of from about 0 % to about 90 % by weight, including from about 30 % to about 80 % by weight of the mixture. The amount of silicon in the composite material can be within a range of from about 0 % to about 35 % by weight, including from about 0 % to about 25 % by weight, from about 10 % to about 35 % by weight, and about 20 % by weight. In further certain embodiments, the amount of silicon in the mixture is at least about 30 % by weight. Additional embodiments of the amount of silicon in the composite material include more than about 50 % by weight, between about 30 % and about 80 % by weight, between about 50 % and about 70 % by weight, and between about 60 % and about 80 % by weight. Furthermore, the silicon particles may or may not be pure silicon. For example, the silicon particles may be substantially silicon or may be a silicon alloy. In one embodiment, the silicon alloy includes silicon as the primary constituent along with one or more other elements.

[0048] As described herein, micron-sized silicon particles can provide good volumetric and gravimetric energy density combined with good cycle life. In certain embodiments, to obtain the benefits of both micron-sized silicon particles (e.g., high energy density) and nanometer-sized silicon particles (e.g., good cycle behavior), silicon particles can have an average particle size in the micron range and a surface including nanometer-sized features. In some embodiments, the silicon particles have an average particle size (e.g.,

average diameter or average largest dimension) between about 0.1 μm and about 30 μm or between about 0.1 μm and all values up to about 30 μm. For example, the silicon particles can have an average particle size between about 0.5 μm and about 25 μm, between about 0.5 μm and about 20 μm, between about 0.5 μm and about 15 μm, between about 0.5 μm and about 10 μm, between about 0.5 μm and about 5 μm, between about 0.5 μm and about 2 μm, between about 1 μm and about 20 μm, between about 1 μm and about 15 μm, between about 1 μm and about 10 μm, between about 5 μm and about 20 μm, etc. Thus, the average particle size can be any value between about 0.1 μm and about 30 μm, e.g., 0.1 μm, 0.5 μm, 1 μm, 5 μm, 10 μm, 15 μm, 20 μm, 25 μm, and 30 μm.

[0049] The composite material can be formed by pyrolyzing a polymer precursor, such as polyamide acid. The amount of carbon obtained from the precursor can be about 50 weight percent by weight of the composite material. In certain embodiments, the amount of carbon from the precursor in the composite material is about 10 % to about 25 % by weight. The carbon from the precursor can be hard carbon. Hard carbon can be a carbon that does not convert into graphite even with heating in excess of 2800 degrees Celsius. Precursors that melt or flow during pyrolysis convert into soft carbons and/or graphite with sufficient temperature and/or pressure. Hard carbon may be selected since soft carbon precursors may flow and soft carbons and graphite are mechanically weaker than hard carbons. Other possible hard carbon precursors can include phenolic resins, epoxy resins, and other polymers that have a very high melting point or are crosslinked. In some embodiments, the amount of hard carbon in the composite material has a value within a range of from about 10 % to about 25 % by weight, about 20 % by weight, or more than about 50 % by weight. In certain embodiments, the hard carbon phase is substantially amorphous. In other embodiments, the hard carbon phase is substantially crystalline. In further embodiments, the hard carbon phase includes amorphous and crystalline carbon. The hard carbon phase can be a matrix phase in the composite material. The hard carbon can also be embedded in the pores of the additives including silicon. The hard carbon may react with some of the additives to create some materials at interfaces. For example, there may be a silicon carbide layer between silicon particles and the hard carbon.

[0050] In certain embodiments, graphite particles are added to the mixture. Advantageously, graphite can be an electrochemically active material in the battery as well as an elastic deformable material that can respond to volume change of the silicon particles. Graphite is the preferred active anode material for certain classes of lithium-ion batteries currently on the market because it has a low irreversible capacity. Additionally, graphite is softer than hard carbon and can better absorb the volume expansion of silicon additives. In certain embodiments, a largest dimension of the graphite particles is between about 0.5 microns and about 20 microns. All, substantially all, or at least some of the graphite particles may comprise the largest dimension described herein. In further embodiments, an average or median largest dimension of the graphite particles is between about 0.5 microns and about 20 microns. In certain embodiments, the mixture includes greater than 0 % and less than about 80 % by weight of graphite particles. In further embodiments, the composite material includes about 40 % to about 75 % by weight graphite particles.

[0051] In certain embodiments, conductive particles which may also be electrochemically active are added to the mixture. Such particles can enable both a more electronically conductive composite as well as a more mechanically deformable composite capable of absorbing the large volumetric change incurred during lithiation and de-lithiation. In certain embodiments, a largest dimension of the conductive particles is between about 10 nanometers and about 7 millimeters. All, substantially all, or at least some of the conductive particles may comprise the largest dimension described herein. In further embodiments, an average or median largest dimension of the conductive particles is between about 10 nm and about 7 millimeters. In certain embodiments, the mixture includes greater than zero and up to about 80 % by weight conductive particles. In further embodiments, the composite material includes about 45 % to about 80 % by weight conductive particles. The conductive particles can be conductive carbon including carbon blacks, carbon fibers, carbon nanofibers, carbon nanotubes, graphite, graphene, etc. Many carbons that are considered as conductive additives that are not electrochemically active become active once pyrolyzed in a polymer matrix. Alternatively, the conductive particles can be metals or alloys including copper, nickel, or stainless steel.

[0052] The composite material may also be formed into a powder. For example, the composite material can be ground into a powder. The composite material powder can be

used as an active material for an electrode. For example, the composite material powder can be deposited on a collector in a manner similar to making a conventional electrode structure, as known in the industry.

[0053] In some embodiments, the full capacity of the composite material may not be utilized during use of the battery to improve battery life (e.g., number charge and discharge cycles before the battery fails or the performance of the battery decreases below a usability level). For example, a composite material with about 70 % by weight silicon particles, about 20 % by weight carbon from a precursor, and about 10 % by weight graphite may have a maximum gravimetric capacity of about 2000 mAh/g, while the composite material may only be used up to a gravimetric capacity of about 550 to about 850 mAh/g. Although, the maximum gravimetric capacity of the composite material may not be utilized, using the composite material at a lower capacity can still achieve a higher capacity than certain lithium ion batteries. In certain embodiments, the composite material is used or only used at a gravimetric capacity below about 70 % of the composite material's maximum gravimetric capacity. For example, the composite material is not used at a gravimetric capacity above about 70 % of the composite material's maximum gravimetric capacity. In further embodiments, the composite material is used or only used at a gravimetric capacity below about 50 % of the composite material's maximum gravimetric capacity or below about 30 % of the composite material's maximum gravimetric capacity.

Electrolyte

[0054] An electrolyte for a lithium ion battery can include a solvent and a lithium ion source, such as a lithium-containing salt. The composition of the electrolyte may be selected to provide a lithium ion battery with improved performance. In some embodiments, the electrolyte may contain an electrolyte additive. As described herein, a lithium ion battery may include a first electrode, a second electrode, a separator between the first electrode and the second electrode, and an electrolyte in contact with the first electrode, the second electrode, and the separator. The electrolyte serves to facilitate ionic transport between the first electrode and the second electrode. In some embodiments, the first electrode and the second electrode can refer to anode and cathode or cathode and anode, respectively.

[0055] In some embodiments, the electrolyte for a lithium ion battery may include a solvent comprising a fluorine-containing component, such as a fluorine-containing cyclic carbonate, a fluorine-containing linear carbonate, and/or a fluoroether. In some embodiments, the electrolyte can include more than one solvent. For example, the electrolyte may include two or more co-solvents. In some embodiments, at least one of the co-solvents in the electrolyte is a fluorine-containing compound. In some embodiments, the fluorine-containing compound may be fluoroethylene carbonate (FEC), 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether, or difluoroethylene carbonate (F2EC). In some embodiments, the co-solvent may be selected from the group consisting of FEC, ethyl methyl carbonate (EMC), 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether, difluoroethylene carbonate (F2EC), ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC), propylene carbonate (PC), and gamma- Butyrolactone (GBL). In some embodiments, the electrolyte contains FEC. In some embodiments, the electrolyte contains both EMC and FEC. In some embodiments, the electrolyte may further contain 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether, EC, DEC, DMC, PC, GBL, and/or F2EC or some partially or fully fluorinated linear or cyclic carbonates, ethers, etc. as a co-solvent. In some embodiments, the electrolyte is free or substantially free of non-fluorine-containing cyclic carbonates, such as EC, GBL, and PC.

[0056] As used herein, a co-solvent of an electrolyte has a concentration of at least about 10% by volume (vol%). In some embodiments, a co-solvent of the electrolyte may be about 20 vol%, about 40 vol%, about 60 vol%, or about 80 vol%, or about 90 vol% of the electrolyte. In some embodiments, a co-solvent may have a concentration from about 10 vol% to about 90 vol%, from about 10 vol% to about 80 vol%, from about 10 vol% to about 60 vol%, from about 20 vol% to about 60 vol%, from about 20 vol% to about 50 vol%, from about 30 vol% to about 60 vol%, or from about 30 vol% to about 50 vol%.

[0057] For example, in some embodiments, the electrolyte may contain a fluorine-containing cyclic carbonate, such as FEC, at a concentration of about 10 vol% to about 60 vol%, including from about 20 vol% to about 50 vol%, and from about 20 vol% to about 40 vol%. In some embodiments, the electrolyte may comprise a linear carbonate that does not contain flourine, such as EMC, at a concentration of about 40 vol% to about 90 vol%, including from about 50 vol% to about 80 vol%, and from about 60 vol% to about 80

vol%. In some embodiments, the electrolyte may comprise 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether at a concentration of from about 10 vol% to about 30 vol%, including from about 10 vol% to about 20 vol%.

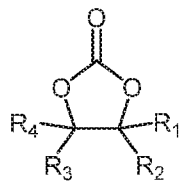
[0058] In some embodiments, the electrolyte is substantially free of cyclic carbonates other than fluorine-containing cyclic carbonates (i.e., non-fluorine-containing cyclic carbonates). Examples of non-fluorine-containing carbonates include EC, PC, GBL, and vinylene carbonate (VC).

Electrolyte Additives

[0059] In some embodiments, the electrolyte may further comprise one or more additives. As used herein, an additive of the electrolyte refers to a component that makes up less than 10 % by weight (wt%) of the electrolyte. In some embodiments, the amount of each additive in the electrolyte may be from about 0.2 wt% to about 1 wt%, 0.1 wt% to about 2 wt%, 0.2 wt% to about 9 wt%, from about 0.5 wt% to about 9 wt%, from about 1 wt% to about 9 wt%, from about 1 wt% to about 8 wt%, from about 1 wt% to about 8 wt%, from about 1 wt% to about 7 wt%, from about 1 wt% to about 6 wt%, from about 1 wt% to about 5 wt%, from about 2 wt% to about 5 wt%, or any value in between. In some embodiments, the total amount of the additive(s) may be from from about 1 wt% to about 9 wt%, from about 1 wt% to about 8 wt%, from about 1 wt% to about 7 wt%, from about 2 wt% to about 7 wt%, or any value in between.

Cyclic Carbonate Compound

[0060] In some embodiments, the cyclic carbonate can be a compound of Formula (A) having the structure:



(A);

[0061] In some embodiments, R_1 is selected from the group consisting of a C1-C8 alkyl substituted by F, an alkoxy-alkyl substituted by F, and alkenyloxy-alkyl. In some embodiments, R_1 is selected from the group consisting of an alkoxy-alkyl substituted by F

and alkenyloxy-alkyl. In some embodiments, R_1 is selected from the group consisting of a C1-C8 alkyl substituted by F and alkenyloxy-alkyl. In some embodiments, R_1 is selected from the group consisting of a C1-C8 alkyl substituted by F and an alkoxy-alkyl substituted by F. In some embodiments, R_1 is C1-C10 alkyl substituted by F or $-CH_2-OR_5$. In some embodiments, R_1 is C1-C10 alkyl substituted by F. In some embodiments, R_1 is $-CH_2-OR_5$.

[0062] In some embodiments, R_5 is a C1-C10 alkyl substituted by F or a C1-C6 alkenyl. In some embodiments, R_5 is a C1-C10 alkyl substituted by F. In some embodiments, R_5 is a C1-C6 alkenyl.

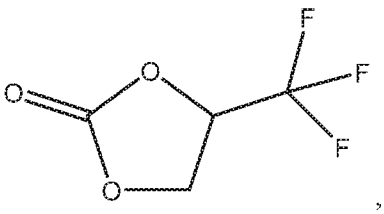
[0063] In some embodiments, each R_2, R_3, and R_4 is independently an –H or a C1-C8 alkyl substituted by F. In some embodiments, each R_2, R_3, and R_4 is independently a C1-C8 alkyl substituted by F. In some embodiments, each R_2, R_3, and R_4 is an –H. In some embodiments, each R_2, R_3, and R_4 is independently an –H or $–CF_3$. In some embodiments, each R_2, R_3, and R_4 is an –H. In some embodiments, each R_2, R_3, and R_4 is a $–CF_3$.

[0064] The electrolyte or additive may comprise a cyclic carbonate. In some embodiments, the additive may be an additive chemical compound comprising cyclic carbonate. In some embodiments, the cyclic carbonate may be included in the electrolyte as a co-solvent. In other embodiments, a cyclic carbonate may be included in the electrolyte as an additive. For example, the electrolyte may contain a cyclic carbonate as a co-solvent at a concentration of about 10 vol % or more. In other embodiments, the electrolyte may contain a cyclic carbonate compound as an additive at less than 10 weight %.

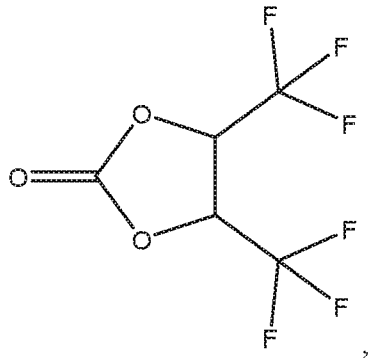
[0065] In some embodiments, the cyclic carbonate compound is selected from 4-(Trifluoromethyl)-1,3-dioxolan-2-one (TFPC), 4,4-Bis(trifluoromethyl)-1,3-dioxolan-2-one (including cis, trans and racemate forms), 4,5-Bis(Trifluoromethyl)-1,3-dioxolan-2-one, 1,1,2-Tris(trifluoromethyl)ethylene carbonate, Tetrakis(trifluoromethyl)ethylene carbonate, 4-(Fluoromethyl)-1,3-dioxolan-2-one, 3,3-Difluoropropylene carbonate, 4-(2,2,3,3,4,4,4-Heptafluorobutyl)-1,3-dioxolan-2-one, 4-(2,2,3,3,4,4,5,5,5-Nonafluoropentyl)-1,3-dioxolan-2-one, 4-(2,2,3,3,4,4,5,5,6,6,7,7,7-Tridecafluoroheptyl)-1,3-dioxolan-2-one, 4-[(2,2,2-Trifluoroethoxy)methyl]-1,3-dioxolan-2-one, 4-[(2,2,3,3,3-Pentafluoropropoxy)methyl]-1,3-dioxolan-2-one, 4-[(2,2,3,3,4,4,4-Heptafluorobutoxy)methyl]-1,3-dioxolan-2-one, 3-[(2,2,3,3-Tetrafluoropropoxy)methyl]-1,3-dioxolan-2-one, 4-[(2,2,3,4,4,4-Hexafluorobutoxy)methyl]-1,3-dioxolan-2-one, 4-[(2,2-Difluoroethoxy)methyl]-1,3-

dioxolan-2-one, 4-[(Hexafluoroisopropoxy)methyl]-1,3-dioxolan-2-one, 4-[(1H,1H-Perfluorohexoxy)methyl]-1,3-dioxolan-2-one, 4-[(1H,1H,9H-Perfluorononoxy)methyl]-1,3-dioxolan-2-one, 4-[(1H,1H,7H-Perfluoroheptoxy)methyl]-1,3-dioxolan-2-one, 4-[(1H,1H,2H,2H-Perfluorohexoxy)methyl]-1,3-dioxolan-2-one, 4-[(4,4,5,5,5-Pentafluoropentoxy)methyl]-1,3-dioxolan-2-one, and their corresponding partially-, or perfluoroalkyl-substituted ethylene carbonates as well as other partially- or per-fluorine-containing heterocyclic carbonates

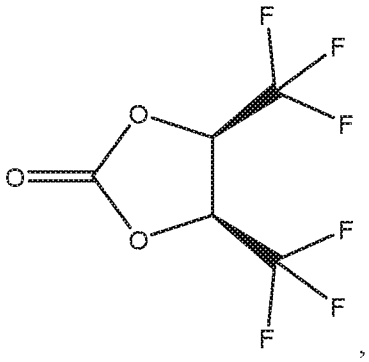
[0066] Example structures of cyclic carbonate compounds and are shown below:



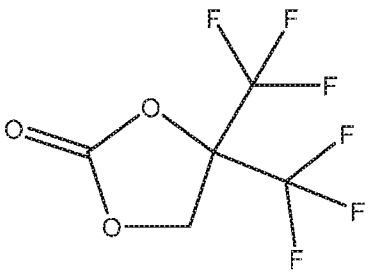
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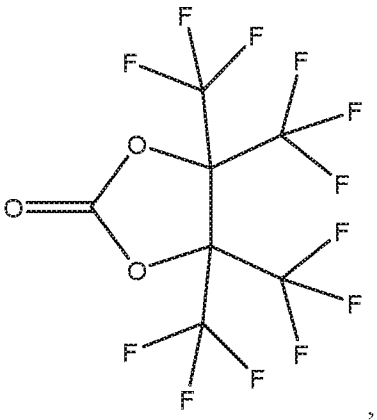
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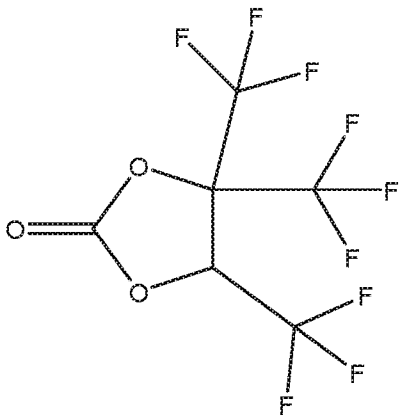
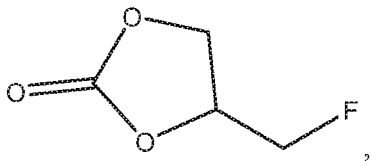
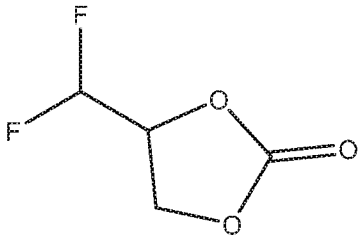
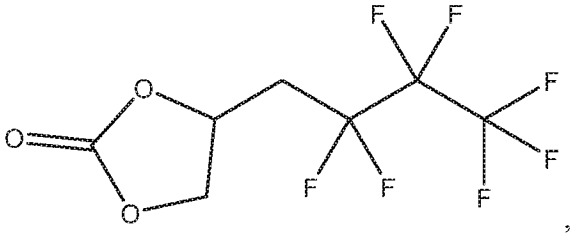
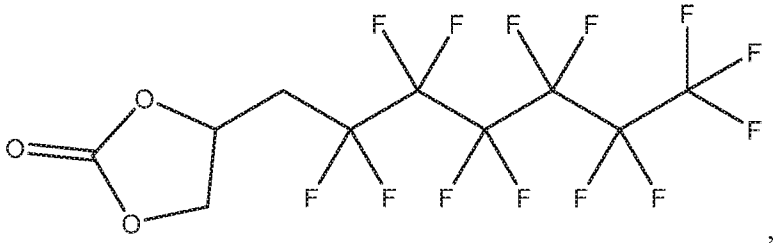
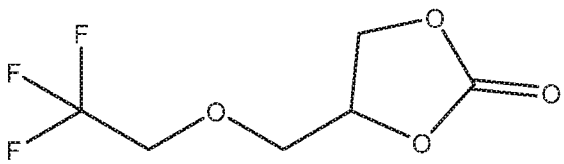
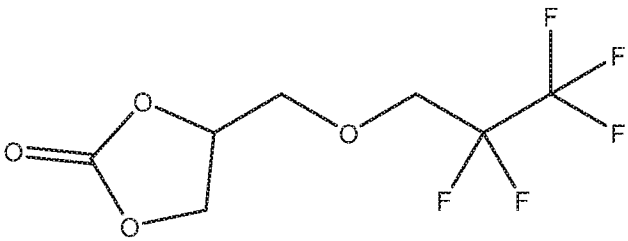
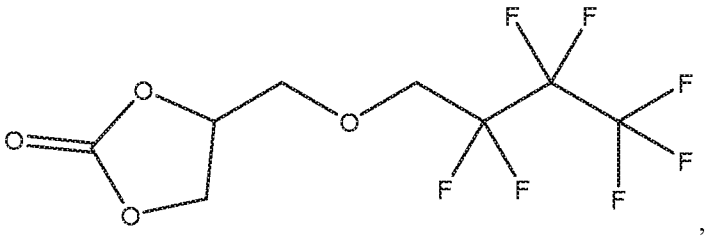
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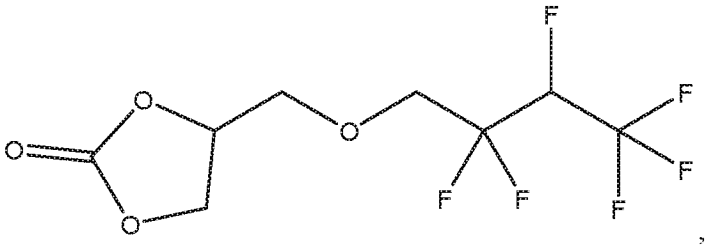


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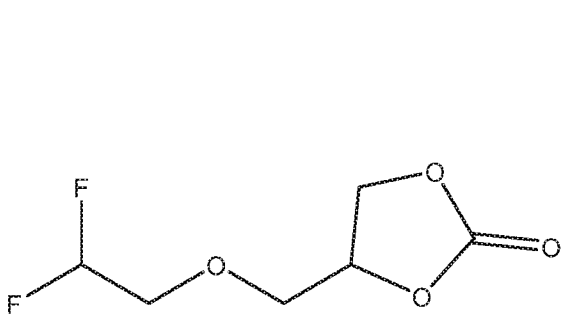


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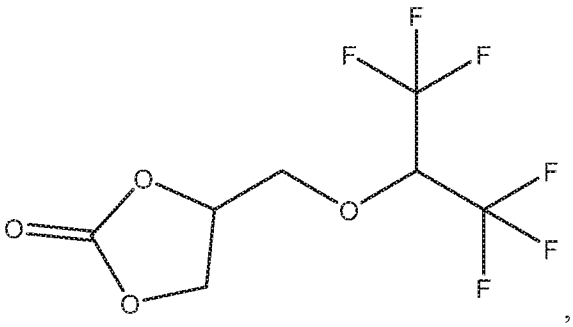

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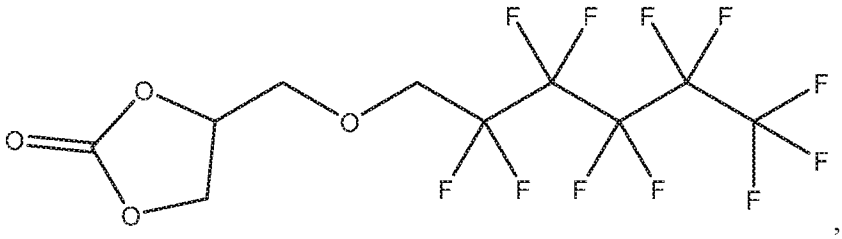
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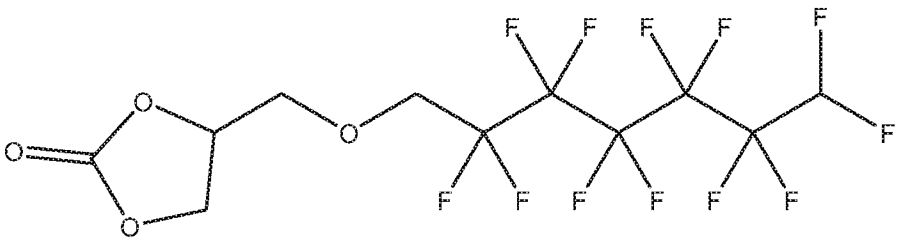
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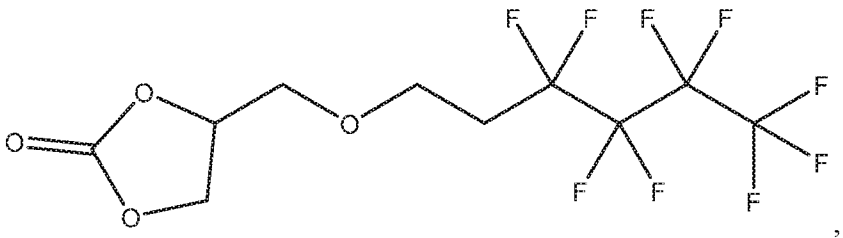
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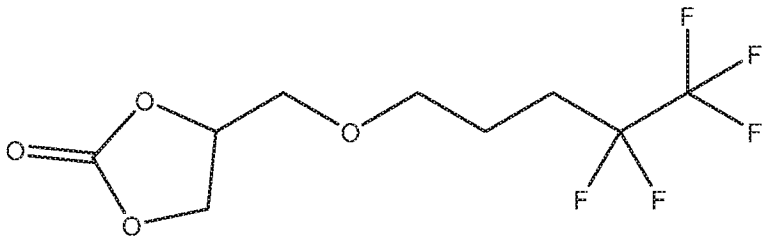
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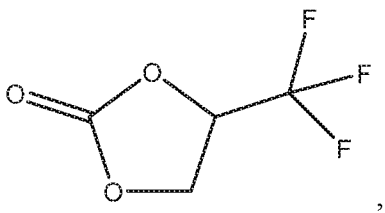
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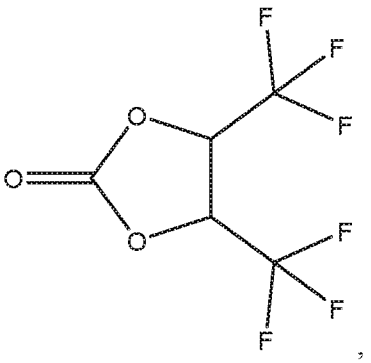
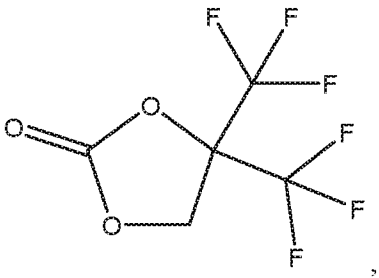
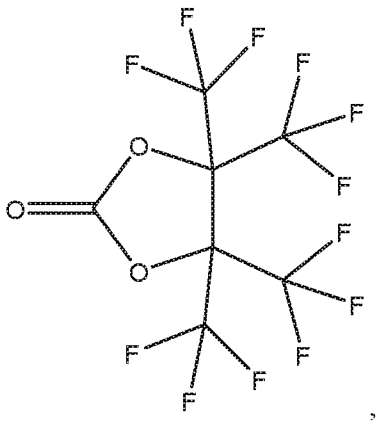
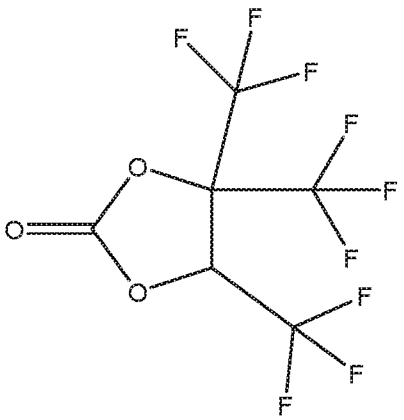
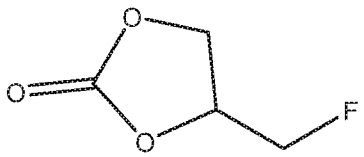
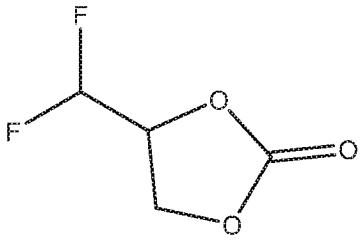
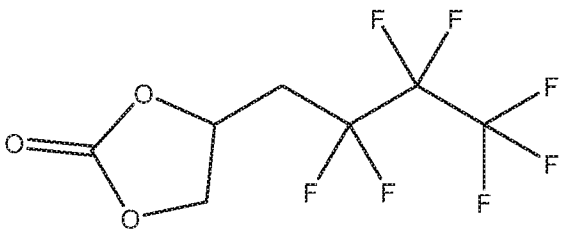
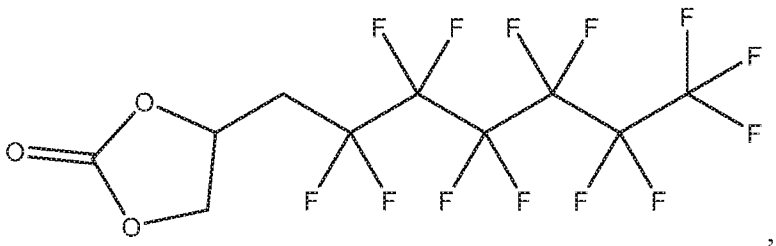
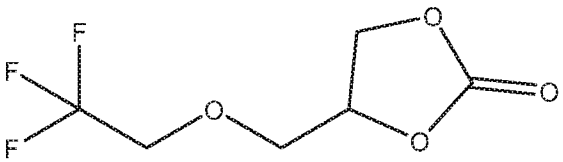
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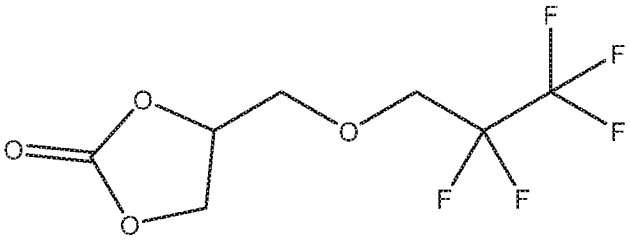


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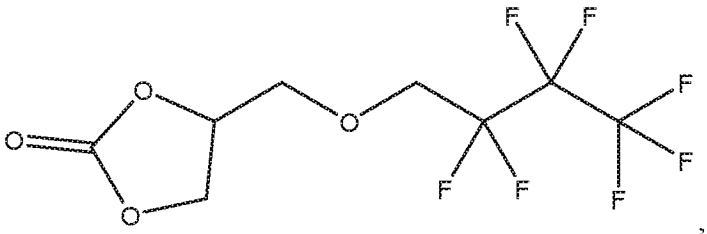


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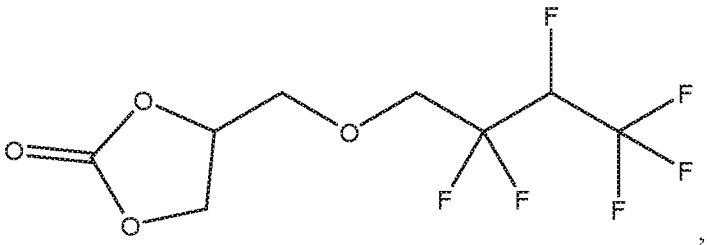

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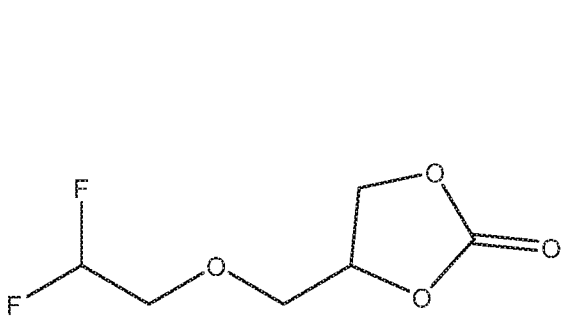
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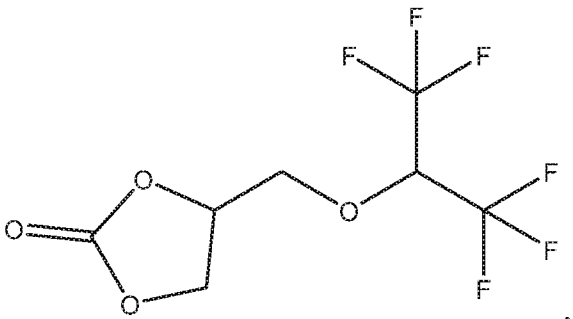
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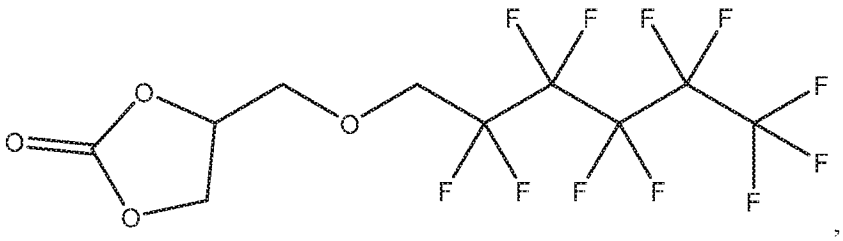
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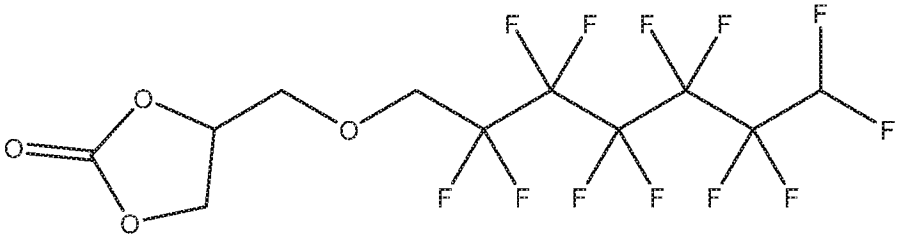
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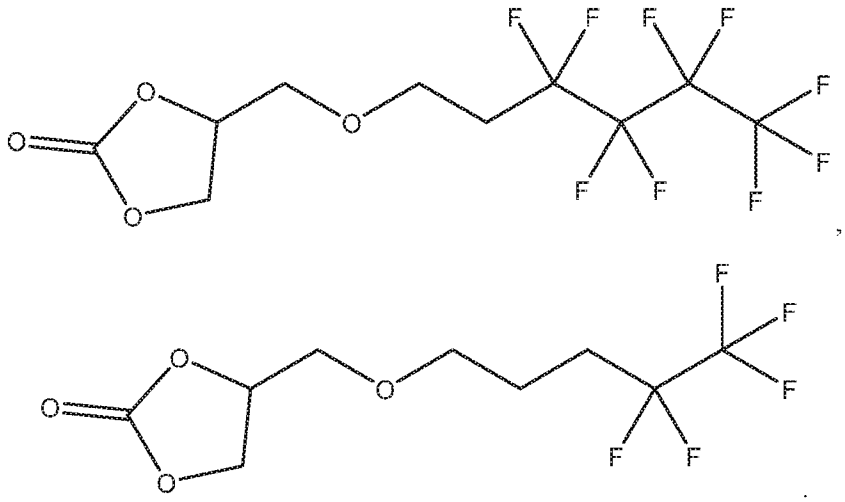
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[0067] In some embodiments, a lithium-containing salt for a lithium ion battery may comprise lithium hexafluorophosphate ($LiPF_6$). In some embodiments, a lithium-containing salt for a lithium ion battery may comprise one or more of lithium tetrafluoroborate ($LiBF_4$), lithium hexafluoroarsenate monohydrate ($LiAsF_6$), lithium perchlorate ($LiClO_4$), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), lithium bis(fluorosulfonyl)imide (LiFSI), lithium bis(oxalato)borate (LiBOB), lithium difluoro(oxalate)borate (LiDFOB), lithium triflate ($LiCF_3SO_3$), lithium tetrafluorooxalato phosphate (LTFOP), lithium difluorophosphate ($LiPO_2F_2$), lithium pentafluoroethyltrifluoroborate (LiFAB), and lithium 2-trifluoromethyl-4,5-dicyanoimidazole (LiTDI), etc. In some embodiments, the electrolyte can have a salt concentration of about 1 moles/L (M).

[0068] These electrolyte additives, along with the electrolytes, can be reduced or self-polymerize on the surface of Si anode to form a SEI layer that can reduce or prevent the crack and/or the continuous reduction of electrolyte solutions as the silicon containing anode expands and contracts during cycling. Furthermore, these electrolyte additives, along with the electrolyte solvents, may be oxidized on a cathode surface to form a CEI layer that can suppress or minimize further decomposition of the electrolyte on the surface of the cathode. Without being bound to the theory or mode of operation, it is believed that the presence of cyclic carbonates in the electrolyte can result in a SEI and/or CEI layer on the surface of electrodes with improved performance. An SEI layer comprising a cyclic carbonate compound may demonstrate improved chemical stability and increased density, for example,

compared to SEI layers formed by electrolytes without additives or with traditional additives. As such, the change in thickness and surface reactivity of the interface layer are limited, which may in turn facilitate reduction in capacity fade and/or generation of excessive gaseous byproducts during operation of the lithium ion battery. A CEI layer comprising a cyclic carbonate compound may demonstrate may help minimize the transition metal ion dissolutions and structure changes on cathode side and may provide favorable kinetics resulting in improved cycling stability and rate capability. In some embodiments, electrolyte solvents comprising cyclic carbonate may be less flammable and more flame retardant.

[0069] In some embodiments, a lithium ion battery comprising an electrolyte composition according to one or more embodiments described herein, and an anode having a composite electrode film according to one or more embodiments described herein, may demonstrate reduced gassing and/or swelling at about room temperature (e.g., about 20°C to about 25°C) or elevated temperatures (e.g., up to temperatures of about 85°C), increased cycle life at about room temperature or elevated temperatures, and/or reduced cell growth/electrolyte consumption per cycle, for example compared to lithium ion batteries comprising conventionally available electrolyte compositions in combination with an anode having a composite electrode film according to one or more embodiments described herein. In some embodiments, a lithium ion battery comprising an electrolyte composition according to one or more embodiments described herein and an anode having a composite electrode film according to one or more embodiments described herein may demonstrate reduced gassing and/or swelling across various temperatures at which the battery may be subject to testing, such as temperatures between about -20°C and about 130°C (e.g., compared to lithium ion batteries comprising conventionally available electrolyte compositions in combination with an anode having a composite electrode film according to one or more embodiments described herein).

[0070] Gaseous byproducts may be undesirably generated during battery operation, for example, due to chemical reactions between the electrolyte and one or more other components of the lithium ion battery, such as one or more components of a battery electrode. Excessive gas generation during operation of the lithium ion battery may adversely affect battery performance and/or result in mechanical and/or electrical failure of the battery. For example, undesired chemical reactions between an electrolyte and one or

more components of an anode may result in gas generation at levels which can mechanically (e.g., structural deformation) and/or electrochemically degrade the battery. In some embodiments, the composition of the anode and the composition of the electrolyte can be selected to facilitate desired gas generation.

Energy Storage Device

[0071] The electrolytes and electrolyte additives described herein may be advantageously utilized within an energy storage device. In some embodiments, energy storage devices may include batteries, capacitors, and battery-capacitor hybrids. In some embodiments, the energy storage device comprise lithium. In some embodiments, the energy storage device may comprise at least one electrode, such as an anode and/or cathode. In some embodiments, at least one electrode may be a Si-based electrode. In some embodiments, the Si-based electrode is a Si-dominant electrode, where silicon is the majority of the active material used in the electrode (e.g., greater than 50% silicon). In some embodiments, the energy storage device comprises a separator. In some embodiments, the separator is between a first electrode and a second electrode.

[0072] In some embodiments, the energy storage device comprises an electrolyte. In some embodiments, the electrolyte comprises a solvent, solvent additive and/or compound as described previously herein. For example, in some embodiments, the electrolyte comprises a cyclic carbonate compound as described previously herein.

Pouch Cell

[0073] As described herein, a battery can be implement as a pouch cell. Figure 1 shows a cross-sectional schematic diagram of an example of a lithium ion battery 300 implemented as a pouch cell, according to some embodiments. The battery 300 comprises an anode 316 in contact with a negative current collector 308, a cathode 304 in contact with a positive current collector 310, a separator 306 disposed between the anode 316 and the cathode 304. In some embodiments, a plurality of anodes 316 and cathode 304 may be arranged into a stacked configuration with a separator 306 separating each anode 316 and cathode 304. Each negative current collector 308 may have one anode 316 attached to each side; each positive current collector 310 may have one cathode 304 attached to each side.

The stacks are immersed in an electrolyte 314 and enclosed in a pouch 312. The anode 302 and the cathode 304 may comprise one or more respective electrode films formed thereon. The number of electrodes of the battery 300 may be selected to provide desired device performance.

[0074] With further reference to Figure 1, the separator 306 may comprise a single continuous or substantially continuous sheet, which can be interleaved between adjacent electrodes of the electrode stack. For example, the separator 306 may be shaped and/or dimensioned such that it can be positioned between adjacent electrodes in the electrode stack to provide desired separation between the adjacent electrodes of the battery 300. The separator 306 may be configured to facilitate electrical insulation between the anode 302 and the cathode 304, while permitting ionic transport between the anode 302 and the cathode 304. In some embodiments, the separator 306 may comprise a porous material, including a porous polyolefin material.

[0075] The lithium ion battery 300 may include an electrolyte 314, for example an electrolyte having a composition as described herein. The electrolyte 314 is in contact with the anode 302, the cathode 304, and the separator 306.

[0076] With continued reference to Figure 1, the anode 302, cathode 304 and separator 306 of the lithium ion battery 300 may be enclosed in a housing comprising a pouch 312. In some embodiments, the pouch 312 may comprise a flexible material. For example, the pouch 312 may readily deform upon application of pressure on the pouch 312, including pressure exerted upon the pouch 312 from within the housing. In some embodiments, the pouch 312 may comprise aluminum. For example, the pouch 312 may comprise a laminated aluminum pouch.

[0077] In some embodiments, the lithium ion battery 300 may comprise an anode connector (not shown) and a cathode connector (not shown) configured to electrically couple the anodes and the cathodes of the electrode stack to an external circuit, respectively. The anode connector and a cathode connector may be affixed to the pouch 312 to facilitate electrical coupling of the battery 300 to an external circuit. The anode connector and the cathode connector may be affixed to the pouch 312 along one edge of the pouch 312. The anode connector and the cathode connector can be electrically insulated from one another, and from the pouch 312. For example, at least a portion of each of the anode connector and

the cathode connector can be within an electrically insulating sleeve such that the connectors can be electrically insulated from one another and from the pouch 312.

EXAMPLES

[0078] The below example devices and processes for device fabrication generally described below, and the performances of lithium ion batteries with different electrolytes and electrolyte additives are evaluated.

[0079] In the examples below, the four IR fields are values calculated by an Arbin pulse function that is depicted in Figure 2, which calculates the average IR of 10 pulses, wherein: B_IR_Res: $T_1 = 100$ ms, performed at the beginning of discharge (cell in charged state at end of rest period); E_IR_Res: $T_1 = 100$ ms, performed at the end of discharge (cell in discharged state at end of rest period); and 5-layer cells: $I_0 + I_{IR} = -100$ mA, $I_0 - I_{IR} = -250$ mA.

Example 1

[0080] The batteries shown in Figures 3A-7B are Si-dominant anode and $LiCoO_2$ cathode 5 layer pouch cells. The Si-dominant anodes contain about 80 wt% Si, 5wt% graphite and 15wt% glass carbon (from resin), and are laminated on 15μm Cu foil. The average loading is about 3.8mg/cm^2. The cathodes contain about 97 wt% $LiCoO_2$, 1wt% Super P and 2wt% PVDF5130, and are laminated on 15μm Al foil. The average loading is about 28 mg/cm^2. The electrolytes of the control cells contain 1M $LiPF_6$ in FEC/EMC (3/7 wt%), while the electrolytes of the cells of one embodiment contain 1M $LiPF_6$ in FEC/EMC (3/7 wt%) and an electrolyte additive of 2wt% TFPC.

[0081] In the examples shown in Figures 3A-7B, the long-term cycling for both control and TFPC additive-containing cells include: (i) At the 1st cycle, charge at 0.5C to 4.3 V for 5 hours, rest 5 minutes, 1ms IR, 100ms IR, discharge at 0.2C to 2.75 V, rest 5 minutes, 1ms IR, 100ms IR; and (ii) from the 2nd cycle, charge at 0.5C to 4.3 V until 0.05C, rest 5 minutes, 1ms IR, 100ms IR, discharge at 0.5 to 3.3 V, rest 5 minutes, 1ms IR, 100ms IR. After each 49 cycles, the test conditions in the 1st cycle were repeated.

[0082] In addition, both control and TFPC-containing cells were formatted for 6 cycles at the following conditions before long-term cycling: (i) At the 1st cycle, Rest 5

minutes, charge at 0.025C to 25% nominal capacity, charge at 0.2C to 4.3 V until 0.05C, rest 5 minutes, discharge at 0.2C to 3.3 V, rest 5 minutes; and (ii) from 2nd to 6th cycles, charge at 0.5C to 4.3 V until 0.05C, rest 5 minutes, discharge at 0.5C to 3.3 V, rest 5 minutes.

[0083] Figure 3A demonstrates the capacity and Figure 3B demonstrates the capacity retention of a control battery (shown as a dotted line) and a battery of one embodiment with 2 wt% TFPC (shown as a solid line). The results of Figures 3A and 3B demonstrate that the TFPC additive-containing electrolyte-based system has a better capacity and capacity retention than the control system after about 200 cycles at 0.5C/0.5C charge/discharge processes.

[0084] Figure 4A demonstrates the average impedance before cycling and Figure 4B demonstrates the average impedance after cycling of a control battery (shown as a dotted line), and a battery of one embodiment with 2 wt% TFPC (shown as a solid line). The results of Figures 4A and 4B demonstrate that the TFPC additive-containing electrolyte system has a lower impedance after about 200 cycles than the control system.

[0085] Figure 5A demonstrates the average resistance before cycling and Figure 5B demonstrates the average resistance after cycling of a control battery (shown as a dotted line), and a battery of one embodiment with 2 wt% TFPC (shown as a solid line). The results of Figures 5A and 5B demonstrate that the TFPC additive-containing electrolyte system has a lower resistance than the control system after about 200 cycles.

[0086] Figure 6A demonstrates the average resistance after 10s charge and Figure 6B demonstrates the average resistance after 10s discharge processes of a control battery (shown as a dotted line), and a battery of one embodiment with 2 wt% TFPC (shown as a solid line). The results of Figures 6A and 6B demonstrate that the TFPC additive-containing electrolyte system has a lower resistance after 10s charge/discharge processes than the control system after about 200 cycles.

[0087] Figure 7A demonstrates the average resistance after 30s charge and Figure 7B demonstrates the average resistance after 30s discharge processes of a control battery (shown as a dotted line), and a battery of one embodiment with 2 wt% TFPC (shown as a solid line). The results of Figures 7A and 7B demonstrate that the TFPC additive-containing electrolyte system has a lower resistance after 30s charge/discharge processes than the control system after about 200 cycles.

Example 2:

[0088] In other embodiments not shown, the electrolytes of the cells contain 1M $LiPF_6$ in FEC/EMC (3/7wt%) with 5wt% TFPC. In other embodiments not shown, the electrolytes of the cells contain 1M $LiPF_6$ in FEC/HFDEC/EMC (3/3.5/3.5wt%) with 2wt% TFPC. In other embodiments not shown, the electrolytes of the cells contain 1M $LiPF_6$ in FEC/HFDEC/EMC (3/3.5/3.5wt%) with 5wt% TFPC. These examples also demonstrated improved battery functions when TFPC was used as an additive as compared to controls.

[0089] Various embodiments have been described above. Although the invention has been described with reference to these specific embodiments, the descriptions are intended to be illustrative and are not intended to be limiting. Various modifications and applications may occur to those skilled in the art without departing from the true spirit and scope of the invention as defined in the appended claims.

WHAT IS CLAIMED IS:

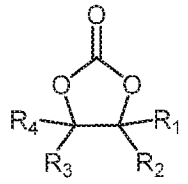
1. An energy storage device comprising:

a first electrode and a second electrode, wherein at least one of the first electrode and the second electrode is a Si-based electrode;

a separator between the first electrode and the second electrode;

an electrolyte; and

at least one electrolyte additive comprising a compound of Formula (A):



(A);

wherein:

R_1 is selected from the group consisting of a C1-C8 alkyl substituted by F, an alkoxy-alkyl substituted by F, and alkenyloxy-alkyl; and

each R_2, R_3, and R_4 is independently an –H or a C1-C8 alkyl substituted by F.

2. The energy storage device of Claim 1, wherein:

R_1 is C1-C10 alkyl substituted by F or $-CH_2-OR_5$; and

R_5 is a C1-C10 alkyl substituted by F or a C1-C6 alkenyl.

3. The energy storage device of Claim 1, wherein:

each R_2, R_3, and R_4 is independently an –H or $–CF_3$.

4. The energy storage device of Claim 1, wherein the second electrode is a Si-dominant electrode.

5. The energy storage device of Claim 1, wherein the second electrode comprises a self-supporting composite material film.

6. The energy storage device of Claim 5, wherein the composite material film comprises:

greater than 0 % and less than about 90 % by weight of silicon particles, and

greater than 0 % and less than about 90 % by weight of one or more types of carbon phases, wherein at least one of the one or more types of carbon phases is a substantially continuous phase that holds the composite material film together such that the silicon particles are distributed throughout the composite material film.

7. The energy storage device of Claim 1, wherein the electrolyte further comprises fluoroethylene carbonate (FEC).

8. The energy storage device of claim 7, wherein the electrolyte is substantially free of non-fluorine containing cyclic carbonate.

9. The energy storage device of Claim 1, wherein the electrolyte additive is selected from the group consisting of 4-(Trifluoromethyl)-1,3-dioxolan-2-one (TFPC), 4,4-Bis(trifluoromethyl)-1,3-dioxolan-2-one (including cis, trans and racemate forms), 4,5-Bis(Trifluoromethyl)-1,3-dioxolan-2-one, 1,1,2-Tris(trifluoromethyl)ethylene carbonate, Tetrakis(trifluoromethyl)ethylene carbonate, 4-(Fluoromethyl)-1,3-dioxolan-2-one, 3,3-Difluoropropylene carbonate, 4-(2,2,3,3,4,4,4-Heptafluorobutyl)-1,3-dioxolan-2-one, 4-(2,2,3,3,4,4,5,5,5-Nonafluoropentyl)-1,3-dioxolan-2-one, 4-(2,2,3,3,4,4,5,5,6,6,7,7,7-Tridecafluoroheptyl)-1,3-dioxolan-2-one, 4-[(2,2,2-Trifluoroethoxy)methyl]-1,3-dioxolan-2-one, 4-[(2,2,3,3,3-Pentafluoropropoxy)methyl]-1,3-dioxolan-2-one, 4-[(2,2,3,3,4,4,4-Heptafluorobutoxy)methyl]-1,3-dioxolan-2-one, 3-[(2,2,3,3-Tetrafluoropropoxy)methyl]-1,3-dioxolan-2-one, 4-[(2,2,3,4,4,4-Hexafluorobutoxy)methyl]-1,3-dioxolan-2-one, 4-[(2,2-Difluoroethoxy)methyl]-1,3-dioxolan-2-one, 4-[(Hexafluoroisopropoxy)methyl]-1,3-dioxolan-2-one, 4-[(1H,1H-Perfluorohexoxy)methyl]-1,3-dioxolan-2-one, 4-[(1H,1H,9H-Perfluorononoxy)methyl]-1,3-dioxolan-2-one, 4-[(1H,1H,7H-Perfluoroheptoxy)methyl]-1,3-dioxolan-2-one, 4-[(1H,1H,2H,2H-Perfluorohexoxy)methyl]-1,3-dioxolan-2-one, and 4-[(4,4,5,5,5-Pentafluoropentoxy)methyl]-1,3-dioxolan-2-one.

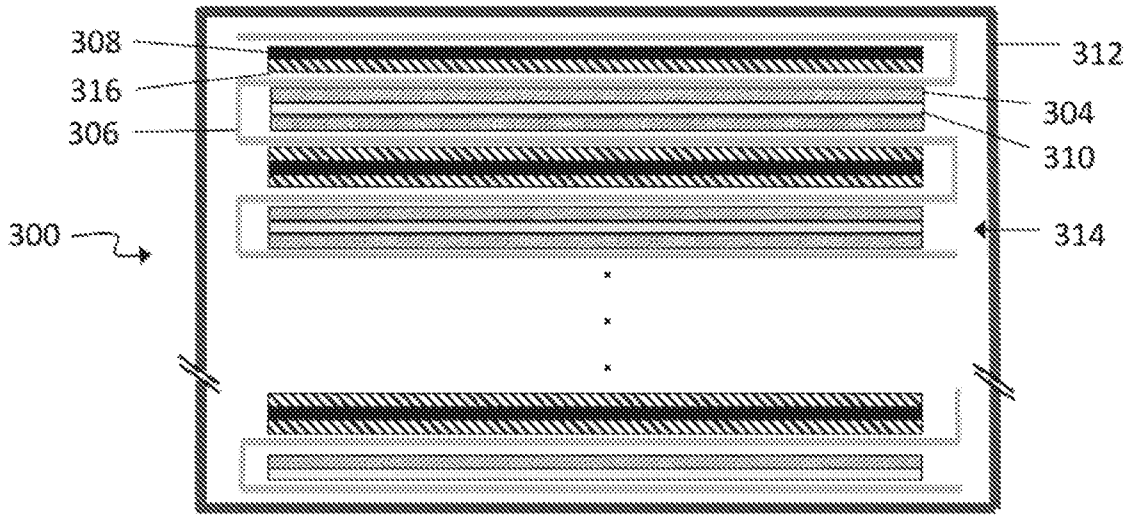


FIG. 1

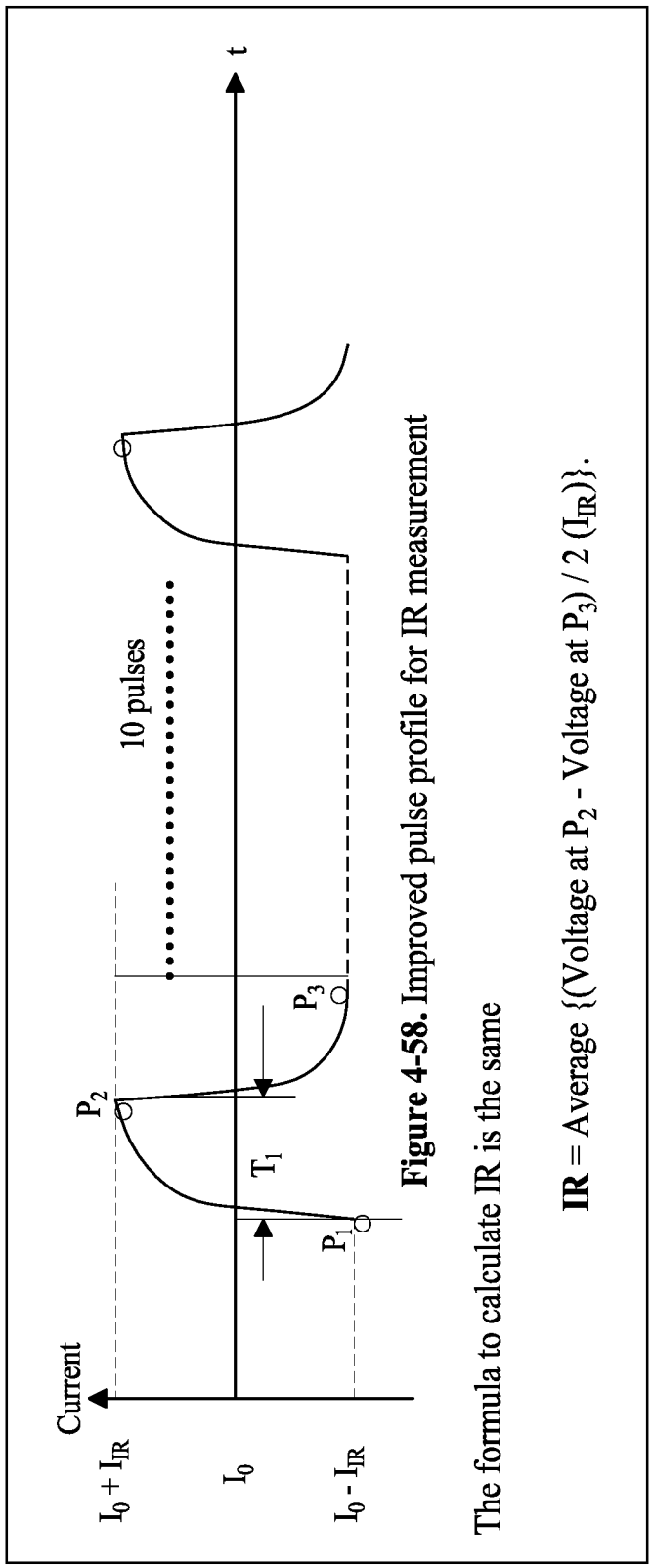


Figure 4-58. Improved pulse profile for IR measurement

The formula to calculate IR is the same

IR = Average {(Voltage at P_2 - Voltage at P_3) / 2 (I_{IR})}.

FIG. 2

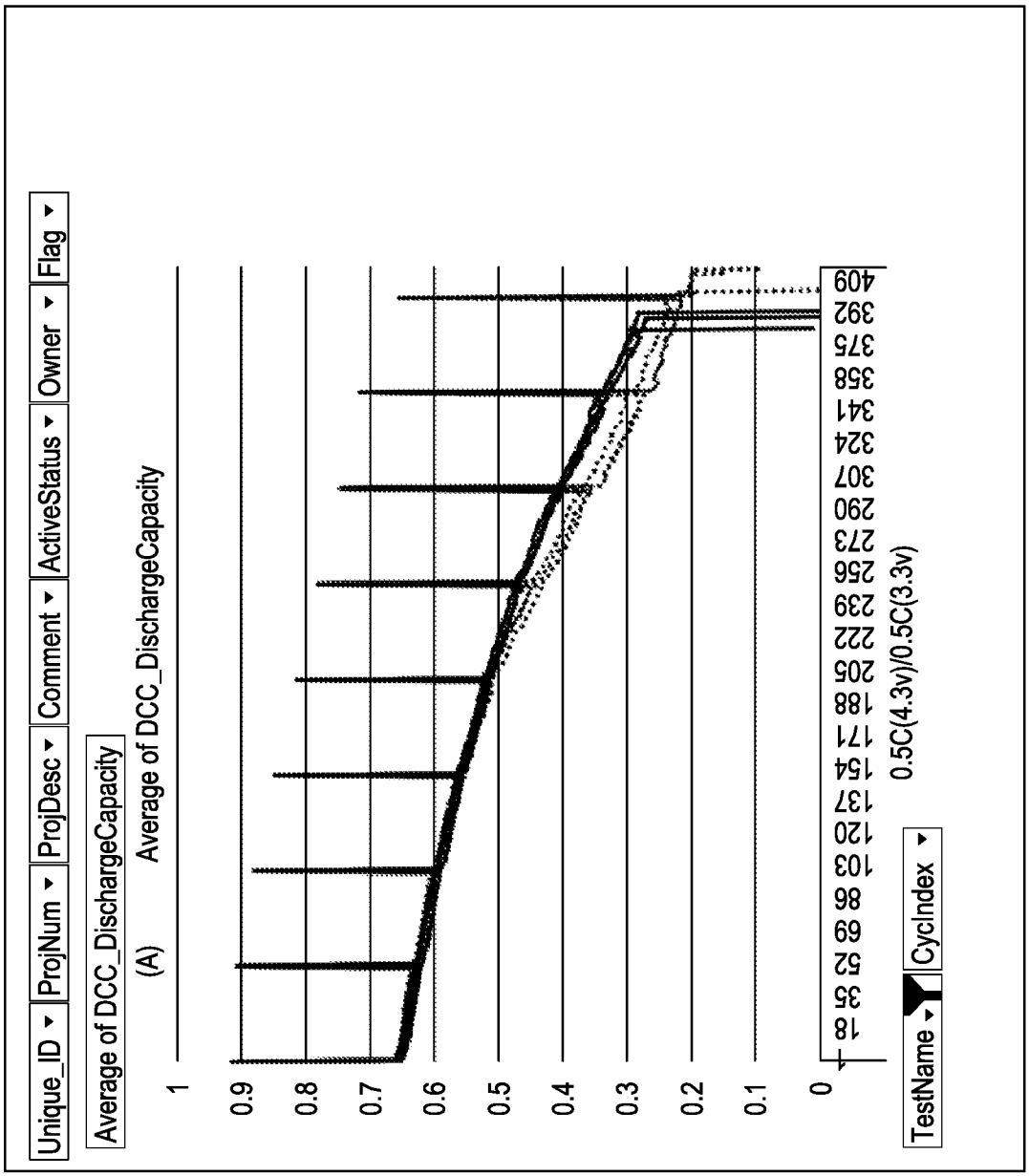

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358
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TestName
CycIndex
0.5C(4.3v)/0.5C(3.3v)

FIG. 3A

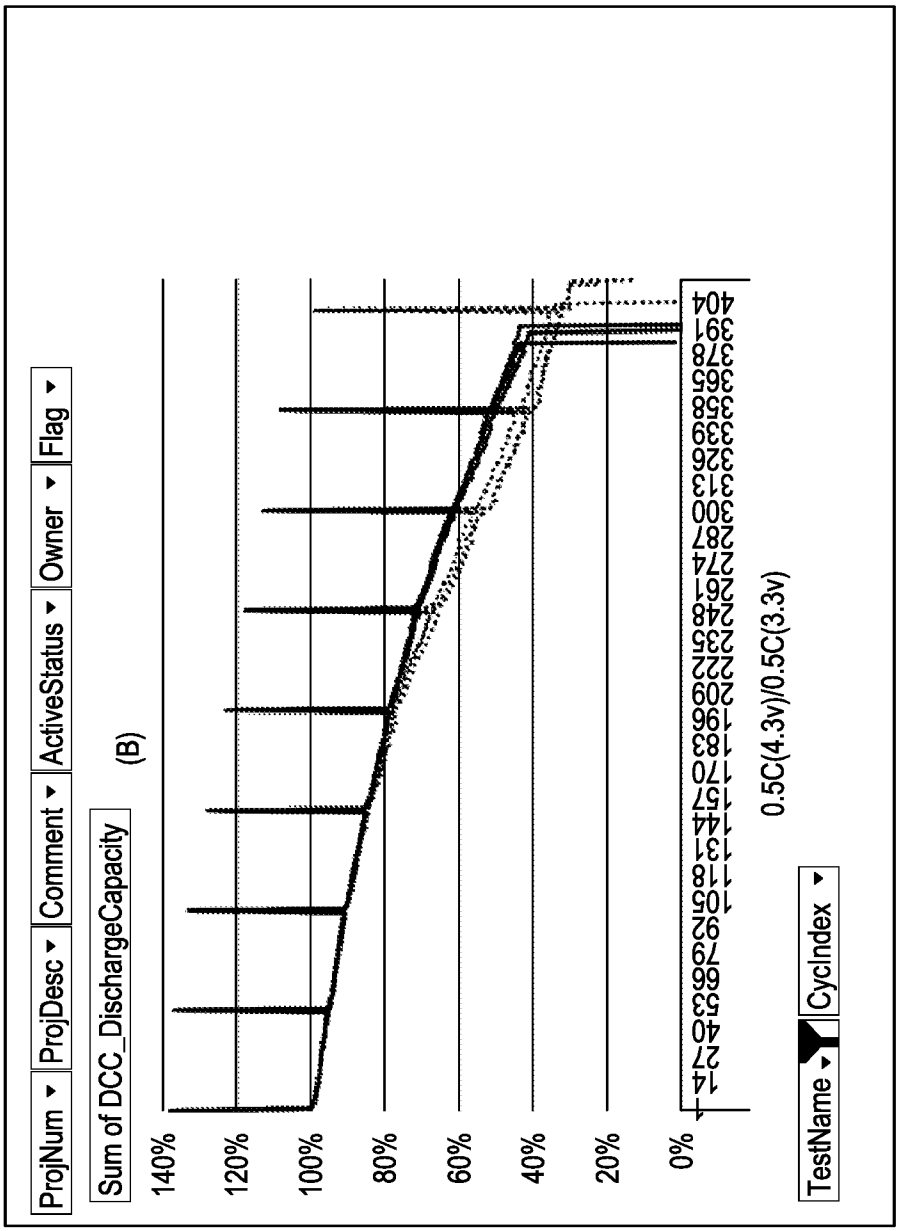

ProjNum
ProjDesc
Comment
ActiveStatus
Owner
Flag
Sum of DCC_DischargeCapacity
(B)
140%
120%
100%
80%
60%
40%
20%
0%
14
27
40
53
66
79
92
105
118
131
144
157
170
183
196
209
222
235
248
261
274
287
300
313
326
339
352
365
378
391
404
0.5C(4.3v)/0.5C(3.3v)
TestName
CycIndex

FIG. 3B

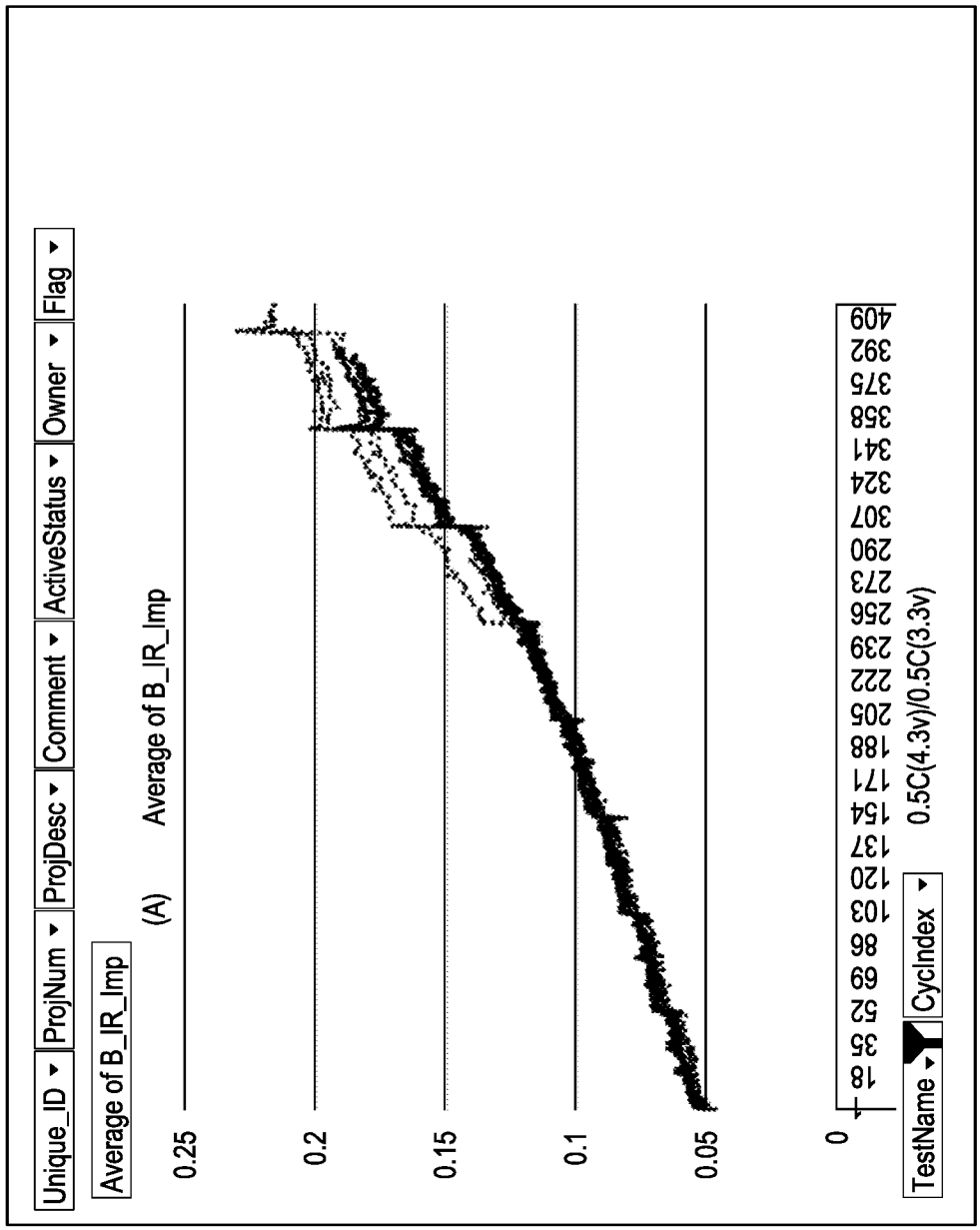

Unique_ID
ProjNum
ProjDesc
Comment
ActiveStatus
Owner
Flag
Average of B_IR_Imp
(A)
Average of B_IR_Imp
0.25
0.2
0.15
0.1
0.05
0
18
35
52
69
86
103
120
137
154
171
188
205
222
239
256
273
290
307
324
341
358
375
392
409
TestName
CycIndex
0.5C(4.3v)/0.5C(3.3v)

FIG. 4A

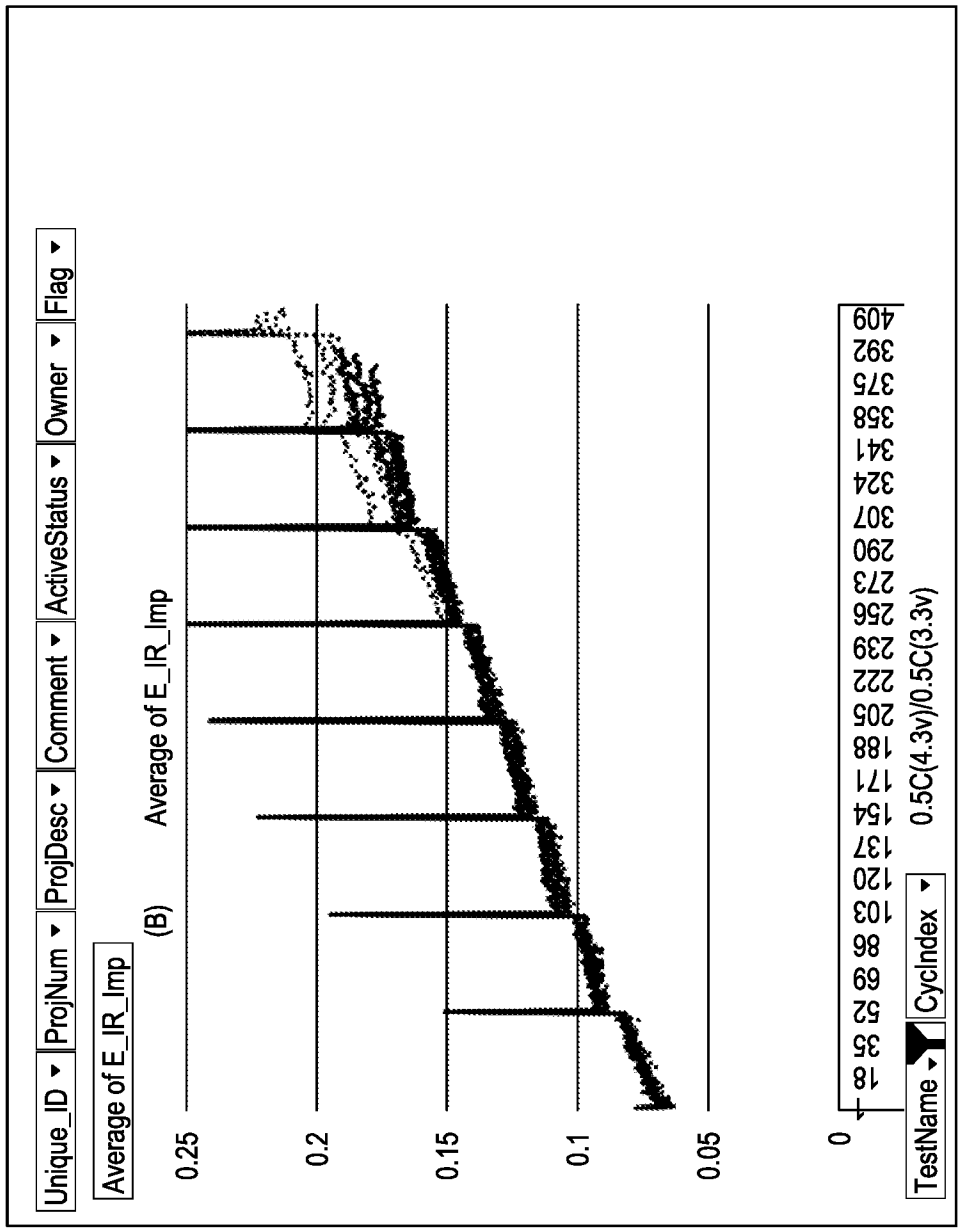

Unique_ID
ProjNum
ProjDesc
Comment
ActiveStatus
Owner
Flag
Average of E_IR_Imp
(B) Average of E_IR_Imp
0.25
0.2
0.15
0.1
0.05
0
18
35
52
69
86
103
120
137
154
171
188
205
222
239
256
273
290
307
324
341
358
375
392
409
TestName
CycIndex
0.5C(4.3v)/0.5C(3.3v)

FIG. 4B

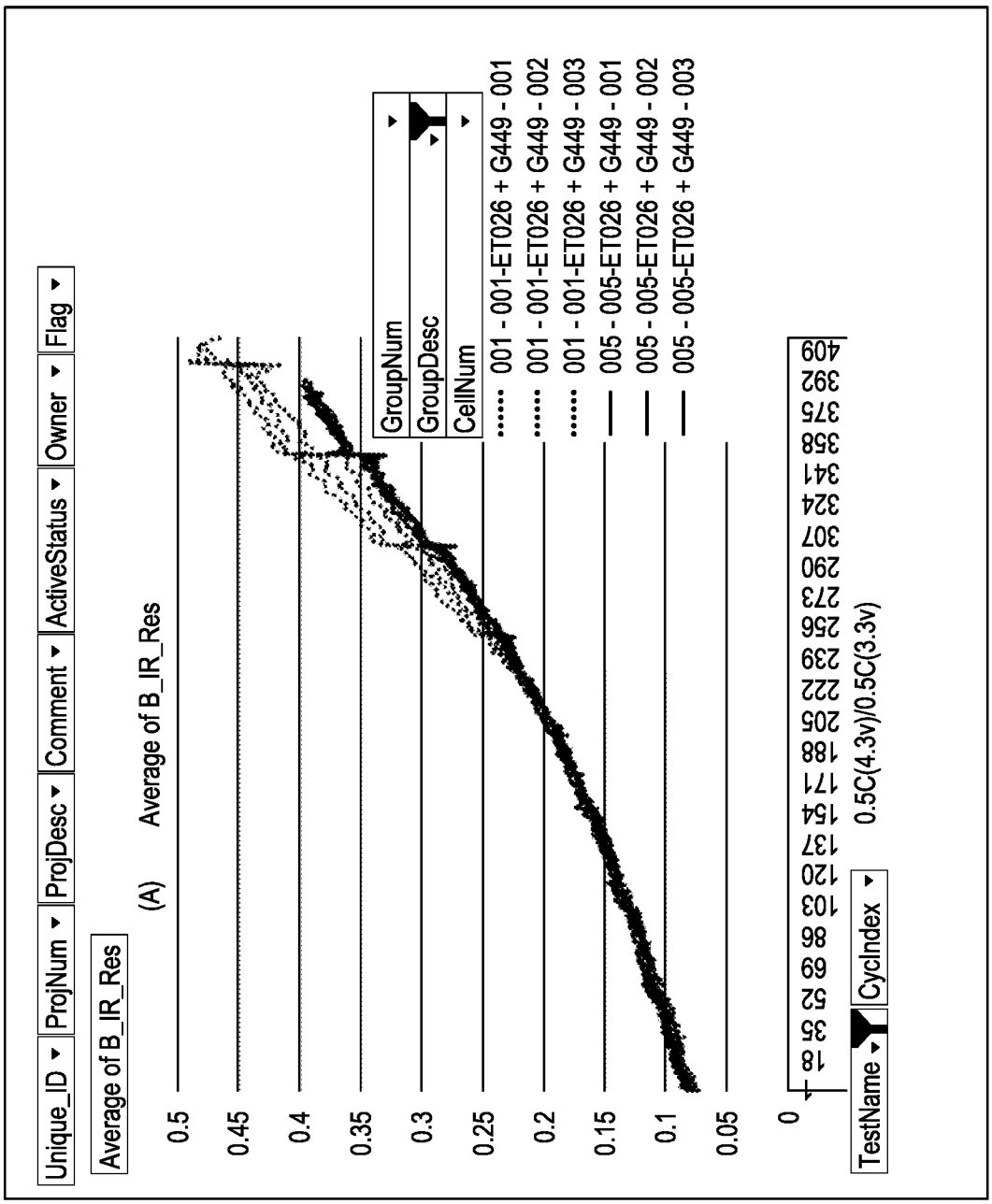

Unique_ID
ProjNum
ProjDesc
Comment
ActiveStatus
Owner
Flag
Average of B_IR_Res
(A) Average of B_IR_Res
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
GroupNum
GroupDesc
CellNum
001 - 001-ET026 + G449 - 001
001 - 001-ET026 + G449 - 002
001 - 001-ET026 + G449 - 003
005 - 005-ET026 + G449 - 001
005 - 005-ET026 + G449 - 002
005 - 005-ET026 + G449 - 003
18
35
52
69
86
103
120
137
154
171
188
205
222
239
256
273
290
307
324
341
358
375
392
409
TestName
CycIndex
0.5C(4.3v)/0.5C(3.3v)

FIG. 5A

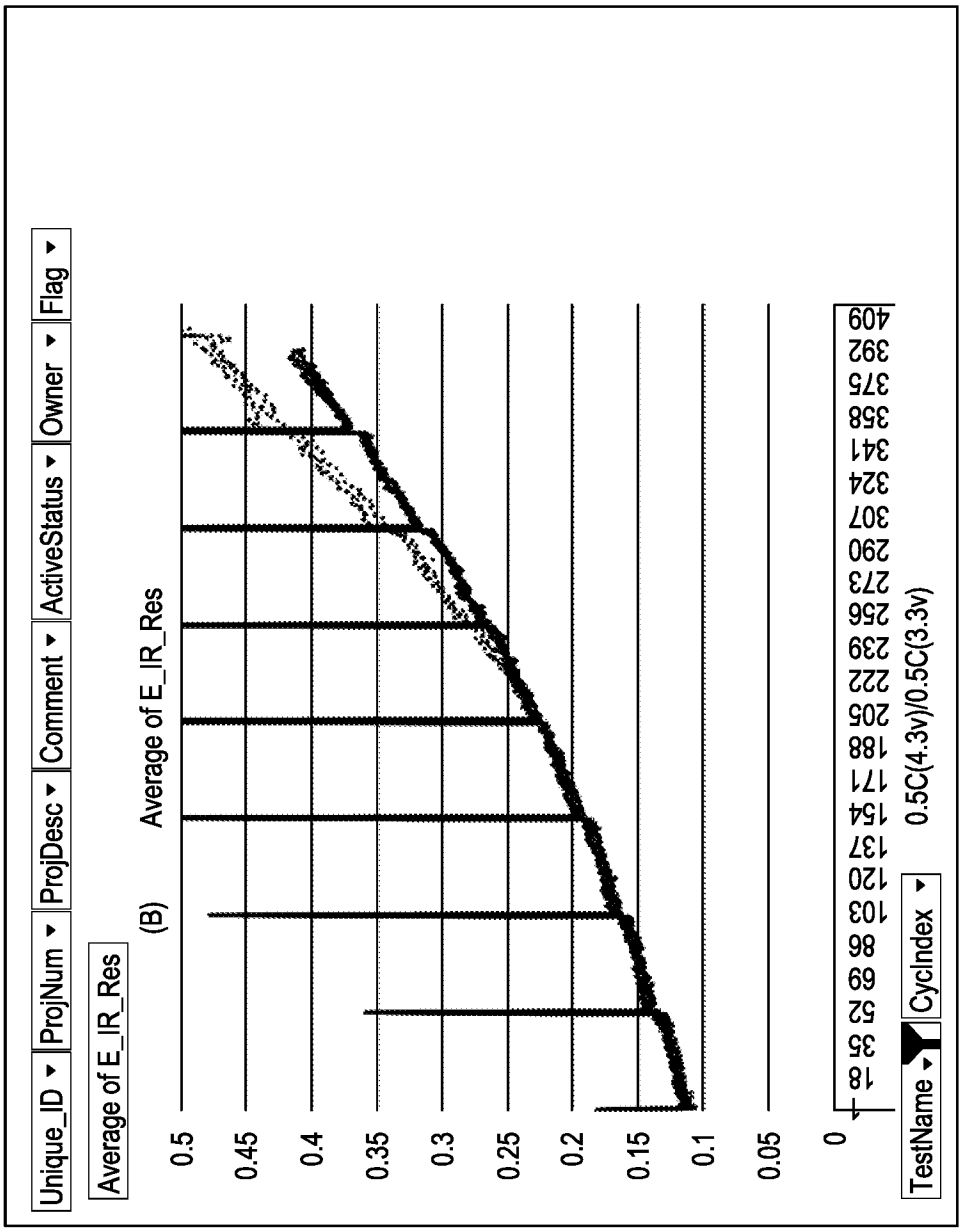

Unique_ID
ProjNum
ProjDesc
Comment
ActiveStatus
Owner
Flag
Average of E_IR_Res
(B)
Average of E_IR_Res
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
18
35
52
69
86
103
120
137
154
171
188
205
222
239
256
273
290
307
324
341
358
375
392
409
TestName
CycIndex
0.5C(4.3v)/0.5C(3.3v)

FIG. 5B

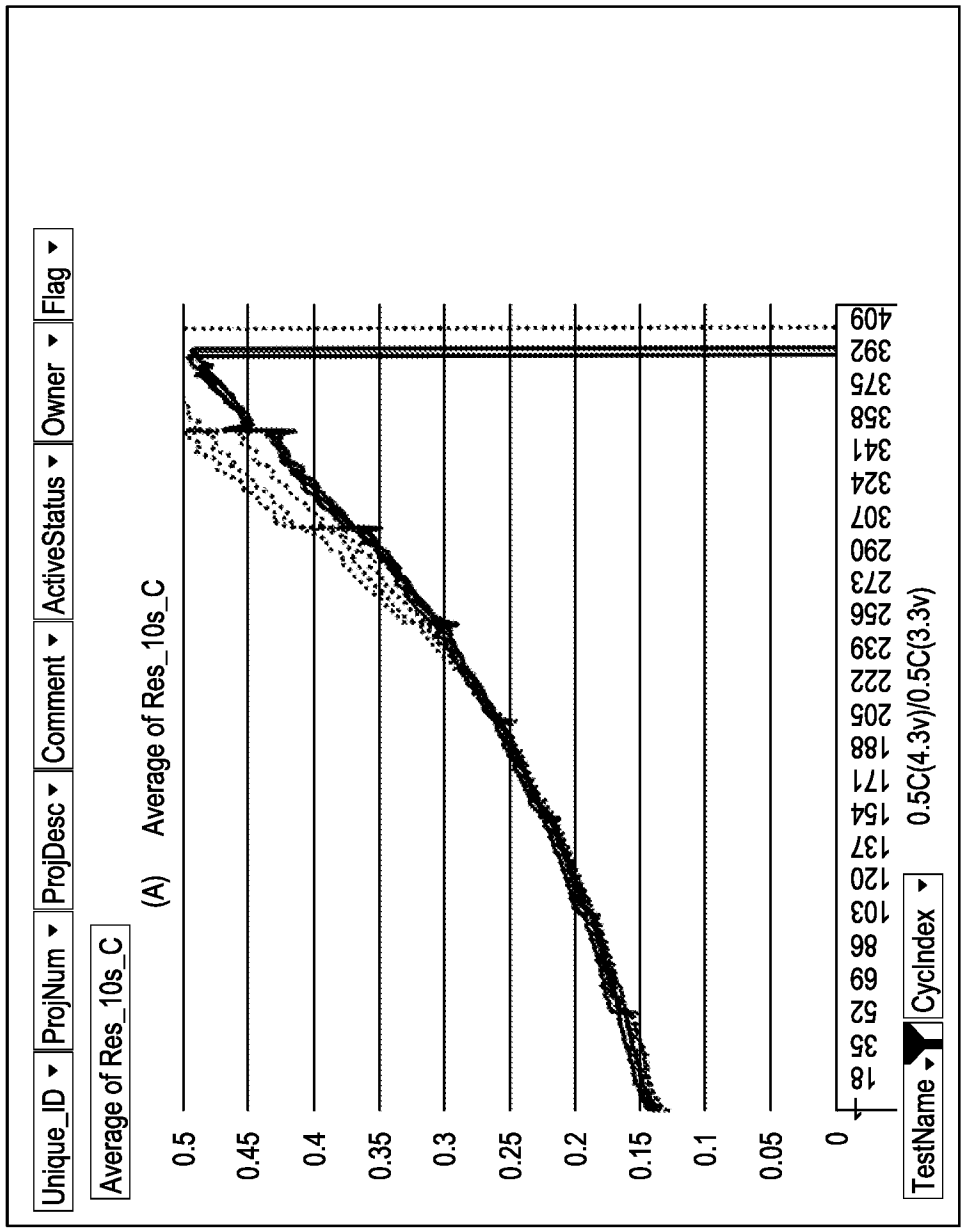

Unique_ID
ProjNum
ProjDesc
Comment
ActiveStatus
Owner
Flag
Average of Res_10s_C
(A) Average of Res_10s_C
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
18
35
52
69
86
103
120
137
154
171
188
205
222
239
256
273
290
307
324
341
358
375
392
409
TestName
CycIndex
0.5C(4.3v)/0.5C(3.3v)

FIG. 6A

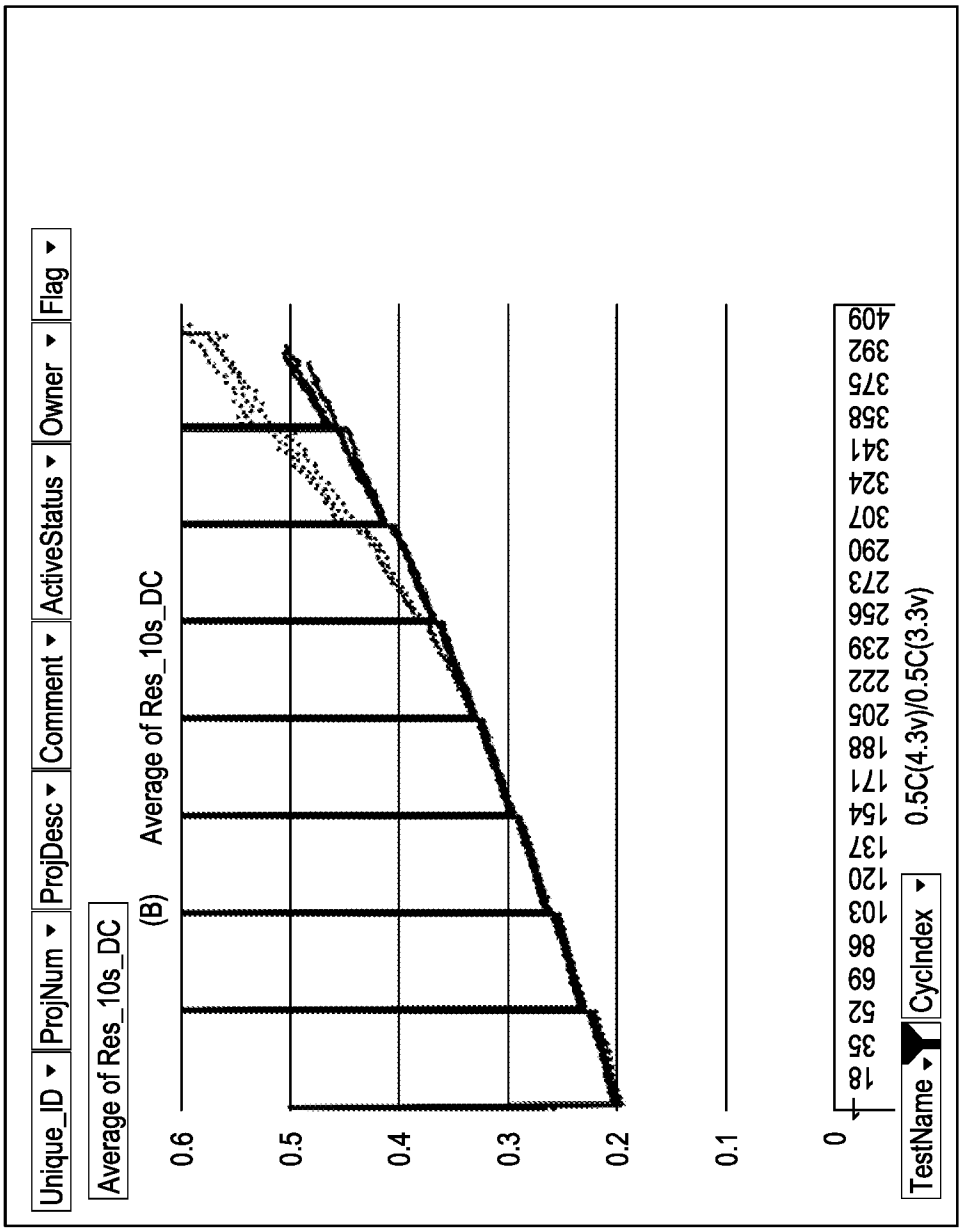

Unique_ID
ProjNum
ProjDesc
Comment
ActiveStatus
Owner
Flag
Average of Res_10s_DC
(B) Average of Res_10s_DC
0.6
0.5
0.4
0.3
0.2
0.1
0
18
35
52
69
86
103
120
137
154
171
188
205
222
239
256
273
290
307
324
341
358
375
392
409
TestName
CycIndex
0.5C(4.3v)/0.5C(3.3v)

FIG. 6B

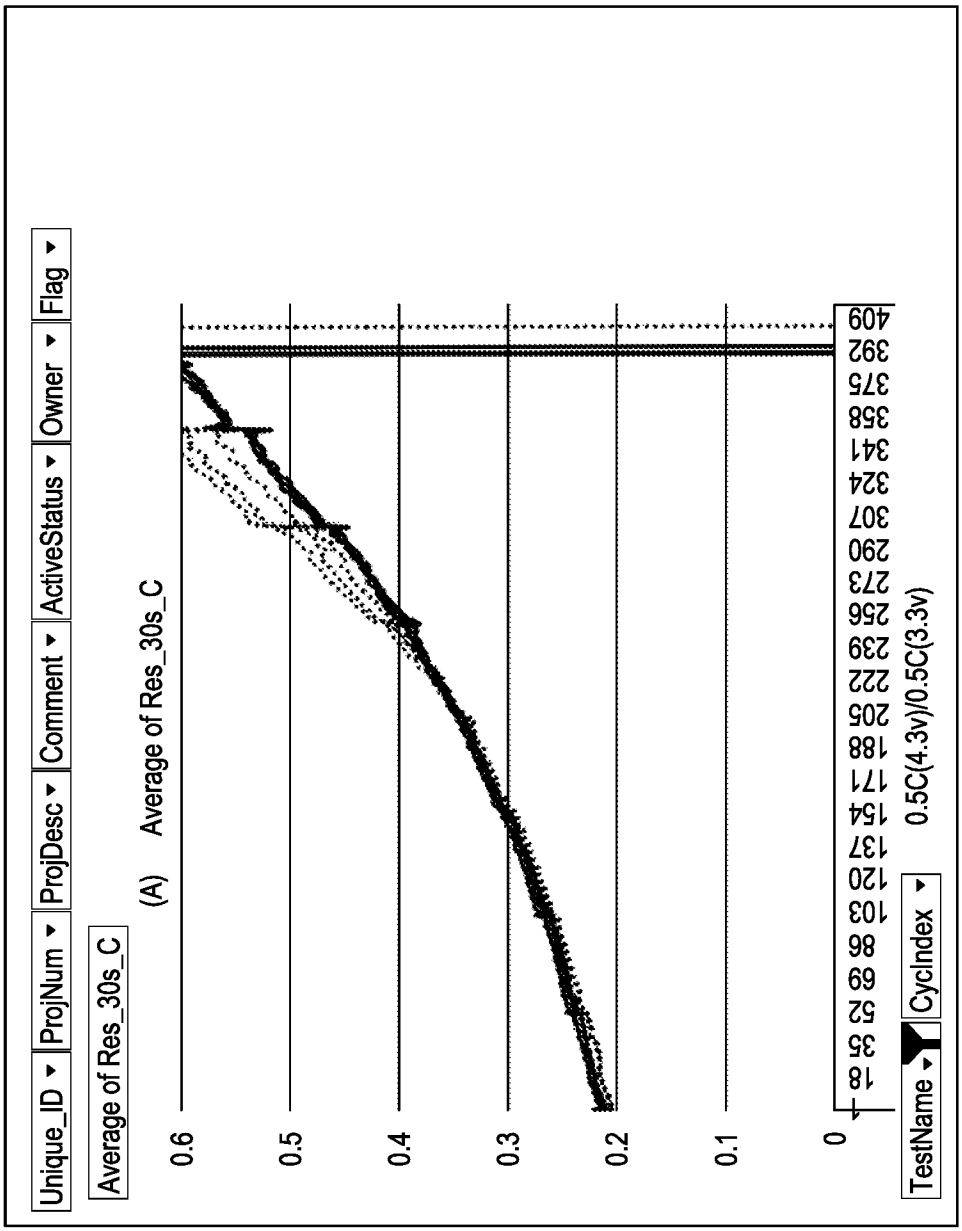

Unique_ID
ProjNum
ProjDesc
Comment
ActiveStatus
Owner
Flag
Average of Res_30s_C
(A) Average of Res_30s_C
0.6
0.5
0.4
0.3
0.2
0.1
0
18
35
52
69
86
103
120
137
154
171
188
205
222
239
256
273
290
307
324
341
358
375
392
409
TestName
CycIndex
0.5C(4.3v)/0.5C(3.3v)

FIG. 7A

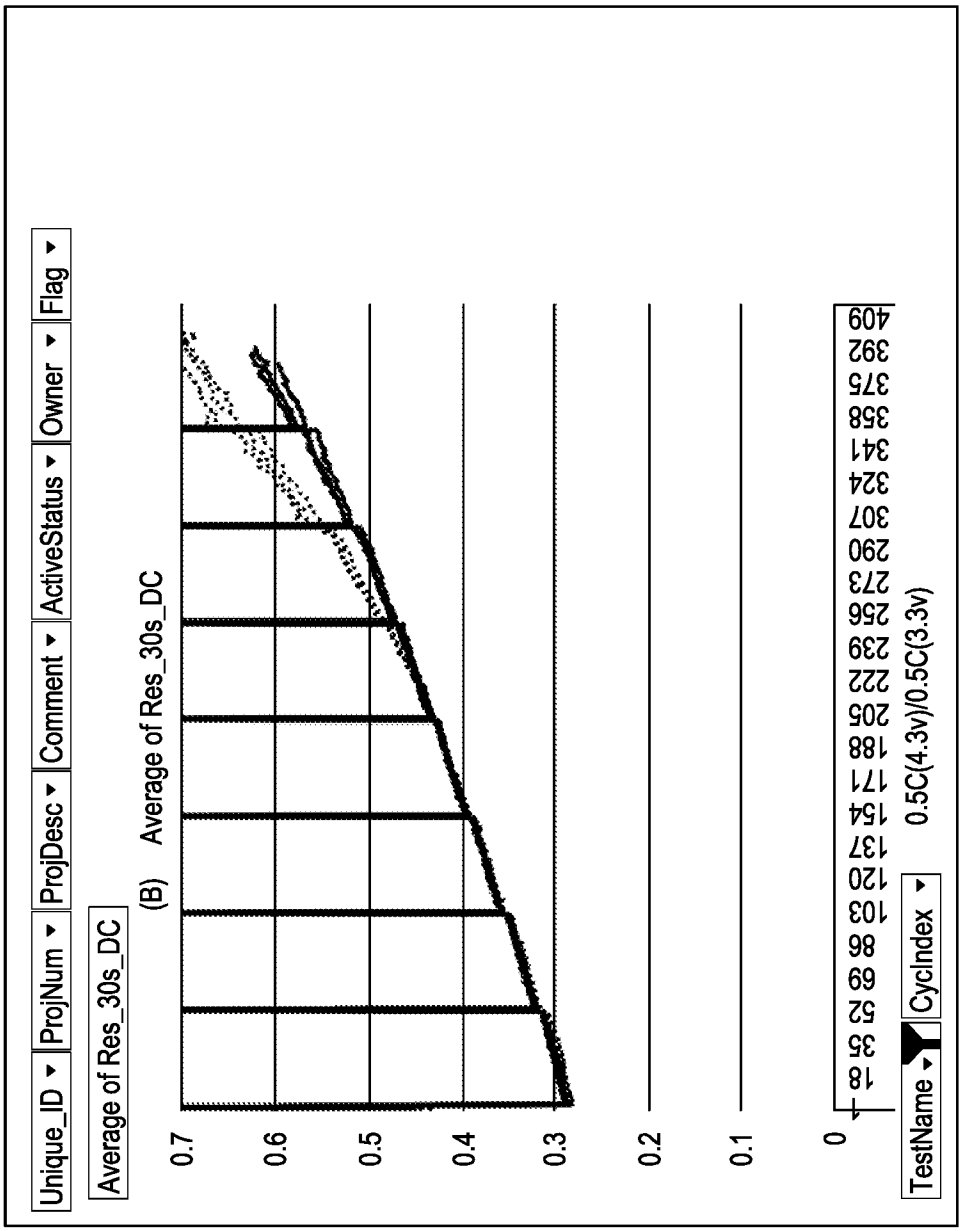

Unique_ID
ProjNum
ProjDesc
Comment
ActiveStatus
Owner
Flag
Average of Res_30s_DC
(B) Average of Res_30s_DC
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
18
35
52
69
86
103
120
137
154
171
188
205
222
239
256
273
290
307
324
341
358
375
392
409
TestName
CycIndex
0.5C(4.3v)/0.5C(3.3v)

FIG. 7B

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2018/064589

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01M4/134 H01G11/00 H01M4/36 H01M4/62 H01M10/0525
H01M10/0567
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01M H01G

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 144 321 A1 (MITSUBISHI CHEM CORP [JP]) 13 January 2010 (2010-01-13) abstract examples 1, 56, 58, 63 claims 1, 14, 29, 39, 41 paragraph [0001] -----	1-9
X	Zhang Zhengcheng: "Fluorinated Electrolyte for 5-V Li-Ion Chemistry", , 12 June 2015 (2015-06-12), XP055556901, Retrieved from the Internet: URL:https://energy.gov/sites/prod/files/2015/06/f23/es218_zhang_2015_o.pdf [retrieved on 2019-02-14] page 1 page 3 pages 21-23 -----	1-4,7-9
	-/--	

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 April 2019	16/04/2019

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Lange, Ronny

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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2018/064589

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2006/127777 A1 (IHARA MASAYUKI [JP] ET AL) 15 June 2006 (2006-06-15) abstract examples 2-1 paragraphs [0002] - [0005], [0097] -----	1-6,9
X	US 2016/233544 A1 (KIM MYUNGHOON [KR] ET AL) 11 August 2016 (2016-08-11) abstract claims 1, 3 paragraphs [0044], [0057] - [0059], [0140] -----	1-9

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2018/064589

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 9(completely); 1-8(partially)

An energy storage device comprising: a first electrode and a second electrode, wherein at least one of the first electrode and the second electrode is a Si-based electrode; a separator between the first electrode and the second electrode; an electrolyte; and at least one electrolyte additive comprising a compound of Formula (A) as defined in claim 1 of the present application, wherein: R1 is selected from the group consisting of a C1-C8 alkyl substituted by F, an alkoxyalkyl substituted by F and each R2 , R3 , and R4 is independently an -H or a C1-C8 alkyl substituted by F, wherein R1 is preferably a C1-C10 alkyl substituted by F or -CH2 -OR5 and R5 is a C1-C10 alkyl substituted by F.

---

2. claims: 1-8(partially)

An energy storage device comprising: a first electrode and a second electrode, wherein at least one of the first electrode and the second electrode is a Si-based electrode; a separator between the first electrode and the second electrode; an electrolyte; and at least one electrolyte additive comprising a compound of Formula (A) as defined in claim 1 of the present application, wherein: R1 is selected from the group consisting of an alkenyloxy-alkyl; and each R2 , R3 , and R4 is independently an -H, wherein R1 is preferably -CH2 -OR5 and R5 is a C1-C6 alkenyl.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2018/064589

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 2144321 A1	13-01-2010	CN 102544585 A	04-07-2012
		CN 102569893 A	11-07-2012
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		WO 2008126800 A1	23-10-2008
US 2006127777 A1	15-06-2006	CN 1790801 A	21-06-2006
		CN 101707261 A	12-05-2010
		JP 4284541 B2	24-06-2009
		JP 2006172811 A	29-06-2006
		KR 20060067852 A	20-06-2006
		TW I332279 B	21-10-2010
		US 2006127777 A1	15-06-2006
US 2016233544 A1	11-08-2016	KR 20160097046 A	17-08-2016
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