



(51) International Patent Classification:

H01M 10/0567 (2010.01) H01M 10/0569 (2010.01)

(21) International Application Number:

PCT/US2024/056465

(22) International Filing Date:

19 November 2024 (19.11.2024)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

63/601,091 20 November 2023 (20.11.2023) US

(71) Applicants: **TESLA, INC.** [US/US]; 1 Tesla Road, Austin, Texas 78725 (US). **UCHICAGO ARGONNE, LLC** [US/US]; 5801 South Ellis Avenue, Chicago, Illinois 60637 (US).

(72) Inventors: **JURNG, Sunhyung**; c/o Tesla, Inc., 1 Tesla Road, Austin, Texas 78725 (US). **MEISNER, Quinton**; c/o Tesla, Inc., 1 Tesla Road, Austin, Texas 78725 (US). **OSTADHOSSEIN, Alireza**; c/o Tesla, Inc., 1 Tesla Road, Austin, Texas 78725 (US). **ABEYWARDANA, Maheeka Yapa**; c/o Tesla, Inc., 1 Tesla Road, Austin, Texas 78725 (US). **ABRAHAM, Jeffin James**; c/o Tesla, Inc.,

1 Tesla Road, Austin, Texas 78725 (US). **AZAM, Saad Mohammad**; c/o Tesla, Inc., 1 Tesla Road, Austin, Texas 78725 (US). **TUUL, Kenneth**; c/o Tesla, Inc., 1 Tesla Road, Austin, Texas 78725 (US). **DAHAN, Jeffery Raymond**; c/o Tesla, Inc., 1 Tesla Road, Austin, Texas 78725 (US). **ZHANG, Zhengcheng**; c/o UChicago Argonne, LLC, 5801 South Ellis Avenue, Chicago, Illinois 60637 (US). **LIU, Qian**; c/o UChicago Argonne, LLC, 5801 South Ellis Avenue, Chicago, Illinois 60637 (US). **WOODS, Eliot**; c/o UChicago Argonne, LLC, 5801 South Ellis Avenue, Chicago, Illinois 60637 (US). **HOSSAIN, Md Anwar**; c/o UChicago Argonne, LLC, 5801 South Ellis Avenue, Chicago, Illinois 60637 (US). **WU, Dezhen**; c/o UChicago Argonne, LLC, 5801 South Ellis Avenue, Chicago, Illinois 60637 (US).

(74) Agent: **FULLER, Michael L.**; KNOBBE MARTENS OLSON & BEAR LLP, 2040 MAIN STREET, FOURTEENTH FLOOR, IRVINE, California 92614 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG,

(54) Title: CYCLIC SULFUR CONTAINING ADDITIVE COMPOUNDS FOR HIGH VOLTAGE ENERGY STORAGE DEVICE ELECTROLYTES, AND PROCESSES THEREOF

(57) Abstract: Provided herein are cyclic sulfite and cyclic sulfate electrolyte additives and formulations for energy storage devices having improved performance. The improved performance may be realized as improved cycling stability at abusive testing conditions.

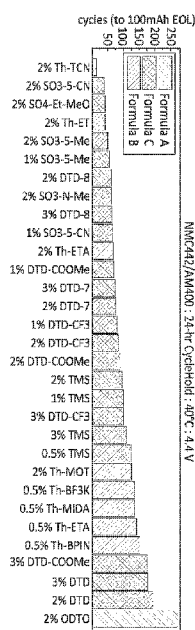


FIG. 21

KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

- *with international search report (Art. 21(3))*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

**CYCLIC SULFUR CONTAINING ADDITIVE COMPOUNDS FOR HIGH
VOLTAGE ENERGY STORAGE DEVICE ELECTROLYTES, AND PROCESSES
THEREOF**

INCORPORATION BY REFERENCE TO ANY PRIORITY APPLICATIONS

[0001] Any and all applications for which a foreign or domestic priority claim is identified in the Application Data Sheet or PCT Request as filed with the present application are hereby incorporated by reference under 37 CFR 1.57, and Rules 4.18 and 20.6. This application claims the benefit of priority to U.S. Provisional Application No. 63/601091, filed November 20, 2023, which is incorporated by reference herein in its entirety for all purposes.

STATEMENT REGARDING FEDERALLY SPONSORED R&D

[0002] This invention was made with government support under Grant No. DE-AC02-06CH11357 awarded by the U.S. Department of Energy (DOE). The government has certain rights in the invention.

PARTIES OF JOINT RESEARCH AGREEMENT

[0003] An invention claimed herein was made by, or on behalf of, and/or in connection with a joint research agreement between the Argonne National Laboratory and Tesla, Inc. The agreement was in effect on and before the date the claimed invention was made, and the claimed invention was made as a result of activities undertaken within the scope of the agreement.

BACKGROUND

Field

[0004] The present disclosure relates generally to energy storage devices, and specifically to improved electrolyte formulations for use in energy storage devices.

Description of the Related Art

[0005] Energy storage devices are widely used to provide power to electronic, electromechanical, electrochemical, and other useful devices. Such cells include primary chemical cells, secondary (rechargeable) cells, fuel cells, and various species of capacitors, including ultracapacitors. Increasing the operating voltage and temperature of energy storage devices, including batteries and capacitors, would be desirable for enhancing energy storage, increasing power capability, and broadening real-world use cases.

[0006] Lithium ion batteries have been relied on as a power source in numerous commercial and industrial uses, for example, in consumer devices, productivity devices, and in battery powered vehicles. However, demands placed on energy storage devices are continuously—and rapidly—growing. For example, the automotive industry is developing vehicles that rely on compact and efficient energy storage, such as plug-in hybrid vehicles and pure electric vehicles. Lithium ion batteries are well suited to meet future demands however improvements in energy density are needed to provide longer life batteries that can travel further on a single charge. The electrolyte is one component in conventional lithium ion batteries that determines electrochemical performance as well as safety of those batteries, where the compatibility between electrode and electrolyte in part governs battery cell performance.

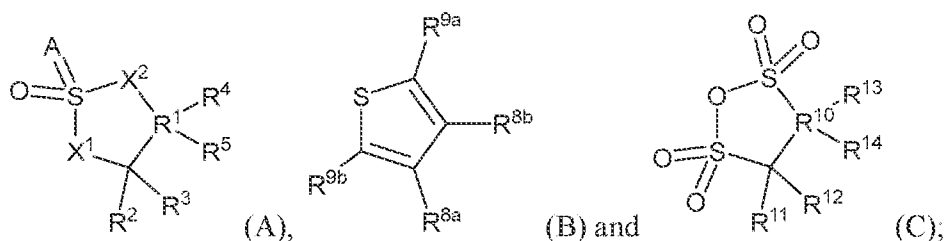
[0007] In conventional lithium ion batteries, discharge rates less than about C/5 are typically manageable by higher energy electrode designs, where C/5 is a discharge current relative to cell capacity such that the cell is drained in 5 hours. However, as the electrodes become thicker (as correlated with higher cell energy), the electrolyte formulation becomes increasingly important to address discharge performance at higher C-rates (1C and above), in addition to improving cell lifetime under high voltage and high temperature conditions.

SUMMARY

[0008] For purposes of summarizing the invention and the advantages achieved over the prior art, certain objects and advantages of the invention are described herein. Not all such objects or advantages may be achieved in any particular embodiment of the invention. Thus, for example, those skilled in the art will recognize that the invention may

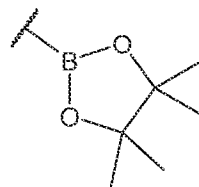
be embodied or carried out in a manner that achieves or optimizes one advantage or group of advantages as taught herein without necessarily achieving other objects or advantages as may be taught or suggested herein.

[0009] In one aspect, an electrolyte composition is disclosed. The electrolyte composition includes: a solvent, a salt, and an additive comprising a compound selected from Formula (A), Formula (B) or Formula (C):

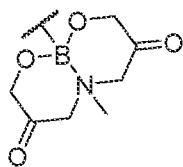


wherein: A is O or absent; X¹ is O or NR⁶; X² is O or NR⁷; R¹ is an optionally substituted C₁-₆ alkylene; R², R³, R⁴ and R⁵ are independently selected from hydrogen, an optionally substituted alkyl, an optionally substituted cycloalkyl, an optionally substituted haloalkyl, an optionally substituted alkenyl, an optionally substituted alkynyl, an optionally substituted cycloalkenyl, a halogen, hydroxy, an optionally substituted alkoxy, an optionally substituted haloalkoxy, an optionally substituted C-amido, an optionally substituted N-amido, an optionally substituted C-carboxy, an optionally substituted O-carboxy, an optionally substituted sulfenyl, an optionally substituted sulfinyl, an optionally substituted sulfonyl,

cyano, nitro, amino, an optionally substituted amine,

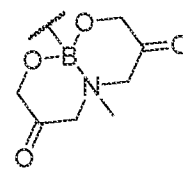
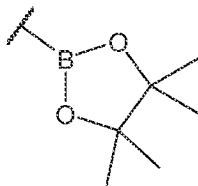


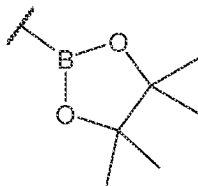
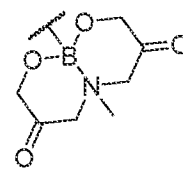
, -BF₃K and

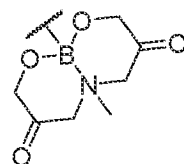
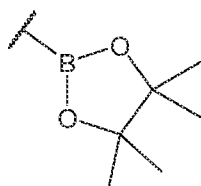


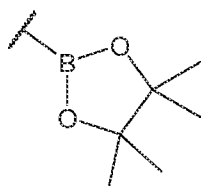
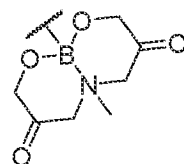
; R⁶ and R⁷ are independently selected from a hydrogen, an optionally substituted alkyl, an optionally substituted cycloalkyl, an optionally substituted haloalkyl, a halogen, hydroxy, an optionally substituted alkoxy and an optionally substituted haloalkoxy; R^{8a} and R^{8b} are independently selected from hydrogen, an optionally substituted alkyl, an optionally substituted cycloalkyl, an optionally substituted haloalkyl, an optionally substituted alkenyl, an optionally substituted alkynyl, an optionally substituted cycloalkenyl,

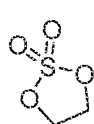
a halogen, hydroxy, an optionally substituted alkoxy, an optionally substituted haloalkoxy, an optionally substituted C-amido, an optionally substituted N-amido, an optionally substituted C-carboxy, an optionally substituted O-carboxy, an optionally substituted sulfinyl, an optionally substituted sulfinyl, an optionally substituted sulfonyl, cyano, nitro, amino, an



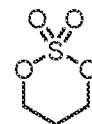
optionally substituted amine, , $-\text{BF}_3\text{K}$ and , or R^{8a} and R^{8b} are taken together to form an optionally substituted cycloalkyl, an optionally substituted cycloalkenyl, an optionally substituted aryl, an optionally substituted heteroaryl or an optionally substituted heterocycle; R^{9a} and R^{9b} are independently selected from a hydrogen, an optionally substituted alkyl, an optionally substituted cycloalkyl, an optionally substituted haloalkyl, a halogen, hydroxy, an optionally substituted alkoxy and an optionally substituted haloalkoxy; R^{10} is an optionally substituted C_{1-6} alkylene; R^{11} , R^{12} , R^{13} and R^{14} are independently selected from hydrogen, an optionally substituted alkyl, an optionally substituted cycloalkyl, an optionally substituted haloalkyl, an optionally substituted alkenyl, an optionally substituted alkynyl, an optionally substituted cycloalkenyl, a halogen, hydroxy, an optionally substituted alkoxy, an optionally substituted haloalkoxy, an optionally substituted C-amido, an optionally substituted N-amido, an optionally substituted C-carboxy, an optionally substituted O-carboxy, an optionally substituted sulfinyl, an optionally substituted sulfinyl, an optionally substituted sulfonyl, cyano, nitro, amino, an optionally



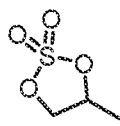
substituted amine, , $-\text{BF}_3\text{K}$ and ; wherein the compound is not



(DTD),



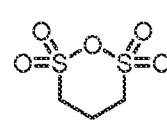
(DTD-6MR or TMS),



(DTD-Me or PLS),



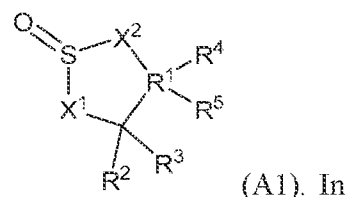
CN (Th-CN) and



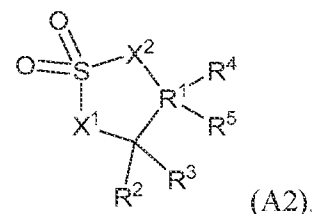
(ODTO).

[0010] In some embodiments, the compound is of Formula (A). In some

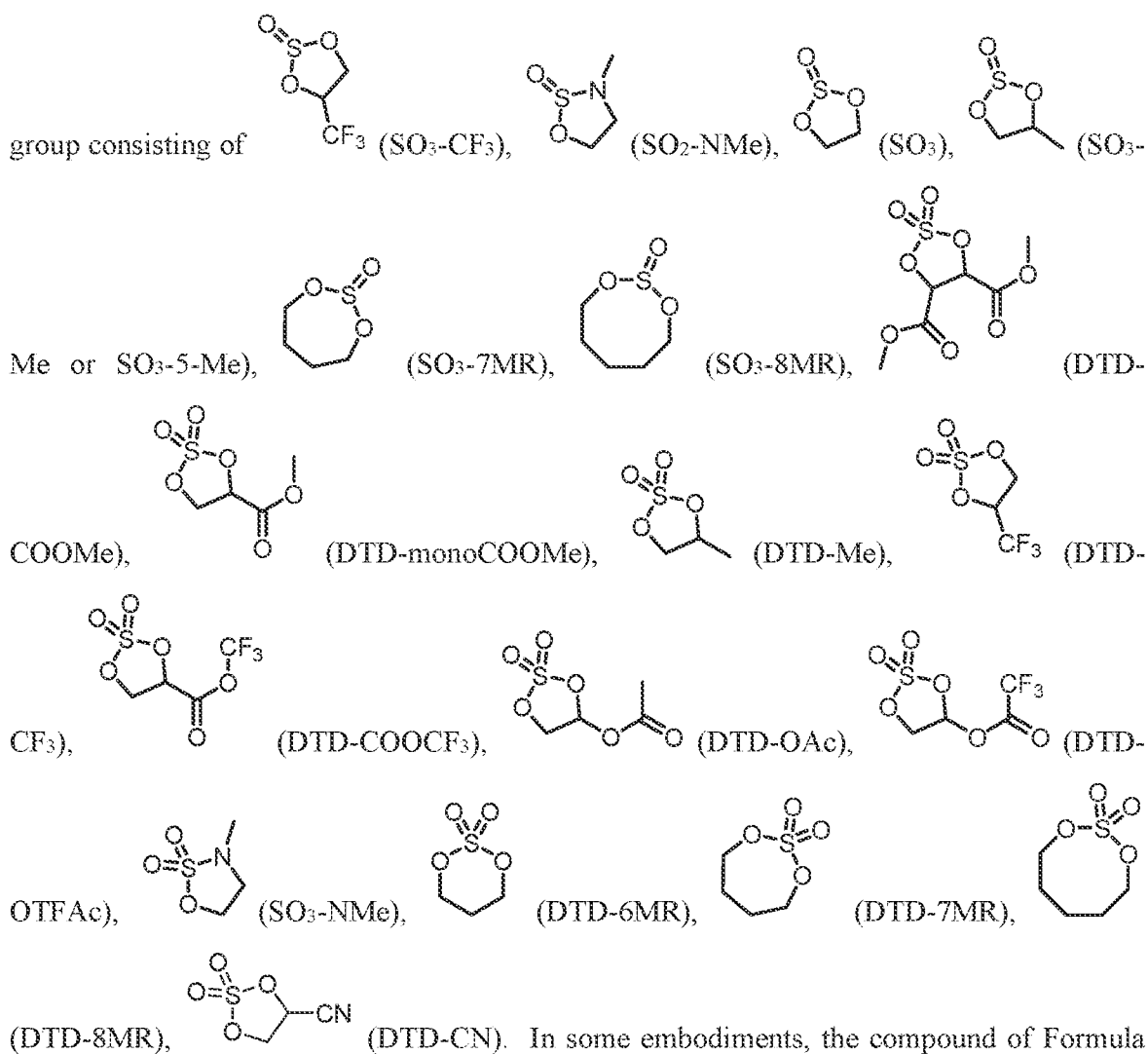
embodiments, is absent and the compound is of Formula (A1):



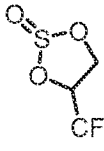
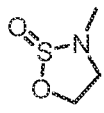
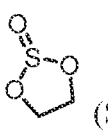
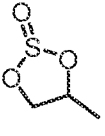
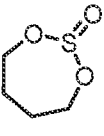
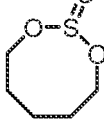
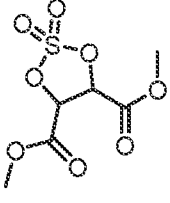
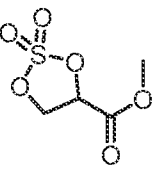
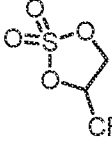
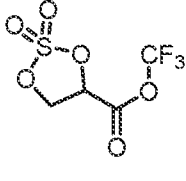
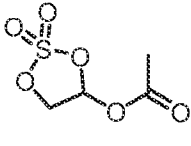
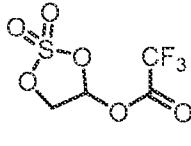
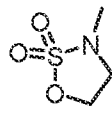
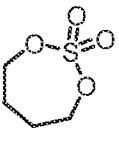
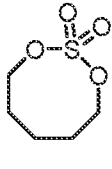
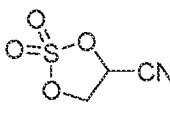
some embodiments, A is O, and the compound is of Formula (A2):



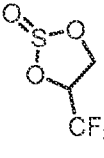
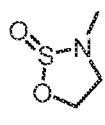
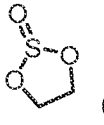
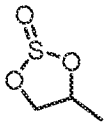
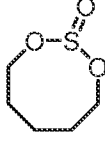
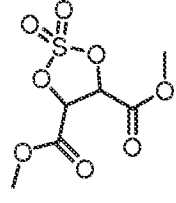
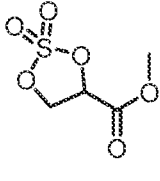
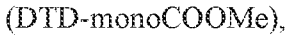
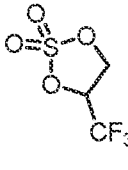
[0011] In some embodiments, the compound of Formula (A) is selected from the

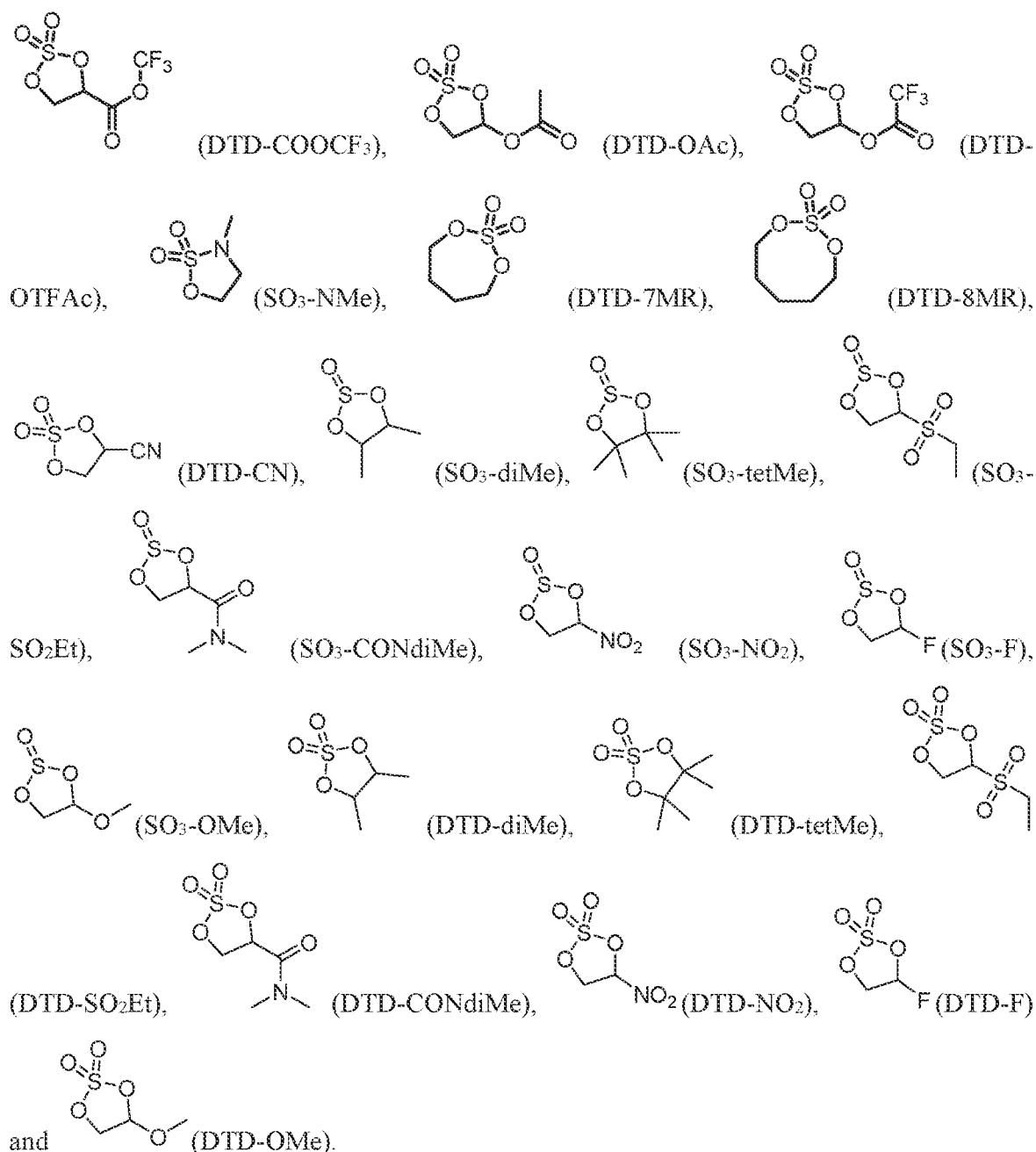


(A) is selected from the group consisting of

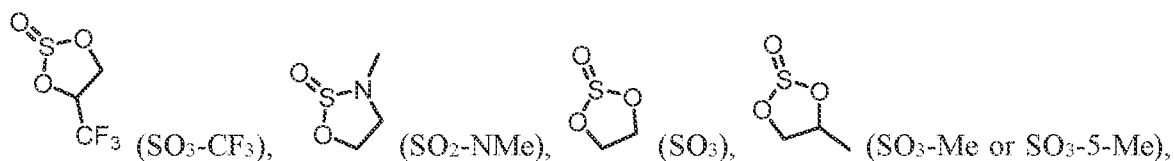
 ($\text{SO}_3\text{-CF}_3$),  ($\text{SO}_2\text{-NMe}$),
 (SO_3),  ($\text{SO}_3\text{-Me}$ or $\text{SO}_3\text{-5-Me}$),  ($\text{SO}_3\text{-7MR}$),  ($\text{SO}_3\text{-8MR}$),
 (DTD-COOMe),  (DTD-monoCOOMe),  (DTD-CF_3),
 (DTD-COOCF_3),  (DTD-OAc),  (DTD-OTFAc),
 ($\text{SO}_3\text{-NMe}$),  (DTD-7MR),  (DTD-8MR) and
 (DTD-CN). In some embodiments, the compound of Formula (A) is selected

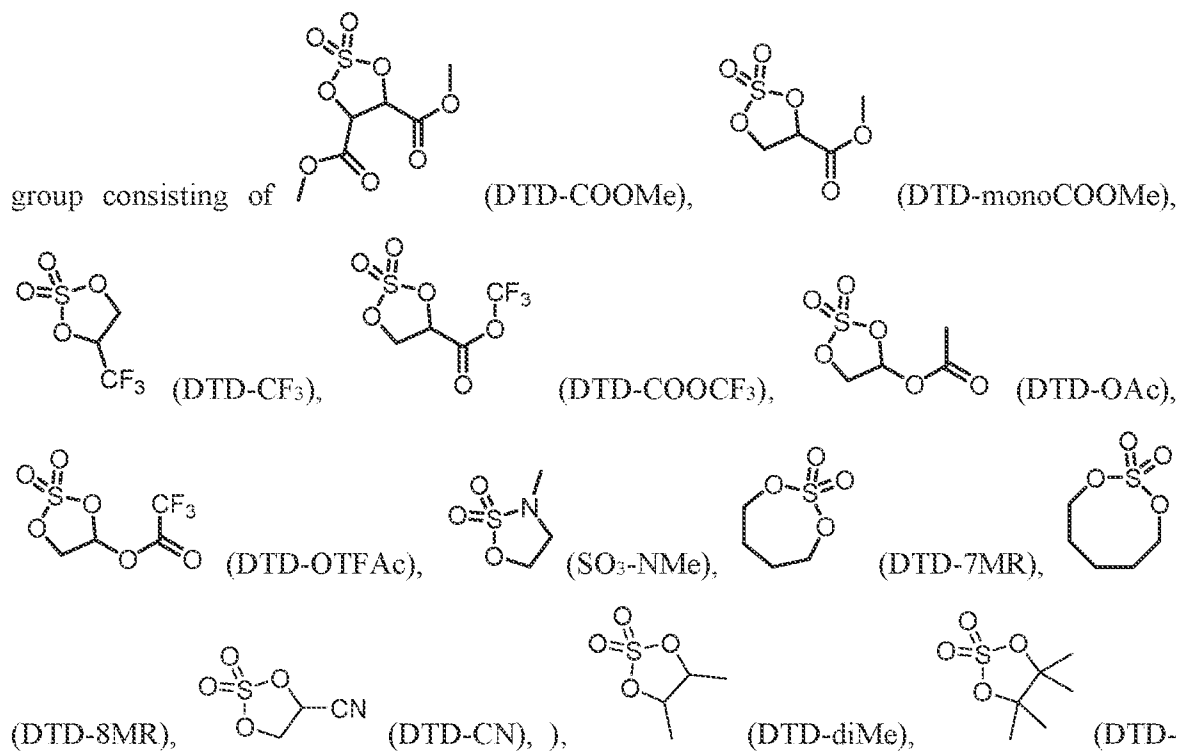
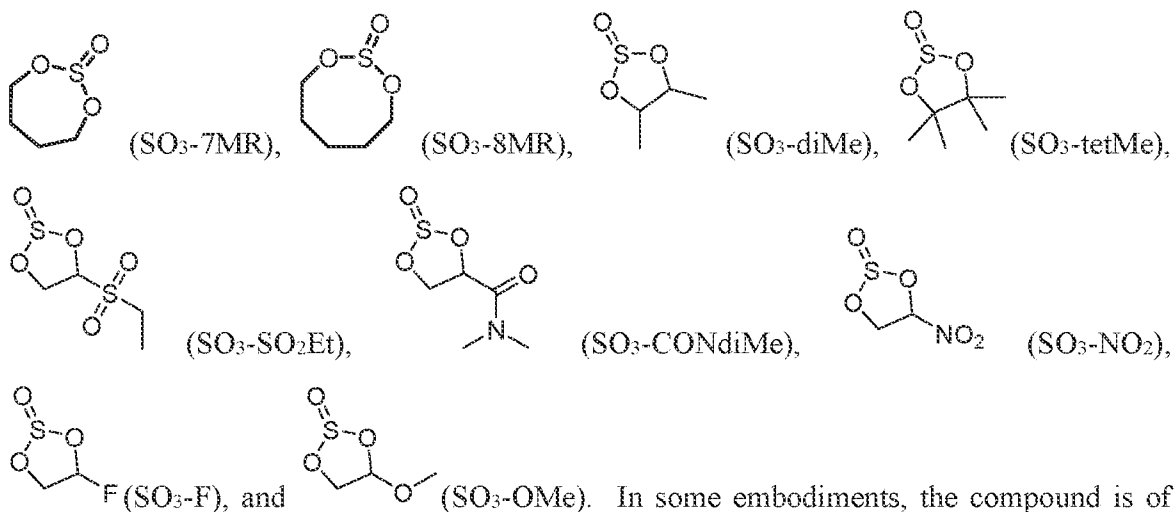
from the group consisting of

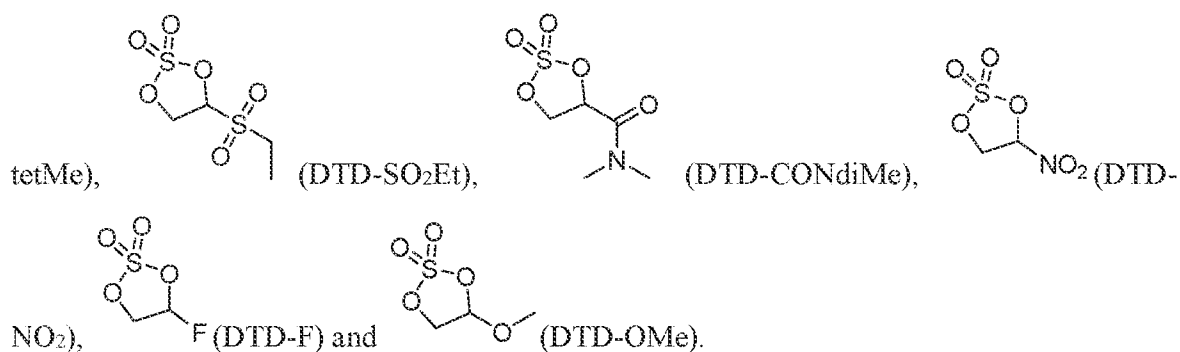
 ($\text{SO}_3\text{-CF}_3$),  ($\text{SO}_2\text{-NMe}$),  (SO_3),
 ($\text{SO}_3\text{-Me}$ or $\text{SO}_3\text{-5-Me}$),  ($\text{SO}_3\text{-7MR}$),  ($\text{SO}_3\text{-8MR}$), 
 (DTD-COOMe),  (DTD-monoCOOMe),  (DTD-CF_3),



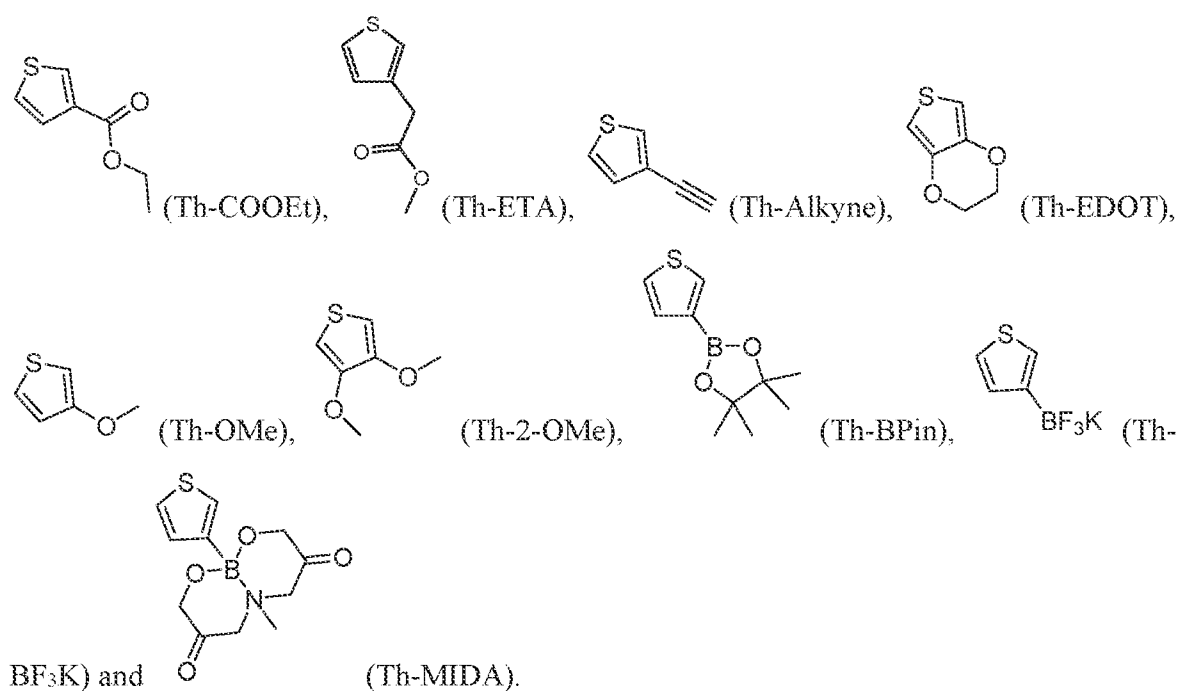
[0012] In some embodiments, the compound is of Formula (A1). In some embodiments, the compound of Formula (A1) is selected from the group consisting of



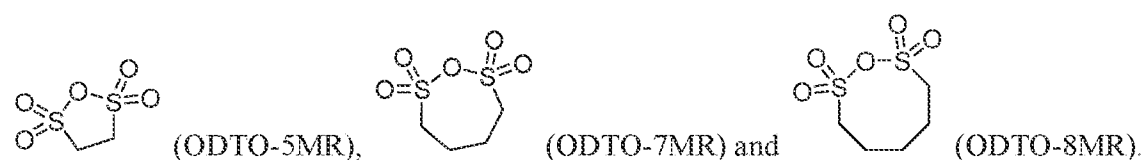




[0013] In some embodiments, the compound is of Formula (B). In some embodiments, the compound of Formula (B) is selected from the group consisting of



[0014] In some embodiments, the compound is of Formula (C). In some embodiments, the compound of Formula (C) is selected from the group consisting of



[0015] In some embodiments, the electrolyte composition includes the additive in about 0.5-3 wt%. In some embodiments, the electrolyte composition may further include an additional additive. In some embodiments, the additional additive can be selected from vinylene chloride (VC), fluoroethylene chloride (FEC), or a combination of VC and FEC. In

some embodiments, the electrolyte composition can include an additional additive of about 0.25 wt% VC, about 0.75 wt% FEC, and about 0.25 wt% VC and about 0.75 wt % FEC. In some embodiments, the solvent can be ethylene chloride (EC), ethyl methyl chloride (EMC), dimethyl chloride (DMC), or combinations thereof. In some embodiments, the electrolyte can comprise EC:DMC at a ratio of 15:85 w/w or EC:EMC at a ratio of 3:7 w/w.

[0016] In another aspect, an energy storage device is described. The energy storage device includes: an electrolyte; a cathode; an anode; and a housing, wherein the electrolyte, cathode and anode are disposed within the housing. In some embodiments, the energy storage device is a lithium-ion battery. In some embodiments, a volume of gas can be produced within the energy storage device including an electrolyte composition having an additive as described herein that is less than or comparable to a volume of gas produced within an energy storage device without the additive.

[0017] In another aspect, a method of preparing an energy storage device is described. The method includes: preparing an electrolyte; and positioning the electrolyte within a housing comprising a cathode and an anode.

[0018] In another aspect, a method of preparing an energy storage device is described. The method includes: positioning an electrolyte composition within a housing comprising a cathode and an anode.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] FIG. 1A is a data chart showing the specific discharge capacity performances of energy storage devices comprising an $\text{SO}_3\text{-CF}_3$ additive, according to some embodiments.

[0020] FIG. 1B is a data chart showing the specific discharge capacity performances of energy storage devices comprising an $\text{SO}_3\text{-CF}_3$ additive and 0.25wt% VC co-additive, according to some embodiments.

[0021] FIG. 1C is a data chart showing the specific discharge capacity performances of energy storage devices comprising an $\text{SO}_3\text{-CF}_3$ additive (0.5 wt%) with VC and/or FEC co-additives, according to some embodiments.

[0022] FIG. 2A is a data chart showing the resistance performances of energy storage devices comprising an $\text{SO}_3\text{-CF}_3$ additive, according to some embodiments.

[0023] FIG. 2B is a data chart showing the resistance performances of energy storage devices comprising an $\text{SO}_3\text{-CF}_3$ additive with FEC and/or VC co-additives, according to some embodiments.

[0024] FIG. 3A is a data chart showing the specific discharge capacity performances of energy storage devices comprising an DTD-COOME additive, according to some embodiments.

[0025] FIG. 3B is a data chart specific discharge capacity performances of energy storage devices comprising an DTD-COOME additive (0.5 wt%) with VC and/or FEC co-additives, according to some embodiments.

[0026] FIG. 4A is a data chart showing the resistance performances of energy storage devices comprising an DTD-COOME additive, according to some embodiments.

[0027] FIG. 4B is a data chart showing the resistance performances of energy storage devices comprising an DTD-COOME additive with VC and/or FEC co-additives, according to some embodiments.

[0028] FIG. 5A is data charts showing the specific discharge capacity and voltage polarization (ΔV) performances of energy storage devices comprising an DTD-COOME additive, according to some embodiments.

[0029] FIG. 5B is data charts showing the specific discharge capacity and voltage polarization (ΔV) performances of energy storage devices comprising an DTD-COOME additive with an FEC co-additive, according to some embodiments

[0030] FIG. 5C are bar graphs showing the gas volume expansion and charge transfer resistance (R_{ct}) measurements of energy storage devices comprising an DTD-COOME additive, according to some embodiments.

[0031] FIG. 6A are data charts showing the specific discharge capacity and voltage polarization (ΔV) performances of energy storage devices comprising an DTD- CF_3 additive, according to some embodiments.

[0032] FIG. 6B are bar graphs showing the gas volume expansion and charge transfer resistance (R_{ct}) measurements of energy storage devices comprising an DTD- CF_3 additive, according to some embodiments.

[0033] FIG. 7A is a data chart showing the specific discharge capacity performances of energy storage devices comprising an SO₃-N-Me additive, according to some embodiments.

[0034] FIG. 7B is a data chart showing the coulombic efficiency performances of energy storage devices comprising an SO₃-N-Me additive, according to some embodiments.

[0035] FIG. 8A is a data chart showing the specific discharge capacity performances of energy storage devices comprising an DTD-7MR additive, according to some embodiments.

[0036] FIG. 8B is a data chart showing the coulombic efficiency performances of energy storage devices comprising an DTD-7MR additive, according to some embodiments.

[0037] FIG. 9A is a data chart showing the specific discharge capacity performances of energy storage devices comprising an ODTO additive, according to some embodiments.

[0038] FIG. 9B is a data chart showing the coulombic efficiency performances of energy storage devices comprising an ODTO additive, according to some embodiments.

[0039] FIG. 10A is a data chart showing the resistance performances of energy storage devices comprising an ODTO additive, according to some embodiments.

[0040] FIG. 10B is an expanded version of the data chart of FIG. 10A showing the resistance performances of energy storage devices comprising an ODTO additive, according to some embodiments.

[0041] FIG. 11A is a bar chart showing the specific discharge capacity performances of energy storage devices comprising DTD-7MR and/or ODTO additives, according to some embodiments.

[0042] FIG. 11B is a bar chart showing the coulombic efficiency performances of energy storage devices comprising DTD-7MR and/or ODTO additives, according to some embodiments.

[0043] FIG. 12A is a data chart showing the resistance performances of energy storage devices comprising efficiency performances of energy storage devices comprising DTD-7MR and/or ODTO additives, according to some embodiments.

[0044] FIG. 12B is an expanded version of the data chart of FIG. 12A showing the resistance performances of energy storage devices comprising efficiency performances of

energy storage devices comprising DTD-7MR and/or ODTO additives, according to some embodiments.

[0045] FIG. 13A is a data chart showing the specific discharge capacity performances of energy storage devices comprising an DTD-6MR additive, according to some embodiments.

[0046] FIG. 13B is a data chart showing the coulombic efficiency performances of energy storage devices comprising an DTD-6MR additive, according to some embodiments.

[0047] FIG. 14 is a data chart showing the specific discharge capacity performances of energy storage devices comprising an SO_3 additive, according to some embodiments.

[0048] FIG. 15A is a data chart showing the specific discharge capacity performances of energy storage devices comprising an $\text{SO}_3\text{-Me}$ additive, according to some embodiments.

[0049] FIG. 15B is a data chart showing the specific discharge capacity performances of energy storage devices comprising an $\text{SO}_3\text{-Me}$ additive and VC co-additive, according to some embodiments.

[0050] FIG. 15C is a data chart showing the specific discharge capacity performances of energy storage devices comprising an $\text{SO}_3\text{-Me}$ additive and VC and FEC co-additives, according to some embodiments.

[0051] FIG. 16A are data charts showing the specific discharge capacity and voltage polarization (ΔV) performances of energy storage devices comprising DTD-7MR or DTD-8MR additives, according to some embodiments.

[0052] FIG. 16B are bar graphs showing the gas volume expansion and charge transfer resistance (R_{ct}) measurements of energy storage devices comprising DTD-7MR or DTD-8MR additives, according to some embodiments.

[0053] FIG. 17A are data charts showing the specific discharge capacity and voltage polarization (ΔV) performances of energy storage devices comprising Th-ETA, Th-TCN, Th-MOT, Th-ET, Th- BR_3K , Th-BPin or Th-MIDA additives, according to some embodiments.

[0054] FIG. 17B are bar graphs showing the gas volume expansion and charge transfer resistance (R_{ct}) measurements of energy storage devices comprising Th-ETA, Th-TCN, Th-MOT, Th-ET, Th- BR_3K , Th-BPin or Th-MIDA additives, according to some embodiments.

[0055] FIG. 18A are data charts showing the specific discharge capacity and voltage polarization (ΔV) performances of energy storage devices comprising TMS, according to some embodiments.

[0056] FIG. 18B are bar graphs showing the gas volume expansion and charge transfer resistance (R_{ct}) measurements of energy storage devices comprising TMS, according to some embodiments.

[0057] FIG. 19A are data charts showing the specific discharge capacity and voltage polarization (ΔV) performances of energy storage devices comprising SO_2N -5-Me, SO_3 -5-Me or SO_3 -N-Me, according to some embodiments.

[0058] FIG. 19B are bar graphs showing the gas volume expansion and charge transfer resistance (R_{ct}) measurements of energy storage devices comprising SO_2N -5-Me, SO_3 -5-Me or SO_3 -N-Me, according to some embodiments.

[0059] FIG. 20A are data charts showing the specific discharge capacity and voltage polarization (ΔV) performances of energy storage devices comprising ODT, according to some embodiments.

[0060] FIG. 20B are bar graphs showing the gas volume expansion and charge transfer resistance (R_{ct}) measurements of energy storage devices comprising ODT, according to some embodiments.

[0061] FIG. 21 is a bar graph showing end of life cycles measured for energy storage devices comprising various additives, according to some embodiments.

[0062] FIG. 22A is a data chart showing the relative decay rate (mol%) of DTD in electrolyte formulations under shelf-storage conditions at ambient temperature (25 °C) and 5 °C over 1 year.

[0063] FIG. 22B is a data chart showing the relative decay rate (mol%) of DTD-Me in electrolyte formulations under shelf-storage conditions at ambient temperature (25 °C) and 5 °C over 40 weeks.

[0064] FIG. 22C is a data chart showing the relative decay rate (mol%) of DTD-diCOOMe in electrolyte formulations at ambient shelf-storage conditions at ambient temperature (25 °C) and 5 °C over 1 year, according to some embodiments.

[0065] FIG. 22D is a data chart showing the relative decay rate (mol%) of DTD-monoCOOMe in electrolyte formulations at ambient under shelf-storage conditions at ambient temperature (25 °C) and 5 °C over 32 weeks, according to some embodiments.

[0066] FIG. 22E is a data chart showing the relative decay rate (mol%) of DTD-diMe in electrolyte formulations at ambient under shelf-storage conditions at ambient temperature (25 °C) and 5 °C over 24 weeks, according to some embodiments.

[0067] FIG. 22F is a data chart showing the relative decay rate (mol%) of DTD-tetMe in electrolyte formulations at ambient under shelf-storage conditions at ambient temperature (25 °C) and 5 °C over 16 weeks, according to some embodiments.

DETAILED DESCRIPTION

[0068] Electrolyte formulations comprising at least one cyclic sulfur containing additive for high-voltage, high-energy density energy storage devices (e.g., lithium ion and/or sodium ion batteries) are described. The electrolyte formulations further include a solvent and a salt (e.g., a lithium salt and/or a sodium salt). Such device improvements may beneficially afford improved cycling stability, particularly under extreme conditions such as high voltages (e.g., at least 4.2 V, 4.3 V or 4.4 V) and high temperature (e.g., about 40-45 °C).

Definitions

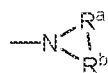
[0069] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as is commonly understood by one of ordinary skill in the art. All patents, applications, published applications and other publications referenced herein are incorporated by reference in their entirety unless stated otherwise. In the event that there are a plurality of definitions for a term herein, those in this section prevail unless stated otherwise.

[0070] Whenever a group is described as being “optionally substituted” that group may be unsubstituted or substituted with one or more of the indicated substituents.

Likewise, when a group is described as being “unsubstituted or substituted” if substituted, the substituent(s) may be selected from one or more of the indicated substituents. If no substituents are indicated, it is meant that the indicated “optionally substituted” or “substituted” group may be substituted with one or more group(s) individually and independently selected from deuterium (D), halogen, hydroxy, C₁₋₄ alkoxy, C₁₋₈ alkyl, C₃₋₂₀ cycloalkyl, aryl, heteroaryl, heterocyclyl, C₁₋₆ haloalkyl, cyano, C₂₋₈ alkenyl, C₂₋₈ alkynyl, C₃₋₂₀ cycloalkenyl, aryl(alkyl), heteroaryl(alkyl), heterocyclyl(alkyl), acyl, thiocarbonyl, C-carboxy, O-carboxy, sulfenyl, sulfinyl, sulfonyl, haloalkoxy, an amino, a mono-substituted amine group and a di-substituted amine group.

[0071] As used herein, “C_a to C_b” in which “a” and “b” are integers refer to the number of carbon atoms in a group. The indicated group can contain from “a” to “b”, inclusive, carbon atoms. Thus, for example, a “C₁ to C₄ alkyl” group refers to all alkyl groups having from 1 to 4 carbons, that is, CH₃-, CH₃CH₂-, CH₃CH₂CH₂-, (CH₃)₂CH-, CH₃CH₂CH₂CH₂-, CH₃CH₂CH(CH₃)- and (CH₃)₃C-. If no “a” and “b” are designated, the broadest range described in these definitions is to be assumed.

[0072] If two “R” groups are described as being “taken together” the R groups and the atoms they are attached to can form a cycloalkyl, cycloalkenyl, aryl, heteroaryl or heterocycle. For example, without limitation, if R^a and R^b of an NR^aR^b group are indicated to be “taken together,” it means that they are covalently bonded, either indirectly through intermediate atoms, or directly to one another, to form a ring, for example:



[0073] As used herein, the term “alkyl” refers to a fully saturated aliphatic hydrocarbon group. The alkyl moiety may be branched or straight chain. Examples of branched alkyl groups include, but are not limited to, isopropyl, sec-butyl, t-butyl and the like. Examples of straight chain alkyl groups include, but are not limited to, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, and the like.

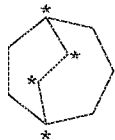
[0074] The term “alkenyl” used herein refers to a monovalent straight or branched chain radical of from two to thirty carbon atoms containing a carbon double bond(s) including, but not limited to, 1-propenyl, 2-propenyl, 2-methyl-1-propenyl, 1-butenyl, 2-butenyl and the like. An alkenyl group may be unsubstituted or substituted.

[0075] The term “alkynyl” used herein refers to a monovalent straight or branched chain radical of from two to thirty carbon atoms containing a carbon triple bond(s) including, but not limited to, 1-propynyl, 1-butyne, 2-butyne and the like. An alkynyl group may be unsubstituted or substituted.

[0076] As used herein, “cycloalkyl” refers to a completely saturated (no double or triple bonds) mono- or multi- cyclic hydrocarbon ring system. When composed of two or more rings, the rings may be joined together in a fused, bridged or spiro fashion. 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 cycloalkyl” 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. Cycloalkyl groups can contain 3 to 30 atoms in the ring(s), 3 to 20 atoms in the ring(s), 3 to 10 atoms in the ring(s), 3 to 8 atoms in the ring(s) or 3 to 6 atoms in the ring(s). A cycloalkyl group may be unsubstituted or substituted. Examples of mono-cycloalkyl groups include, but are in no way limited to, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl and cyclooctyl. 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.

[0077] As used herein, “cycloalkenyl” refers to a mono- or multi- cyclic hydrocarbon ring system that contains one or more double bonds in at least one ring; although, if there is more than one, the double bonds cannot form a fully delocalized pi-electron system throughout all the rings (otherwise the group would be “aryl,” as defined herein). Cycloalkenyl groups can contain 3 to 30 atoms in the ring(s), 3 to 20 atoms in the

ring(s), 3 to 10 atoms in the ring(s), 3 to 8 atoms in the ring(s) or 3 to 6 atoms in the ring(s). When composed of two or more rings, the rings may be connected together in a fused, bridged or spiro fashion. A cycloalkenyl group may be unsubstituted or substituted.

[0078] As used herein, “cycloalkynyl” refers to a mono- or multi- cyclic hydrocarbon ring system that contains one or more triple bonds in at least one ring. If there is more than one triple bond, the triple bonds cannot form a fully delocalized pi-electron system throughout all the rings. Cycloalkynyl groups can contain 8 to 30 atoms in the ring(s), 8 to 20 atoms in the ring(s) or 8 to 10 atoms in the ring(s). When composed of two or more rings, the rings may be joined together in a fused, bridged or spiro fashion. A cycloalkynyl group may be unsubstituted or substituted.

[0079] As used herein, “aryl” refers to a carbocyclic (all carbon) monocyclic or polycyclic aromatic ring system (including fused ring systems where two carbocyclic rings share a chemical bond) that has a fully delocalized pi-electron system throughout all the rings. The number of carbon atoms in an aryl group can vary. For example, the aryl group can be a C₆-C₁₄ aryl group, a C₆-C₁₀ aryl group, or a C₆ aryl group. Examples of aryl groups include, but are not limited to, benzene, naphthalene and azulene. An aryl group may be substituted or unsubstituted.

[0080] As used herein, “heteroaryl” refers to a monocyclic or polycyclic aromatic ring system (a ring system with fully delocalized pi-electron system) that contain(s) one or more heteroatoms (for example, 1, 2 or 3 heteroatoms), that is, an element other than carbon, including but not limited to, nitrogen, oxygen and sulfur. The number of atoms in the ring(s) of a heteroaryl group can vary. For example, the heteroaryl group can contain 4 to 14 atoms in the ring(s), 5 to 10 atoms in the ring(s) or 5 to 6 atoms in the ring(s). Furthermore, the term “heteroaryl” includes fused ring systems where two rings, such as at least one aryl ring and at least one heteroaryl ring, or at least two heteroaryl rings, share at least one chemical bond. Examples of heteroaryl rings include, but are not limited to, furan, furazan, thiophene, benzothiophene, phthalazine, pyrrole, oxazole, benzoxazole, 1,2,3-oxadiazole, 1,2,4-oxadiazole, thiazole, 1,2,3-thiadiazole, 1,2,4-thiadiazole, benzothiazole, imidazole, benzimidazole, indole, indazole, pyrazole, benzopyrazole, isoxazole, benzoisoxazole, isothiazole, triazole, benzotriazole, thiadiazole, tetrazole, pyridine,

pyridazine, pyrimidine, pyrazine, purine, pteridine, quinoline, isoquinoline, quinazoline, quinoxaline, cinnoline and triazine. A heteroaryl group may be substituted or unsubstituted.

[0081] As used herein, “heterocyclyl” or “heteroalicyclyl” refers to three-, four-, five-, six-, seven-, eight-, nine-, ten-, up to 18-membered monocyclic, bicyclic and tricyclic ring system wherein carbon atoms together with from 1 to 5 heteroatoms constitute said ring system. A heterocycle may optionally contain one or more unsaturated bonds situated in such a way, however, that a fully delocalized pi-electron system does not occur throughout all the rings. The heteroatom(s) is an element other than carbon including, but not limited to, oxygen, sulfur and nitrogen. A heterocycle may further contain one or more carbonyl or thiocarbonyl functionalities, so as to make the definition include oxo-systems and thio-systems such as lactams, lactones, cyclic imides, cyclic thioimides and cyclic carbamates. When composed of two or more rings, the rings may be joined together in a fused or spiro fashion. Additionally, any nitrogens in a heteroalicyclic may be quaternized. Heterocyclyl or heteroalicyclic groups may be unsubstituted or substituted. Examples of such “heterocyclyl” or “heteroalicyclyl” groups include but are not limited to, 1,3-dioxin, 1,3-dioxane, 1,4-dioxane, 1,2-dioxolane, 1,3-dioxolane, 1,4-dioxolane, 1,3-oxathiane, 1,4-oxathiin, 1,3-oxathiolane, 1,3-dithiole, 1,3-dithiolane, 1,4-oxathiane, tetrahydro-1,4-thiazine, 2H-1,2-oxazine, maleimide, succinimide, barbituric acid, thiobarbituric acid, dioxopiperazine, hydantoin, dihydrouracil, trioxane, hexahydro-1,3,5-triazine, imidazoline, imidazolidine, isoxazoline, isoxazolidine, oxazoline, oxazolidine, oxazolidinone, thiazoline, thiazolidine, morpholine, oxirane, piperidine N-Oxide, piperidine, piperazine, pyrrolidine, pyrrolidone, pyrrolidione, 4-piperidone, pyrazoline, pyrazolidine, 2-oxopyrrolidine, tetrahydropyran, 4H-pyran, tetrahydrothiopyran, thiamorpholine, thiamorpholine sulfoxide, thiamorpholine sulfone and their benzo-fused analogs (e.g., benzimidazolidinone, tetrahydroquinoline and/or 3,4-methylenedioxyphenyl).

[0082] As used herein, “aralkyl” and “aryl(alkyl)” refer to an aryl group connected, as a substituent, via a lower alkylene group. The lower alkylene and aryl group of an aralkyl may be substituted or unsubstituted. Examples include but are not limited to benzyl, 2-phenylalkyl, 3-phenylalkyl and naphthylalkyl.

[0083] As used herein, “heteroaralkyl” and “heteroaryl(alkyl)” refer to a heteroaryl group connected, as a substituent, via a lower alkylene group. The lower alkylene

and heteroaryl group of heteroaralkyl may be substituted or unsubstituted. Examples include but are not limited to 2-thienylalkyl, 3-thienylalkyl, furylalkyl, thienylalkyl, pyrrolylalkyl, pyridylalkyl, isoxazolylalkyl and imidazolylalkyl and their benzo-fused analogs.

[0084] A “heteroalicycyl(alkyl)” and “heterocycyl(alkyl)” refer to a heterocyclic or a heteroalicyclic group connected, as a substituent, via a lower alkylene group. The lower alkylene and heterocycyl of a (heteroalicycyl)alkyl may be substituted or unsubstituted. Examples include but are not limited tetrahydro-2H-pyran-4-yl(methyl), piperidin-4-yl(ethyl), piperidin-4-yl(propyl), tetrahydro-2H-thiopyran-4-yl(methyl) and 1,3-thiazinan-4-yl(methyl).

[0085] “Alkylene groups” and “lower alkylene groups” are straight-chained -CH₂- tethering groups, forming bonds to connect molecular fragments via their terminal carbon atoms. Examples include but are not limited to methylene (-CH₂-), ethylene (-CH₂CH₂-), propylene (-CH₂CH₂CH₂-), and butylene (-CH₂CH₂CH₂CH₂-). An alkylene group can be substituted by replacing one or more hydrogen of the alkylene group with a substituent(s) listed under the definition of “substituted” and/or by substituting both

hydrogens on the same carbon with a cycloalkyl group (e.g., ).

[0086] As used herein, the term “hydroxy” refers to a -OH group.

[0087] As used herein, “alkoxy” refers to the formula -OR wherein R is an alkyl, an alkenyl, an alkynyl, a cycloalkyl, a cycloalkenyl, aryl, heteroaryl, heterocycyl, cycloalkyl(alkyl), aryl(alkyl), heteroaryl(alkyl) or heterocycyl(alkyl) is defined herein. A non-limiting list of alkoxys is methoxy, ethoxy, n-propoxy, 1-methylethoxy (isopropoxy), n-butoxy, iso-butoxy, sec-butoxy, tert-butoxy, phenoxy and benzoxy. An alkoxy may be substituted or unsubstituted.

[0088] As used herein, “acyl” refers to a hydrogen, alkyl, alkenyl, alkynyl, aryl, heteroaryl, heterocycyl, aryl(alkyl), heteroaryl(alkyl) and heterocycyl(alkyl) connected, as substituents, via a carbonyl group. Examples include formyl, acetyl, propanoyl, benzoyl and acryl. An acyl may be substituted or unsubstituted.

[0089] A “cyano” group refers to a “-CN” group.

[0090] The term “halogen atom” or “halogen” as used herein, means any one of the radio-stable atoms of column 7 of the Periodic Table of the Elements, such as, fluorine, chlorine, bromine and iodine.

[0091] A “thiocarbonyl” group refers to a “-C(=S)R” group in which R can be the same as defined with respect to O-carboxy. A thiocarbonyl may be substituted or unsubstituted.

[0092] An “O-carbamyl” group refers to a “-OC(=O)N(R_AR_B)” group in which R_A and R_B can be independently hydrogen, an alkyl, an alkenyl, an alkynyl, a cycloalkyl, a cycloalkenyl, aryl, heteroaryl, heterocyclyl, cycloalkyl(alkyl), aryl(alkyl), heteroaryl(alkyl) or heterocyclyl(alkyl). An O-carbamyl may be substituted or unsubstituted.

[0093] An “N-carbamyl” group refers to an “ROC(=O)N(R_A)-” group in which R and R_A can be independently hydrogen, an alkyl, an alkenyl, an alkynyl, a cycloalkyl, a cycloalkenyl, aryl, heteroaryl, heterocyclyl, cycloalkyl(alkyl), aryl(alkyl), heteroaryl(alkyl) or heterocyclyl(alkyl). An N-carbamyl may be substituted or unsubstituted.

[0094] An “O-thiocarbamyl” group refers to a “-OC(=S)-N(R_AR_B)” group in which R_A and R_B can be independently hydrogen, an alkyl, an alkenyl, an alkynyl, a cycloalkyl, a cycloalkenyl, aryl, heteroaryl, heterocyclyl, cycloalkyl(alkyl), aryl(alkyl), heteroaryl(alkyl) or heterocyclyl(alkyl). An O-thiocarbamyl may be substituted or unsubstituted.

[0095] An “N-thiocarbamyl” group refers to an “ROC(=S)N(R_A)-” group in which R and R_A can be independently hydrogen, an alkyl, an alkenyl, an alkynyl, a cycloalkyl, a cycloalkenyl, aryl, heteroaryl, heterocyclyl, cycloalkyl(alkyl), aryl(alkyl), heteroaryl(alkyl) or heterocyclyl(alkyl). An N-thiocarbamyl may be substituted or unsubstituted.

[0096] A “C-amido” group refers to a “-C(=O)N(R_AR_B)” group in which R_A and R_B can be independently hydrogen, an alkyl, an alkenyl, an alkynyl, a cycloalkyl, a cycloalkenyl, aryl, heteroaryl, heterocyclyl, cycloalkyl(alkyl), aryl(alkyl), heteroaryl(alkyl) or heterocyclyl(alkyl). A C-amido may be substituted or unsubstituted.

[0097] An “N-amido” group refers to a “RC(=O)N(R_A)-” group in which R and R_A can be independently hydrogen, an alkyl, an alkenyl, an alkynyl, a cycloalkyl, a

cycloalkenyl, aryl, heteroaryl, heterocyclyl, cycloalkyl(alkyl), aryl(alkyl), heteroaryl(alkyl) or heterocyclyl(alkyl). An N-amido may be substituted or unsubstituted.

[0098] A “C-thioamido” group refers to a “-C(=S)N(R_AR_B)” group in which R_A and R_B can be independently hydrogen, an alkyl, an alkenyl, an alkynyl, a cycloalkyl, a cycloalkenyl, aryl, heteroaryl, heterocyclyl, cycloalkyl(alkyl), aryl(alkyl), heteroaryl(alkyl) or heterocyclyl(alkyl). A C-thioamido may be substituted or unsubstituted.

[0099] An “N-thioamido” group refers to a “RC(=S)N(R_A)-” group in which R and R_A can be independently hydrogen, an alkyl, an alkenyl, an alkynyl, a cycloalkyl, a cycloalkenyl, aryl, heteroaryl, heterocyclyl, cycloalkyl(alkyl), aryl(alkyl), heteroaryl(alkyl) or heterocyclyl(alkyl). An N-thioamido may be substituted or unsubstituted.

[0100] An “S-sulfonamido” group refers to a “-SO₂N(R_AR_B)” group in which R_A and R_B can be independently hydrogen, an alkyl, an alkenyl, an alkynyl, a cycloalkyl, a cycloalkenyl, aryl, heteroaryl, heterocyclyl, cycloalkyl(alkyl), aryl(alkyl), heteroaryl(alkyl) or heterocyclyl(alkyl). An S-sulfonamido may be substituted or unsubstituted.

[0101] An “N-sulfonamido” group refers to a “RSO₂N(R_A)-” group in which R and R_A can be independently hydrogen, an alkyl, an alkenyl, an alkynyl, a cycloalkyl, a cycloalkenyl, aryl, heteroaryl, heterocyclyl, cycloalkyl(alkyl), aryl(alkyl), heteroaryl(alkyl) or heterocyclyl(alkyl). An N-sulfonamido may be substituted or unsubstituted.

[0102] An “O-carboxy” group refers to a “RC(=O)O-” group in which R can be hydrogen, an alkyl, an alkenyl, an alkynyl, an alkoxy, a cycloalkyl, a cycloalkenyl, aryl, heteroaryl, heterocyclyl, cycloalkyl(alkyl), aryl(alkyl), heteroaryl(alkyl) or heterocyclyl(alkyl), as defined herein. An O-carboxy may be substituted or unsubstituted.

[0103] The terms “ester” and “C-carboxy” refer to a “-C(=O)OR” group in which R can be the same as defined with respect to O-carboxy. An ester and C-carboxy may be substituted or unsubstituted.

[0104] A “sulfenyl” group refers to an “-SR” group in which R can be hydrogen, an alkyl, an alkenyl, an alkynyl, a cycloalkyl, a cycloalkenyl, aryl, heteroaryl, heterocyclyl, cycloalkyl(alkyl), aryl(alkyl), heteroaryl(alkyl) or heterocyclyl(alkyl). A sulfenyl may be substituted or unsubstituted.

[0105] A “sulfinyl” group refers to an “-S(=O)-R” group in which R can be the same as defined with respect to sulfenyl. A sulfinyl may be substituted or unsubstituted.

[0106] A “sulfonyl” group refers to an “SO₂R” group in which R can be the same as defined with respect to sulfenyl. A sulfonyl may be substituted or unsubstituted.

[0107] As used herein, “haloalkyl” refers to an alkyl group in which one or more of the hydrogen atoms are replaced by a halogen (e.g., mono-haloalkyl, di-haloalkyl and tri-haloalkyl). Such groups include but are not limited to, chloromethyl, fluoromethyl, difluoromethyl, trifluoromethyl, 1-chloro-2-fluoromethyl and 2-fluoroisobutyl. A haloalkyl may be substituted or unsubstituted.

[0108] As used herein, “haloalkoxy” refers to an alkoxy group in which one or more of the hydrogen atoms are replaced by a halogen (e.g., mono-haloalkoxy, di-haloalkoxy and tri-haloalkoxy). Such groups include but are not limited to, chloromethoxy, fluoromethoxy, difluoromethoxy, trifluoromethoxy, 1-chloro-2-fluoromethoxy and 2-fluoroisobutoxy. A haloalkoxy may be substituted or unsubstituted.

[0109] The term “nitro” as used herein refers to a –NO₂ group.

[0110] The term “amino” as used herein refers to a –NH₂ group.

[0111] A “mono-substituted amine” group refers to a “-NHR” group in which R can be an alkyl, an alkenyl, an alkynyl, a haloalkyl, a cycloalkyl, a cycloalkenyl, aryl, heteroaryl, heterocyclyl, cycloalkyl(alkyl), aryl(alkyl), heteroaryl(alkyl) or heterocyclyl(alkyl), as defined herein. A mono-substituted amino may be substituted or unsubstituted. Examples of mono-substituted amino groups include, but are not limited to, –NH(methyl), –NH(phenyl) and the like.

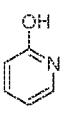
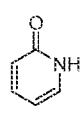
[0112] A “di-substituted amine” group refers to a “-NR_AR_B” group in which R_A and R_B can be independently an alkyl, an alkenyl, an alkynyl, a haloalkyl, a cycloalkyl, a cycloalkenyl, aryl, heteroaryl, heterocyclyl, cycloalkyl(alkyl), aryl(alkyl), heteroaryl(alkyl) or heterocyclyl(alkyl), as defined herein. A di-substituted amino may be substituted or unsubstituted. Examples of di-substituted amino groups include, but are not limited to, –N(methyl)₂, –N(phenyl)(methyl), –N(ethyl)(methyl) and the like.

[0113] Where the numbers of substituents is not specified (e.g. haloalkyl), there may be one or more substituents present. For example, “haloalkyl” may include one or more of the same or different halogens. As another example, “C₁-C₃ alkoxyphenyl” may include one or more of the same or different alkoxy groups containing one, two or three atoms.

[0114] As used herein, a radical indicates species with a single, unpaired electron such that the species containing the radical can be covalently bonded to another species. Hence, in this context, a radical is not necessarily a free radical. Rather, a radical indicates a specific portion of a larger molecule. The term “radical” can be used interchangeably with the term “group.”

[0115] It is understood that, in any compound described herein having one or more chiral centers, if an absolute stereochemistry is not expressly indicated, then each center may independently be of R-configuration or S-configuration or a mixture thereof. Thus, the compounds provided herein may be enantiomerically pure, enantiomerically enriched, racemic mixture, diastereomerically pure, diastereomerically enriched, or a stereoisomeric mixture. In addition, it is understood that in any compound described herein having one or more double bond(s) generating geometrical isomers that can be defined as E or Z, each double bond may independently be E or Z, or a mixture thereof.

[0116] In some embodiments, in any compound described, all tautomeric forms are also intended to be included. For example, without limitation, a reference to the

compound  may be interpreted to include tautomer .

[0117] It is to be understood that where compounds disclosed herein have unfilled valencies, then the valencies are to be filled with hydrogens or isotopes thereof, e.g., hydrogen-1 (protium) and hydrogen-2 (deuterium).

[0118] It is understood that the compounds described herein can be labeled isotopically. Substitution with isotopes such as deuterium may afford certain therapeutic advantages resulting from greater metabolic stability, such as, for example, increased *in vivo* half-life or reduced dosage requirements. Each chemical element as represented in a compound structure may include any isotope of said element. For example, in a compound structure a hydrogen atom may be explicitly disclosed or understood to be present in the compound. At any position of the compound that a hydrogen atom may be present, the hydrogen atom can be any isotope of hydrogen, including but not limited to hydrogen-1 (protium) and hydrogen-2 (deuterium). Thus, reference herein to a compound encompasses all potential isotopic forms unless the context clearly dictates otherwise.

[0119] It is understood that the methods and combinations described herein include crystalline forms (also known as polymorphs, which include the different crystal packing arrangements of the same elemental composition of a compound), amorphous phases, salts, solvates, and hydrates. In some embodiments, the compounds described herein exist in solvated forms with pharmaceutically acceptable solvents such as water, ethanol, or the like. In other embodiments, the compounds described herein exist in unsolvated form. Solvates contain either stoichiometric or non-stoichiometric amounts of a solvent, and may be formed during the process of crystallization with pharmaceutically acceptable solvents such as water, ethanol, or the like. Hydrates are formed when the solvent is water, or alcoholates are formed when the solvent is alcohol. In addition, the compounds provided herein can exist in unsolvated as well as solvated forms. In general, the solvated forms are considered equivalent to the unsolvated forms for the purposes of the compounds and methods provided herein.

[0120] Where a range of values is provided, it is understood that the upper and lower limit, and each intervening value between the upper and lower limit of the range is encompassed within the embodiments.

[0121] Terms and phrases used in this application, and variations thereof, especially in the appended claims, unless otherwise expressly stated, should be construed as open ended as opposed to limiting. As examples of the foregoing, the term 'including' should be read to mean 'including, without limitation,' 'including but not limited to,' or the like; the term 'comprising' as used herein is synonymous with 'including,' 'containing,' or 'characterized by,' and is inclusive or open-ended and does not exclude additional, unrecited elements or method steps; the term 'having' should be interpreted as 'having at least;' the term 'includes' should be interpreted as 'includes but is not limited to;' the term 'example' is used to provide exemplary instances of the item in discussion, not an exhaustive or limiting list thereof; and use of terms like 'preferably,' 'preferred,' 'desired,' or 'desirable,' and words of similar meaning should not be understood as implying that certain features are critical, essential, or even important to the structure or function, but instead as merely intended to highlight alternative or additional features that may or cannot be utilized in a particular embodiment. In addition, the term "comprising" is to be interpreted synonymously with the phrases "having at least" or "including at least". When used in the context of a

process, the term "comprising" means that the process includes at least the recited steps, but may include additional steps. When used in the context of a compound, composition or device, the term "comprising" means that the compound, composition or device includes at least the recited features or components, but may also include additional features or components.

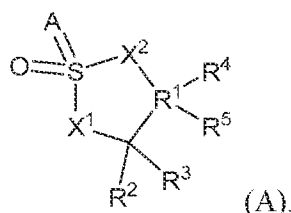
[0122] With respect to the use of substantially any plural and/or singular terms herein, those having skill in the art can translate from the plural to the singular and/or from the singular to the plural as is appropriate to the context and/or application. The various singular/plural permutations may be expressly set forth herein for sake of clarity. The indefinite article "a" or "an" does not exclude a plurality. The mere fact that certain measures are recited in mutually different dependent claims does not indicate that a combination of these measures cannot be used to advantage. Any reference signs in the claims should not be construed as limiting the scope.

Cyclic Sulfur Containing Additives

[0123] Cyclic sulfur containing electrolyte additives are generally disclosed. In some embodiments, the cyclic sulfur containing electrolyte additives is a cyclic sulfite and/or a cyclic sulfate electrolyte additive.

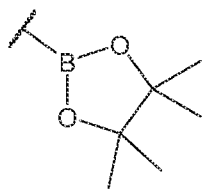
Formula (A)

[0124] In some embodiments, the cyclic sulfur containing electrolyte additives are of Formula (A):

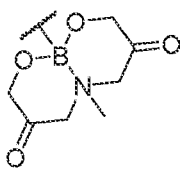


[0125] In some embodiments, A is O or absent; X¹ is O or NR⁶; X² is O or NR⁷; R¹ is an optionally substituted C₁₋₆ alkylene; R², R³, R⁴ and R⁵ are independently selected from hydrogen, an optionally substituted alkyl, an optionally substituted cycloalkyl, an optionally substituted haloalkyl, an optionally substituted alkenyl, an optionally substituted alkynyl, an optionally substituted cycloalkenyl, a halogen, hydroxy, an optionally substituted

alkoxy, an optionally substituted haloalkoxy, an optionally substituted C-amido, an optionally substituted N-amido, an optionally substituted C-carboxy, an optionally substituted O-carboxy, an optionally substituted sulfenyl, an optionally substituted sulfinyl, an optionally substituted sulfonyl, cyano, nitro, amino, an optionally substituted amine,



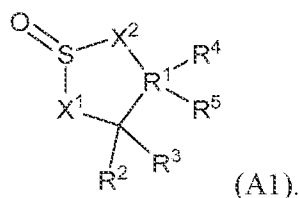
,

-BF₃K and

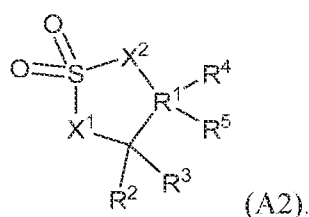
;

and R⁶ and R⁷ are independently selected from a hydrogen, an optionally substituted alkyl, an optionally substituted cycloalkyl, an optionally substituted haloalkyl, a halogen, hydroxy, an optionally substituted alkoxy and an optionally substituted haloalkoxy.

[0126] In some embodiments, the cyclic sulfur containing electrolyte additives of Formula (A) are of Formula (A1):



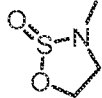
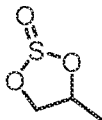
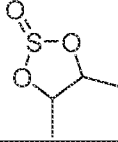
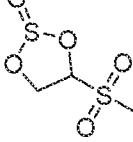
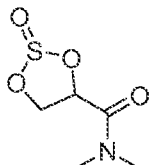
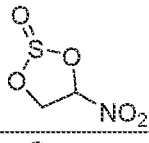
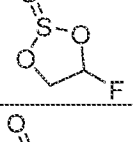
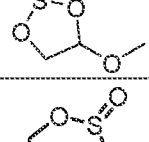
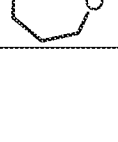
[0127] In some embodiments, the cyclic sulfur containing electrolyte additives of Formula (A) are of Formula (A2):

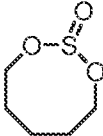
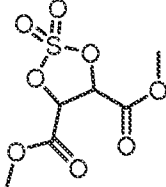
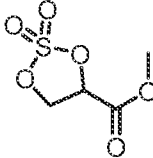
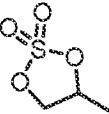
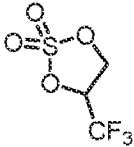
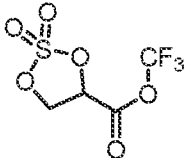
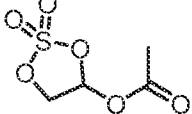
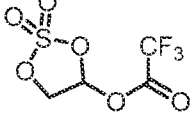
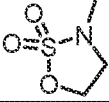
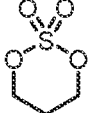
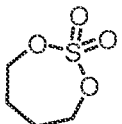


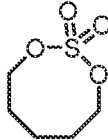
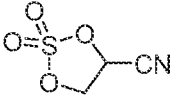
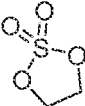
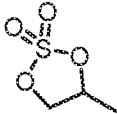
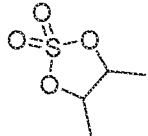
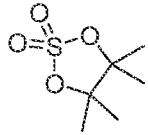
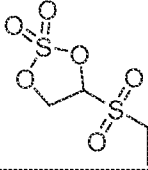
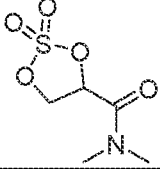
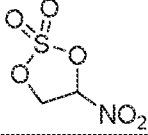
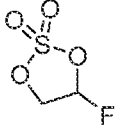
[0128] In some embodiments, the electrolyte additive of Formula (A) is selected from any one of or any combination of the compounds shown in Table A.

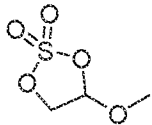
Table A

Name	Structure
SO ₃ -CF ₃	

Name	Structure
SO ₂ -NMe or SO ₂ N-5-Me	
SO ₃	
SO ₃ -Me or SO ₃ -5-Me	
SO ₃ -diMe	
SO ₃ -tetMe	
SO ₃ -SO ₂ Et	
SO ₃ -CONdiMe	
SO ₃ -NO ₂	
SO ₃ -F	
SO ₃ -OMe	
SO ₃ -7MR	

Name	Structure
SO ₃ -8MR	
DTD-COOMe	
DTD-monoCOOMe	
DTD-Me	
DTD-CF ₃	
DTD-COOCF ₃	
DTD-OAc	
DTD-OTFAc	
SO ₃ -NMe or SO ₃ -N-Me	
DTD-6MR	
DTD-7MR	

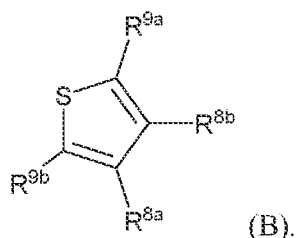
Name	Structure
DTD-8MR	
DTD-CN	
DTD	
DTD-6MR or TMS	
DTD-Me or PLS	
DTD-diMe	
DTD-tetMe	
DTD-SO ₂ Et	
DTD-CONdiMe	
DTD-NO ₂	
DTD-F	

Name	Structure
DTD-OMe	

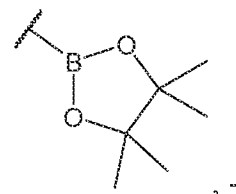
[0129] In some embodiments, the electrolyte additive of Formula (A) is not selected from any one of or any combination of the of the compounds shown in Table A. For example, in some embodiments the compound is not selected from DTD, TMS or PLS (i.e., DTD-Me), or any combinations thereof.

Formula (B)

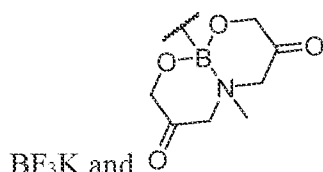
[0130] In some embodiments, the cyclic sulfur containing electrolyte additives are of Formula (B):

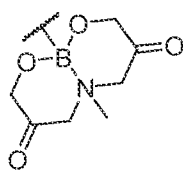


[0131] In some embodiments, R^{8a} and R^{8b} are independently selected from hydrogen, an optionally substituted alkyl, an optionally substituted cycloalkyl, an optionally substituted haloalkyl, an optionally substituted alkenyl, an optionally substituted alkynyl, an optionally substituted cycloalkenyl, a halogen, hydroxy, an optionally substituted alkoxy, an optionally substituted haloalkoxy, an optionally substituted C-amido, an optionally substituted N-amido, an optionally substituted C-carboxy, an optionally substituted O-carboxy, an optionally substituted sulfinyl, an optionally substituted sulfonyl, cyano, nitro, amino, an optionally substituted amine,



substituted sulfonyl, cyano, nitro, amino, an optionally substituted amine,

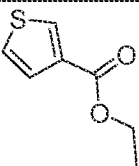
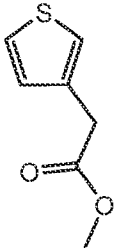
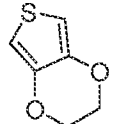
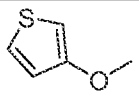
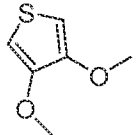
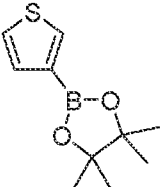


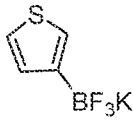
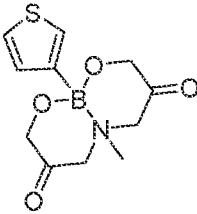
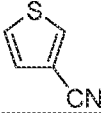
BF₃K and , or R^{8a} and R^{8b} are taken together to form an optionally substituted

cycloalkyl, an optionally substituted cycloalkenyl, an optionally substituted aryl, an optionally substituted heteroaryl or an optionally substituted heterocycle; and R^{9a} and R^{9b} are independently selected from a hydrogen, an optionally substituted alkyl, an optionally substituted cycloalkyl, an optionally substituted haloalkyl, a halogen, hydroxy, an optionally substituted alkoxy and an optionally substituted haloalkoxy.

[0132] In some embodiments, the electrolyte additive of Formula (A) is selected from any one of or any combination of the compounds shown in Table B.

Table B

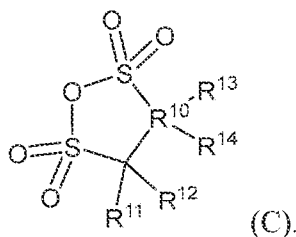
Name	Structure
Th-COOEt	
Th-ETA	
Th-Alkyne or Th-ET	
Th-EDOT	
Th-OMe or Th-MOT	
Th-2-OMe	
Th-BPin	

Name	Structure
Th-BF ₃ K	
Th-MIDA	
Th-CN or Th-TCN	

[0133] In some embodiments, the electrolyte additive of Formula (B) is not selected from any one of or any combination of the of the compounds shown in Table B. For example, in some embodiments the compound is not Th-CN.

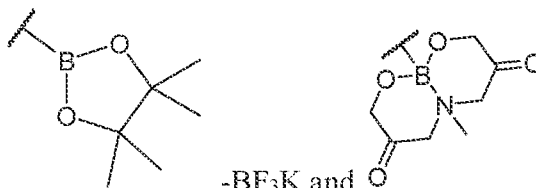
Formula (C)

[0134] In some embodiments, the cyclic sulfur containing electrolyte additives are of Formula (C):



[0135] In some embodiments, R¹⁰ is an optionally substituted C₁₋₆ alkylene; and R¹¹, R¹², R¹³ and R¹⁴ are independently selected from hydrogen, an optionally substituted alkyl, an optionally substituted cycloalkyl, an optionally substituted haloalkyl, an optionally substituted alkenyl, an optionally substituted alkynyl, an optionally substituted cycloalkenyl, a halogen, hydroxy, an optionally substituted alkoxy, an optionally substituted haloalkoxy, an optionally substituted C-amido, an optionally substituted N-amido, an optionally substituted C-carboxy, an optionally substituted O-carboxy, an optionally substituted sulfenyl, an

optionally substituted sulfinyl, an optionally substituted sulfonyl, cyano, nitro, amino, an



optionally substituted amine,

, -BF₃K and

[0136] In some embodiments, the electrolyte additive of Formula (C) is selected from any one of or any combination of the compounds shown in Table C.

Table C

Name	Structure
ODTO-5MR	
ODTO-7MR	
ODTO-8MR	
ODTO	

[0137] In some embodiments, the electrolyte additive of Formula (C) is not selected from any one of or any combination of the of the compounds shown in Table C. For example, in some embodiments the compound is not ODTO.

Electrolytes

[0138] The electrolyte formulations described herein can include a salt (e.g., lithium salt), an electrolyte solvent, and one or more of the additives discussed herein. In some embodiments, the electrolyte further comprises one or more additional additives. In some embodiments, the electrolyte comprises the additive in, in about, in at most, or in at most about, 0.1 wt.%, 0.5 wt. %, 1 wt.%, 1.5 wt.%, 2 wt.%, 2.5 wt.%, 3 wt.%, 3.5 wt.%, 4 wt.%, 4.5 wt.%, 5 wt.%, 5.5 wt.%, 6 wt.%, 7 wt.% or 8 wt.%, or any range of values

therebetween. In some embodiments, the electrolyte composition comprises the additive in about 0.5-3 wt%, or any range of values therebetween. In some embodiments, the electrolyte comprises a plurality of additives that total to, to about, to at most, or to at most about, 0.5 wt. %, 1 wt. %, 1.5 wt. %, 2 wt. %, 2.5 wt. %, 3 wt. %, 3.5 wt. %, 4 wt. %, 4.5 wt. %, 5 wt. %, 5.5 wt. %, 6 wt. %, 6.5 wt. %, 7 wt. %, 7.5 wt. %, 8 wt. %, 8.5 wt. %, 9 wt. %, 9.5 wt. %, 10 wt. %, 11 wt. % or 12 wt. %, or any range of values therebetween.

[0139] Generally, the salt comprises a cation and an anion. In some embodiments, the anion is redox stable. In some embodiments, the anion can be monovalent. In some embodiments, the salt is a lithium salt and/or a sodium salt. In some embodiments, a lithium salt can be selected from lithium hexafluorophosphate (LiPF_6), lithium tetrafluoroborate (LiBF_4), lithium difluoro(oxalato)borate (LiDFOB), lithium bisfluorosulfonyl imide (LiFSI), lithium tetrafluoro(oxalate)phosphate (LiTFOP), lithium difluoro(dioxalato)phosphate (LiDFDOP), and combinations thereof. In some embodiments, a sodium salt can be selected from sodium hexafluorophosphate (NaPF_6), sodium tetrafluoroborate (NaBF_4), sodium difluoro(oxalato)borate (NaDFOB), sodium bisfluorosulfonyl imide (NaFSI), sodium bistrifluoromethylsulfonyl imide (NaTFSI), sodium tetrafluoro(oxalate)phosphate (NaTFOP), sodium difluoro(dioxalato)phosphate (NaDFDOP), and combinations thereof. In some embodiments, the salt can include an anion selected from hexafluorophosphate, tetrafluoroborate, bisfluorosulfonyl imide, tetrafluoro(oxalate)phosphate, difluoro(dioxalato)phosphate, difluoro(oxalato)borate, and combinations thereof. In certain embodiments, the salt concentration of the electrolyte can be, be about, be at most, or be at most about, 0.1 M, 0.2 M, 0.3 M, 0.4 M, 0.5 M, 0.6 M, 0.7 M, 0.8 M, 0.9 M, 1 M, 1.1 M, 1.2 M, 1.3 M, 1.4 M, 1.5 M, 1.6 M, 1.7 M, 1.8 M, 1.9 M, 2 M, 2.1 M, 2.2 M, 2.3 M, 2.4 M, 2.5 M, 2.6 M, 2.7 M, 2.8 M, 2.9 M, 3 M, 3.1 M, 3.2 M, 3.3 M, 3.4 M, 3.5 M, 3.6 M, 3.7 M, 3.8 M, 3.9 M, 4 M, 4.1 M, 4.2 M, 4.3 M, 4.4 M, 4.5 M, 4.6 M, 4.7 M, 4.8 M, 4.9 M, 5 M, 5.1 M, 5.2 M, 5.3 M, 5.4 M, 5.5 M, 5.6 M, 5.7 M, 5.8 M, 5.9 M, 6 M, 6.1 M, 6.2 M, 6.3 M, 6.4 M, 6.5 M, 6.6 M, 6.7 M, 6.8 M, 6.9 M, or 7 M, or any range of values therebetween. For example, in some embodiments, the salt concentration can be about 0.1 M to about 5 M, about 0.2 M to about 3 M, about 0.3 M to about 2 M, or about 0.7 M to about 1 M.

[0140] In some embodiments, the electrolyte includes a liquid solvent. A solvent as provided herein need not dissolve every component, and need not completely dissolve each component of the electrolyte. In further embodiments, the solvent can include an organic solvent. In some embodiments, a solvent can include one or more functional groups selected from carbonates, ethers and/or esters. In some embodiments, the solvent can comprise a carbonate. In further embodiments, the carbonate can be selected from cyclic carbonates such as, for example, ethylene carbonate (EC), propylene carbonate (PC), vinyl ethylene carbonate (VEC), vinylene carbonate (VC), fluoroethylene carbonate (FEC), and combinations thereof, or acyclic carbonates such as, for example, dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC), and combinations thereof. In some embodiments, the solvent can comprise an ester. In some embodiments, the ester is selected from methyl acetate (MA), methyl propionate (MP), ethyl acetate (EA), methyl butyrate (MB), and combinations thereof. In some embodiments, the solvent may include EC, PC, VEC, VC, FEC, DMC, DEC, EMC, MA, MP, EA, MB, and combinations thereof. In some embodiments, the solvent may include EC, DMC, DEC, EMC, MA, and combinations thereof. In some embodiments, the solvent may include EC, DMC, EMC, and combinations thereof.

[0141] In some embodiments, the electrolyte includes a first solvent:second solvent w/w ratio of, of about, of at least, or of at least about 1:10, 2:10, 18:85, 3:10, 4:10, 3:7, 5:10, 6:10, 7:10, 8:10, 9:10, 1:1, 10:9, 10:8, 10:7, 10:6, 10:5, 7:3, 10:4, 10:3, 85:18, 10:2 or 10:1, or any range of values therebetween. In some embodiments, the solvent may include EC:DMC at a ratio of 18:85 w/w. In other embodiments, the solvent may include EC:EMC at a ratio of 3:7 w/w.

[0142] In some embodiments, the electrolyte comprises the solvent in, in about, in at least, or in at least about, 80 wt.%, 81 wt.%, 82 wt.%, 83 wt.%, 84 wt.%, 85 wt.%, 86 wt.%, 87 wt.%, 88 wt.%, 89 wt.%, 90 wt.%, 91 wt.%, 92 wt.%, 93 wt.%, 94 wt.%, 95 wt.%, 96 wt.%, 97 wt.% or 98 wt.%, or any range of values therebetween.

[0143] In some embodiments, the electrolyte includes one or more additional additives. In some embodiments, an additional additive can include one or more functional groups selected from carbonates, ethers and/or esters. In some embodiments, the additional additive may be selected from a carbonate, an ether, an ester, a salt (e.g., lithium salt, sodium

salt), and combinations thereof. In some embodiments, the additional additive can comprise a carbonate. In further embodiments, the carbonate can be selected from cyclic carbonates such as, for example, ethylene carbonate (EC), propylene carbonate (PC), vinyl ethylene carbonate (VEC), vinylene carbonate (VC), fluoroethylene carbonate (FEC), and combinations thereof, or acyclic carbonates such as, for example, dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC), and combinations thereof. In some embodiments, the additional additive can comprise an ester. In some embodiments, the ester is selected from methyl acetate (MA), methyl propionate (MP), ethyl acetate (EA), methyl butyrate (MB), and combinations thereof. In some embodiments, the additional additive can comprise a lithium salt additive and/or a sodium salt additive. In some embodiments, the lithium salt additive is selected from lithium difluoro(oxalato)borate (LiDFOB), lithium difluorophosphate (LiPO_2F_2), and combinations thereof. In some embodiments, the sodium salt additive is selected from sodium difluoro(oxalato)borate (NaDFOB), sodium difluorophosphate (NaPO_2F_2), and combinations thereof. In some embodiments, the additional additive may be selected from polyethersulfone (PES), 1,3-propylene sultone (PRS), 1,3,2-dioxathiolane-2,2-dioxide (“DTD”), EC, PC, VEC, VC, FEC, DMC, DEC, EMC, MA, MP, EA, MB, LiDFOB, LiPO_2F_2 , and combinations thereof.

[0144] In some embodiments, the electrolyte comprises the additional additive in, in about, in at most, or in at most about, 0.1 wt.%, 0.25%, 0.5 wt. %, 1 wt.%, 1.5 wt.%, 2 wt.%, 2.5 wt.%, 3 wt.%, 3.5 wt.%, 4 wt.%, 4.5 wt.%, 5 wt.%, 5.5 wt.%, 6 wt.%, 7 wt.% or 8 wt.%, or any range of values therebetween. In some embodiments, the electrolyte comprises an additional additive of about 0.25 wt% VC. In other embodiments, the electrolyte composition comprises an additional additive of about 0.75% wt% FEC. In other embodiments, the electrolyte composition comprises the additional additive of about 0.25 wt% VC and about 0.75 wt% FEC.

Electrode Materials, Electrode Films, Electrodes and Energy Storage Device

[0145] Energy storage devices of the present disclosure include the electrolyte discussed herein, a cathode, an anode, and a housing, wherein the electrolyte, cathode and anode are disposed within the housing. In some embodiments, the energy storage devices of the present enclosure may further include a separator, wherein the separator is placed

between the anode electrode and the cathode electrode. In some embodiments, the energy storage device comprises an anode electrode positioned between two cathode electrodes. In some embodiments, the anode electrode and/or the cathode electrode comprises a shaped electrode film. In some embodiments, an energy storage device as provided herein is a lithium-ion battery and/or sodium-ion battery. In some embodiments, the energy storage devices may be a battery, capacitor, capacitor-battery hybrid, fuel cell, or combinations thereof. In some embodiments, an energy storage device as provided herein has a discharge capacity retention when cycled up to 4.2 V, 4.3 V or 4.4 V of at least about 90% after 50 cycles. Each of the cathode and anode include an electrode film and a current collected that form the electrode.

[0146] An active material (e.g., cathode active material, anode active material) may be used in the preparation of an electrode film mixture, electrode film and/or electrode for an energy storage device, such as the shaped electrode films and shaped electrodes described herein. In some embodiments, an electrode comprises a current collector and an electrode film.

[0147] In some embodiments, the active material is a cathode active material. In some embodiments, the cathode active material is selected from at least one of a metal oxide, metal sulfide, a sulfur-carbon composite, a lithium metal oxide, and a material including sulfur. In some embodiments, the lithium metal oxide can be, for example, a lithium nickel manganese cobalt oxide ((i.e., $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$ or “NMC”), a lithium manganese oxide (LMO), a lithium cobalt oxide (“LCO”), a lithium titanate (“LTO”), and/or a lithium nickel cobalt aluminum oxide (i.e., $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$ or “NCA”). In some embodiments, cathode active materials can comprise, for example, a layered transition metal oxide (such as LiCoO_2 (LCO), $\text{Li}(\text{NiMnCo})\text{O}_2$ (NMC) and/or $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (i.e., $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$ or NCA)). In some embodiments, the cathode active material can be an iron phosphate-based active material. In some embodiments, iron phosphate-based active materials include LiFePO_4 (i.e., “lithium iron phosphate” and “LFP”) and $\text{LiMn}_{1-x}\text{Fe}_x\text{PO}_4$ (i.e., “lithium manganese iron phosphate” and “LMFP”) (e.g., $\text{LiMn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$ or $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$). In some embodiments, the iron phosphate-based active material includes LFP. In some embodiments, the iron phosphate-based active material includes an LMFP. In some embodiments, the iron phosphate-based active material includes an LFP and/or an LMFP. The cathode active

material can comprise sulfur or a material including sulfur, such as lithium sulfide (Li_2S), molybdenum disulfide (MoS_2), or other sulfur-based materials, or a mixture thereof. In some embodiments, the cathode active material can be a spinel manganese oxide (such as LiMn_2O_4 (LMO) and/or $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (LMNO)), an olivine (such as LiFePO_4), silicon, silicon oxide (SiO_x), aluminum, tin, tin oxide (SnO_x), manganese oxide (MnO_x), molybdenum oxide (MoO_2), nickel oxide (NiO_x), or copper oxide (CuO_x). In some embodiments, the cathode active material includes at least two of LFP, LMFP, NMC, NCA, LMO, LNMO, LCO, LTO, and combinations thereof.

[0148] In some embodiments, an electrode film includes an anode active material. In some embodiments, anode active materials can include, for example, an insertion material (such as carbon or graphite), an alloying/dealloying material (such as silicon, silicon oxide, tin, and/or tin oxide), a metal alloy or compound (such as Si-Al, and/or Si-Sn), and/or a conversion material (such as manganese oxide, molybdenum oxide, nickel oxide, and/or copper oxide). The anode active materials can be used alone or mixed together to form multi-phase materials (such as Si-C, Sn-C, $\text{SiO}_x\text{-C}$, $\text{SnO}_x\text{-C}$, Si-Sn, Si- SiO_x , Sn- SnO_x , Si- $\text{SiO}_x\text{-C}$, Sn- $\text{SnO}_x\text{-C}$, Si-Sn-C, $\text{SiO}_x\text{-SnO}_x\text{-C}$, Si- $\text{SiO}_x\text{-Sn}$, or Sn- $\text{SiO}_x\text{-SnO}_x$). Anode active materials include common natural graphite, synthetic or artificial graphite, surface modified graphite, spherical-shaped graphite, flake-shaped graphite and blends or combinations of these types of graphite, metallic elements and its compound as well as metal-C composite for anode.

[0149] In some embodiments, an electrode film as provided herein includes at least one active material. In some embodiments, the electrode film mixture and/or electrode film comprises the active material in an amount of, of about, of at least, or at least about, 70 wt.%, 75 wt.%, 80 wt.%, 85 wt.%, 86 wt.%, 87 wt.%, 88 wt.%, 89 wt.%, 90 wt.%, 91 wt.%, 92 wt.%, 93 wt.%, 94 wt.%, 95 wt.%, 96 wt.%, 97 wt.%, 98 wt.%, 98.5 wt.%, 99 wt.%, 99.5 wt.%, 99.8 wt.% or 99.9 wt.%, or any range of values therebetween.

[0150] In some embodiments, an electrode film mixture and/or electrode film (e.g., shaped electrode film) comprises a carbon material configured to reversibly intercalate lithium ions. In some embodiments, the lithium intercalating carbon is selected from a graphitic carbon, graphite, hard carbon, soft carbon and combinations thereof. For example, the electrode film of the electrode can include a binder material, one or more of graphitic

carbon, graphite, graphene-containing carbon, hard carbon and soft carbon, and an electrical conductivity promoting material. In some embodiments, an electrode is mixed with lithium metal and/or lithium ions. In some embodiments, the electrode comprises the carbon material in a total amount of, of about, of at most, or at most about, 20 wt.%, 15 wt.%, 10 wt.%, 9 wt.%, 8 wt.%, 7 wt.%, 6 wt.%, 5 wt.%, 4 wt.%, 3 wt.%, 2 wt.%, 1 wt.%, or any range of values therebetween.

[0151] In some embodiments, an electrode film mixture and/or electrode film includes a conductive additive. In some embodiments, the conductive additive may comprise a conductive carbon additive, such as a carbon black. In some embodiments, the conductive additive may comprise a conductive carbon additive. In some embodiments, the conductive carbon additive comprises carbon black, carbon nanotubes, such as single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). In some embodiments, the electrode film comprises the conductive additive in a total amount of, of about, of at most, or at most about, 10 wt.%, 9 wt.%, 8 wt.%, 7 wt.%, 6 wt.%, 5 wt.%, 4 wt.%, 3 wt.%, 2 wt.%, 1 wt.%, 0.5 wt.%, 0.25 wt.%, 0.1 wt.%, or any range of values therebetween. In some embodiments, each of the conductive additive is in an amount of, of about, of at most, or at most about, 10 wt.%, 9 wt.%, 8 wt.%, 7 wt.%, 6 wt.%, 5 wt.%, 4 wt.%, 3 wt.%, 2 wt.%, 1 wt.%, 0.5 wt.%, 0.25 wt.%, 0.1 wt.%, of the electrode film, or any range of values therebetween. In some embodiments, the conductive additive is carbon black.

[0152] In some embodiments, the electrode film further comprises at least one binder. In some embodiments, binders can include polytetrafluoroethylene (PTFE), a polyolefin, polyalkylenes, polyethers, styrene-butadiene, co-polymers of polysiloxanes and polysiloxane, branched polyethers, polyvinylethers, a carboxymethylcellulose (CMC), co-polymers thereof, and/or combinations thereof. In some embodiments, the polyolefin can include polyethylene (PE), polypropylene (PP), polyvinylidene fluoride (PVDF), co-polymers thereof, and/or combinations thereof. For example, the binder can include polyvinylene chloride, poly(phenylene oxide) (PPO), polyethylene-block-poly(ethylene glycol), poly(ethylene oxide) (PEO), poly(phenylene oxide) (PPO), polyethylene-block-poly(ethylene glycol), polydimethylsiloxane (PDMS), polydimethylsiloxane-coalkylmethylsiloxane, co-polymers thereof, and/or combinations thereof. In some

embodiments, the binder may include a thermoplastic. In some embodiments, the binder comprises a fibrillizable and/or fibrillized polymer. In certain embodiments, the binder comprises, consists essentially, or consists of a single fibrillizable and/or fibrillized binder, such as PTFE. In some embodiments, the electrode film includes, includes about, includes at most, or includes at most about, 1 wt.%, 2 wt.%, 3 wt.%, 4 wt.%, 5 wt.%, 6 wt.%, 7 wt.%, 8 wt.%, 9 wt.%, 10 wt.%, or any range of values therebetween, of a binder.

[0153] As provided herein, a “solvent-free” electrode film (e.g., shaped, unshaped) is an electrode film that contains no detectable processing solvents, processing solvent residues, or processing solvent impurities. A dry electrode film, such as a cathode electrode film or an anode electrode film that is manufactured with only dry components, may be solvent-free.

[0154] A “wet” electrode, “wet process” electrode, or slurry electrode, is an electrode or comprises an electrode film (e.g., shaped, unshaped) prepared by at least one step involving a slurry of active material(s), binder(s), and optionally additive(s), even if a subsequent drying step removes moisture from the electrode or electrode film. Thus, a wet electrode or wet electrode film will include at least one or more processing solvents, processing solvent residues, and/or processing solvent impurities.

[0155] In some embodiments, the electrode film can be a wet processed electrode film. In some embodiments, the electrode film is prepared by a wet or slurry-based electrode fabrication process. In some embodiments, the electrode film of the present disclosure can be a dry processed electrode film. In some embodiments, the electrode film is prepared by a dry electrode fabrication process. As used herein, a dry electrode fabrication process can refer to a process in which no or substantially no solvents are used to form a dry electrode film. For example, components of the active layer or electrode film, including carbon materials and binders, may comprise, consist of, or consist essentially of dry particles. The dry particles for forming the active layer or electrode film may be combined to provide a dry particle active layer mixture. In some embodiments, the active layer or electrode film may be formed from the dry particle active layer mixture such that weight percentages of the components of the active layer or electrode film and weight percentages of the components of the dry particles active layer mixture are substantially the same. In some embodiments, the active layer or electrode film formed from the dry particle active layer mixture using the dry fabrication

process may be free from, or substantially free from, any processing additives such as solvents and solvent residues resulting therefrom. In some embodiments, the resulting active layer or electrode films are self-supporting films formed using the dry process from the dry particle mixture. In some embodiments, the resulting active layer or electrode films are free-standing films formed using the dry process from the dry particle mixture. A process for forming an active layer or electrode film can include fibrillizing the fibrillizable binder component(s) such that the film comprises fibrillized binder. In further embodiments, a free-standing active layer or electrode film may be formed in the absence of a current collector. In still further embodiments, an active layer or electrode film may comprise a fibrillized polymer matrix such that the film is self-supporting. It is thought that a matrix, lattice, or web of fibrils can be formed to provide mechanical structure to the electrode film.

[0156] In some embodiments, an electrode film is disposed on a current collector to form an electrode (e.g., shaped electrode). In some embodiments, a current collector can include a metallic material, such as a material comprising aluminum, nickel, copper, combinations of the foregoing. In some embodiments, a current collector comprises a pure metal. In some embodiments, a current collector comprises a metallized polymer film or metal coated polymer film. In some embodiments, the polymer comprises polyethylene terephthalate (PET), biaxially oriented polypropylene (BOPP) or a combination thereof. In some embodiments, the metal coating comprises aluminum. In some embodiments, coating the final electrode film mixture comprises forming a uniform electrode film mixture coating. In some embodiments, the current collector comprises a thickness of, of about, of at most, or at most about, 200 μm , 100 μm , 50 μm , 40 μm , 30 μm , 20 μm , 15 μm , 10 μm , 5 μm , or any range of values therebetween.

[0157] In some embodiments, the electrode is a single-sided electrode. In some embodiments, an electrode is a double-sided electrode. In some embodiments, at least a portion of the electrode is a single-sided electrode and/or double-sided electrode (e.g., wherein the portion is located at an end of the electrode). In some embodiments, the double-sided electrode includes two electrode films. In some embodiments, the double-sided electrode may include a current collector, a top electrode film, and a bottom electrode film. In some embodiments, each of the two electrode films can have any suitable shape, size and thickness.

[0158] An electrode assembly includes a cathode, an anode, and a separator positioned between the anode and cathode. In some embodiments, the electrode assembly is a wound electrode (i.e., rolled electrode) assembly (e.g., a jelly roll). In some embodiments, the energy storage device is selected from the group consisting of a cylindrical energy storage device, a stacked prismatic energy storage device, and a spiral-wound prismatic energy storage device. In some embodiments, the shaped edge substantially prevents the formation of an electrode buckling zone or kink within the electrode.

[0159] An energy storage device as provided herein can be of any suitable configuration, for example planar, spirally wound, button shaped, or pouch. An energy storage device as provided herein can be a component of a system, for example, a power generation system, an uninterruptible power source systems (UPS), a photo voltaic power generation system, an energy recovery system for use in, for example, industrial machinery and/or transportation. An energy storage device as provided herein may be used to power various electronic device and/or motor vehicles, including hybrid electric vehicles (HEV), plug-in hybrid electric vehicles (PHEV), and/or electric vehicles (EV). In some embodiments, the energy storage device used in motor vehicles, including hybrid electric vehicles (HEV), plug-in hybrid electric vehicles (PHEV), and/or electric vehicles (EV) reduces greenhouse gas emissions.

[0160] In some embodiments, an energy storage device including an electrolyte formulation as provided herein may demonstrate a higher discharge rate capability in comparison to energy storage devices that do not use the electrolyte formulations described herein. Such higher discharge rate capability is desirable in high energy, high power applications such as electric vehicle propulsion.

[0161] In some embodiments, an energy storage device including an electrolyte formulation as provided herein may produce a smaller volume of gas within the energy storage device in comparison to energy storage devices without the electrolyte formulations described herein.

[0162] An energy storage device including an electrolyte formulation described herein may be characterized by improved capacity retention over the life of the device. Further improvements that may be realized in various embodiments include improved cycling performance, including improved storage stability during cycling and reduced

capacity fade. In some embodiments, improved cycling performance were also achieved under aggressive or stressed conditions (e.g., long constant voltage hold at 4.2 V or 4.4 V).

[0163] It will be understood that an electrolyte formulation provided herein, can be used in various embodiments with any of a number of energy storage devices and systems, such as one or more batteries, capacitors, capacitor-battery hybrids, fuel cells, or other energy storage systems or devices and combinations thereof. In some embodiments, an electrolyte additive or electrolyte including an additive described herein may be implemented in lithium ion and/or sodium ion batteries.

[0164] In some embodiments, the lithium ion or sodium ion battery is configured to operate at about 2.5 to 4.5 V, or 3.0 to 4.2 V. In further embodiments, the lithium ion or sodium ion battery is configured to have a minimum operating voltage of about 2.5 V to about 3 V, respectively. In still further embodiments, the lithium ion or sodium ion battery is configured to have a maximum operating voltage of or of about 4.0 V, 4.1 V, 4.2 V, 4.3 V, 4.4 V, 4.5 V or 4.6 V, or any range of values thereof.

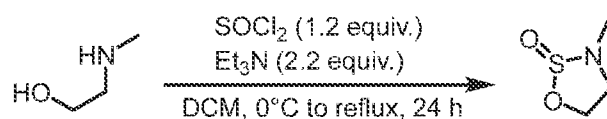
[0165] In some embodiments, an energy storage device is created such that one electrode (e.g., anode) is larger than and overhangs the other electrode (e.g., cathode). One electrode may overhang the other in the winding direction and/or non-winding direction of the electrode assembly. Such electrode overhangs may avoid yield losses. In some embodiments, where there is no, or is substantially no, overlap and/or intermingling of the separator and the shaped electrode film (e.g., cathode electrode film), the boundary of the shaped electrode film is easier to identify and therefore improves the ability to form a counter electrode (e.g., anode electrode) with an overhang.

Methods of Preparing

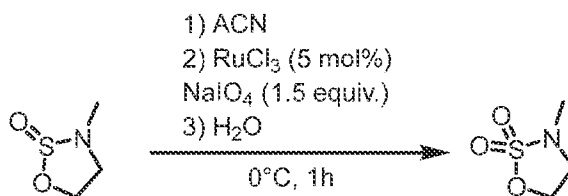
[0166] Additives, electrolytes and energy storage devices discussed herein may be synthesized or manufactured. In some embodiments, a method for preparing an energy storage device includes preparing the electrolyte discussed herein and positioning the electrolyte within a housing comprising a cathode and an anode. In some embodiments, a method for preparing an electrolyte includes combining a compound of Formula (A), a solvent and a salt to form the electrolyte.

EXAMPLES

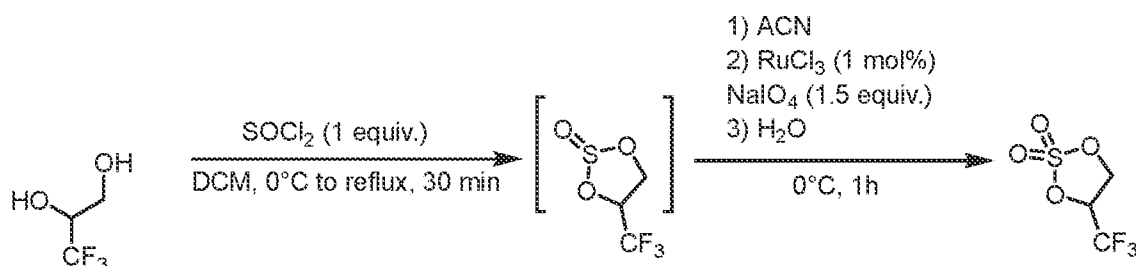
[0167] Example embodiments of the present disclosure, including processes, materials and/or resultant products, are described in the following examples.

Example 1 – SO₂-N-Me Synthesis*Scheme 1*

[0168] SO₂-N-Me was synthesized according to Scheme 1 depicted herein. Purification was performed by extraction of reaction solution with saturated NaCl and concentration of organic fractions *in vacuo*, followed by high vacuum distillation of organic fractions (~0.1 torr, 45°C).

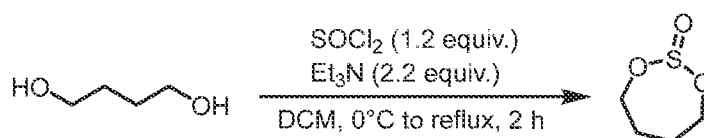
Example 2 – SO₃-N-Me Synthesis*Scheme 2*

[0169] SO₃-N-Me was synthesized according to Scheme 2 depicted herein. Purification was performed by extraction of reaction solution with saturated NaCl and concentration of organic fractions *in vacuo*, followed by high vacuum distillation of organic fractions (~0.1 torr, 165°C)

Example 3 – DTD-CF₃ Synthesis

Scheme 3

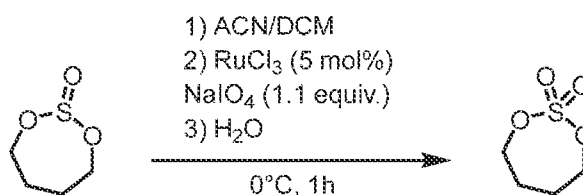
[0170] DTD-CF₃ was synthesized according to Scheme 3 depicted herein. Purification was performed by extraction of reaction solution with saturated NaCl, followed by saturated NaHCO₃, and concentration of organic fractions *in vacuo*, followed by high vacuum distillation of organic fractions (~0.1 torr, 65°C)

Example 4 – SO₃-7MR Synthesis

Scheme 4

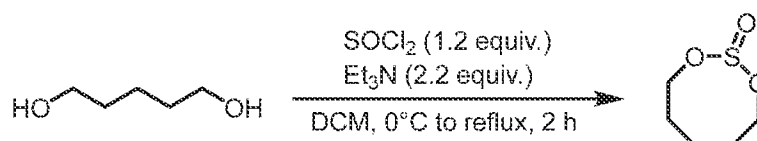
[0171] SO₃-7MR was synthesized according to Scheme 4 depicted herein. Purification was performed by extraction of reaction solution with saturated NaCl and concentration of organic fractions *in vacuo*, followed by high vacuum distillation of organic fractions (~0.1 torr, 70°C)

Example 5 – DTD-7MR Synthesis



Scheme 5

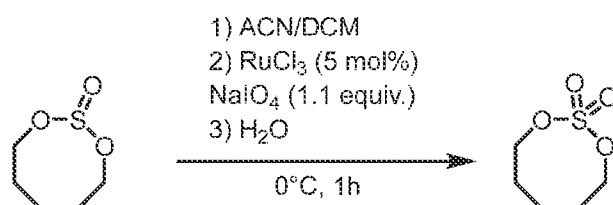
[0172] DTD-7MR was synthesized according to Scheme 5 depicted herein. Purification was performed by extraction of reaction solution with saturated NaCl and concentration of organic fractions *in vacuo*, followed by high vacuum distillation of organic fractions (~0.1 torr, 100°C)

Example 6 – SO₃-8MR Synthesis

Scheme 6

[0173] SO₃-8MR was synthesized according to Scheme 6 depicted herein. Purification was performed by extraction of reaction solution with saturated NaCl and concentration of organic fractions *in vacuo*, followed by high vacuum distillation of organic fractions (~0.1 torr, 85°C)

Example 7 – DTD-8MR Synthesis



Scheme 7

[0174] DTD-8MR was synthesized according to Scheme 7 depicted herein. Purification was performed by extraction of reaction solution with saturated NaCl and concentration of organic fractions *in vacuo*, followed by high vacuum distillation of organic fractions (~0.1 torr, 120°C)

Example 8 – SO₃-CF₃ Performance

[0175] An NMC622/Graphite cell was charged with an electrolyte and tested at a cutoff voltage of 3.0V to 4.4 V, with cycling at C/3 (CCCV for charging and CC for discharge), at a testing temperature of 40°C, and an HPPC test every 20 cycles.

[0176] FIGS. 1A-2B show the testing results for a control electrolyte of 1.2 M LiPF₆ and EC/EMC (3/7 w/w) (i.e., “Gen-2”), the Gen-2 electrolytes with SO₃-CF₃ additives, and the Gen-2 electrolytes with SO₃-CF₃ additives and VC and/or FEC co-additives.

Example 9 – DTD-COOMe Performance

[0177] An NMC622/Graphite cell was charged with an electrolyte and tested at a cutoff voltage of 3.0V to 4.4 V, with cycling at C/3 (CCCV for charging and CC for discharge), at a testing temperature of 40°C, and an HPPC test every 20 cycles.

[0178] FIGS. 3A-4B show the testing results for a control electrolyte of 1.2 M LiPF₆ and EC/EMC (3/7 w/w) (i.e., “Gen-2”), the Gen-2 electrolytes with DTD-COOME additives, and the Gen-2 electrolytes with DTD-COOME additives and VC and/or FEC co-additives.

Example 10 – DTD-COOME Performance Compared to DTD Control

[0179] NMC442/graphite pouch cells were charged with an electrolyte, a formation cycle was performed at 40°C of a 1.5V hold for 24 hrs, a C/20 CC up to 4.4 V, a C/20 CC down to 3.0 V and back up to 3.8V for EIS measurements. Cells were tested using a cycle-hold protocol of two cycles between 3.0 and 4.4 V at C/3 followed by a 24 hour hold at 4.4 V, all at 40°C. This sequence was repeated until the cell capacity reached 100 mAh. All electrolytes included 1.5M LiPF₆, the control electrolyte included EC:EMC:DMC at weight ratios of 25:5:70, and all other electrolytes included EC:DMC at weight ratios of 15:85 in addition to the wt.% of additive compound(s) noted.

[0180] FIGS. 5A-5C show the testing results for a control electrolyte, electrolytes with an DTD additive, FEC additive, DTD-COOME additives, DTD and FEC additives, or DTD-COOME and FEC additives. The results shown in FIG. 5C were measured after the initial formation cycle was performed.

[0181] As can be seen in FIGS. 5A and 5B, although the 2% DTD electrolyte formulation demonstrated a high capacity retention, the energy storage device begins to suffer from impedance growth. The 3% DTD-COOME electrolyte formulation demonstrated 175 cycles to end of life (EOL) with the lowest ΔV . Similar trends were demonstrated for when adding FEC as a co-additive along with DTD-COOME.

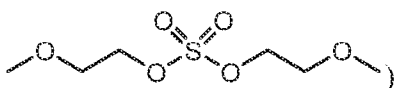
[0182] As can be seen in FIG. 5C, DTD-COOME electrolyte formulations demonstrated lower gas volume generation relative to the control electrolyte and the electrolyte with a DTD additive alone, and acceptable charge transfer resistances.

Example 11 – DTD-CF₃ Performance

[0183] NMC442/graphite pouch cells were charged with an electrolyte, a formation cycle was performed at 40°C of a 1.5V hold for 24 hrs, a C/20 CC up to 4.4 V, a C/20 CC down to 3.0 V and back up to 3.8V for EIS measurements. Cells were tested using

a cycle-hold protocol of two cycles between 3.0 and 4.4 V at C/3 followed by a 24 hour hold at 4.4 V, all at 40°C. This sequence was repeated until the cell capacity reached 100 mAh. All electrolytes included 1.5M LiPF₆, the control electrolyte included EC:EMC:DMC at weight ratios of 25:5:70, and all other electrolytes included EC:DMC at weight ratios of 15:85 in addition to the wt.% of additive compound(s) noted.

[0184] FIGS. 6A and 6B show the testing results for a control electrolyte, electrolytes with a DTD additive, DTD-CF₃ additives, or SO₄-Et-MeO (i.e.,



) additive. The results shown in FIG. 6B were measured after the initial formation cycle was performed. FIG. 6A demonstrates that DTD-CF₃ reduces ΔV growth, and FIG. 6B demonstrates DTD-CF₃ show comparable or reduced gas volume generation and charge transfer resistance.

Example 12 – SO₃-N-Me Performance

[0185] An NMC62/Graphite cell was charged with an electrolyte and tested at a cutoff voltage of 3.0V to 4.4 V, with cycling at C/3 (CCCV for charging and CC for discharge), at a testing temperature of 40°C, and an HPPC test every 20 cycles.

[0186] FIGS. 7A and 7B show the performance results of a control electrolyte of 1.2 M LiPF₆ and EC/EMC (3/7 w/w) (i.e., “Gen-2”), the Gen-2 electrolytes with SO₃-N-Me additives, and the Gen-2 electrolytes with SO₃-N-Me additives and VC, FEC, PES or LiDFOB co-additives.

Example 11 – DTD-7MR Performance

[0187] An NMC622/Graphite cell was charged with an electrolyte and tested at a cutoff voltage of 3.0V to 4.4 V, with cycling at C/3 (CCCV for charging and CC for discharge), at a testing temperature of 40°C, and an HPPC test every 20 cycles.

[0188] FIGS. 8A and 8B show the performance results of a control electrolyte of 1.2 M LiPF₆ and EC/EMC (3/7 w/w) (i.e., “Gen-2”), the Gen-2 electrolytes with DTD-6MR additives, and the Gen-2 electrolytes with DTD-7MR additives.

Example 12 – ODTO Performance

[0189] An NMC622/Graphite cell was charged with an electrolyte and tested at a cutoff voltage of 3.0V to 4.4 V, with cycling at C/3 (CCCV for charging and CC for discharge), at a testing temperature of 40°C, and an HPPC test every 20 cycles.

[0190] FIGS. 9A-10B show the performance results of a control electrolyte of 1.2 M LiPF₆ and EC/EMC (3/7 w/w) (i.e., “Gen-2”), and the Gen-2 electrolytes with ODTO additives.

Example 13 – ODTO and DTD-7MR Performance

[0191] An NMC622/Graphite cell was charged with an electrolyte and tested at a cutoff voltage of 3.0V to 4.4 V, with cycling at C/3 (CCCV for charging and CC for discharge), at a testing temperature of 40°C, and an HPPC test every 20 cycles.

[0192] FIGS. 11A-12B show the performance results of a control electrolyte of 1.2 M LiPF₆ and EC/EMC (3/7 w/w) (i.e., “Gen-2”), the Gen-2 electrolytes with DTD-7MR additives, the Gen-2 electrolytes with ODTO additives, and the Gen-2 electrolytes with DTD-7MR and ODTO additives.

Example 14 – DTD-8MR Performance

[0193] An NMC622/Graphite cell was charged with an electrolyte and tested at a cutoff voltage of 3.0V to 4.4 V, with cycling at C/3 (CCCV for charging and CC for discharge), at a testing temperature of 40°C, and an HPPC test every 20 cycles.

[0194] FIGS. 13A and 13B show the performance results of a control electrolyte of 1.2 M LiPF₆ and EC/EMC (3/7 w/w) (i.e., “Gen-2”), the Gen-2 electrolytes with DTD-6MR additives, and the Gen-2 electrolytes with DTD-8MR additives.

Example 15 – SO₃ Performance

[0195] An NMC622/Graphite cell was charged with an electrolyte and tested at a cutoff voltage of 3.0V to 4.4 V, with cycling at C/3 (CCCV for charging and CC for discharge), at a testing temperature of 40°C, and an HPPC test every 20 cycles.

[0196] FIG. 14 shows the performance results for a control electrolyte of 1.2 M LiPF₆ and EC/EMC (3/7 w/w) (i.e., “Gen-2”), and the Gen-2 electrolytes with SO₃ additives.

Example 16 – SO₃-5-Me Performance

[0197] An NMC622/Graphite cell was charged with an electrolyte and tested at a cutoff voltage of 3.0V to 4.4 V, with cycling at C/3 (CCCV for charging and CC for discharge), at a testing temperature of 40°C, and an HPPC test every 20 cycles.

[0198] FIGS. 15A-15C show the performance results for a control electrolyte of 1.2 M LiPF₆ and EC/EMC (3/7 w/w) (i.e., “Gen-2”), the Gen-2 electrolytes with SO₃-Me additives, the Gen-2 electrolytes with SO₃-Me additives with VC and/or FEC co-additives, and the Gen-2 electrolytes with SO₃-Me additives with VC and FEC co-additives.

Example 17 – DTD-7MR and DTD-8MR Performance

[0199] NMC442/graphite pouch cells were charged with an electrolyte, a formation cycle was performed at 40°C of a 1.5V hold for 24 hrs, a C/20 CC up to 4.4 V, a C/20 CC down to 3.0 V and back up to 3.8V for EIS measurements. Cells were tested using a cycle-hold protocol of two cycles between 3.0 and 4.4 V at C/3 followed by a 24 hour hold at 4.4 V, all at 40°C. This sequence was repeated until the cell capacity reached 100 mAh. All electrolytes included 1.5M LiPF₆, the control electrolyte included EC:EMC:DMC at weight ratios of 25:5:70, and all other electrolytes included EC:DMC at weight ratios of 15:85 in addition to the wt.% of additive compound(s) noted.

[0200] FIGS. 16A and 16B show the testing results for a control electrolyte, an electrolyte with a DTD additive, electrolytes with a DTD-7MR additive, and electrolytes with a DTD-8MR additive. The results shown in FIG. 16B were measured after the initial formation cycle was performed.

[0201] FIG. 16B demonstrates DTD-7MR and DTD-8MR show comparable or reduced gas volume generation and charge transfer resistance.

Example 17 – Th-ETA, Th-TCN, Th-MOT, Th-ET, Th-BF₃K, Th-BPin and Th-MIDA Performance

[0202] NMC442/graphite pouch cells were charged with an electrolyte, a formation cycle was performed at 40°C of a 1.5V hold for 24 hrs, a C/20 CC up to 4.4 V, a C/20 CC down to 3.0 V and back up to 3.8V for EIS measurements. Cells were tested using

a cycle-hold protocol of two cycles between 3.0 and 4.4 V at C/3 followed by a 24 hour hold at 4.4 V, all at 40°C. This sequence was repeated until the cell capacity reached 100 mAh. All electrolytes included 1.5M LiPF₆, the control electrolyte included EC:EMC:DMC at weight ratios of 25:5:70, and all other electrolytes included EC:DMC at weight ratios of 15:85 in addition to the wt.% of additive compound(s) noted.

[0203] FIGS. 17A and 17B show the testing results for a control electrolyte, and electrolytes with Th-ETA, Th-TCN, Th-MOT, Th-ET, Th-BF₃K, Th-BPin and Th-MIDA additives. The results shown in FIG. 17B were measured after the initial formation cycle was performed.

[0204] FIG. 17B demonstrates Th-ETA, Th-TCN, Th-MOT, Th-ET, Th-BF₃K, Th-BPin and Th-MIDA show comparable gas volume generation and charge transfer resistance.

Example 18

[0205] NMC442/graphite pouch cells were charged with an electrolyte, a formation cycle was performed at 40°C of a 1.5V hold for 24 hrs, a C/20 CC up to 4.4 V, a C/20 CC to either 4.4 V and back up to 3.8V for EIS measurements. Cells were tested using a cycle-hold protocol of two cycles between 3.0 and 4.4 V at C/3 followed by a 24 hour hold at 4.4 V, all at 40°C. This sequence was repeated until the cell capacity reached 100 mAh. All electrolytes included 1.5M LiPF₆, the control electrolyte included EC:EMC:DMC at weight ratios of 25:5:70, and all other electrolytes included EC:DMC at weight ratios of 15:85 in addition to the wt.% of additive compound(s) noted.

[0206] FIGS. 18A and 18B show the testing results for a control electrolyte, an electrolyte with a DTD additive, and electrolytes with a TMS additives. The results shown in FIG. 18B were measured after the initial formation cycle was performed.

Example 19

[0207] NMC442/graphite pouch cells were charged with an electrolyte, a formation cycle was performed at 40°C of a 1.5V hold for 24 hrs, a C/20 CC up to 4.4 V, a C/20 CC down to 3.0 V and back up to 3.8V for EIS measurements. Cells were tested using a cycle-hold protocol of two cycles between 3.0 and 4.4 V at C/3 followed by a 24 hour hold

at 4.4 V, all at 40°C. This sequence was repeated until the cell capacity reached 100 mAh. All electrolytes included 1.5M LiPF₆, the control electrolyte included EC:EMC:DMC at weight ratios of 25:5:70, and all other electrolytes included EC:DMC at weight ratios of 15:85 in addition to the wt.% of additive compound(s) noted.

[0208] FIGS. 19A and 19B show the testing results for a control electrolyte, electrolytes with SO₂N-5-Me additives, electrolytes with SO₃-5-Me additives, and electrolytes with SO₃-N-Me additives. The results shown in FIG. 19B were measured after the initial formation cycle was performed.

Example 20

[0209] NMC442/graphite pouch cells were charged with an electrolyte, a formation cycle was performed at 40°C of a 1.5V hold for 24 hrs, a C/20 CC up to 4.4 V, a C/20 CC down to 3.0 V and back up to 3.8V for EIS measurements. Cells were tested using a cycle-hold protocol of two cycles between 3.0 and 4.4 V at C/3 followed by a 24 hour hold at 4.4 V, all at 40°C. This sequence was repeated until the cell capacity reached 100 mAh. All electrolytes included 1.5M LiPF₆, the control electrolyte included EC:EMC:DMC at weight ratios of 25:5:70, and all other electrolytes included EC:DMC at weight ratios of 15:85 in addition to the wt.% of additive compound(s) noted.

[0210] FIGS. 20A and 20B show the testing results for a control electrolyte, and an electrolyte with an ODTO additive. The results shown in FIG. 20B were measured after the initial formation cycle was performed. The cell with the ODTO additive shows exceptional performance.

Example 21

[0211] NMC442/graphite pouch cells were charged with an electrolyte, a formation cycle was performed at 40°C of a 1.5V hold for 24 hrs, a C/20 CC up to 4.4 V, a C/20 CC down to 3.0 V and back up to 3.8V for EIS measurements. Cells were tested using a cycle-hold protocol of two cycles between 3.0 and 4.4 V at C/3 followed by a 24 hour hold at 4.4 V, all at 40°C. This sequence was repeated until the cell capacity reached 100 mAh. All electrolytes included 1.5M LiPF₆ with EC:DMC at weight ratios of 15:85 in addition to the wt.% of additive compound(s) noted.

[0212] FIG. 21 is a bar graph showing the number of C/3 cycles in the cycle-hold protocol described above until end of life, measured or predicted for NMC442/graphite pouch-type energy storage devices comprising various additives, according to some embodiments.

Example 22 – Electrolyte Shelf-Storage Stability

[0213] Decomposition of electrolyte additives described herein was determined under ambient shelf-storage conditions (25°C) and at 5°C to determine the relative decay rates (mol%) of additives in electrolyte formulations over time. FIG. 22A shows the relative amounts of DTD (mol%) at 5 °C and under ambient conditions over the course of 1 year. After 1 year under ambient storage conditions, less than 20% of DTD remained. At 5°C, DTD degraded to approximately 80% of the original amount. FIG. 22B shows the relative amounts of DTD-Me (mol%) over the course of 40 weeks at both 5 °C and ambient storage conditions. FIGS. 22C, 22D, 22E and 22F show relative decay rates of DTD-diCOOMe, DTD-mCOOMe (i.e., DTD-monoCOOMe), DTD-diMe and DTD-tetMe at 5 °C and 25 °C over the course of 1 year, 32 weeks, 24 weeks, and 16 weeks, respectively. The results of FIGS. 22B-22E show similar or less degradation of DTD-diCOOMe, DTD-mCOOMe, DTD-diMe and DTD-tetMe additives compared to DTD and DTD-Me shown in FIG. 22A and FIG. 22B, respectively, at both 5 °C and ambient storage conditions.

[0214] While certain embodiments of the inventions have been described, these embodiments have been presented by way of example only, and are not intended to limit the scope of the disclosure. Indeed, the novel methods and systems described herein may be embodied in a variety of other forms. Furthermore, various omissions, substitutions and changes in the systems and methods described herein may be made without departing from the spirit of the disclosure. The accompanying claims and their equivalents are intended to cover such forms or modifications as would fall within the scope and spirit of the disclosure. Accordingly, the scope of the present inventions is defined only by reference to the appended claims.

[0215] Features, materials, characteristics, or groups described in conjunction with a particular aspect, embodiment, or example are to be understood to be applicable to any other aspect, embodiment or example described in this section or elsewhere in this

specification unless incompatible therewith. All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive. The protection is not restricted to the details of any foregoing embodiments. The protection extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

[0216] Furthermore, certain features that are described in this disclosure in the context of separate implementations can also be implemented in combination in a single implementation. Conversely, various features that are described in the context of a single implementation can also be implemented in multiple implementations separately or in any suitable subcombination. Moreover, although features may be described above as acting in certain combinations, one or more features from a claimed combination can, in some cases, be excised from the combination, and the combination may be claimed as a subcombination or variation of a subcombination.

[0217] Moreover, while operations may be depicted in the drawings or described in the specification in a particular order, such operations need not be performed in the particular order shown or in sequential order, or that all operations be performed, to achieve desirable results. Other operations that are not depicted or described can be incorporated in the example methods and processes. For example, one or more additional operations can be performed before, after, simultaneously, or between any of the described operations. Further, the operations may be rearranged or reordered in other implementations. Those skilled in the art will appreciate that in some embodiments, the actual steps taken in the processes illustrated and/or disclosed may differ from those shown in the figures. Depending on the embodiment, certain of the steps described above may be removed, others may be added. Furthermore, the features and attributes of the specific embodiments disclosed above may be combined in different ways to form additional embodiments, all of which fall within the scope of the present disclosure. Also, the separation of various system components in the implementations described above should not be understood as requiring such separation in all implementations, and it should be understood that the described components and systems can

generally be integrated together in a single product or packaged into multiple products. For example, any of the components for an energy storage system described herein can be provided separately, or integrated together (e.g., packaged together, or attached together) to form an energy storage system.

[0218] For purposes of this disclosure, certain aspects, advantages, and novel features are described herein. Not necessarily all such advantages may be achieved in accordance with any particular embodiment. Thus, for example, those skilled in the art will recognize that the disclosure may be embodied or carried out in a manner that achieves one advantage or a group of advantages as taught herein without necessarily achieving other advantages as may be taught or suggested herein.

[0219] Conditional language, such as “can,” “could,” “might,” or “may,” unless specifically stated otherwise, or otherwise understood within the context as used, is generally intended to convey that certain embodiments include, while other embodiments do not include, certain features, elements, and/or steps. Thus, such conditional language is not generally intended to imply that features, elements, and/or steps are in any way required for one or more embodiments or that one or more embodiments necessarily include logic for deciding, with or without user input or prompting, whether these features, elements, and/or steps are included or are to be performed in any particular embodiment.

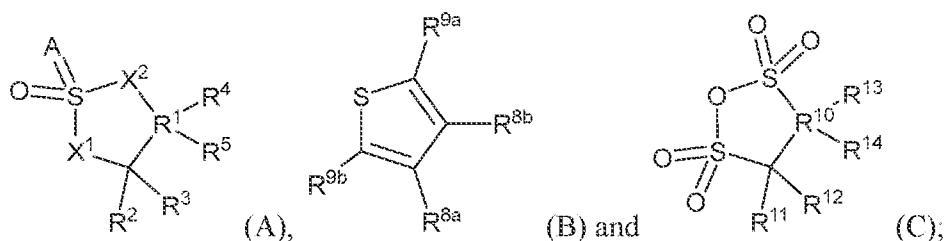
[0220] Conjunctive language such as the phrase “at least one of X, Y, and Z,” unless specifically stated otherwise, is otherwise understood with the context as used in general to convey that an item, term, etc. may be either X, Y, or Z. Thus, such conjunctive language is not generally intended to imply that certain embodiments require the presence of at least one of X, at least one of Y, and at least one of Z.

[0221] Language of degree used herein, such as the terms “approximately,” “about,” “generally,” and “substantially” as used herein represent a value, amount, or characteristic close to the stated value, amount, or characteristic that still performs a desired function or achieves a desired result. For example, the terms “approximately,” “about,” “generally,” and “substantially” may refer to an amount that is within less than 10% of, within less than 5% of, within less than 1% of, within less than 0.1% of, and within less than 0.01% of the stated amount, depending on the desired function or desired result.

[0222] The scope of the present disclosure is not intended to be limited by the specific disclosures of preferred embodiments in this section or elsewhere in this specification, and may be defined by claims as presented in this section or elsewhere in this specification or as presented in the future. The language of the claims is to be interpreted broadly based on the language employed in the claims and not limited to the examples described in the present specification or during the prosecution of the application, which examples are to be construed as non-exclusive.

WHAT IS CLAIMED IS:

1. An electrolyte composition, comprising:
 a solvent;
 a salt; and
 an additive comprising a compound selected from Formula (A), Formula (B) or Formula (C):



wherein:

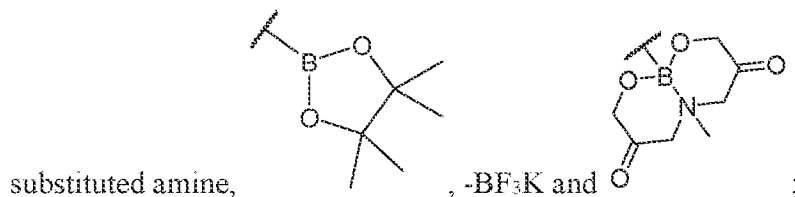
A is O or absent;

X¹ is O or NR⁶;

X² is O or NR⁷;

R¹ is an optionally substituted C₁₋₆ alkylene;

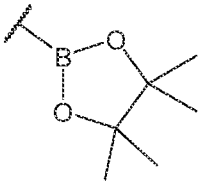
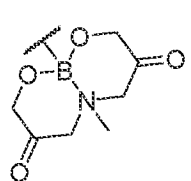
R², R³, R⁴ and R⁵ are independently selected from hydrogen, an optionally substituted alkyl, an optionally substituted cycloalkyl, an optionally substituted haloalkyl, an optionally substituted alkenyl, an optionally substituted alkynyl, an optionally substituted cycloalkenyl, a halogen, hydroxy, an optionally substituted alkoxy, an optionally substituted haloalkoxy, an optionally substituted C-amido, an optionally substituted N-amido, an optionally substituted C-carboxy, an optionally substituted O-carboxy, an optionally substituted sulfenyl, an optionally substituted sulfinyl, an optionally substituted sulfonyl, cyano, nitro, amino, an optionally



R⁶ and R⁷ are independently selected from a hydrogen, an optionally substituted alkyl, an optionally substituted cycloalkyl, an optionally

substituted haloalkyl, a halogen, hydroxy, an optionally substituted alkoxy and an optionally substituted haloalkoxy;

R^{8a} and R^{8b} are independently selected from hydrogen, an optionally substituted alkyl, an optionally substituted cycloalkyl, an optionally substituted haloalkyl, an optionally substituted alkenyl, an optionally substituted alkynyl, an optionally substituted cycloalkenyl, a halogen, hydroxy, an optionally substituted alkoxy, an optionally substituted haloalkoxy, an optionally substituted C-amido, an optionally substituted N-amido, an optionally substituted C-carboxy, an optionally substituted O-carboxy, an optionally substituted sulfenyl, an optionally substituted sulfinyl, an optionally substituted sulfonyl, cyano, nitro, amino, an optionally

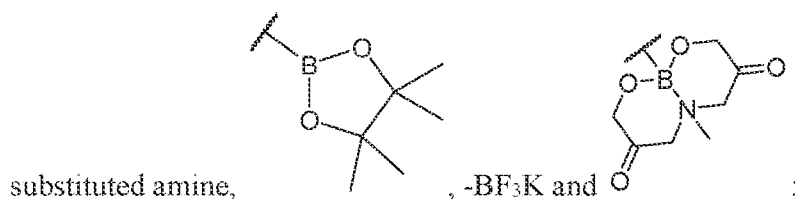
substituted amine, , $-\text{BF}_3\text{K}$ and , or R^{8a} and R^{8b} are taken together to form an optionally substituted cycloalkyl, an optionally substituted cycloalkenyl, an optionally substituted aryl, an optionally substituted heteroaryl or an optionally substituted heterocycle;

R^{9a} and R^{9b} are independently selected from a hydrogen, an optionally substituted alkyl, an optionally substituted cycloalkyl, an optionally substituted haloalkyl, a halogen, hydroxy, an optionally substituted alkoxy and an optionally substituted haloalkoxy;

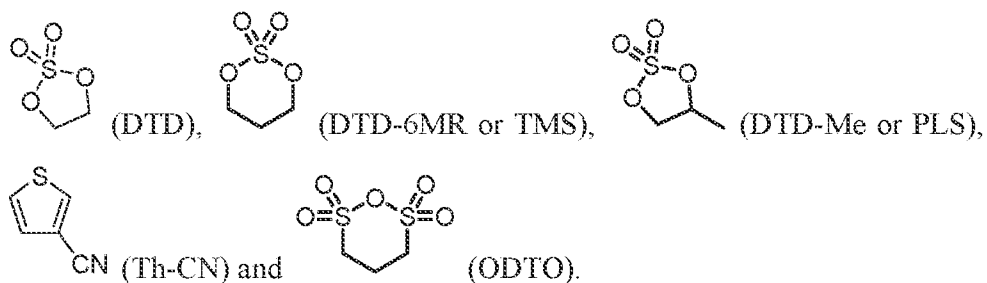
R^{10} is an optionally substituted C_{1-6} alkylene;

R^{11} , R^{12} , R^{13} and R^{14} are independently selected from hydrogen, an optionally substituted alkyl, an optionally substituted cycloalkyl, an optionally substituted haloalkyl, an optionally substituted alkenyl, an optionally substituted alkynyl, an optionally substituted cycloalkenyl, a halogen, hydroxy, an optionally substituted alkoxy, an optionally substituted haloalkoxy, an optionally substituted C-amido, an optionally substituted N-amido, an optionally substituted C-carboxy, an optionally substituted O-carboxy, an optionally substituted sulfenyl, an optionally substituted

sulfinyl, an optionally substituted sulfonyl, cyano, nitro, amino, an optionally

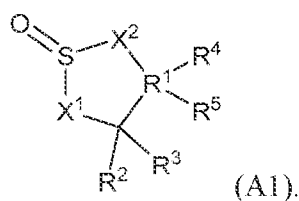


wherein the compound is not selected from the group consisting of

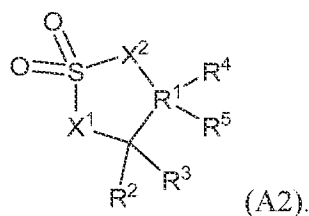


2. The electrolyte composition of Claim 1, wherein the compound is of Formula (A).

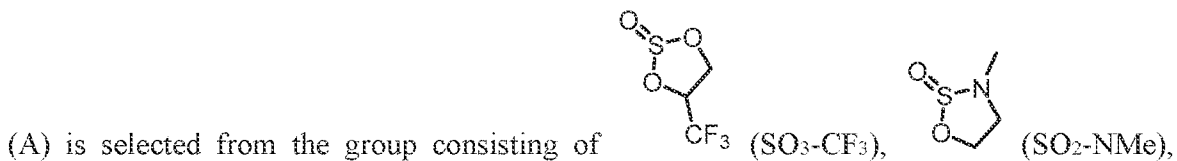
3. The electrolyte composition of Claim 2, wherein A is absent and the compound is of Formula (A1):

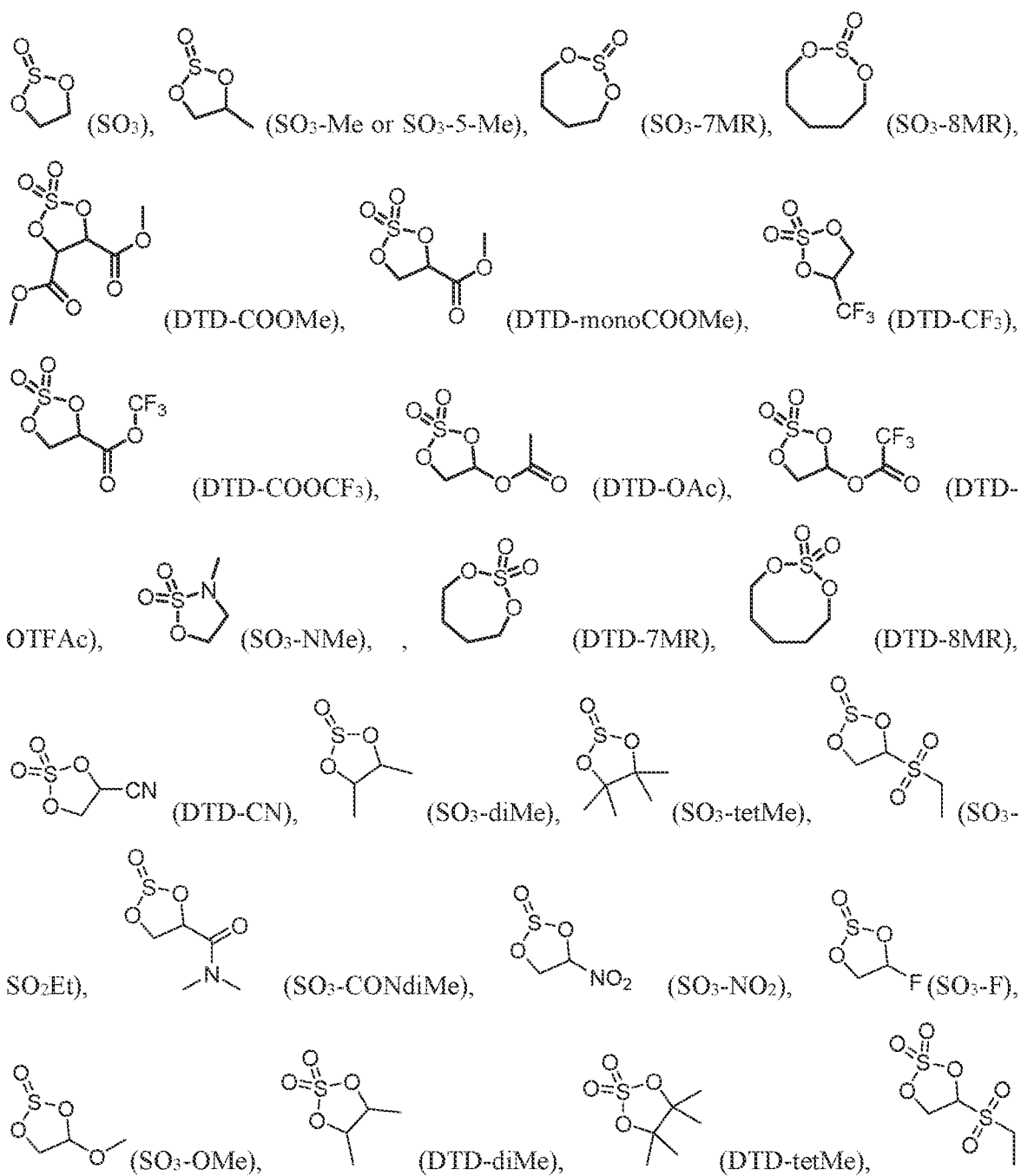


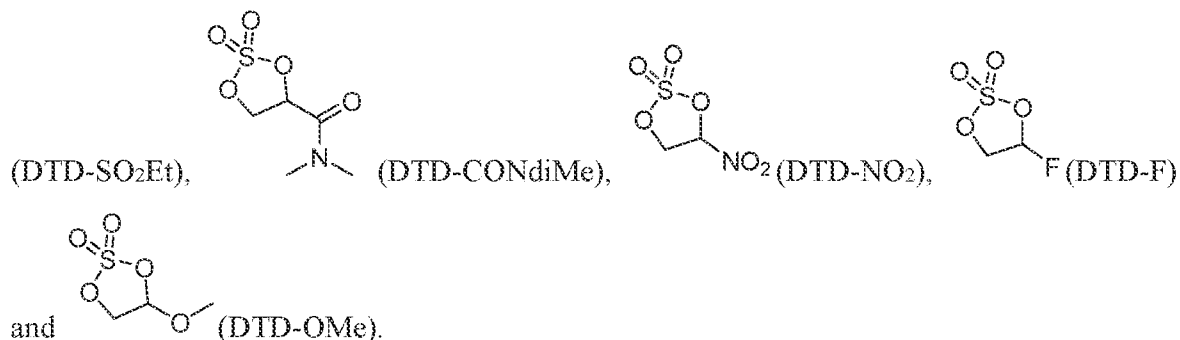
4. The electrolyte composition of Claim 2, wherein A is O, and the compound is of Formula (A2):



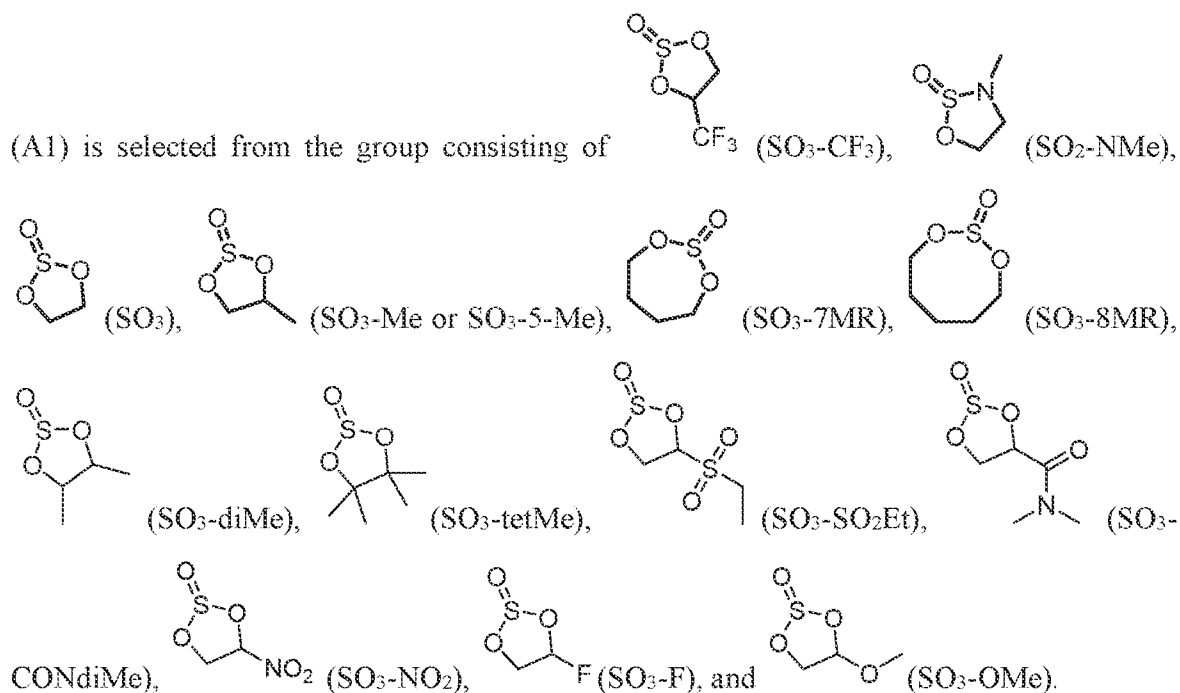
5. The electrolyte composition of Claim 2, wherein the compound of Formula



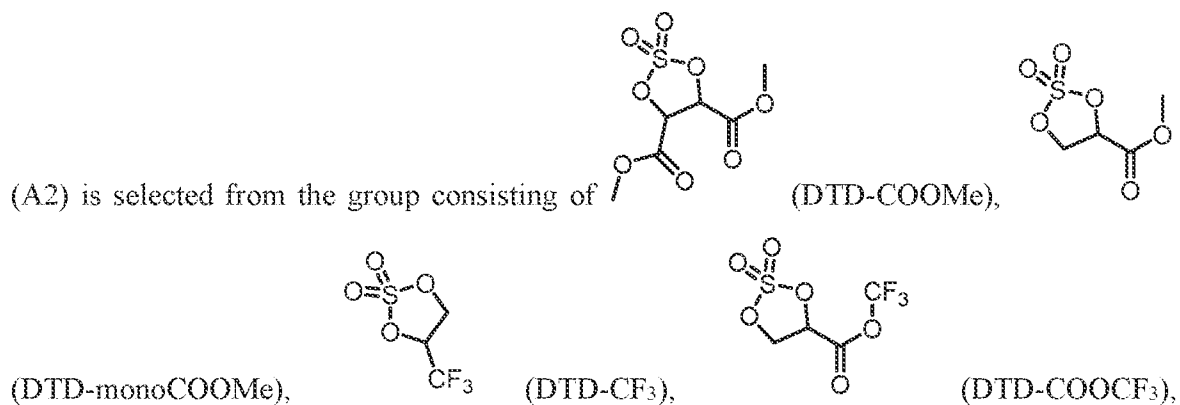


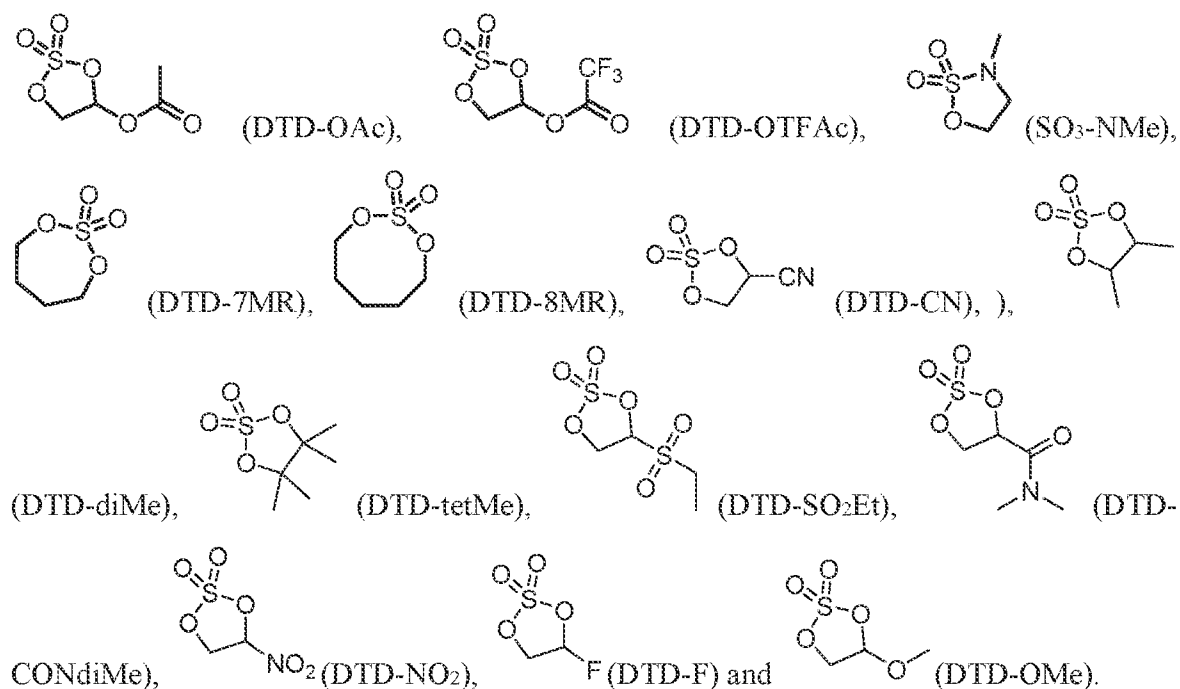


6. The electrolyte composition of Claim 3, wherein the compound of Formula



7. The electrolyte composition of Claim 4, wherein the compound of Formula

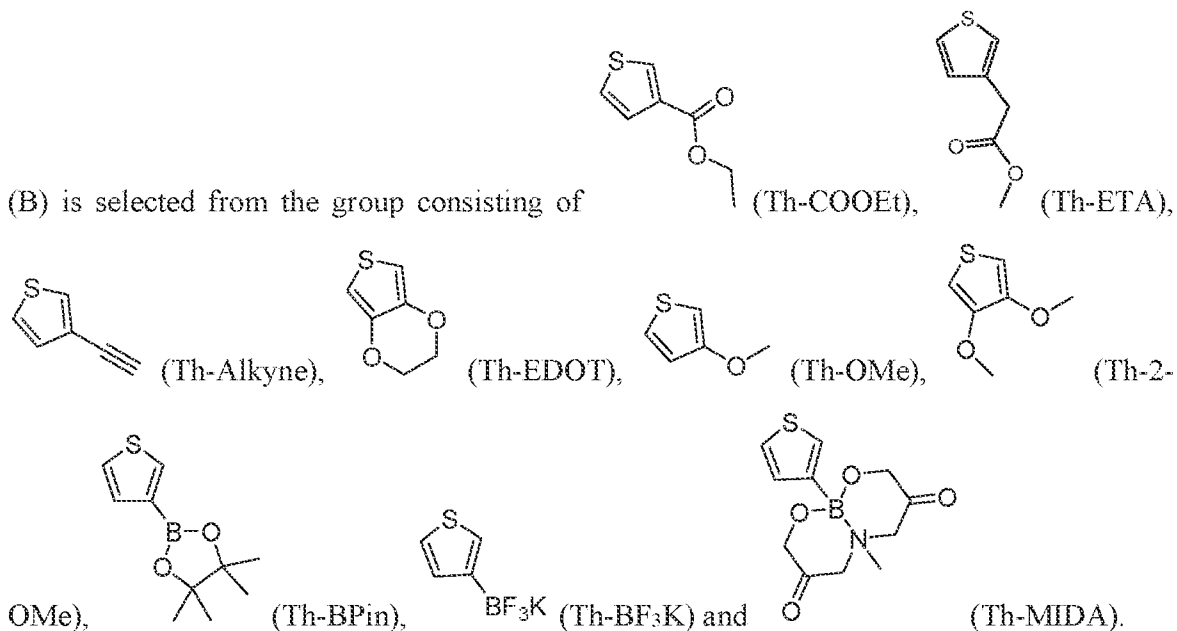




8. The electrolyte composition of Claim 1, wherein the compound is of Formula (B).

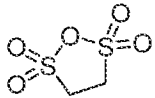
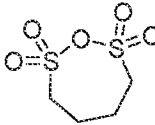
9. The electrolyte composition of Claim 8, wherein the compound of Formula

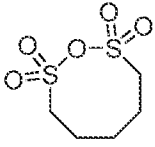
(B) is selected from the group consisting of



10. The electrolyte composition of Claim 1, wherein the compound is of Formula (C).

11. The electrolyte composition of Claim 10, wherein the compound of Formula

(C) is selected from the group consisting of  (ODTO-5MR), 

(ODTO-7MR) and  (ODTO-8MR).

12. The electrolyte composition of any one of Claims 1-11, wherein the electrolyte composition comprises the additive in about 0.5-3 wt%.

13. The electrolyte composition of any one of Claims 1-12, further comprising an additional additive.

14. The electrolyte composition of Claim 13, wherein the additional additive is selected from the group consisting of VC, FEC, and combinations thereof.

15. The electrolyte composition of Claim 14, wherein the electrolyte composition comprises the additional additive selected from the group consisting of about 0.25 wt% VC, about 0.75 wt% FEC, and about 0.25 wt% VC and about 0.75 wt% FEC.

16. The electrolyte composition of any one of Claims 1-15, wherein the solvent is selected from the group consisting of EC, EMC, DMC, and combinations thereof.

17. The electrolyte composition of Claim 16, wherein electrolyte comprises EC:DMC at a ratio of 15:85 w/w or EC:EMC at a ratio of 3:7 w/w.

18. An energy storage device, comprising:

the electrolyte of any one of Claims 1-17;

a cathode;

an anode; and

a housing, wherein the electrolyte, cathode and anode are disposed within the housing.

19. The energy storage device of Claim 18, wherein a volume of gas produced within the energy storage device is less than or comparable to a volume of gas produced within an energy storage device without the additive.

20. The energy storage device of Claim 18 or 19, wherein the energy storage device is a lithium-ion battery.

21. A method of preparing an energy storage device, comprising:
positioning the electrolyte composition of any one of Claims 1-17 within a housing comprising a cathode and an anode.

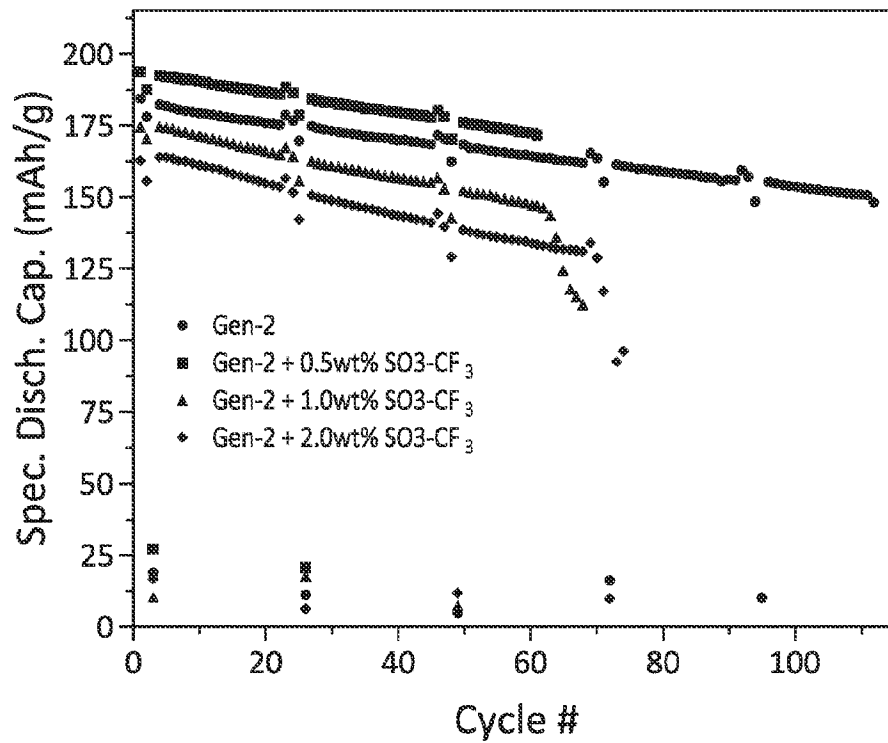


FIG. 1A

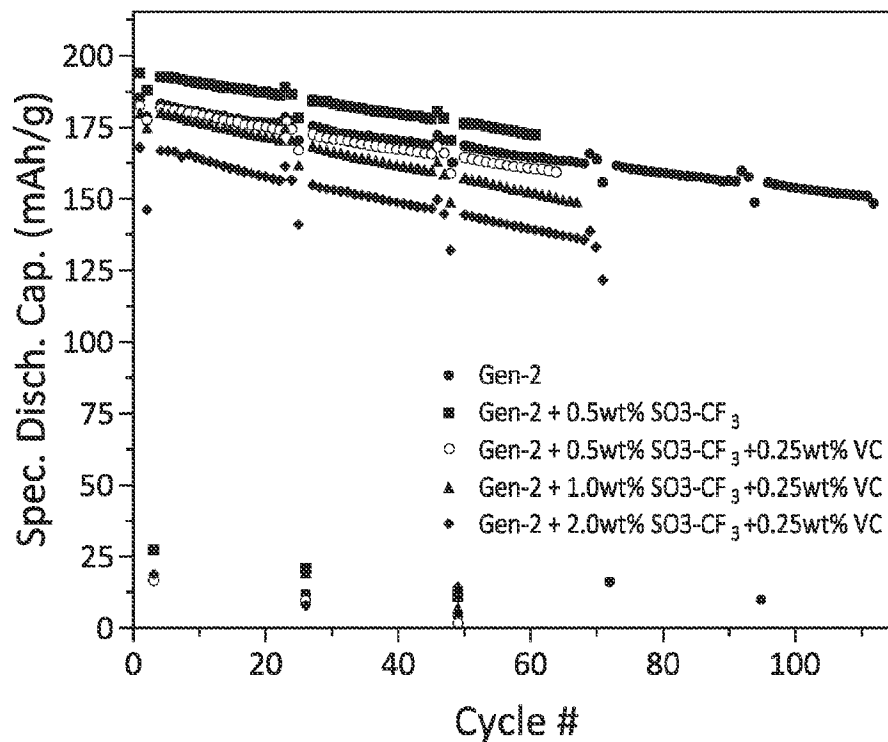


FIG. 1B

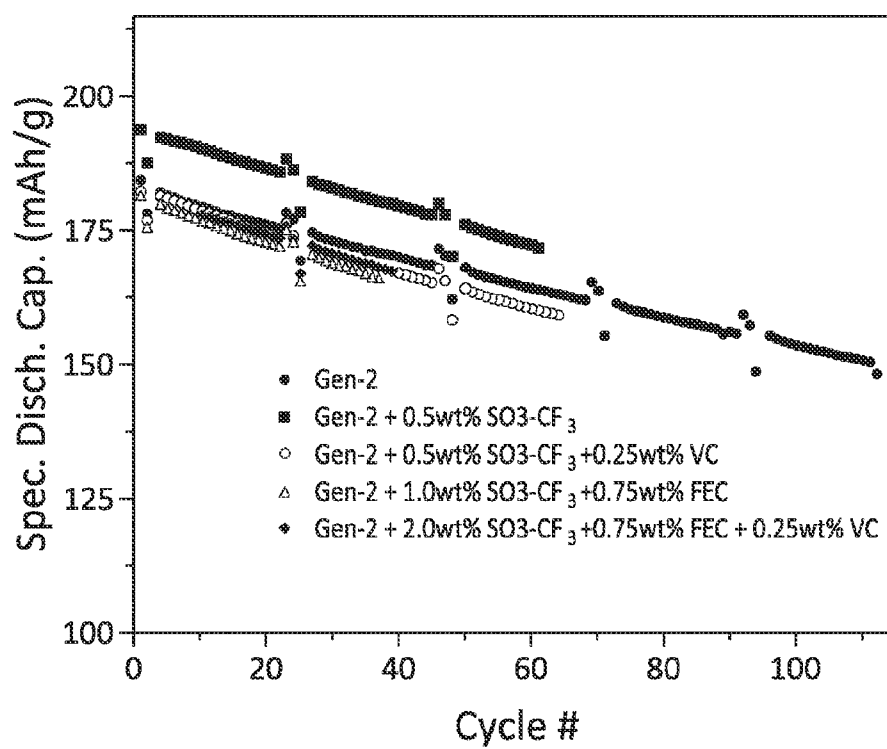


FIG. 1C

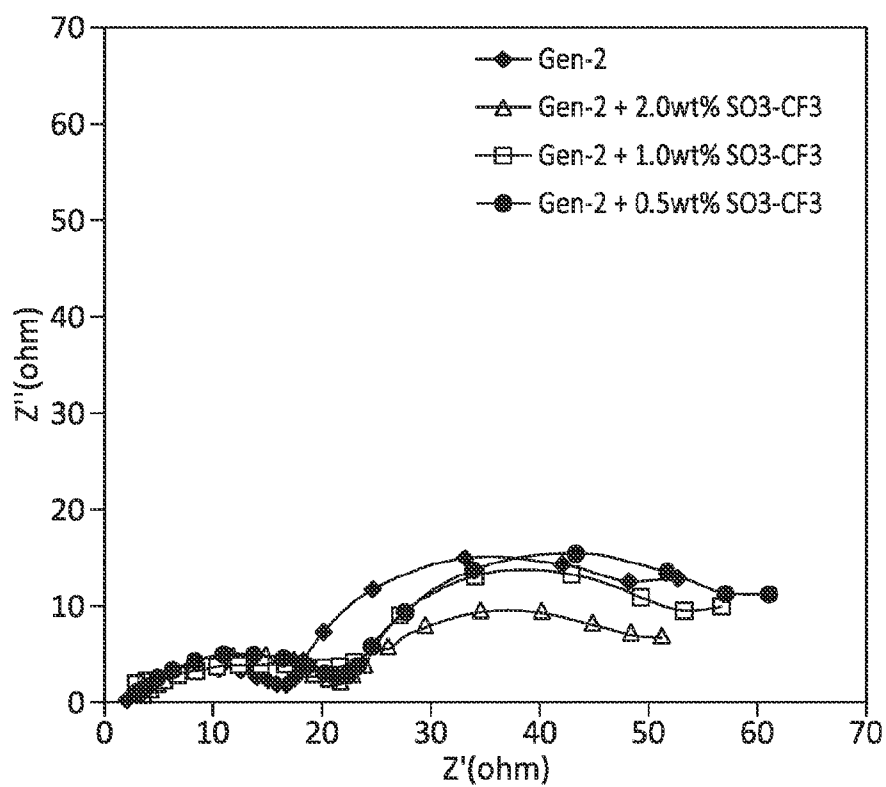


FIG. 2A

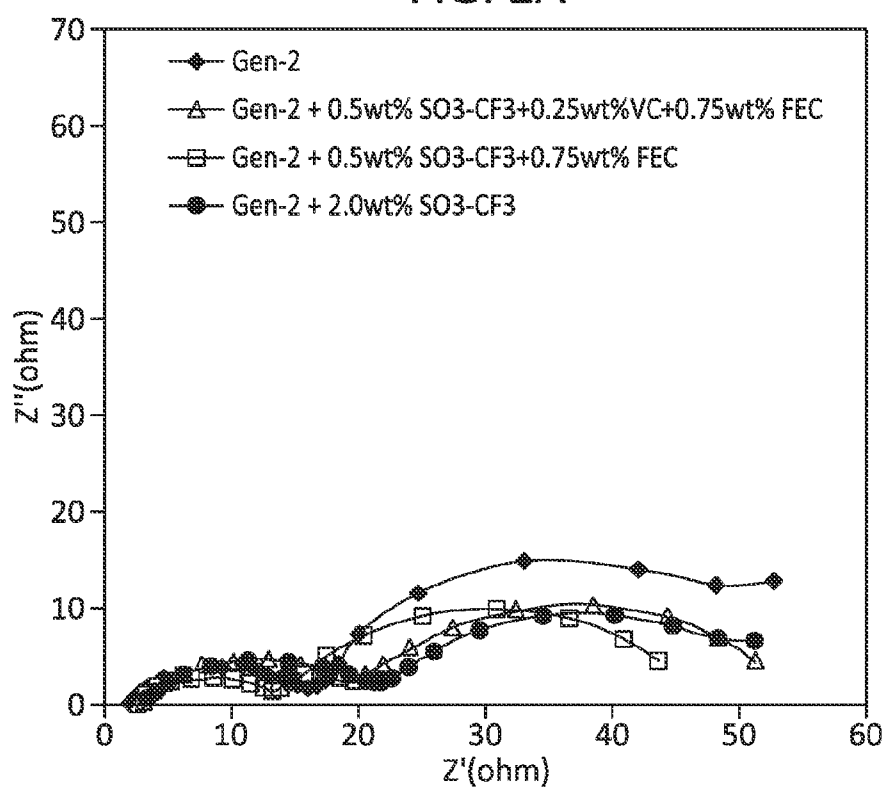


FIG. 2B

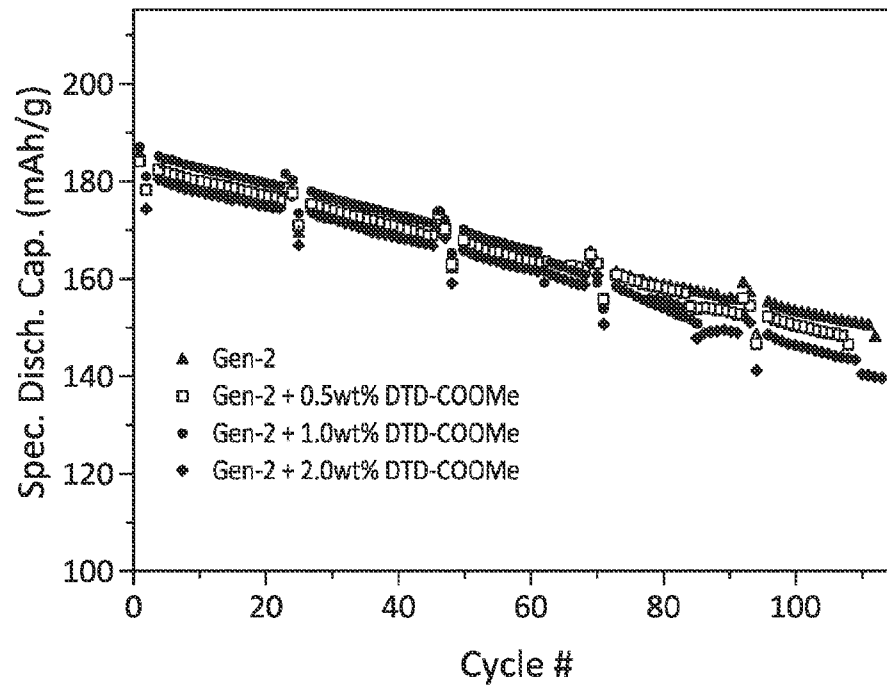


FIG. 3A

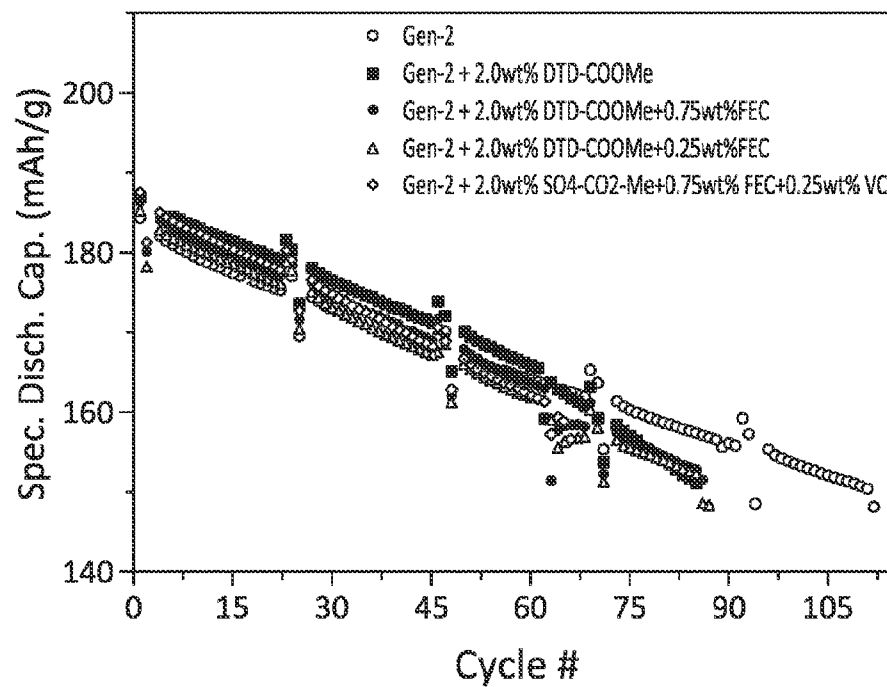


FIG. 3B

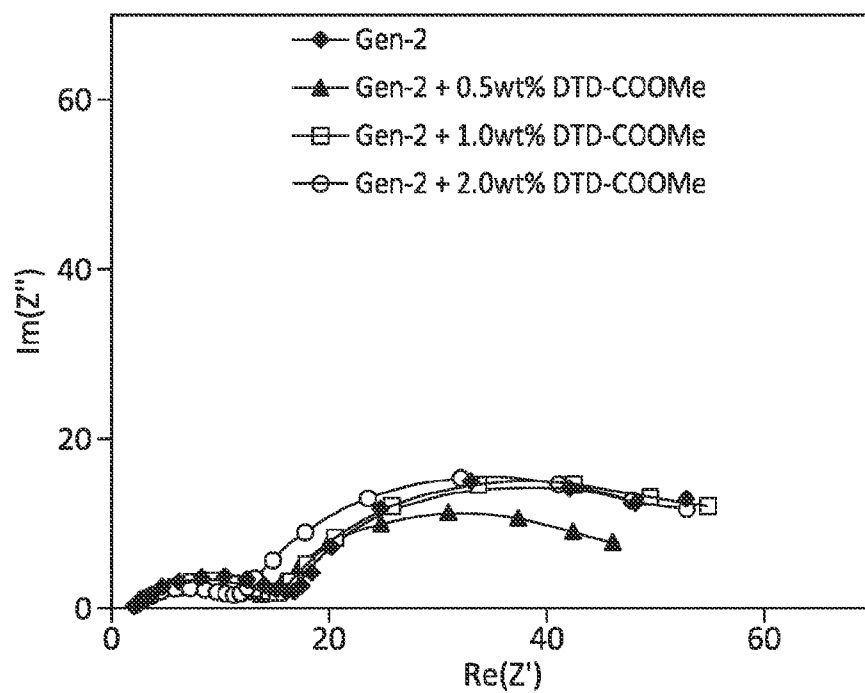


FIG. 4A

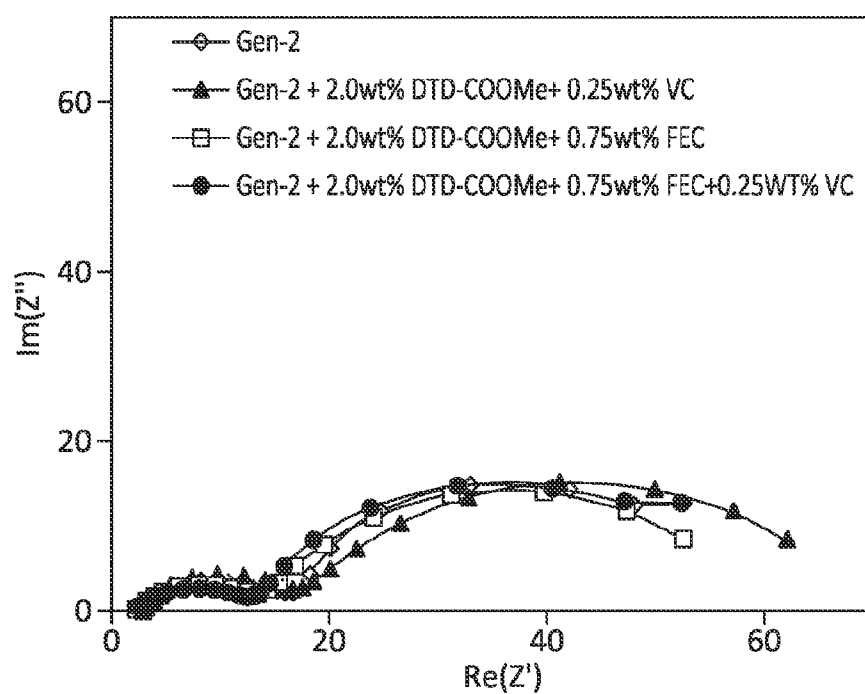


FIG. 4B

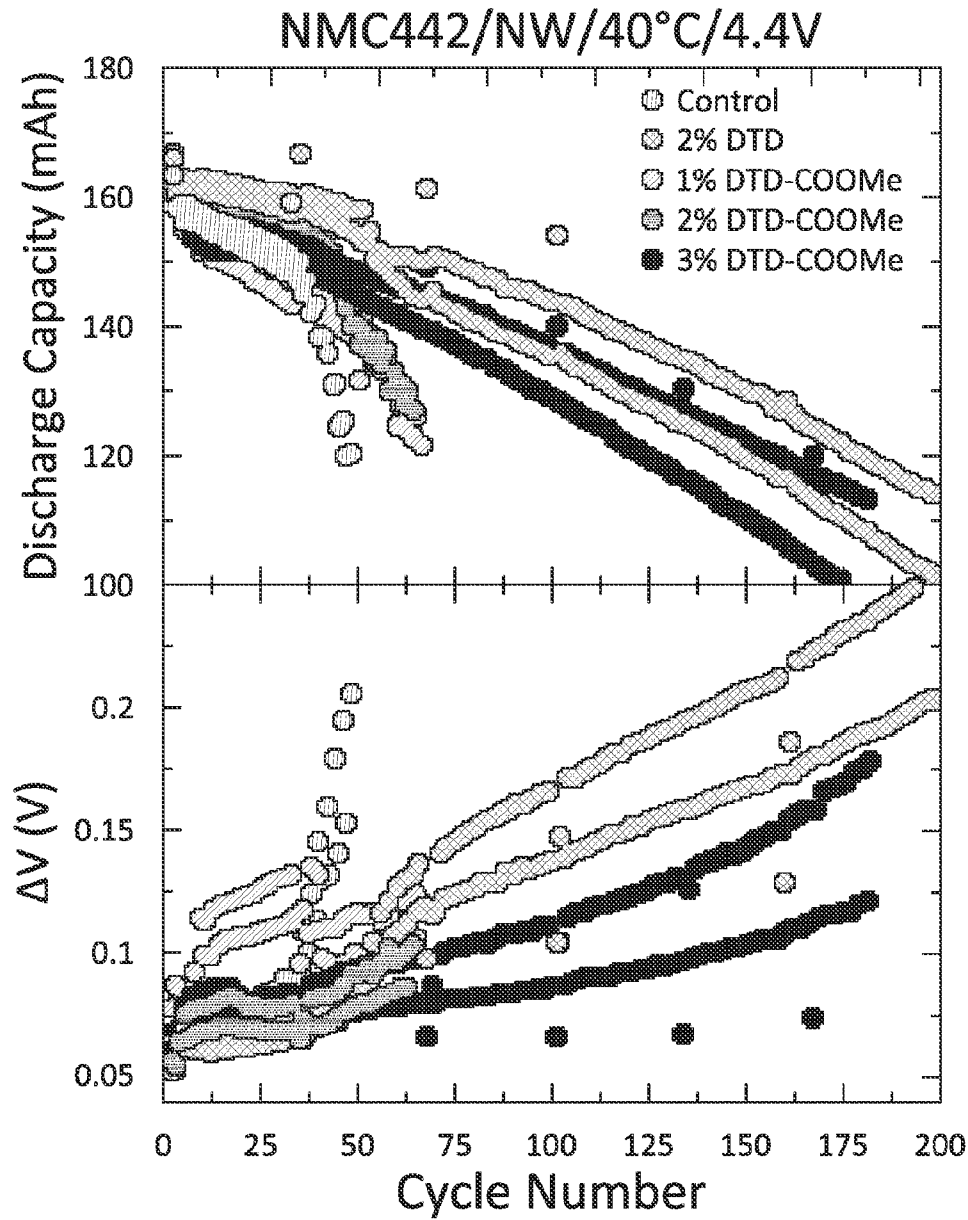


FIG. 5A

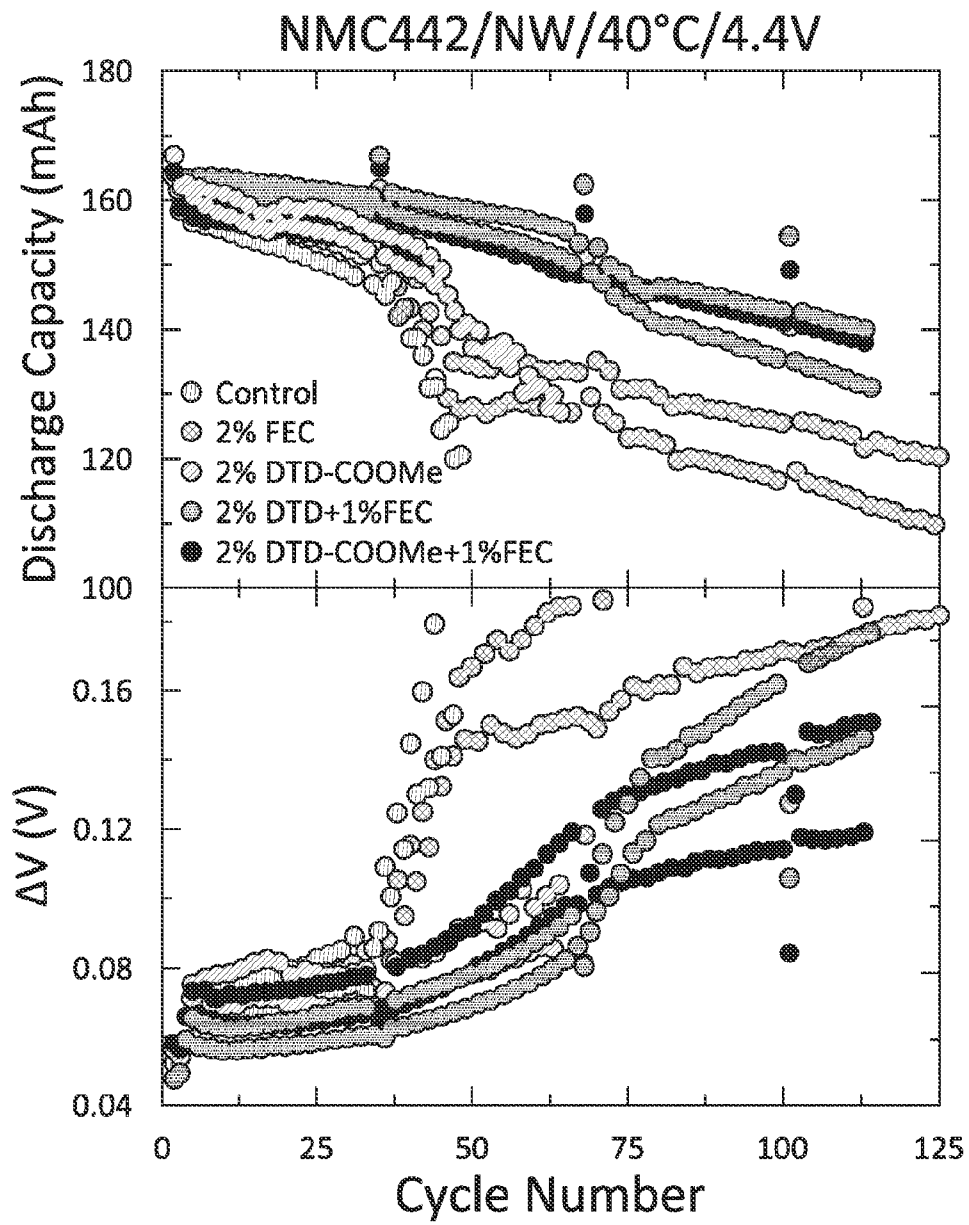


FIG. 5B

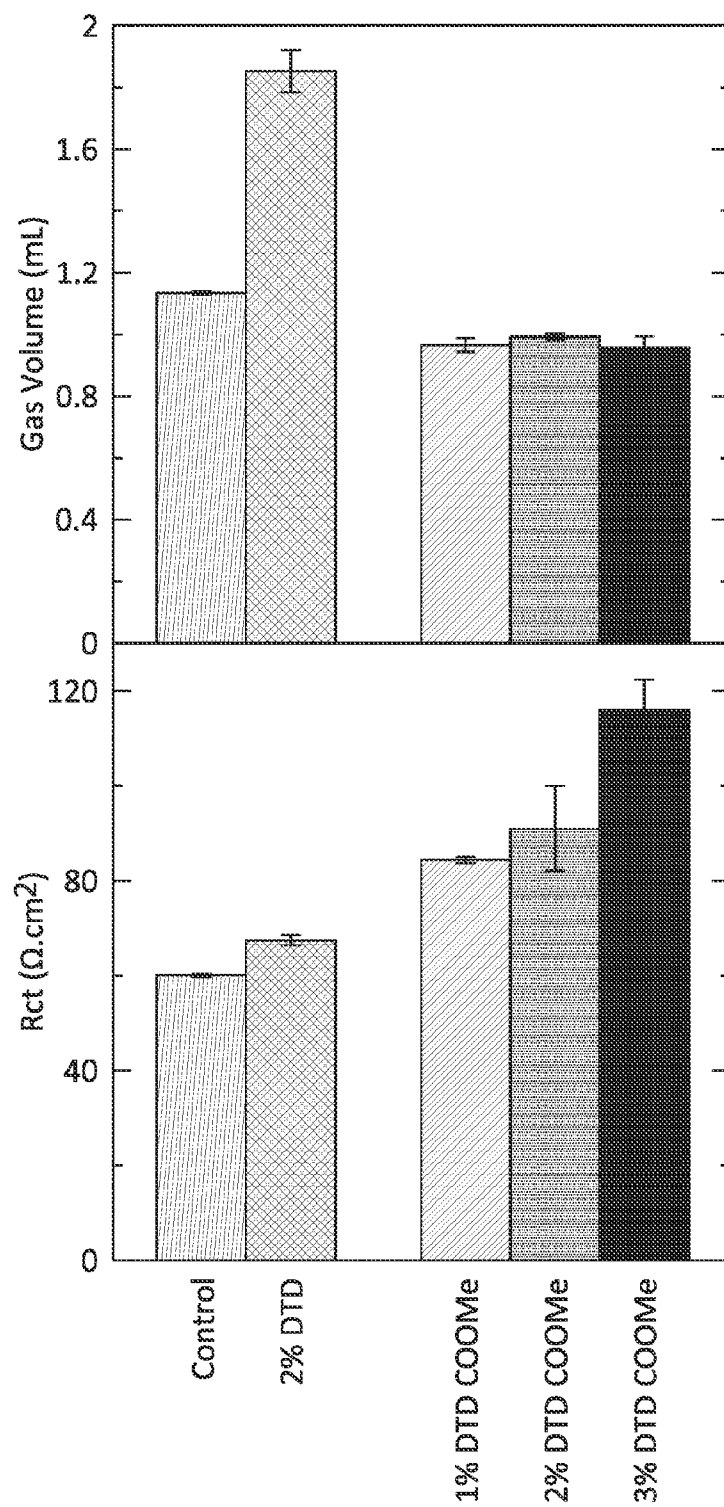


FIG. 5C

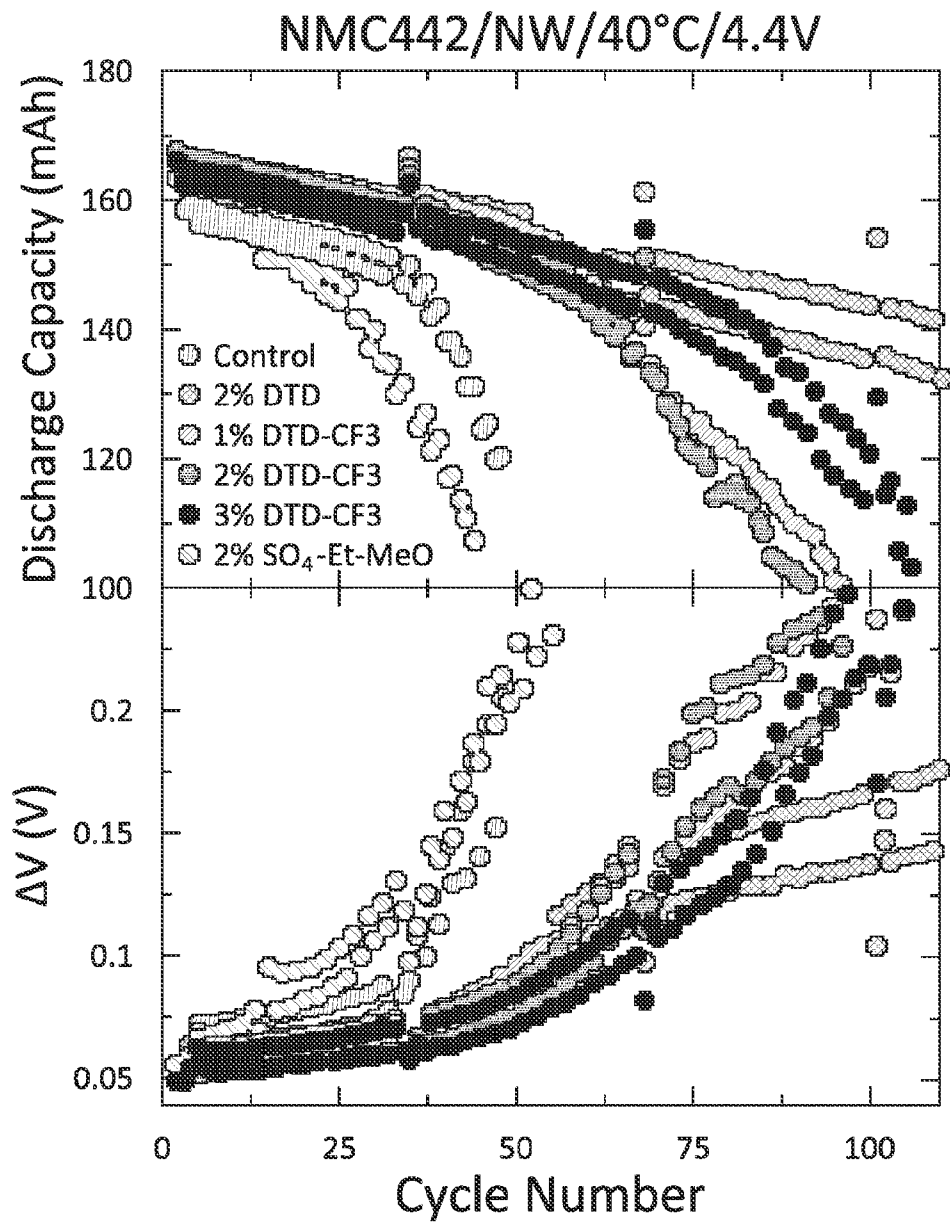


FIG. 6A

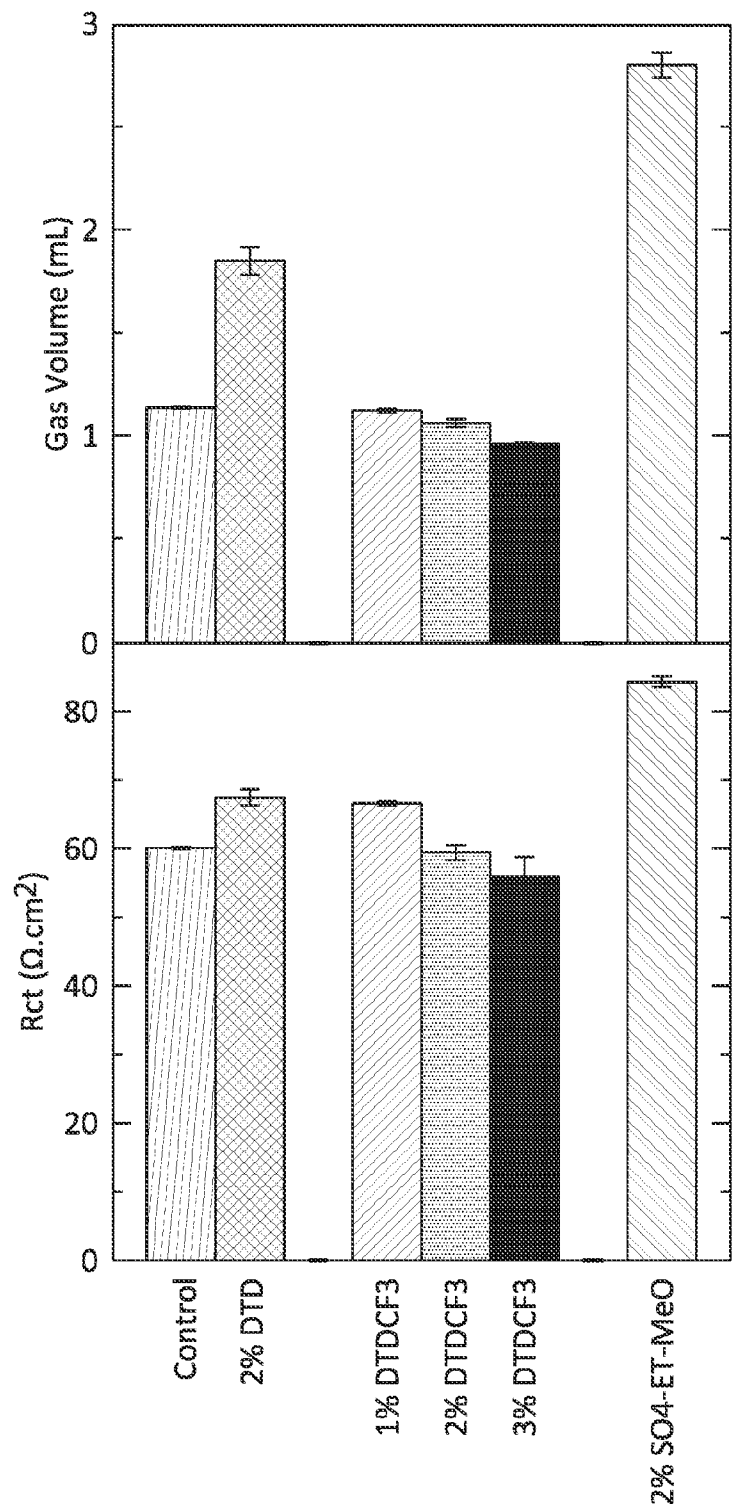


FIG. 6B

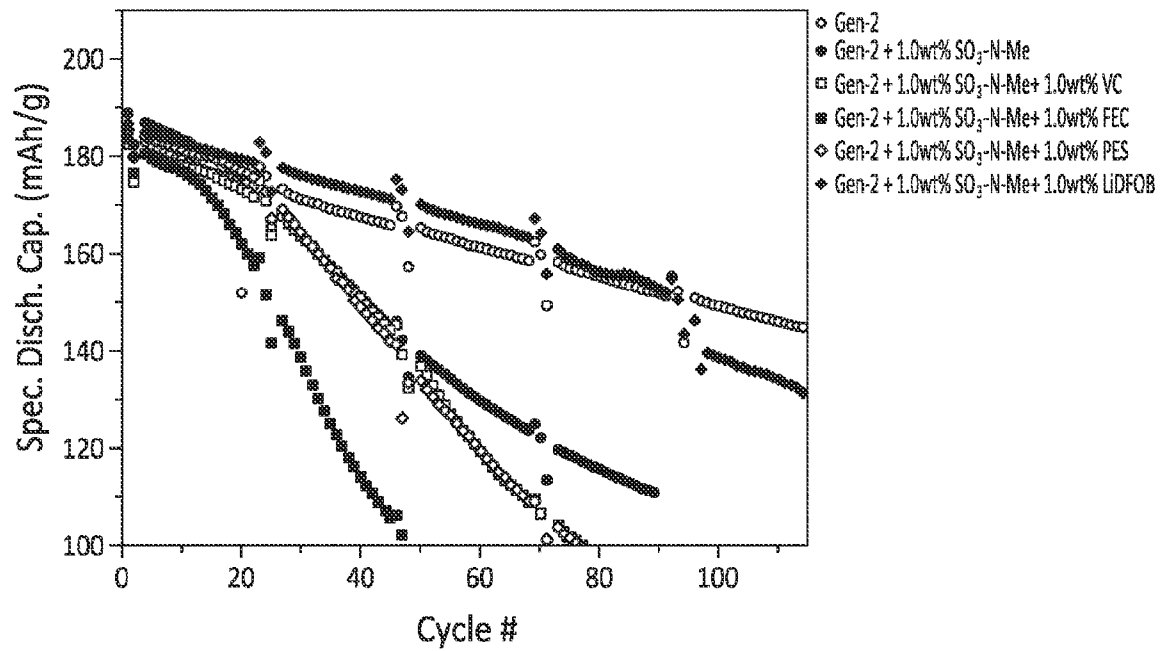


FIG. 7A

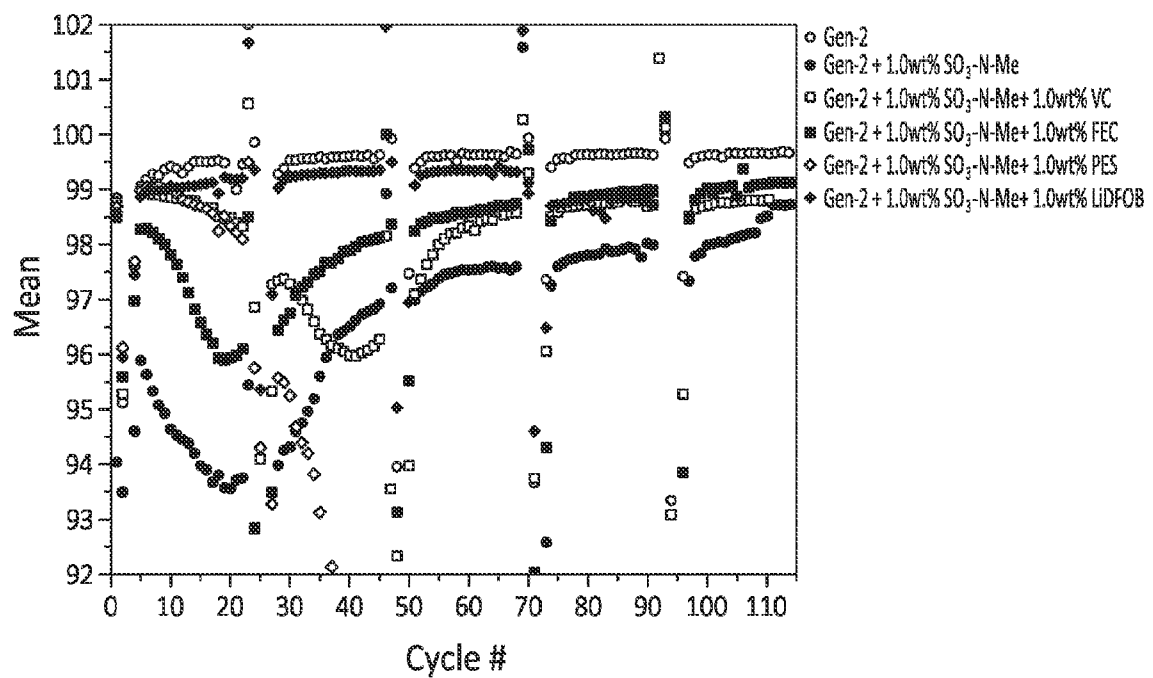


FIG. 7B

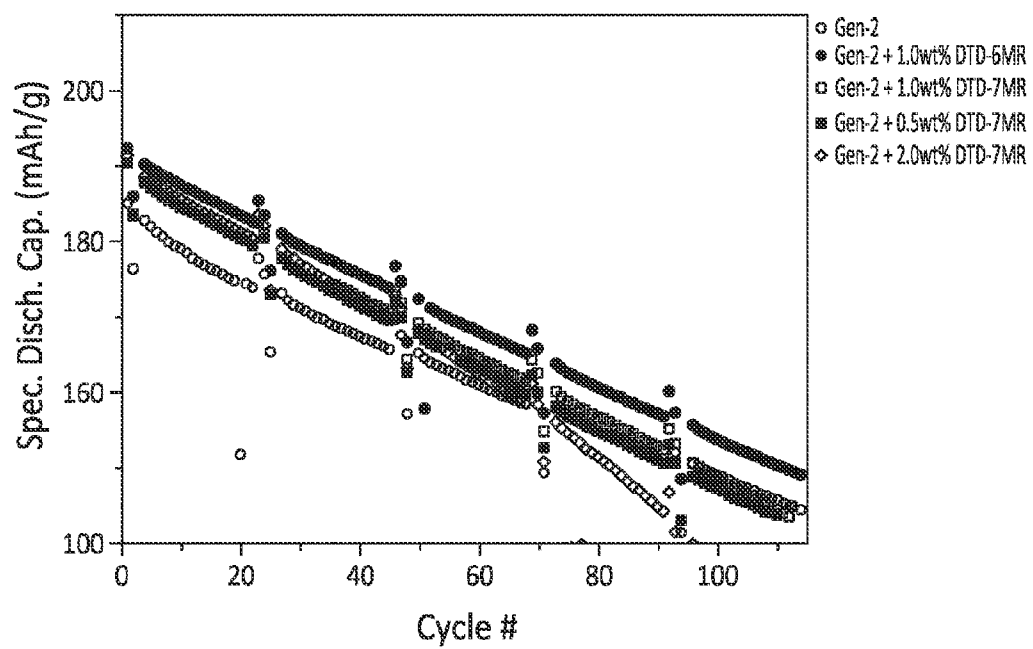


FIG. 8A

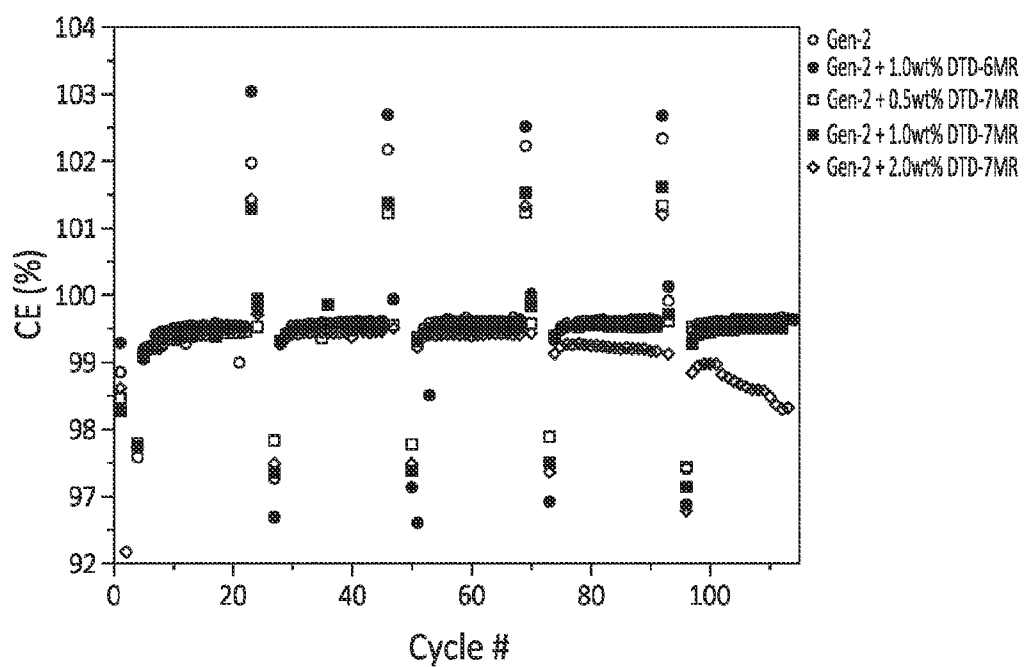


FIG. 8B

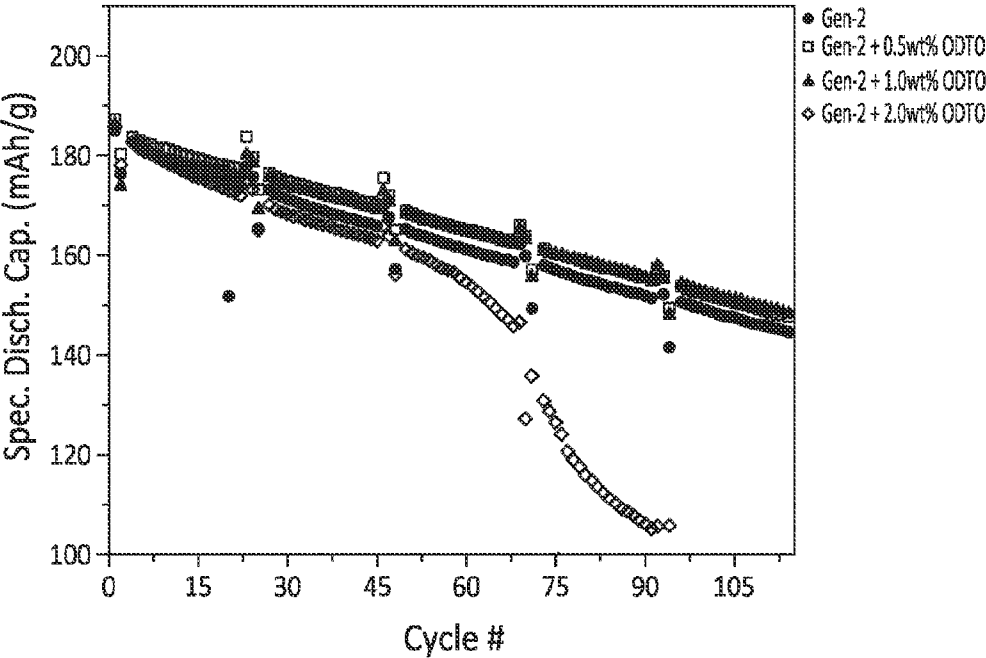


FIG. 9A

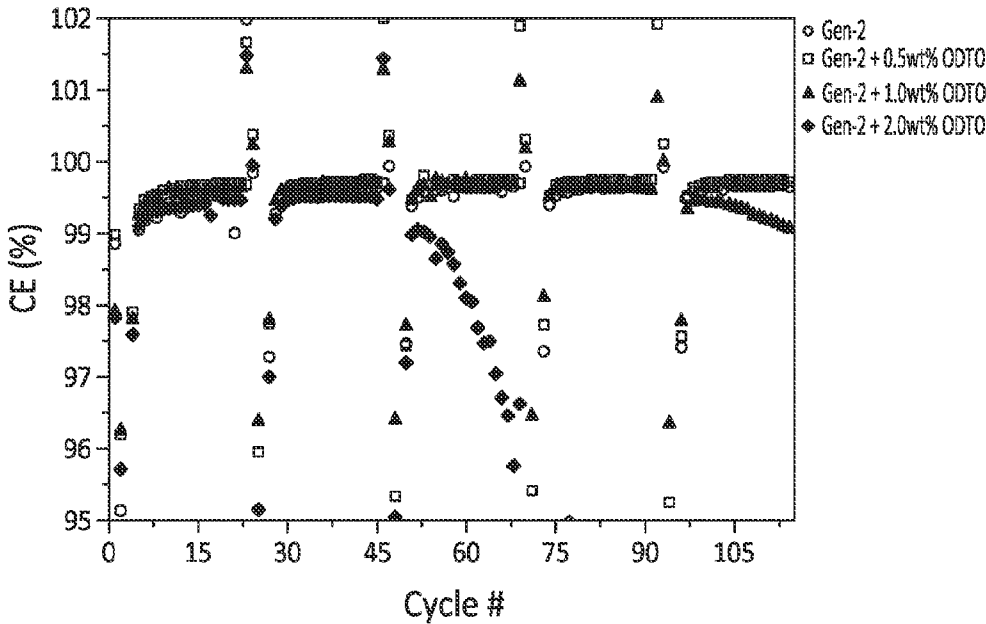


FIG. 9B

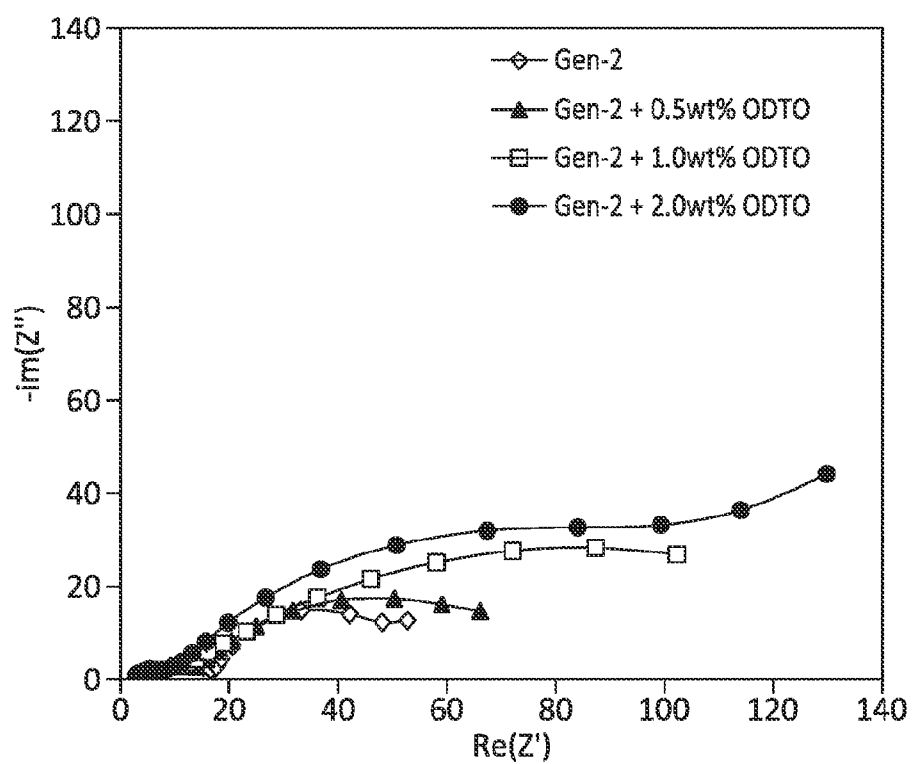


FIG. 10A

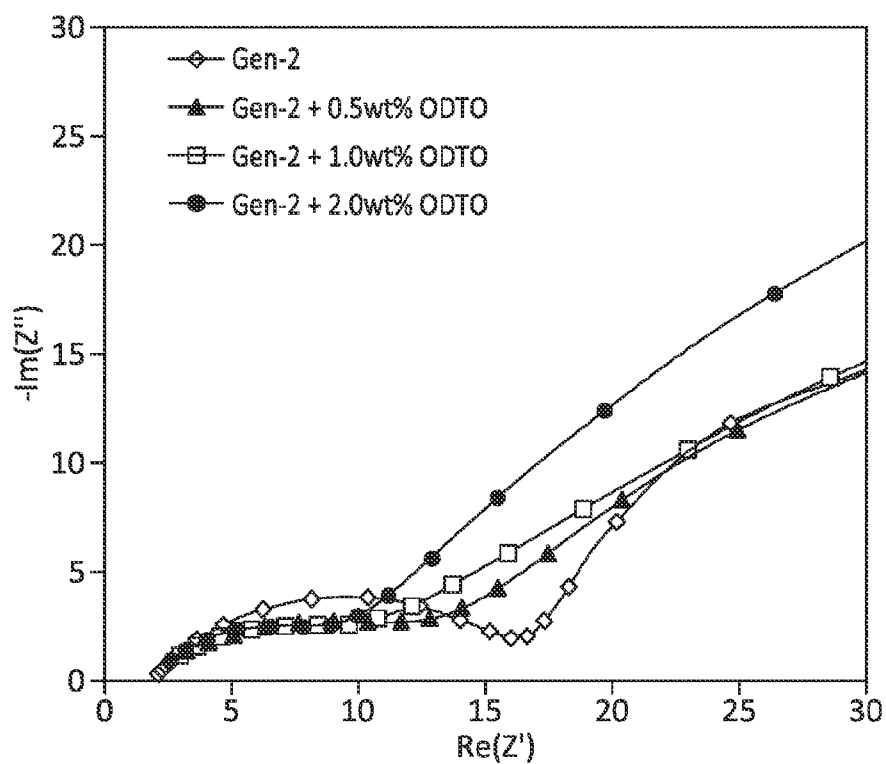


FIG. 10B

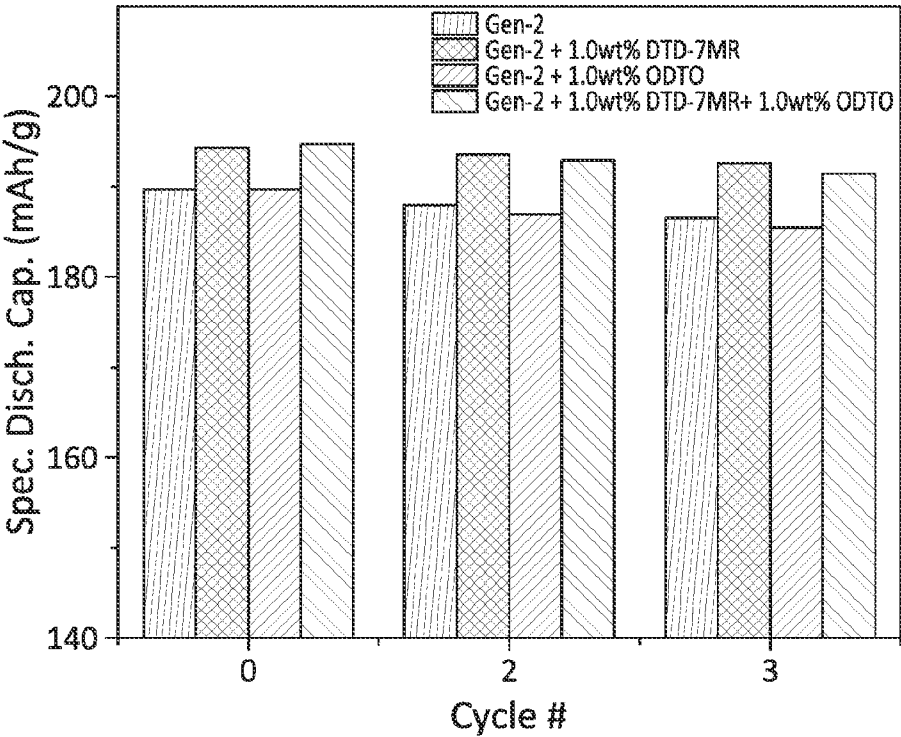


FIG. 11A

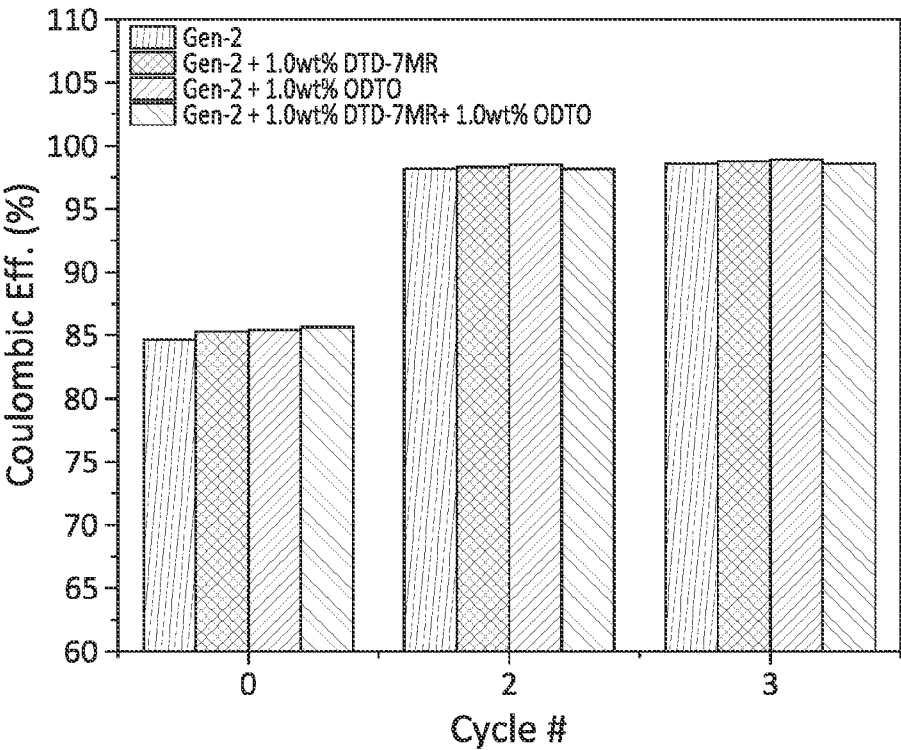


FIG. 11B

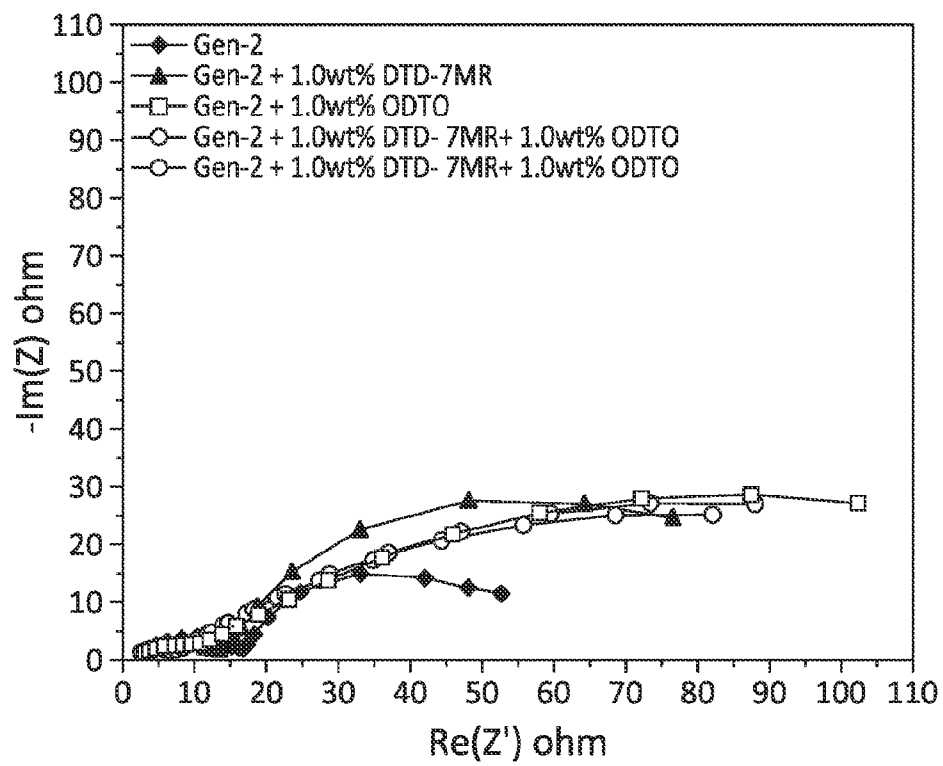


FIG. 12A

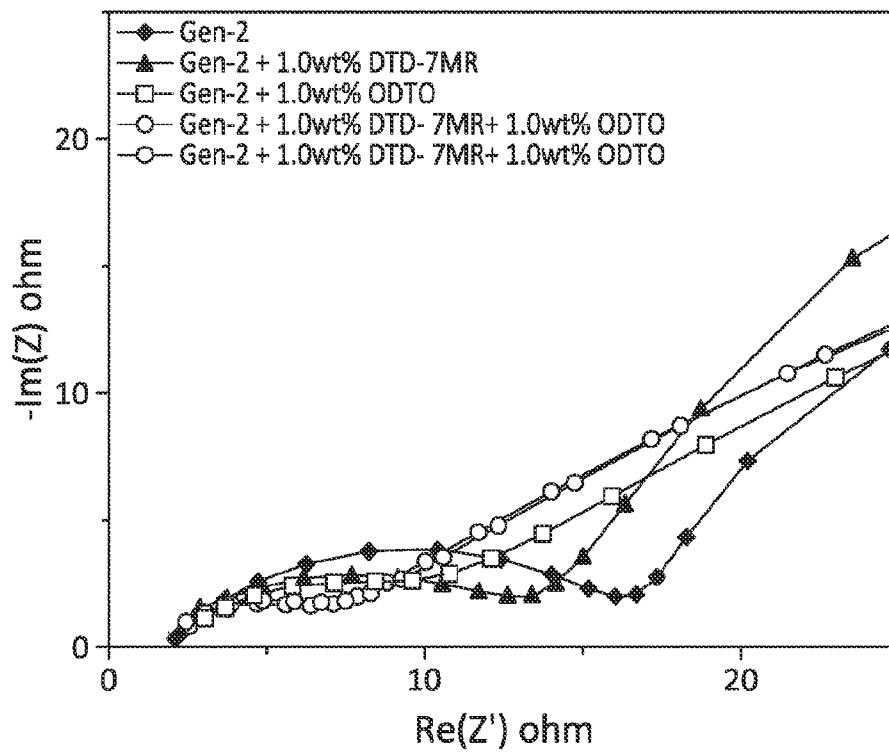


FIG. 12B

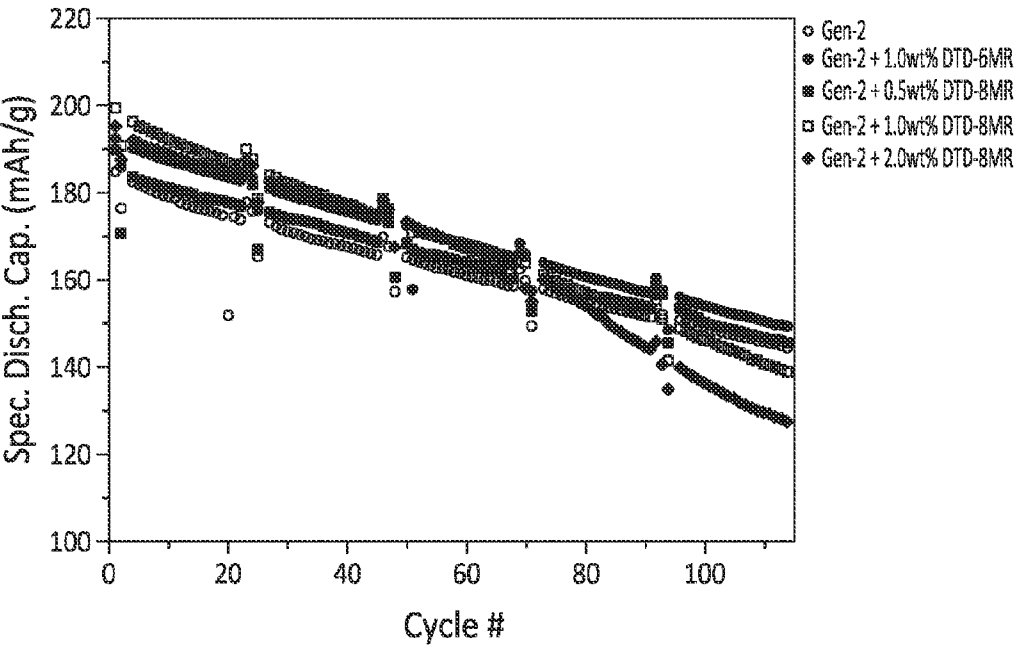


FIG. 13A

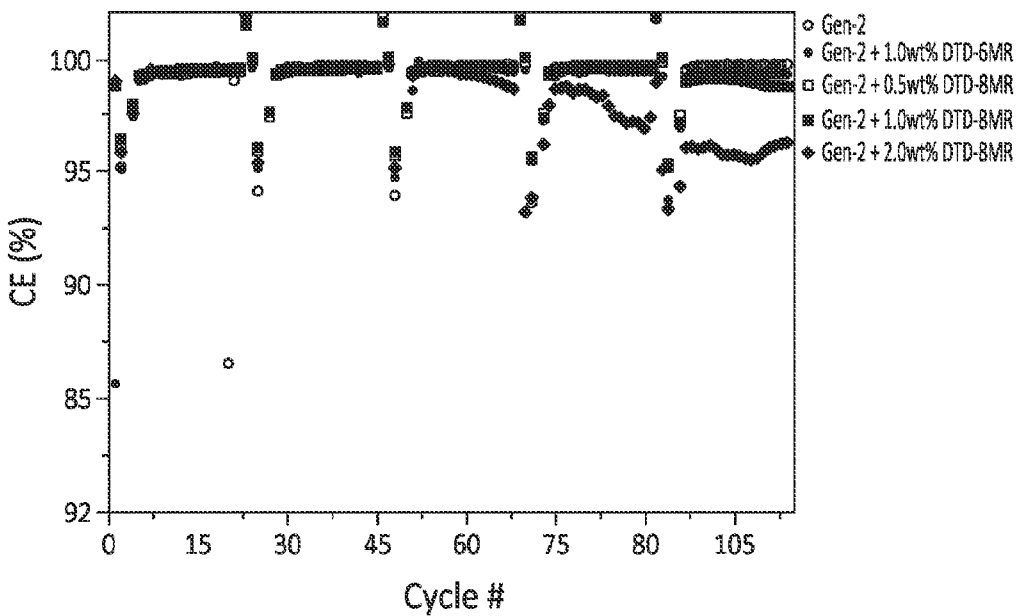


FIG. 13B

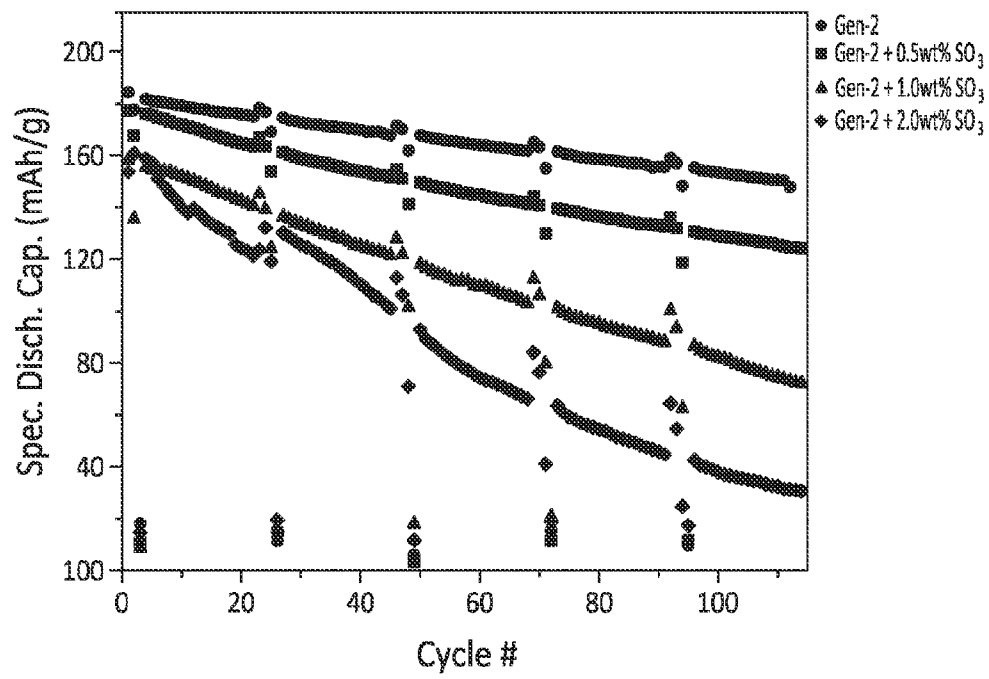


FIG. 14

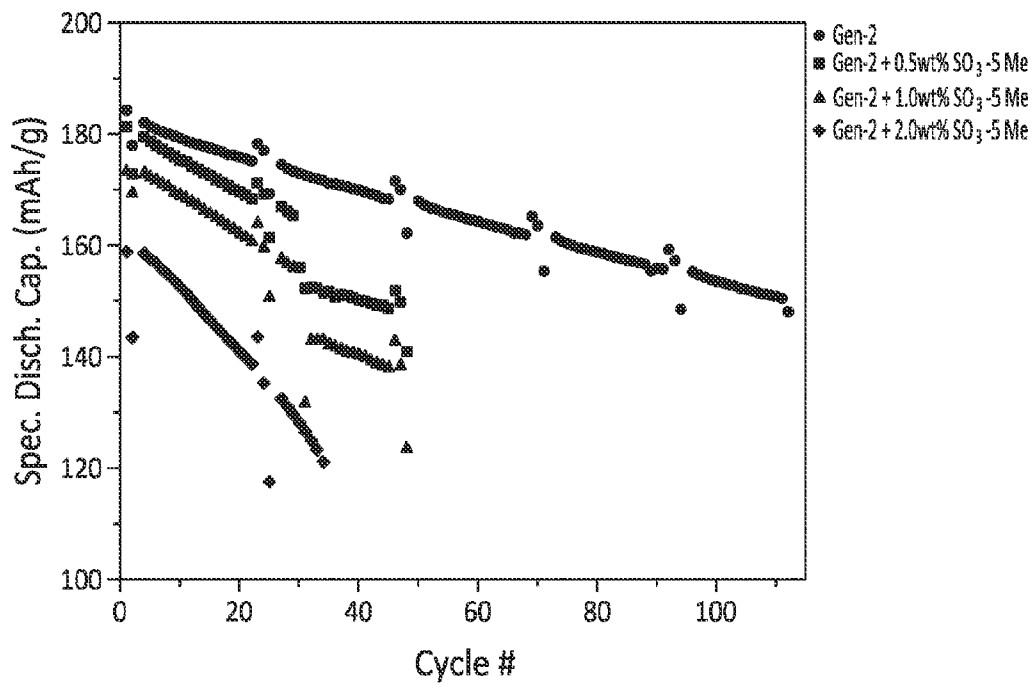


FIG. 15A

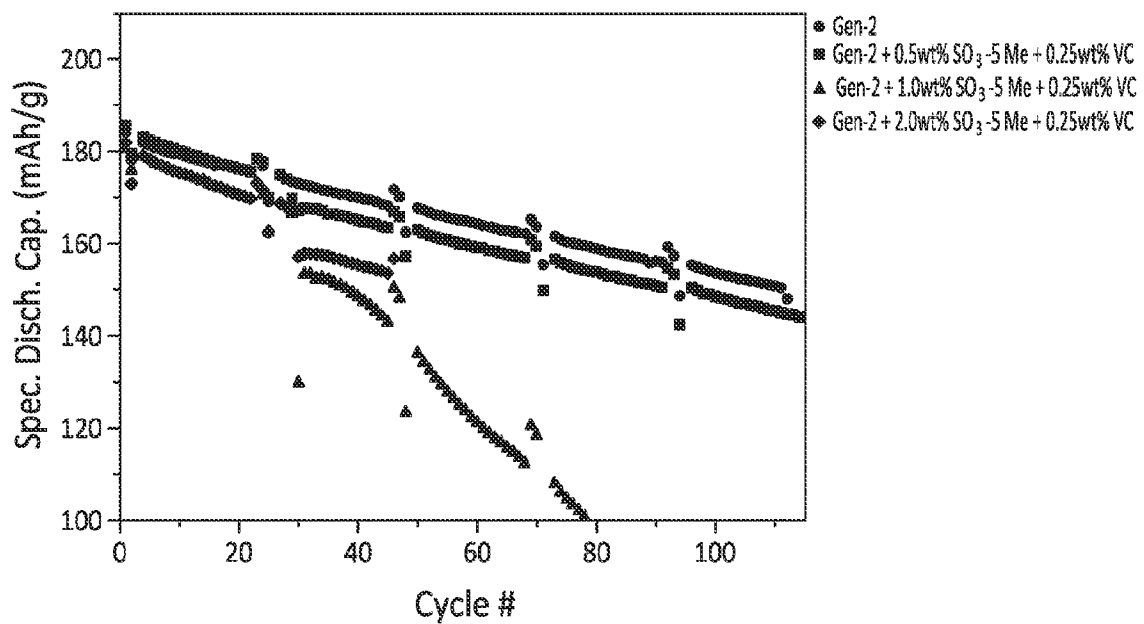


FIG. 15B

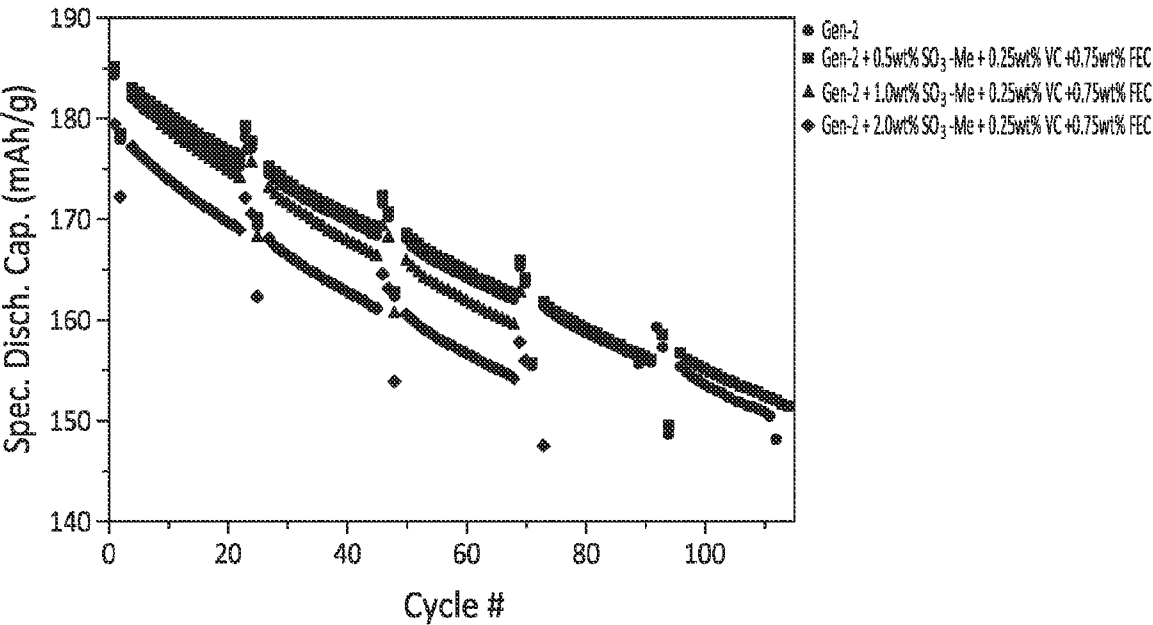


FIG. 15C

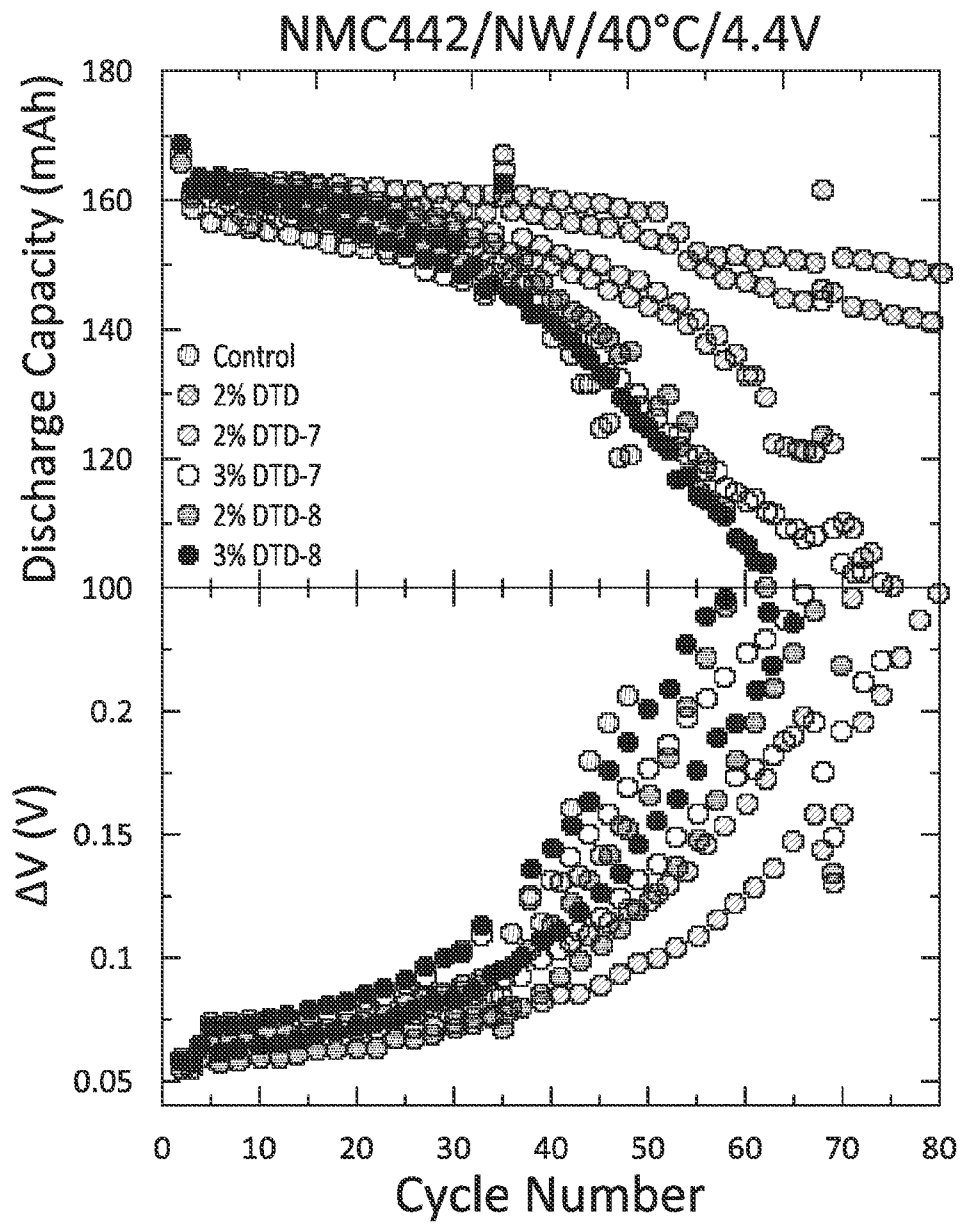


FIG. 16A

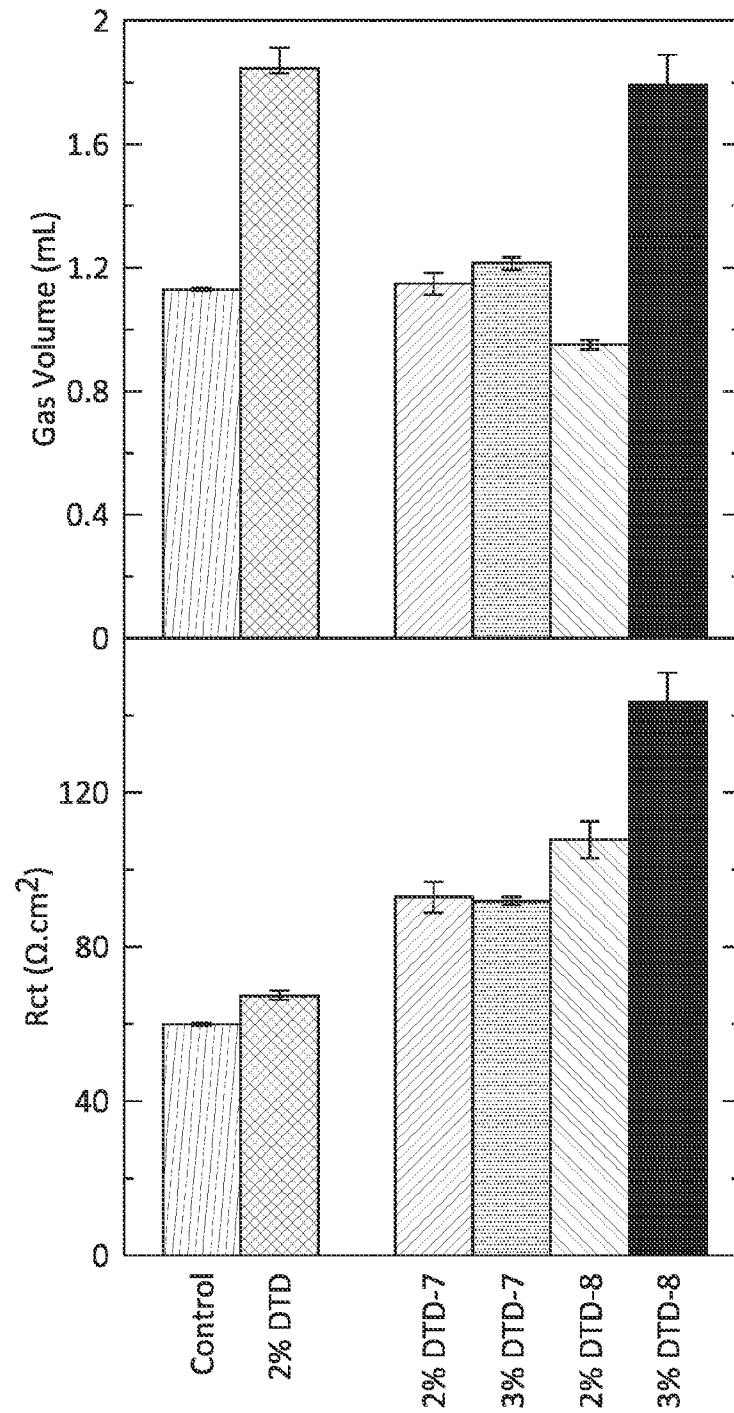


FIG. 16B

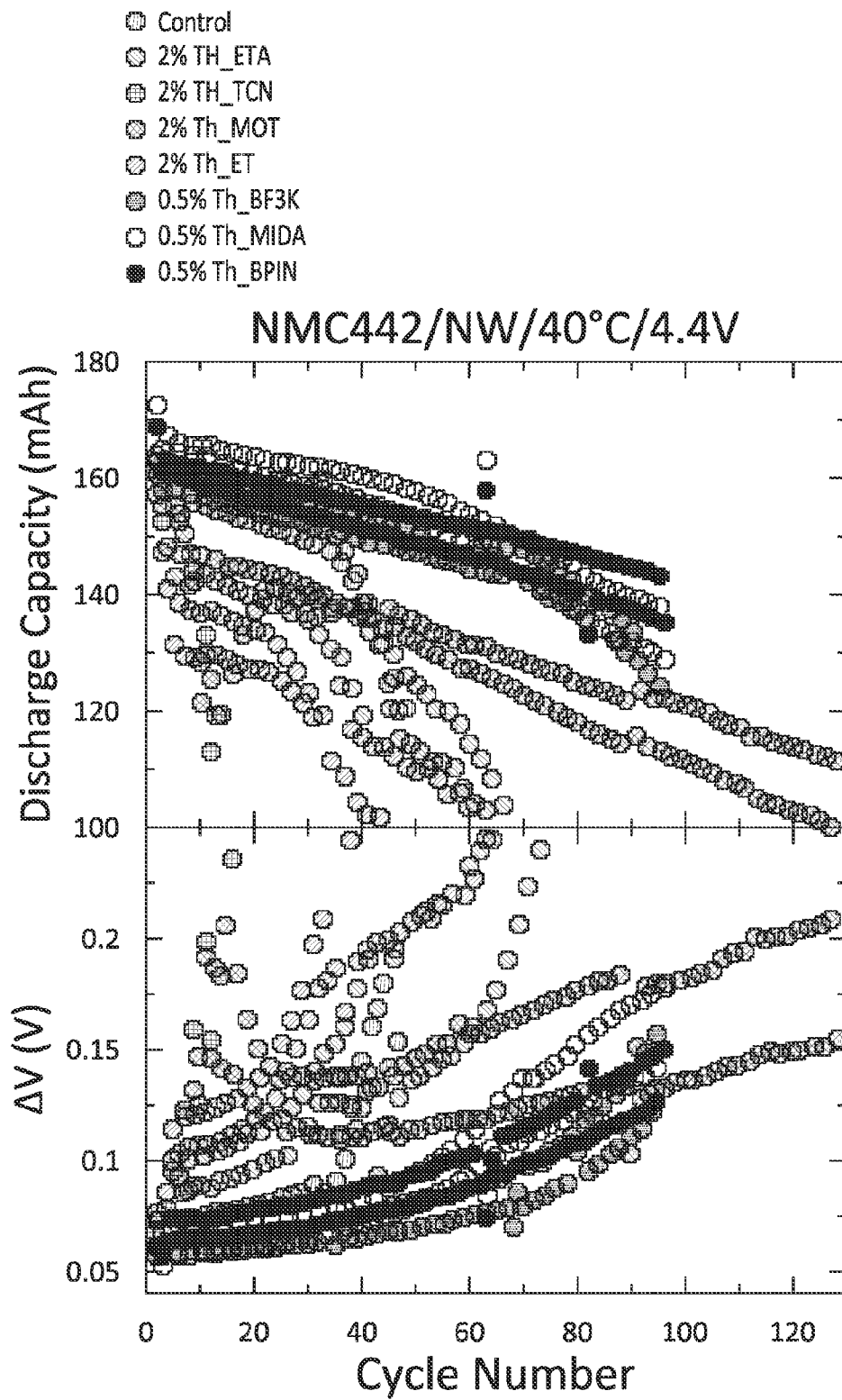


FIG. 17A

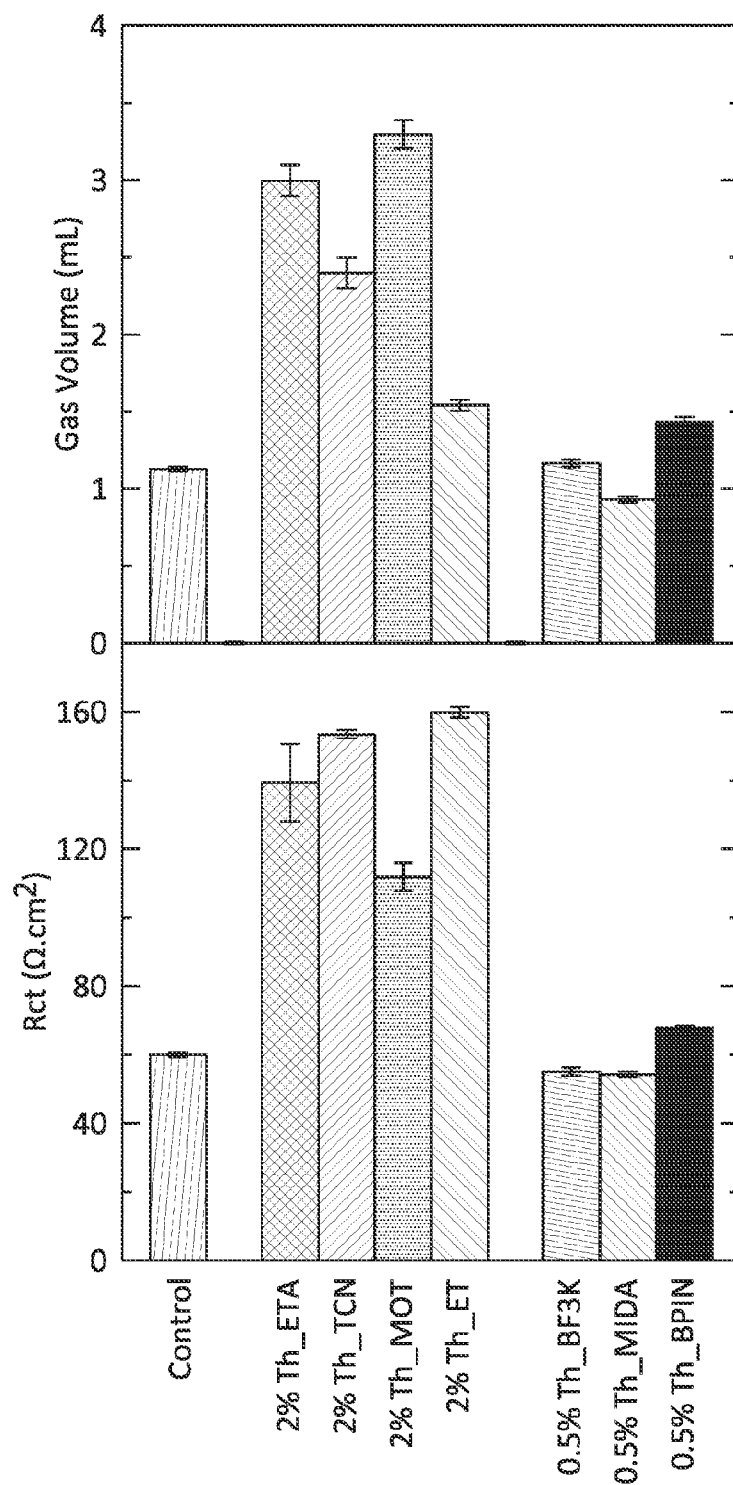


FIG. 17B

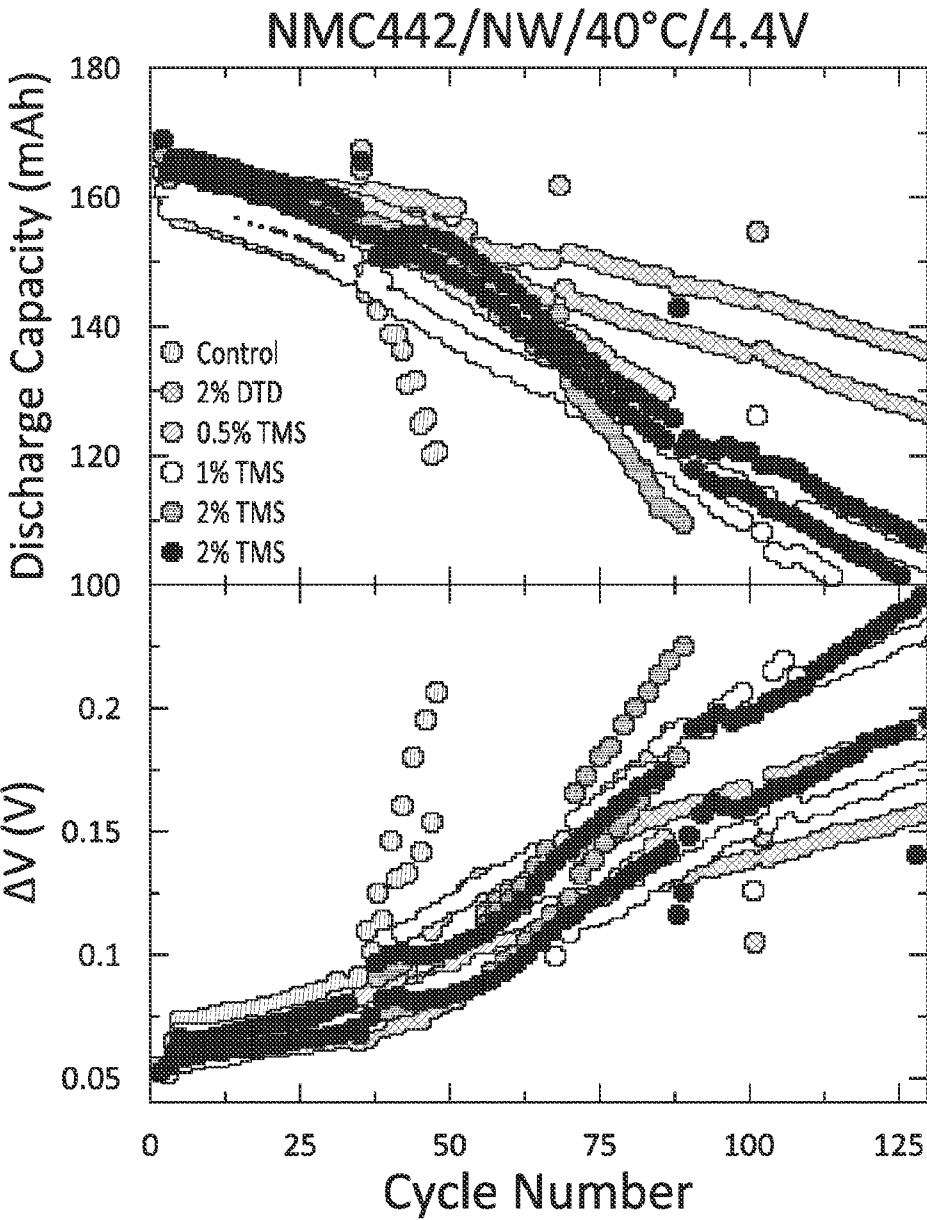


FIG. 18A

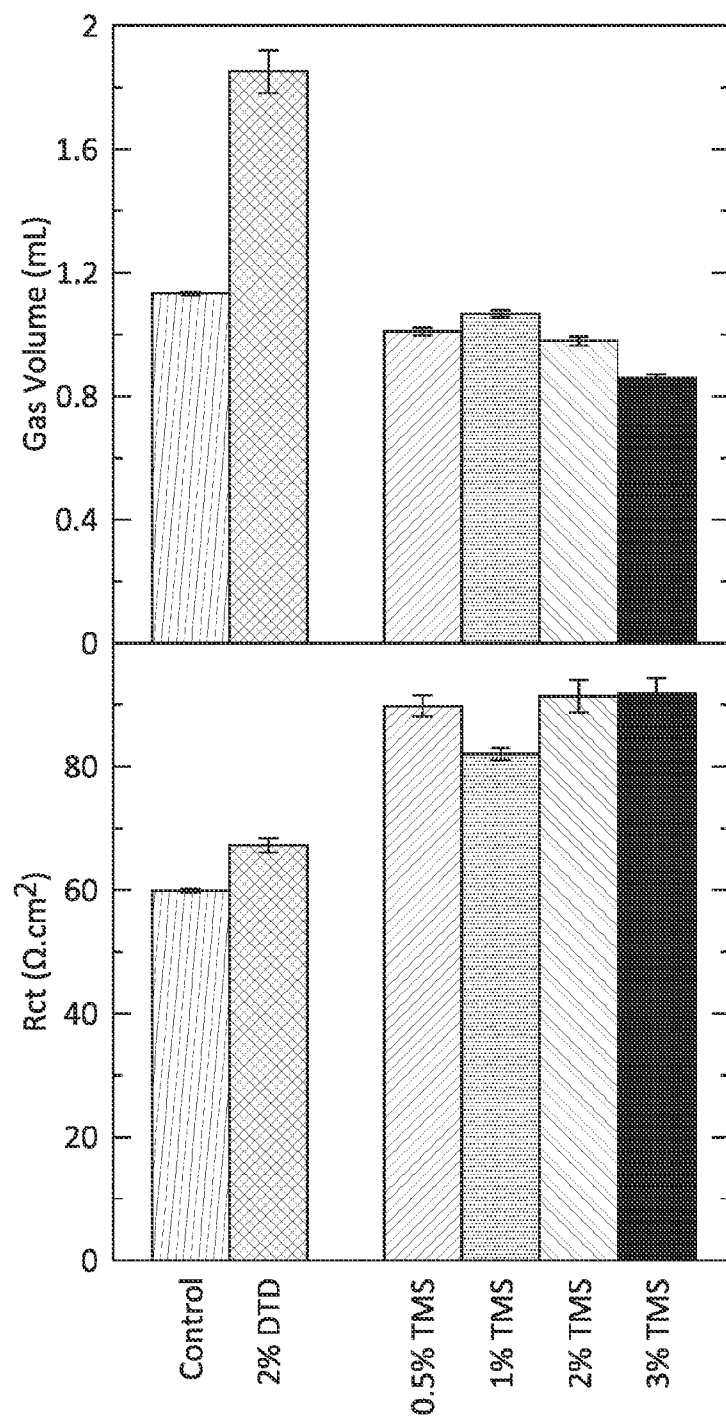


FIG. 18B

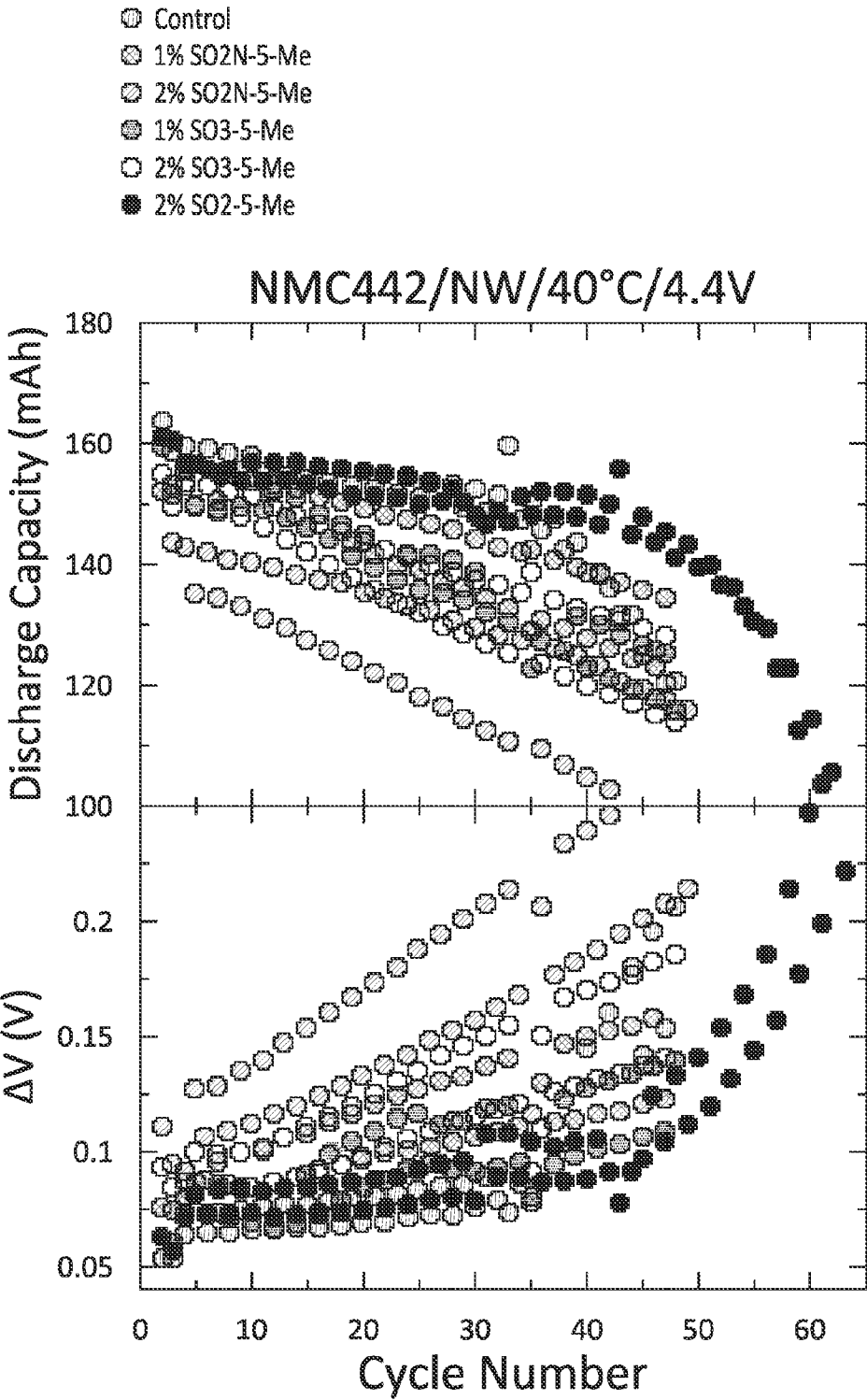


FIG. 19A

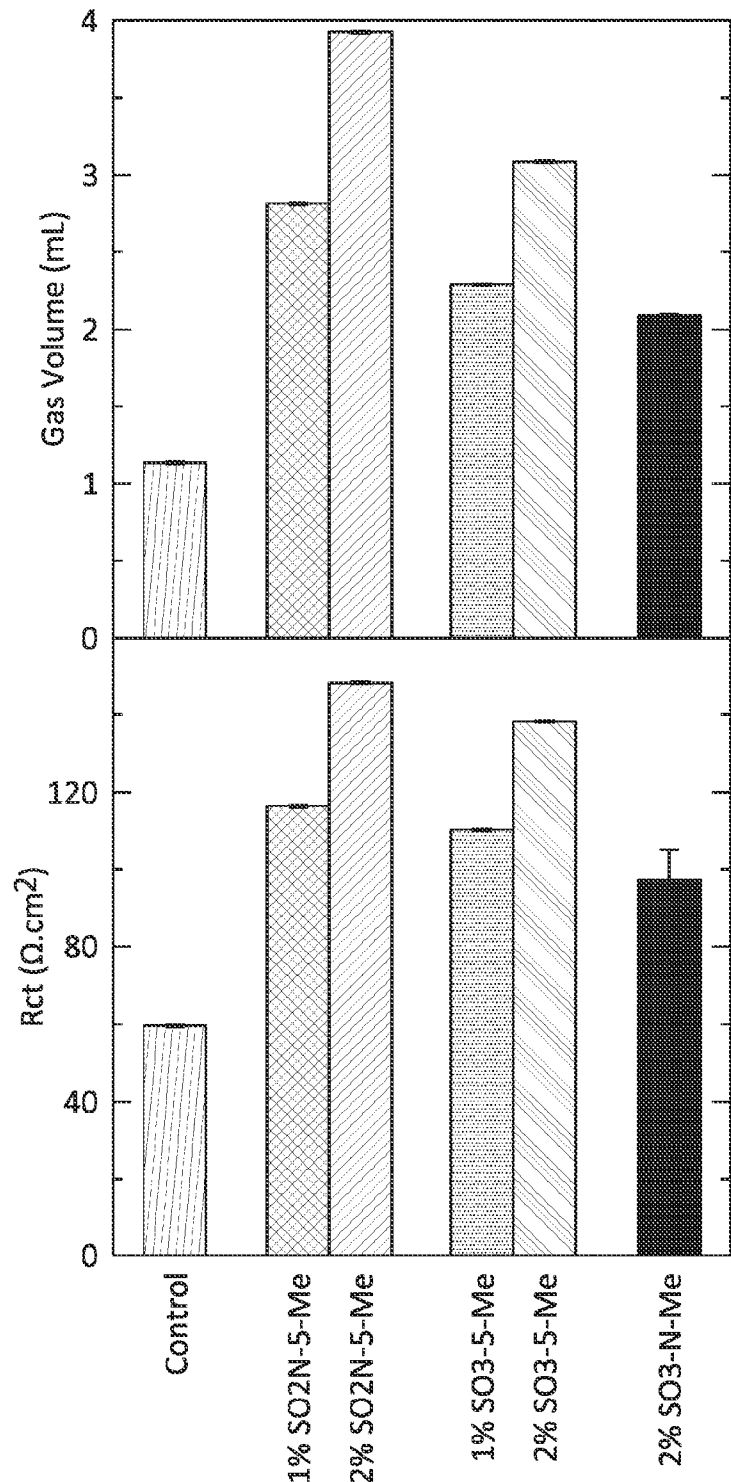


FIG. 19B

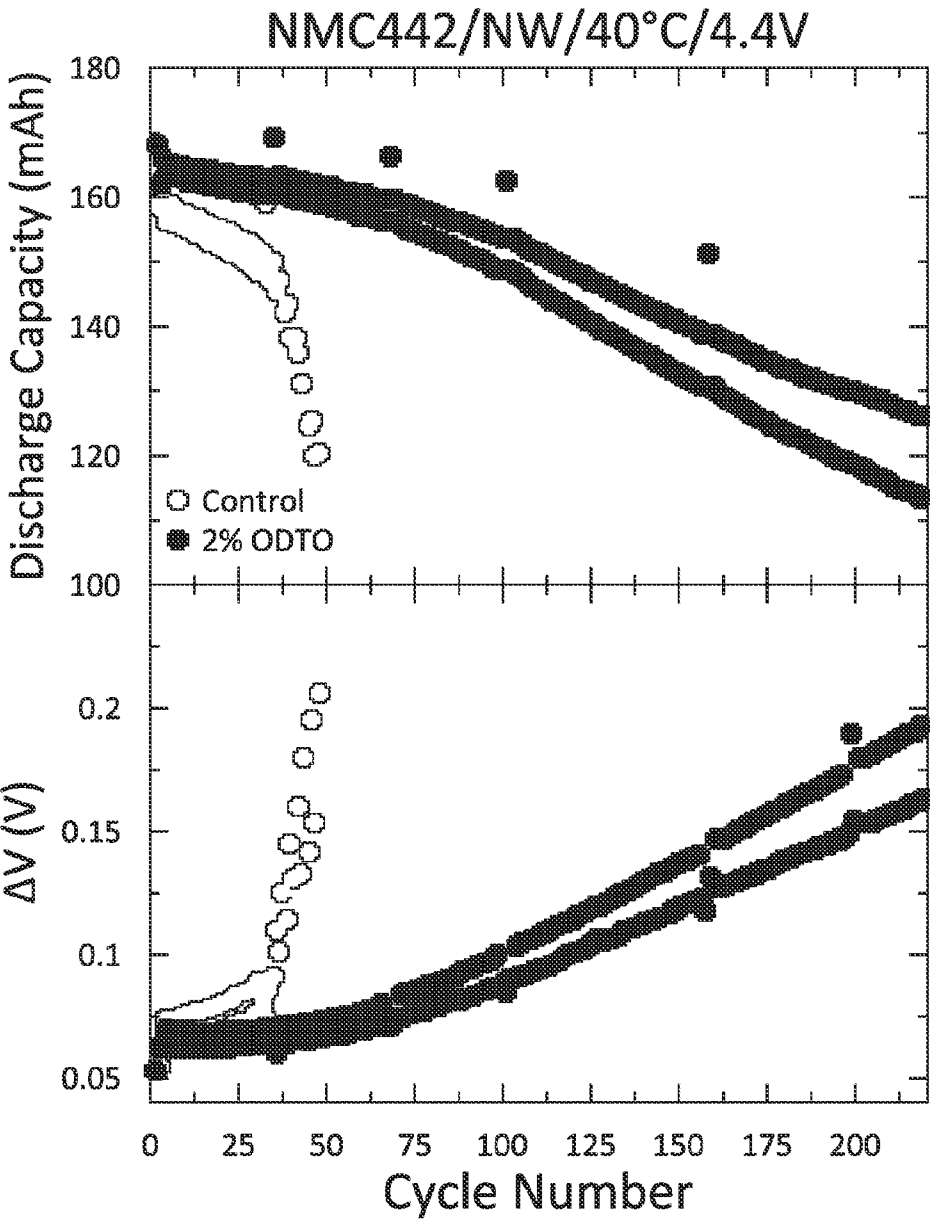


FIG. 20A

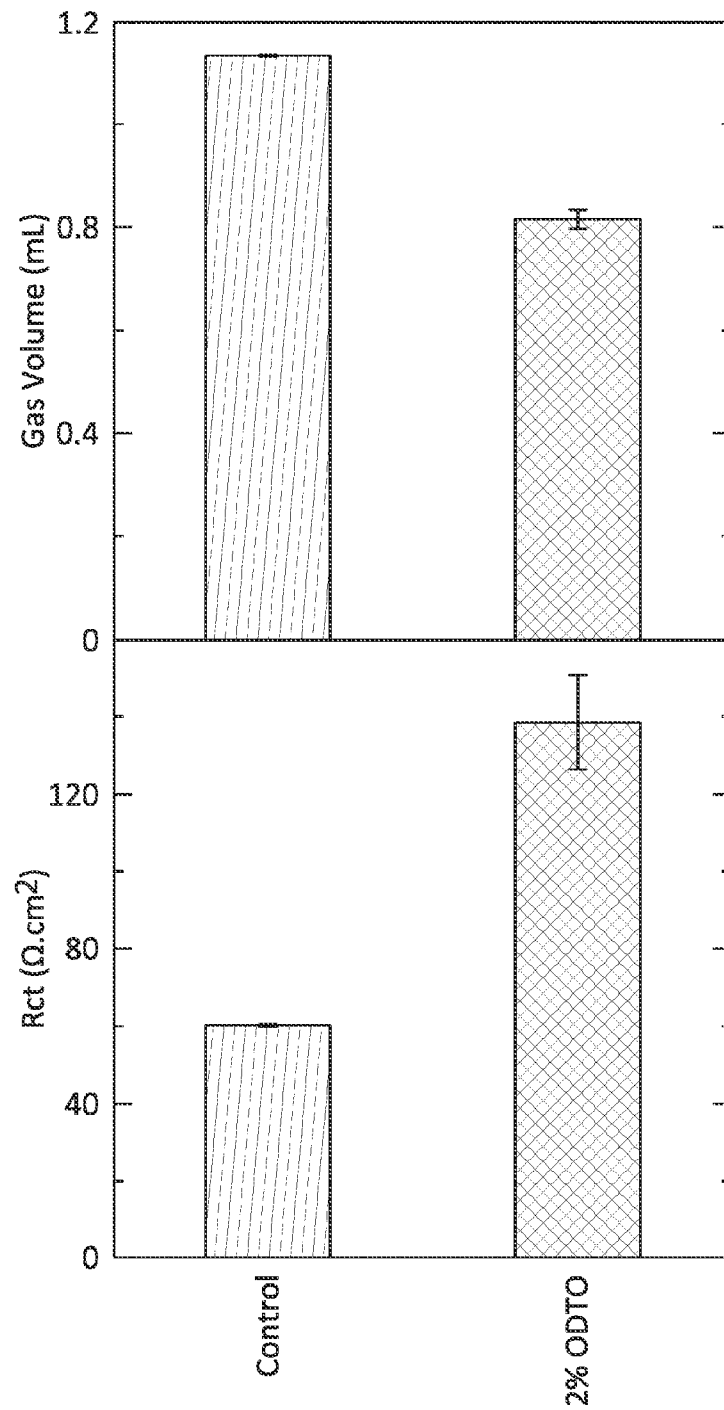


FIG. 20B

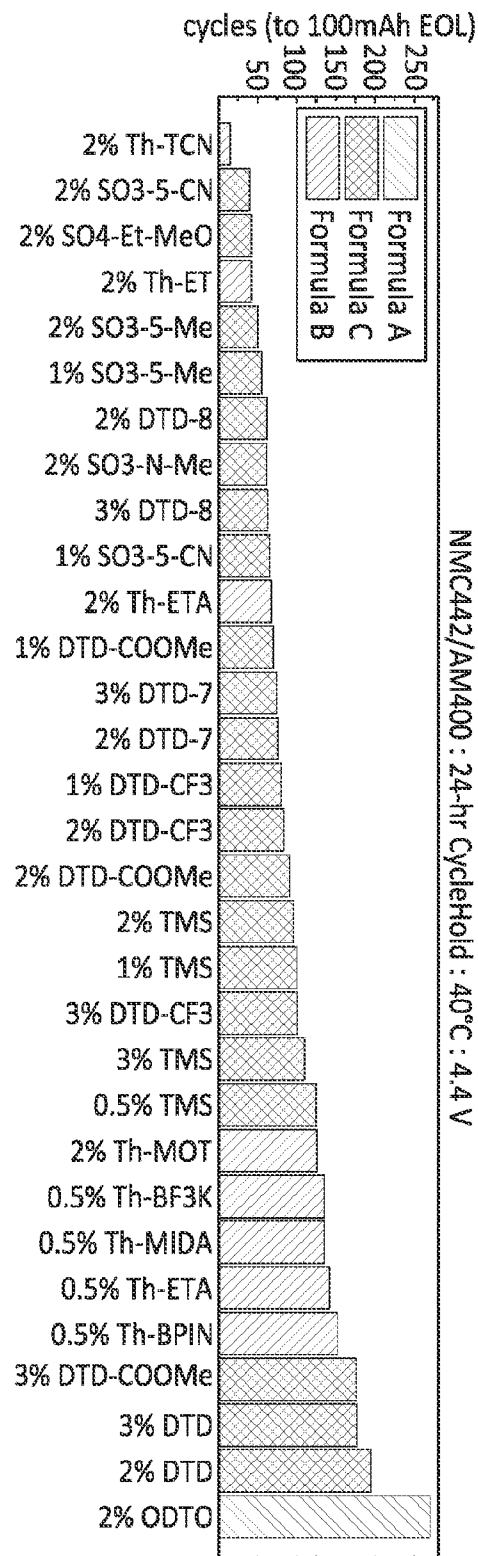


FIG. 21

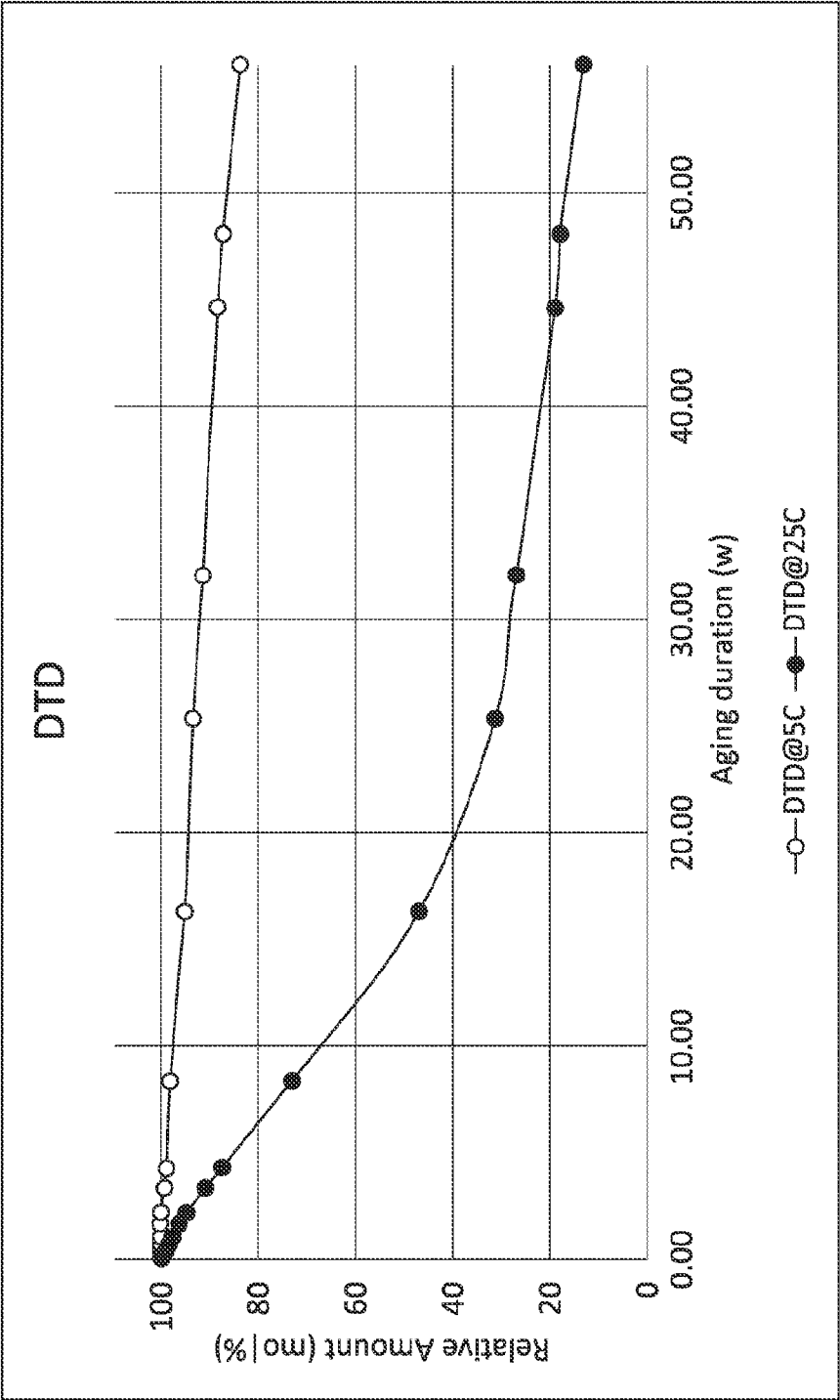


FIG. 22A

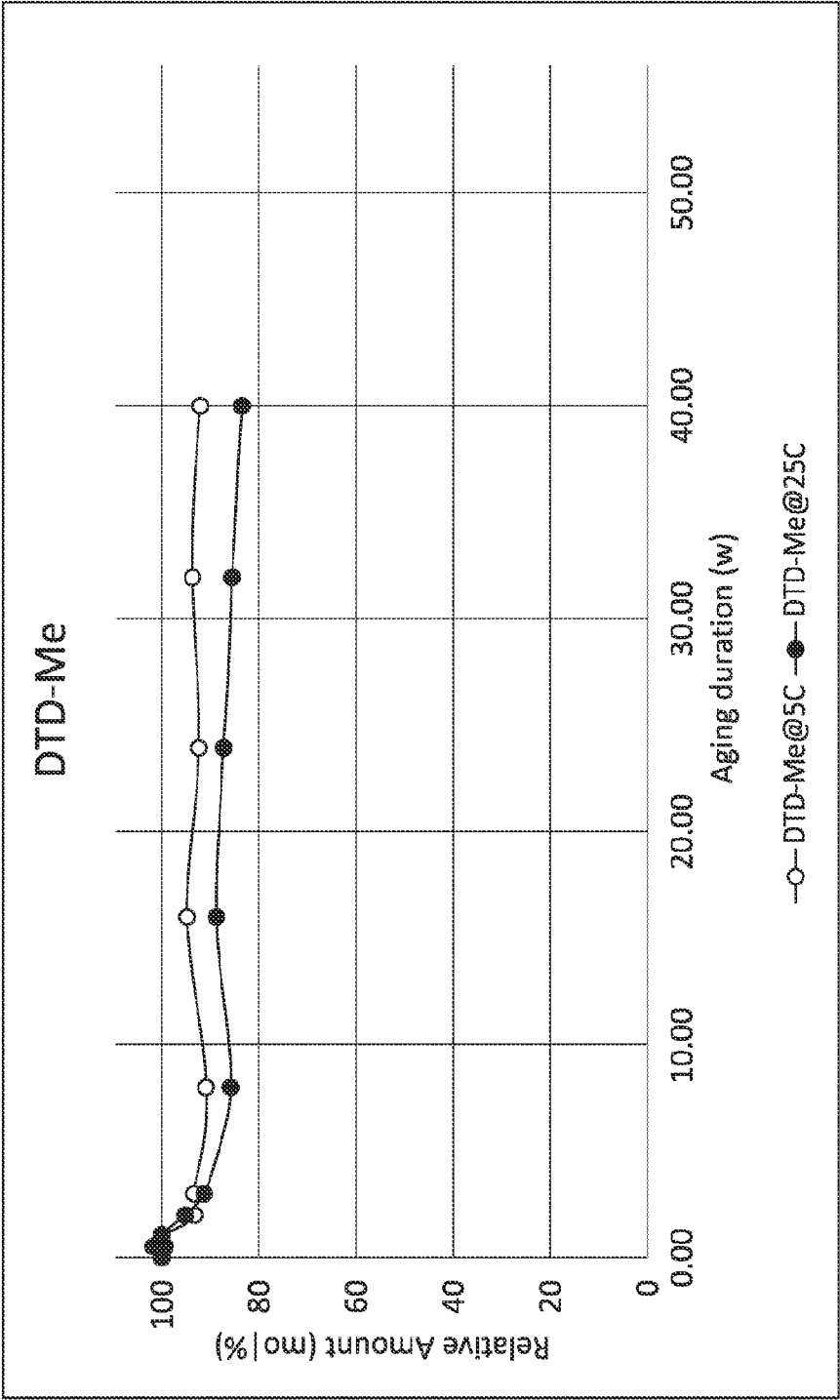


FIG. 22B

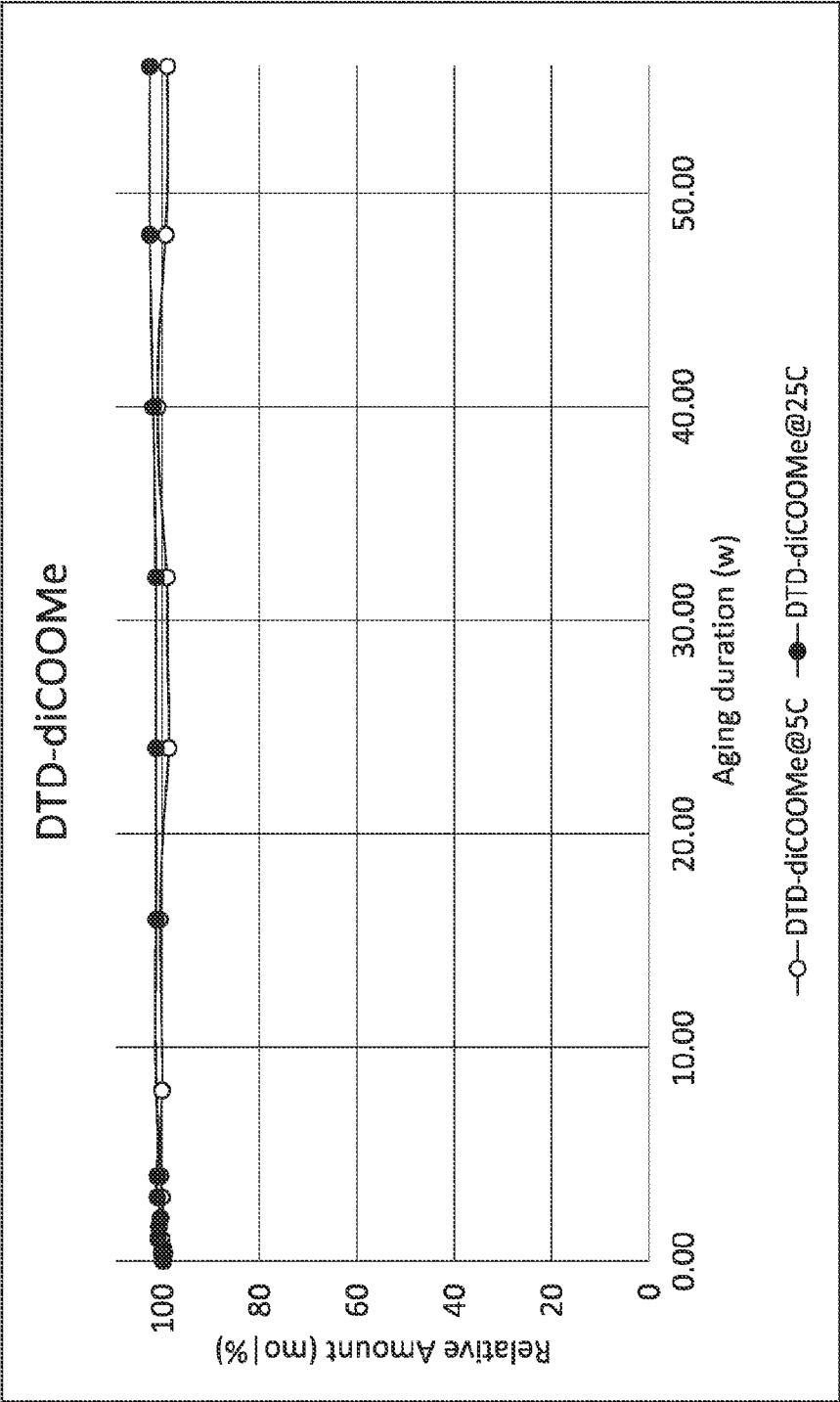


FIG. 22C

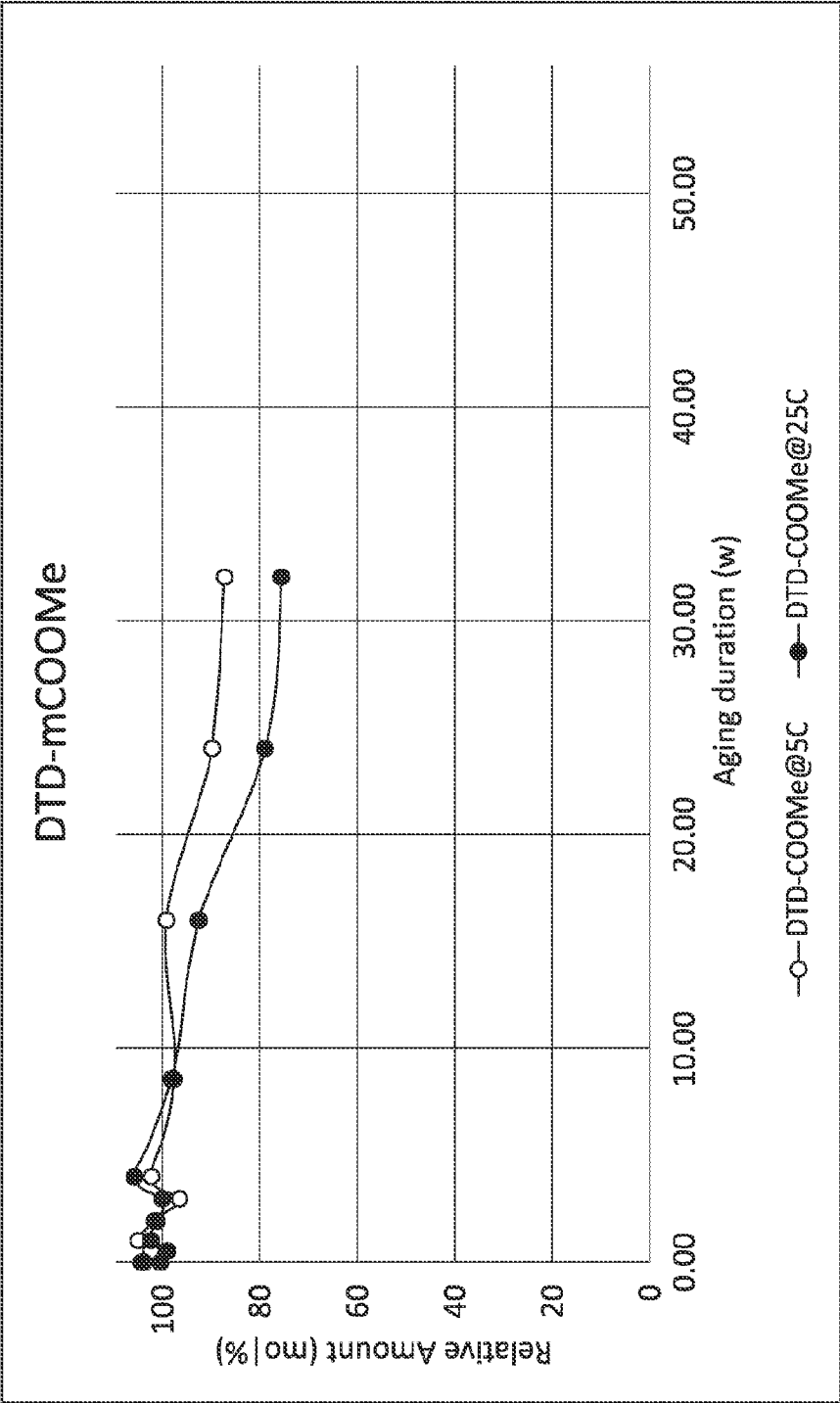


FIG. 22D

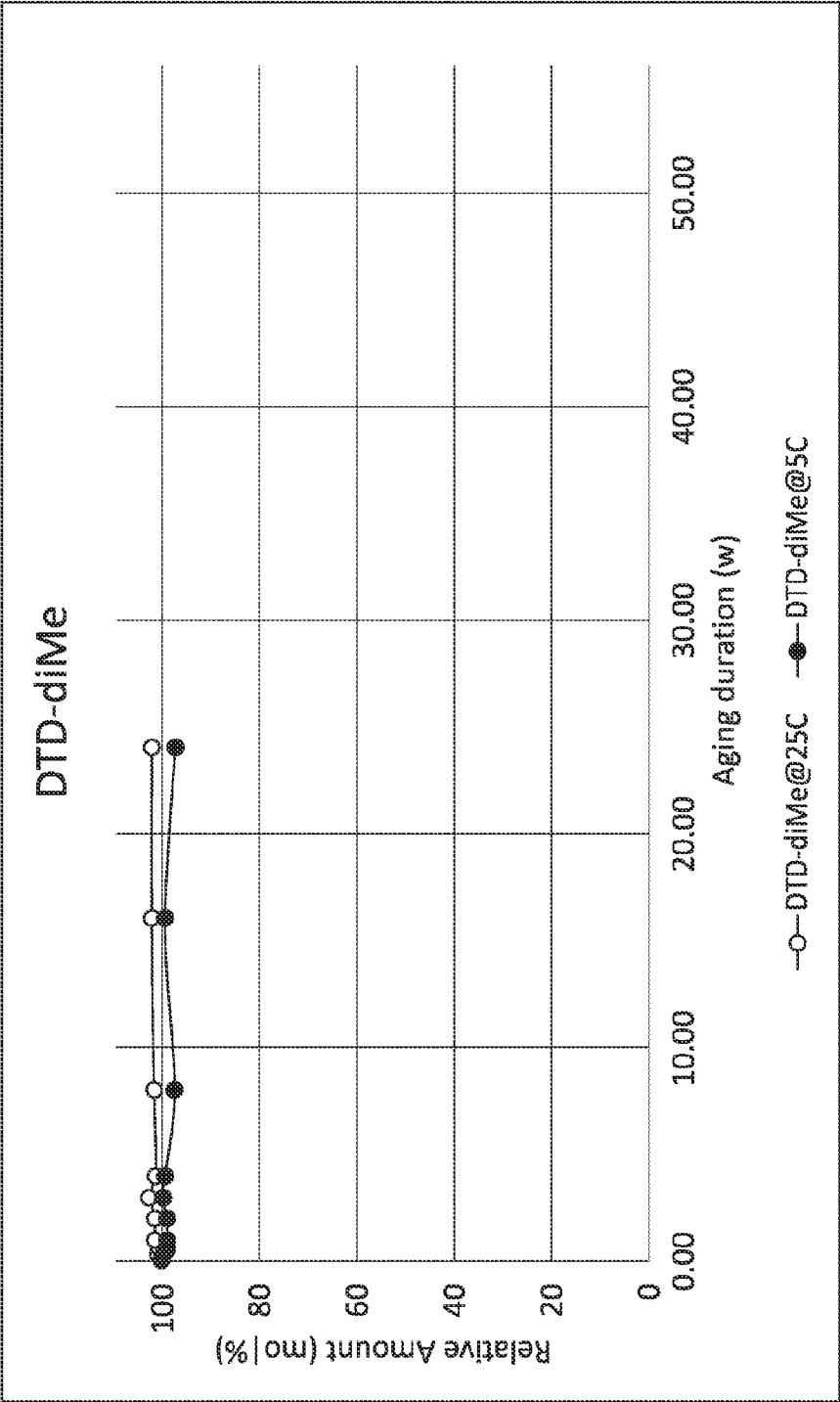


FIG. 22E

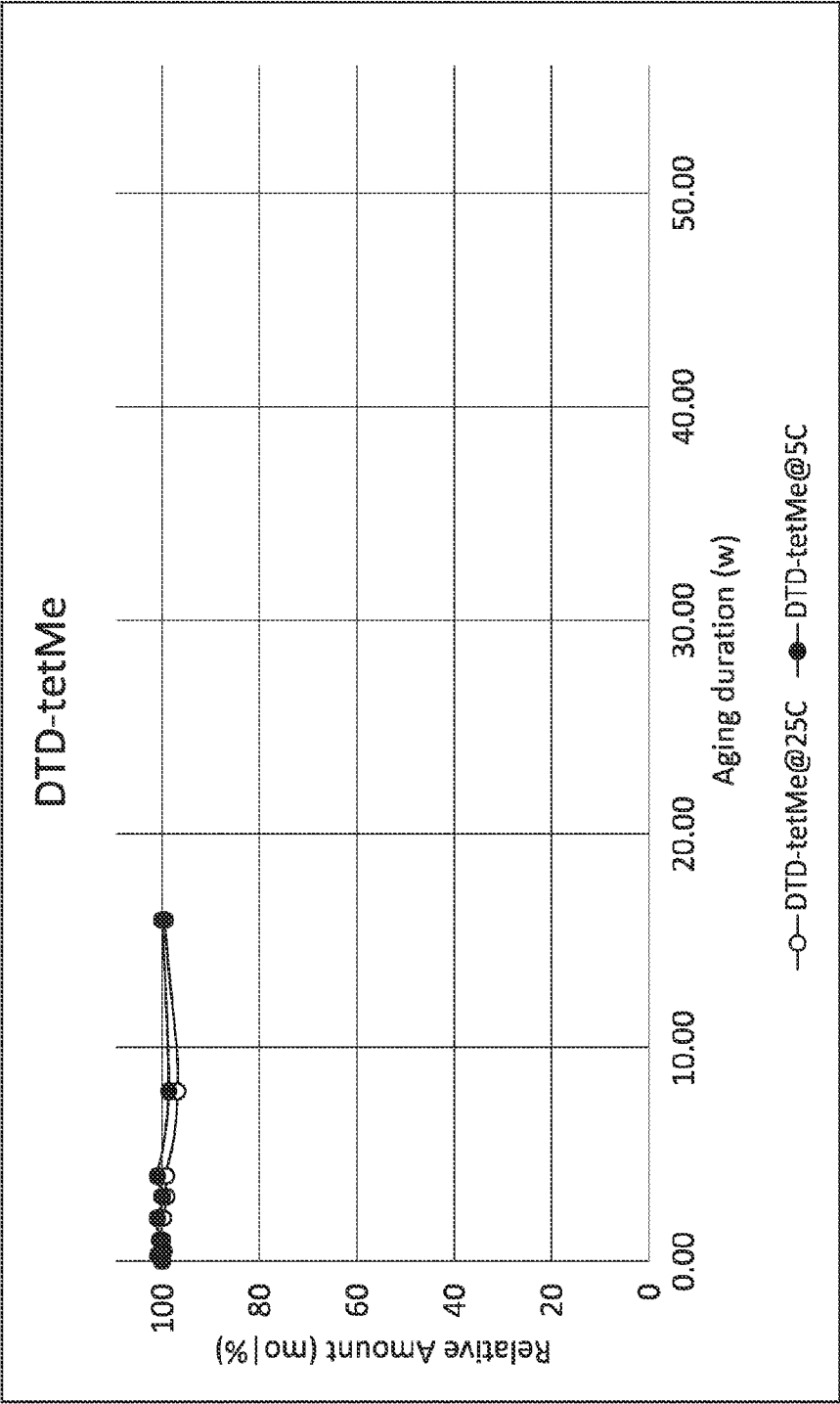


FIG. 22F

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2024/056465

A. CLASSIFICATION OF SUBJECT MATTER

INV. H01M10/0567 H01M10/0569

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

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	US 9 601 808 B2 (TDK CORP [JP]) 21 March 2017 (2017-03-21) example 12; table 1 column 2, line 27 - column 4, line 17 column 7, line 45 - column 8, line 62 -----	1, 2, 4, 12-14, 16-21
X	US 2017/317385 A1 (ZHANG ZHENGHUA [CN] ET AL) 2 November 2017 (2017-11-02) claims 1-2 paragraph [0114] -----	1, 2, 4, 18-21
X	US 11 108 086 B2 (UCHICAGO ARGONNE LLC [US]) 31 August 2021 (2021-08-31) claim 1; figures 4, 6, 7, 9; examples 1-4 column 1, line 10 - line 55 -----	1, 2, 4, 5, 7, 13-15, 18-21



Further documents are listed in the continuation of Box C.



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

25 January 2025

Date of mailing of the international search report

31/03/2025

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2

NL - 2280 HV Rijswijk

Tel. (+31-70) 340-2040,

Fax: (+31-70) 340-3016

Authorized officer:

Agra-Gutierrez, C

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2024/056465

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.:
12-21 (completely); 1, 2, 4, 5, 7 (partially)

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.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2024/056465

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 9601808	B2	21-03-2017	CN 103367807 A	23-10-2013
			JP 5664685 B2	04-02-2015
			JP 2013229307 A	07-11-2013
			US 2013260261 A1	03-10-2013

US 2017317385	A1	02-11-2017	US 2017317385 A1	02-11-2017
			WO 2016095116 A1	23-06-2016

US 11108086	B2	31-08-2021	NONE	

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

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

1. claims: 12-21(completely); 1, 2, 4, 5, 7(partially)

Electrolyte composition comprising a solvent, a salt, and an additive selected from a substituted glycol cyclic sulfate (alkylene or cyclic sulfate), as defined by formula (A) of claim 1 with A, X 1 and X2 = O and R1 to R5 defined as in claims 1-2, 4, 5, 7, and 12-17 and the corresponding energy storage devices of claims 18-21.

2. claims: 12-21(completely); 1-3, 5, 6(partially)

Electrolyte composition comprising a solvent, a salt, and an additive selected from a substituted glycol cyclic sulfite (alkylene or cyclic sulfite), as defined by formula (A) of claim 1 with A=absent, X 1 and X2 = O and R1 to R5 defined as in claims 1-3, 5-6, and 12-17 and the corresponding energy storage devices of claims 18-21.

3. claims: 12-21(completely); 1, 2, 4, 5, 7(partially)

Electrolyte composition comprising a solvent, a salt, and an additive selected from is a substituted amidated sulfate, as defined by formula (A) of claim 1 with A=O and with at least one of X1 or X2 being N and the other one O, or both X1 and X2 being N, and R1 to R5 defined as in claims 1-2, 4, 5, 7, and 12-17 and the corresponding energy storage devices of claims 18-21.

4. claims: 12-21(completely); 1-3, 5, 6(partially)

Electrolyte composition comprising a solvent, a salt, and an additive selected from a heterocyclic compound comprising sulfur is a substituted amidated sulfite, as defined by formula (A) of claim 1 with A=O, with at least one of X1 or X2 being N and the other one O, or both X1 and X2 being N, and R1 to R5 defined as in claims 1-3, 5-6, and 12-17 and the corresponding energy storage devices of claims 18-21.

5. claims: 8, 9, 12-21(completely); 1(partially)

Electrolyte composition comprising a solvent, a salt, and an additive selected from a substituted thiophene, as defined by formula (B) of claim 1 with R 8a to R9b defined as in claims 1, 8-9, and 12-17 and the corresponding energy storage devices of claims 18-21.

6. claims: 10-21(completely); 1(partially)

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Electrolyte composition comprising a solvent, a salt, and an additive selected from a substituted cyclic compound having the moiety: cyclic $-(R^{11}R^{12})C-S(=O)_2-O-S(=O)_2-R^{10}(R^{13}R^{14})-$, as defined by formula (C) of claim 1 with R¹⁰ to R¹⁴ defined as in claims 1, and 10-17, 12-17 and the corresponding energy storage devices of claims 18-21.
