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(54) Title: FLUORINATED SULFONAMIDE-BASED ELECTROLYTES FOR NON-LITHIUM BATTERIES THEREOF

(57) Abstract: Disclosed are compositions, electrolytes, electrochemical cells, and batteries comprising a halogenated sodium salt; a halogenated sulfonate; and a co-solvent.

FLUORINATED SULFONAMIDE-BASED ELECTROLYTES FOR NON-LITHIUM BATTERIES THEREOF

RELATED APPLICATIONS

This application claims the benefit of priority to U.S. Provisional Patent Application No. 63/514,181, filed July 18, 2023; the contents of which are hereby incorporated by reference in their entirety.

BACKGROUND

The commonly used electrolytes use strongly solvating solvents, which enhance the cation-dipole interaction and facilitate the formation of solvent-separated ion pairs (SSIPs) as shown in **Fig. 1A**, allowing solubility and high ion conductivity (*ACS Nano* **18**, 8350-8359 (2024)). Unfortunately, the free solvent molecules can be vulnerable to parasitic reactions with the electrode during cycling (*Chem* **9**, 2943-2955 (2023)). On the other hand, weakly solvating solvents allow the incorporation of anions within the first solvation sheath, contributing to the accumulation of contact-ion pairs (CIPs) and ion aggregates (AGGs) with higher electrochemical stability against sodium metal anodes and cathodes. This low solvation ability can cause insufficient salt solubility and limited cation conductivity, however, limiting practical cycling performance with current densities of $\geq$ 1 mA cm^{-2} (*Nat. Energy* **8**, 814-826 (2023)). Combining strongly and weakly solvating solvents can enable fine-tuning of the solvation ability to balance the salt association strength, which improves the cation conductivity without compromising electrochemical stability against sodium metal anodes and cathodes.

Compared with weakly solvating electrolytes (WSEs), high-concentration electrolytes (HCEs) and localized HCEs (LHCEs), there is a larger material space with higher degree of freedom to design hybrid solvating electrolytes (HSEs), since different types of hybrid solvents with varied ratios can be explored (**Fig. 1B**). Therefore, optimization of key electrochemical parameters, such as CE and overpotential, can be achieved by fast initial screening and subsequent fine-tuning.

SUMMARY OF THE INVENTION

In one aspect, the present disclosure provides compositions comprising: a halogenated sodium salt; a halogenated sulfonate; and a co-solvent.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGs. 1A & 1B. shows the preparation of DMTMSA-based electrolytes with (a) sodium bis(trifluoromethylsulfonyl)imide (NaTFSI) salt and (b) sodium bis(fluorosulfonyl)imide (NaFSI) salt.

FIGs. 2A & 2B. shows the Coulombic efficiency results of DMTMSA-contained electrolyte in Na-Cu cells. The blue and red curves show the result from duplicate trials. The Coulombic efficiency at the stable region reaches >99%.

FIGs. 3A-3C. shows a comparison of voltage profiles and Coulombic efficiency among (a) the commercial carbonate electrolytes and (b-c) DMTMSA-contained electrolytes in Na-Cu cells.

FIGs. 4A-4D. shows a comparison of (a) discharge capacity and (b-d) voltage profiles among the commercial carbonate electrolytes and DMTMSA-contained electrolytes in Na-NMO cells.

FIGs. 5A & 5B. shows the voltage profiles of DMTMSA-contained electrolyte in Na-Cu cells. (a) and (b) show the result from duplicate trials.

FIG. 6. shows Raman spectra of NaFSI and DMTMSA-contained electrolytes without other additives. Optical images of the white precipitation formed directly between NaFSI and DMTMSA without addition of other additives. Blue-shifts (6~8 cm^{-1}) of the Raman bands reflect the electron density changes around NaFSI, indicating DMTMSA coordination and complex formation between NaFSI and DMTMSA.

FIGs. 7A & 7B. Shows a comparison of Coulombic efficiency among recent literature and DMTMSA-contained electrolytes. The round and square points show the testing results without and with current collector modification, respectively. The star shows our result without current collector modification.

FIGs. 8A-8D. shows the design concept of hybrid solvating electrolytes**. a,** Comparison between strongly and weakly solvating electrolytes, and design of hybrid solvating electrolytes combined with strongly and weakly solvating solvents. **b,** Scheme about the design space of hybrid solvating electrolytes. Components-properties relationships between THF ratio and **c,** cycling overpotential, and **d,** logarithm coulombic efficiency (LCE) for hybrid solvating electrolytes. WSE, weakly solvating electrolytes; HCE: high-concentration electrolyte; LHCE,

localized high-concentration electrolyte; LCE, low-concentration electrolyte. LCE = $-\log_{10}(1-CE)$.

FIGs. 9A-9G. shows the polarization curves of hybrid various solvating electrolytes. **a-g,** The hybrid solvating electrolytes use different molar ratios between DMTMSA and THF solvents in this example. The number followed by THF indicates the molar ratio of THF solvent. The same nomenclature is used below. For example, "DMTMSA/THF13" means the molar ratio of THF is 13% and therefore, DMTMSA accounts for 87%. The tests are carried out using Na||Cu half-cell at 1 mA cm^{-2} with the areal capacity of 1 mAh cm^{-2} for all the hybrid solvating electrolytes.

FIGs. 10A-10H. shows the components-properties relationships between THF ratio and CE_{Aur}**.** The CE_{Aur} reflects the value evaluated by modified Aurbach method using Na||Cu half-cell at 1 mA cm^{-2} with the areal capacity of 1 mAh cm^{-2}. $LCE_{Aur} = -\log_{10}(1-CE_{Aur})$.

FIG. 11. shows Aurbach method measurements of Na^0 coulombic efficiency. The current density was 1 mA cm^{-2}.

FIG. 12. shows the electrochemical oxidative stability of various electrolytes. The cell configuration was Na||stainless steel.

FIG. 13. shows the ionic conductivity of different electrolytes under various temperatures. The values indicated the activation energy.

FIGs. 14A & 14B. shows the viscosity of hybrid solvating electrolytes at different temperatures. **a**, The tests are carried out one day after the electrolyte preparation. **b**, The viscosity of hybrid solvating electrolytes after 24 days.

FIGs. 15A-15C. shows the electrochemical cycling performance of hybrid solvating electrolytes. **a-c,** Cycling performance of three parallel Na||Cu half cells at 1.0 mA cm^{-2} with the areal capacity of 1 mAh cm^{-2} using hybrid solvating electrolytes.

FIG. 16. shows the cycling performance of 1 m NaFSI DMTMSA/THF. The current density was 3.0 mA cm^{-2} and areal capacity was 1.0 mAh cm^{-2}.

FIG. 17. shows the electrochemical cycling performance using $Na_3V_2(PO_4)_3$ cathode. The areal capacity was 1.5 mAh cm^{-2} and the cycling rate was 0.2 C.

FIG. 18. shows the electrochemical cycling performance using $Na_{0.44}MnO_2$ cathode. The areal capacity was 1.0 mAh cm^{-2} and the cycling rate was 0.3 C.

FIG. 19. shows a comparison of electrochemical rate performance using $Na_3V_2(PO_4)_3$ cathode. The area capacity was 1.5 mAh cm^{-2}.

FIG. 20. shows electrochemical fast cycling performance using $Na_3V_2(PO_4)_3$ cathode. The area capacity was 1.0 mAh cm^{-2} and the cycling current density was 5.0 mA cm^{-2} (5.0 C).

FIGs. 21A-21C. shows microscopic characterization of hybrid solvating electrolytes. Top-view SEM images of Cu electrodes after 200 cycles using different electrolytes at plating stage. The scheme below describes the morphology features of electrochemically deposited Na^0. **a,** 1 m NaFSI in DMTMSA. **b,** 1 m NaFSI in DMTMSA and THF mixture. **c,** 1 m NaFSI in THF.

FIGs. 22A-22L. shows electrochemically deposited Na^0 microparticles labeled using computer vision method. **a, d,** Weakly solvating electrolyte. **b, e,** hybrid solvating electrolyte. **c, f,** Strongly solvating electrolyte. Distinct color area is used to label and distinguish different Na metal microparticles electrochemically deposited on the Cu current collectors. **g-l,** Statistically results about the particle area and perimeter of labeled electrochemically deposited Na0 microparticles. **g, j,** Weakly solvating electrolyte. **h, k,** hybrid solvating electrolyte. **i, l,** Strongly solvating electrolyte.

FIGs. 23A-23C. shows exemplary properties of hybrid solvating electrolytes. NMR spectra of **a,** ^{23}Na, **b,** ^{1}H and **c,** ^{19}F for hybrid solvating electrolytes with different molar ratios between DMTMSA and THF solvents.

FIG. 24. shows Raman results of different hybrid solvating electrolytes. The solvation structure analysis of hybrid solvating electrolytes with different molar ratios between

FIG. 25. Molecular snapshots and solvation structures of different electrolytes.

FIGs. 26A & 26B shows generalized strategy for hybrid solvating electrolytes. **a,** The general recipes of hybrid solvating electrolytes including various sodium salts (blue region), fluorinated sulfonated-based weak solvents (green region) and different types of co-solvents (orange region). **b,** The calculated minimum electrostatic potentials (ESP_{min}) of reported non-solvating diluents, fluorinated sulfonated-based weak solvents, and different types of co-solvents.

FIGs. 27A-27F. shows oxidative stability of various electrolytes. Hybrid solvating electrolytes with **a,** different sodium salts. **b,** different fluorinated sulfonate-based weakly solvating solvents. **c,** different types of strong solvating co-solvents, including fluorinated carbonate, ionic liquid, and partially fluorinated sulfonates. **d,** different types of acyclic ether-based strong solvating co-solvents. **e,** different strong and weak solvating electrolyte mixtures. **f,** Commercial carbonate electrolytes. The oxidation stability of various electrolytes was tested using NalSS half cells with scanning rate of 1 mV s^{-1}. SS, stainless steel.

FIGs. 28A-28F. shows Na^0 cycling stability of various electrolytes. Hybrid solvating electrolytes with **a,** different sodium salts. **b,** different fluorinated sulfonate-based weakly solvating solvents. **c-e,** different types of strong solvating co-solvents, including fluorinated

carbonate, ionic liquid, acyclic ether, and partially fluorinated sulfonates. **f,** different strong and weak solvating electrolyte mixtures.

FIGs. 29A-29I. shows Na^0 cycling stability of various hybrid solvating electrolytes. **a,** 1 m NaFSI DMTMSA/THF/[Pyr14][FSI]. **b,** 1 m NaFSI DMTMSA/DETMSA/Pyr-TMSA/Pip-TMSA/THF. **c,** 1 m NaFSI DETMSA/THF. **d,** 1 m NaFSI Pyr-TMSA/THF. **e,** 1 m NaFSI DMTMSA/FEC. **f,** 1 m NaFSI Pip-TMSA/THF. **g,** 1 m NaFSI Pip-TMSA/DME. **h,** 1 m NaFSI DMTMSA/THF/[Pyr14][FSI] (combination 2). **i,** 1 m NaFSI DMTMSA/DEE. **j,** 1 m NaFSI DMTMSA/Diglyme.

FIGs. 30A-30F. shows Na^0 cycling stability of various hybrid solvating electrolytes. Aurbach method measurement of Na^0 coulombic efficiency in NalCu half cells using different electrolytes.

FIG. 31 shows generalized strategy for hybrid solvating electrolytes. The stability against Na^0 anode and oxidative stability for different types of hybrid solvating electrolytes.

DETAILED DESCRIPTION OF THE INVENTION

This disclosure describes a series of novel electrolytes with fluorinated sulfonamide as the components, such as N,N-dimethyltrifluoromethane sulfonamide (DMTMSA) and its derivatives, including but not limited to ethyl-, morpholine-, piperidine-, pyrrolidine-substituted compounds. These electrolytes demonstrate superior electrochemical performance, outperforming the commercial carbonate electrolytes and advanced electrolytes reported in recent literature. (*Adv. Funct. Mater.* **2023**, 33, 2214195., *Adv. Energy Mater.* **2023**, 13, 2204125., *ACS Energy Lett.* **2018**, 3, 315–321., *Small* **2022**, 18, 2203409.) Compared with the commercial carbonate electrolytes and other advanced electrolytes reported in recent years (*Adv. Funct. Mater.* **2023**, 33, 2214195., *Adv. Energy Mater.* **2023**, 13, 2204125., *ACS Energy Lett.* **2018**, 3, 315–321., *Small* **2022**, 18, 2203409.), DMTMSA-contained electrolytes show lower overpotential during cycling (~53 mV at 1 mA cm^{-2}), more stable cycling (negligible polarization buildup after 400 h-cycling), and higher Coulombic efficiency (>99% at 1 mA cm^{-2}) in Na-Cu cell tests. These improvements are related to the contact ion pairs (CIP), and aggregate (AGG) species in the DMTMSA-contained electrolytes. The electrochemical performance has the potential to be further improved by the surface modification of current collector (*Small* **2022**, 18, 2203409).

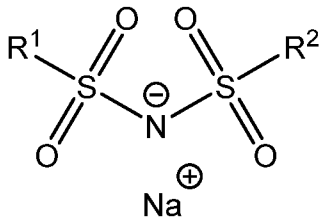
The sulfonamide-based solvent represents a unique and substantial improvement to both sodium-ion and -metal battery technologies. When synergistically combined with sodium salts such as sodium hexafluorophosphate and/or sodium bis(fluorosulfonyl)imide, the results

are electrolytes demonstrating marked improvements in performance, stability, and cyclability, distinguishing them from currently available solutions.

In one aspect, the present disclosure provides a composition, comprising:

a halogenated sodium salt; a halogenated sulfonate; and a co-solvent.

In certain embodiments, the halogenated sodium salt is a fluorinated sodium salt. In certain embodiments, the fluorinated sodium salt has a structure represented by formula I:



I

wherein

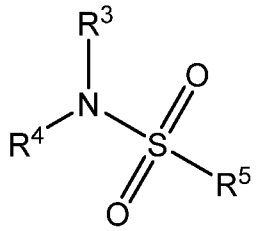
R^1 and R^2 are each independently fluoro or fluoroalkyl.

In certain embodiments, R^2 is fluoro. In other embodiments, R^2 is fluoroalkyl.

In certain embodiments, R^2 is fluoro. In other embodiments, R^2 is fluoroalkyl.

In certain preferred embodiments, the halogenated sodium salt is NFSI. In other embodiments, the halogenated sodium salt is NaFTFSI. In yet other embodiments, the halogenated sodium salt is NaTFSI. In yet other embodiments, the halogenated sodium salt is $NaPF_6$.

In certain embodiments, the halogenated sulfonate is a fluorinated sulfonate. In certain embodiments, the halogenated sulfonate has a structure represented by formula II:



II

wherein

R^3 and R^4 are each independently alkyl, aryl, cycloalkyl, or arakyl; or R^3 and R^4 combine with the intervening nitrogen atom to form a heterocyclyl; and

R^5 is fluoroalkyl.

In certain embodiments, R^3 is alkyl (*e.g.,* methyl or ethyl).

In certain embodiments, R^4 is alkyl (*e.g.,* methyl or ethyl).

In certain embodiments, R^3 and R^4 combine with the intervening nitrogen atom to form a heterocyclyl (*e.g.,* pyrrolidinyl, piperidinyl, or morpholinyl).

In certain embodiments, the co-solvent is an organic co-solvent. In certain embodiments, the organic co-solvent is an ethereal solvent (*e.g.,* THF, diglyme, 1-methoxy-2-(2-methoxyethoxy)ethane, dimethyl ether, or tetraethylene glycol dimethyl ether). In certain preferred embodiments the organic co-solvent is THF. In certain embodiments, the organic co-solvent comprises THF, [Pyr14][FSI], FEC, or TM; or a mixture of any of the foregoing.

In certain embodiments, the molar ratio of the halogenated sulfonate:co-solvent is about 1:1, about 2:1, about 3:1, about 4:1, about 5:1, about 6:1, about 7:1, or about 8:1.

In another aspect, the present disclosure provides electrolytes comprising the compositions disclosed herein.

In yet another aspect, the present disclosure provides electrochemical cells comprising the electrolytes disclosed herein. In certain embodiments, the cell comprises sodium. In certain embodiments, the electrochemical cell comprises copper. In certain embodiments, the coulombic efficiency (CE) of the electrochemical cell is greater than about 98%. In certain embodiments, the coulombic efficiency (CE) of the electrochemical cell is greater than about 99%.

In yet another aspect, the present disclosure provides batteries comprising the electrolytes or electrochemical cells disclosed herein. In certain embodiments, the battery is not a lithium battery. In certain embodiments, the battery is a barium, calcium, sodium, magnesium, or aluminum battery. In certain preferred embodiments, the battery is a sodium battery. In certain preferred embodiments, the battery comprises a sodium cathode (*e.g.,* $Na_3V_2(PO_4)_3$ or $Na_{0.44}MnO_2$).

In yet another aspect, the present disclosure provides a non-lithium battery comprising

$R^1–S(=O)_2–NR^2R^3$, wherein

i. R^1 is trifluoromethane, and

ii. R^2 and R^3 are the same or different and are selected from the group consisting of alkyl-, morpholine-, piperidine-, and pyrrolidine.

In certain embodiments, the disclosed non-lithium battery further comprises a salt or a metal, wherein the salt or metal is selected from the group consisting of barium, calcium, sodium, magnesium, and aluminum. In certain embodiments, R^2 and R^3 are the same or different and comprise an alkyl selected from methyl, ethyl, propyl, or butyl. In certain

embodiments, the battery comprises N,N-dimethyltrifluoromethane sulfonamide (DMTMSA). In certain embodiments, the battery further comprises sodium bis(fluorosulfonyl)imide (NaFSI). In certain embodiments, the battery further comprises sodium bis(trifluoromethylsulfonyl)imide (NaTFSI) salt. In certain embodiments, the battery comprises a Na-Cu cell. In certain embodiments, the Coulombic efficiency is greater than 80%, 85% 90%, 95%, or 99%.

Definitions

Unless otherwise defined herein, scientific and technical terms used in this application shall have the meanings that are commonly understood by those of ordinary skill in the art. Generally, nomenclature used in connection with, and techniques of, chemistry described herein, are those well-known and commonly used in the art.

Chemistry terms used herein, unless otherwise defined herein, are used according to conventional usage in the art, as exemplified by "The McGraw-Hill Dictionary of Chemical Terms", Parker S., Ed., McGraw-Hill, San Francisco, C.A. (1985).

All of the above, and any other publications, patents and published patent applications referred to in this application are specifically incorporated by reference herein. In case of conflict, the present specification, including its specific definitions, will control.

As used herein, the terms "optional" or "optionally" mean that the subsequently described event or circumstance may occur or may not occur, and that the description includes instances where the event or circumstance occurs as well as instances in which it does not. For example, "optionally substituted alkyl" refers to the alkyl may be substituted as well as where the alkyl is not substituted.

It is understood that substituents and substitution patterns on the compounds of the present invention can be selected by one of ordinary skilled person in the art to result chemically stable compounds which can be readily synthesized by techniques known in the art, as well as those methods set forth below, from readily available starting materials. If a substituent is itself substituted with more than one group, it is understood that these multiple groups may be on the same carbon or on different carbons, so long as a stable structure results.

As used herein, the term "optionally substituted" refers to the replacement of one to six hydrogen radicals in a given structure with the radical of a specified substituent including, but not limited to: hydroxyl, hydroxyalkyl, alkoxy, halogen, alkyl, nitro, silyl, acyl, acyloxy, aryl, cycloalkyl, heterocyclyl, amino, aminoalkyl, cyano, haloalkyl, haloalkoxy, -OCO-CH_2-O-alkyl, -OP(O)(O-alkyl)$_2$ or –CH_2-OP(O)(O-alkyl)$_2$. Preferably, "optionally substituted" refers

to the replacement of one to four hydrogen radicals in a given structure with the substituents mentioned above. More preferably, one to three hydrogen radicals are replaced by the substituents as mentioned above. It is understood that the substituent can be further substituted.

As used herein, the term "alkyl" refers to saturated aliphatic groups, including but not limited to C_1-C_{10} straight-chain alkyl groups or C_1-C_{10} branched-chain alkyl groups. Preferably, the "alkyl" group refers to C_1-C_6 straight-chain alkyl groups or C_1-C_6 branched-chain alkyl groups. Most preferably, the "alkyl" group refers to C_1-C_4 straight-chain alkyl groups or C_1-C_4 branched-chain alkyl groups. Examples of "alkyl" include, but are not limited to, methyl, ethyl, 1-propyl, 2-propyl, n-butyl, sec-butyl, tert-butyl, 1-pentyl, 2-pentyl, 3-pentyl, neo-pentyl, 1-hexyl, 2-hexyl, 3-hexyl, 1-heptyl, 2-heptyl, 3-heptyl, 4-heptyl, 1-octyl, 2-octyl, 3-octyl or 4-octyl and the like. The "alkyl" group may be optionally substituted.

The term "acyl" is art-recognized and refers to a group represented by the general formula hydrocarbylC(O)-, preferably alkylC(O)-.

The term "acylamino" is art-recognized and refers to an amino group substituted with an acyl group and may be represented, for example, by the formula hydrocarbylC(O)NH-.

The term "acyloxy" is art-recognized and refers to a group represented by the general formula hydrocarbylC(O)O-, preferably alkylC(O)O-.

The term "alkoxy" refers to an alkyl group having an oxygen attached thereto. Representative alkoxy groups include methoxy, ethoxy, propoxy, tert-butoxy and the like.

The term "alkoxyalkyl" refers to an alkyl group substituted with an alkoxy group and may be represented by the general formula alkyl-O-alkyl.

The term "alkyl" refers to saturated aliphatic groups, including straight-chain alkyl groups, branched-chain alkyl groups, cycloalkyl (alicyclic) groups, alkyl-substituted cycloalkyl groups, and cycloalkyl-substituted alkyl groups. In preferred embodiments, a straight chain or branched chain alkyl has 30 or fewer carbon atoms in its backbone (e.g., C_{1-30} for straight chains, C_{3-30} for branched chains), and more preferably 20 or fewer.

Moreover, the term "alkyl" as used throughout the specification, examples, and claims is intended to include both unsubstituted and substituted alkyl groups, the latter of which refers to alkyl moieties having substituents replacing a hydrogen on one or more carbons of the hydrocarbon backbone, including haloalkyl groups such as trifluoromethyl and 2,2,2-trifluoroethyl, etc.

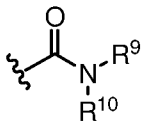
The term "C_{x-y}" or "C_x-C_y", when used in conjunction with a chemical moiety, such as, acyl, acyloxy, alkyl, alkenyl, alkynyl, or alkoxy is meant to include groups that contain from x to y carbons in the chain. C_0alkyl indicates a hydrogen where the group is in a terminal position,

a bond if internal. A $C_{1\text{-}6}$alkyl group, for example, contains from one to six carbon atoms in the chain.

The term "alkylamino", as used herein, refers to an amino group substituted with at least one alkyl group.

The term "alkylthio", as used herein, refers to a thiol group substituted with an alkyl group and may be represented by the general formula alkylS-.

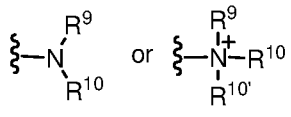
The term "amido", as used herein, refers to a group



,

wherein R^9 and R^{10} each independently represent a hydrogen or hydrocarbyl group, or R^9 and R^{10} taken together with the N atom to which they are attached complete a heterocycle having from 4 to 8 atoms in the ring structure.

The terms "amine" and "amino" are art-recognized and refer to both unsubstituted and substituted amines and salts thereof, e.g., a moiety that can be represented by



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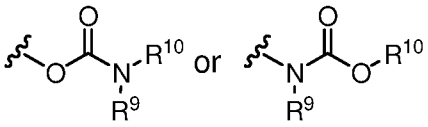
wherein R^9, R^{10}, and $R^{10'}$ each independently represent a hydrogen or a hydrocarbyl group, or R^9 and R^{10} taken together with the N atom to which they are attached complete a heterocycle having from 4 to 8 atoms in the ring structure.

The term "aminoalkyl", as used herein, refers to an alkyl group substituted with an amino group.

The term "aralkyl", as used herein, refers to an alkyl group substituted with an aryl group.

The term "aryl" as used herein include substituted or unsubstituted single-ring aromatic groups in which each atom of the ring is carbon. Preferably the ring is a 5- to 7-membered ring, more preferably a 6-membered ring. The term "aryl" also includes polycyclic ring systems having two or more cyclic rings in which two or more carbons are common to two adjoining rings wherein at least one of the rings is aromatic, e.g., the other cyclic rings can be cycloalkyls, cycloalkenyls, cycloalkynyls, aryls, heteroaryls, and/or heterocyclyls. Aryl groups include benzene, naphthalene, phenanthrene, phenol, aniline, and the like.

The term "carbamate" is art-recognized and refers to a group



wherein R^9 and R^{10} independently represent hydrogen or a hydrocarbyl group.

The term "carbocyclylalkyl", as used herein, refers to an alkyl group substituted with a carbocycle group.

The term "carbocycle" includes 5-7 membered monocyclic and 8-12 membered bicyclic rings. Each ring of a bicyclic carbocycle may be selected from saturated, unsaturated and aromatic rings. Carbocycle includes bicyclic molecules in which one, two or three or more atoms are shared between the two rings. The term "fused carbocycle" refers to a bicyclic carbocycle in which each of the rings shares two adjacent atoms with the other ring. Each ring of a fused carbocycle may be selected from saturated, unsaturated and aromatic rings. In an exemplary embodiment, an aromatic ring, e.g., phenyl, may be fused to a saturated or unsaturated ring, e.g., cyclohexane, cyclopentane, or cyclohexene. Any combination of saturated, unsaturated and aromatic bicyclic rings, as valence permits, is included in the definition of carbocyclic. Exemplary "carbocycles" include cyclopentane, cyclohexane, bicyclo[2.2.1]heptane, 1,5-cyclooctadiene, 1,2,3,4-tetrahydronaphthalene, bicyclo[4.2.0]oct-3-ene, naphthalene and adamantane. Exemplary fused carbocycles include decalin, naphthalene, 1,2,3,4-tetrahydronaphthalene, bicyclo[4.2.0]octane, 4,5,6,7-tetrahydro-1H-indene and bicyclo[4.1.0]hept-3-ene. "Carbocycles" may be substituted at any one or more positions capable of bearing a hydrogen atom.

The term "carbocyclylalkyl", as used herein, refers to an alkyl group substituted with a carbocycle group.

The term "carbonate" is art-recognized and refers to a group $-OCO_2-$.

The term "carboxy", as used herein, refers to a group represented by the formula $-CO_2H$.

The term "cycloalkyl" includes substituted or unsubstituted non-aromatic single ring structures, preferably 4- to 8-membered rings, more preferably 4- to 6-membered rings. The term "cycloalkyl" also includes polycyclic ring systems having two or more cyclic rings in which two or more carbons are common to two adjoining rings wherein at least one of the rings is cycloalkyl and the substituent (e.g., R^{100}) is attached to the cycloalkyl ring, e.g., the other cyclic rings can be cycloalkyls, cycloalkenyls, cycloalkynyls, aryls, heteroaryls, and/or heterocyclyls. Heteroaryl groups include, for example, pyrrole, furan, thiophene, imidazole,

oxazole, thiazole, pyrazole, pyridine, pyrazine, pyridazine, pyrimidine, denzodioxane, tetrahydroquinoline, and the like.

The term "ester", as used herein, refers to a group $-C(O)OR^9$ wherein R^9 represents a hydrocarbyl group.

The term "ether", as used herein, refers to a hydrocarbyl group linked through an oxygen to another hydrocarbyl group. Accordingly, an ether substituent of a hydrocarbyl group may be hydrocarbyl-O-. Ethers may be either symmetrical or unsymmetrical. Examples of ethers include, but are not limited to, heterocycle-O-heterocycle and aryl-O-heterocycle. Ethers include "alkoxyalkyl" groups, which may be represented by the general formula alkyl-O-alkyl.

The terms "halo" and "halogen" as used herein means halogen and includes chloro, fluoro, bromo, and iodo.

The terms "hetaralkyl" and "heteroaralkyl", as used herein, refers to an alkyl group substituted with a hetaryl group.

The terms "heteroaryl" and "hetaryl" include substituted or unsubstituted aromatic single ring structures, preferably 5- to 7-membered rings, more preferably 5- to 6-membered rings, whose ring structures include at least one heteroatom, preferably one to four heteroatoms, more preferably one or two heteroatoms. The terms "heteroaryl" and "hetaryl" also include polycyclic ring systems having two or more cyclic rings in which two or more carbons are common to two adjoining rings wherein at least one of the rings is heteroaromatic, e.g., the other cyclic rings can be cycloalkyls, cycloalkenyls, cycloalkynyls, aryls, heteroaryls, and/or heterocyclyls. Heteroaryl groups include, for example, pyrrole, furan, thiophene, imidazole, oxazole, thiazole, pyrazole, pyridine, pyrazine, pyridazine, and pyrimidine, and the like.

The term "heteroatom" as used herein means an atom of any element other than carbon or hydrogen. Preferred heteroatoms are nitrogen, oxygen, and sulfur.

The term "heterocyclylalkyl", as used herein, refers to an alkyl group substituted with a heterocycle group.

The terms "heterocyclyl", "heterocycle", and "heterocyclic" refer to substituted or unsubstituted non-aromatic ring structures, preferably 3- to 10-membered rings, more preferably 3- to 7-membered rings, whose ring structures include at least one heteroatom, preferably one to four heteroatoms, more preferably one or two heteroatoms. The terms "heterocyclyl" and "heterocyclic" also include polycyclic ring systems having two or more cyclic rings in which two or more carbons are common to two adjoining rings wherein at least one of the rings is heterocyclic, e.g., the other cyclic rings can be cycloalkyls, cycloalkenyls,

cycloalkynyls, aryls, heteroaryls, and/or heterocyclyls. Heterocyclyl groups include, for example, piperidine, piperazine, pyrrolidine, morpholine, lactones, lactams, and the like.

The term "hydrocarbyl", as used herein, refers to a group that is bonded through a carbon atom that does not have a =O or =S substituent, and typically has at least one carbon-hydrogen bond and a primarily carbon backbone, but may optionally include heteroatoms. Thus, groups like methyl, ethoxyethyl, 2-pyridyl, and even trifluoromethyl are considered to be hydrocarbyl for the purposes of this application, but substituents such as acetyl (which has a =O substituent on the linking carbon) and ethoxy (which is linked through oxygen, not carbon) are not. Hydrocarbyl groups include, but are not limited to aryl, heteroaryl, carbocycle, heterocycle, alkyl, alkenyl, alkynyl, and combinations thereof.

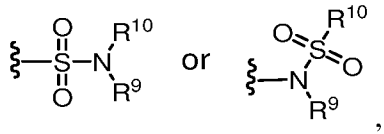
The term "hydroxyalkyl", as used herein, refers to an alkyl group substituted with a hydroxy group.

The term "lower" when used in conjunction with a chemical moiety, such as, acyl, acyloxy, alkyl, alkenyl, alkynyl, or alkoxy is meant to include groups where there are ten or fewer atoms in the substituent, preferably six or fewer. A "lower alkyl", for example, refers to an alkyl group that contains ten or fewer carbon atoms, preferably six or fewer. In certain embodiments, acyl, acyloxy, alkyl, alkenyl, alkynyl, or alkoxy substituents defined herein are respectively lower acyl, lower acyloxy, lower alkyl, lower alkenyl, lower alkynyl, or lower alkoxy, whether they appear alone or in combination with other substituents, such as in the recitations hydroxyalkyl and aralkyl (in which case, for example, the atoms within the aryl group are not counted when counting the carbon atoms in the alkyl substituent).

The terms "polycyclyl", "polycycle", and "polycyclic" refer to two or more rings (e.g., cycloalkyls, cycloalkenyls, cycloalkynyls, aryls, heteroaryls, and/or heterocyclyls) in which two or more atoms are common to two adjoining rings, e.g., the rings are "fused rings". Each of the rings of the polycycle can be substituted or unsubstituted. In certain embodiments, each ring of the polycycle contains from 3 to 10 atoms in the ring, preferably from 5 to 7.

The term "sulfate" is art-recognized and refers to the group $-OSO_3H$, or a pharmaceutically acceptable salt thereof.

The term "sulfonamido" is art-recognized and refers to the group represented by the general formulae



wherein R^9 and R^{10} independently represents hydrogen or hydrocarbyl.

The term "sulfoxide" is art-recognized and refers to the group–S(O)-.

The term "sulfonate" is art-recognized and refers to the group SO_3H, or a pharmaceutically acceptable salt thereof.

The term "sulfone" is art-recognized and refers to the group $–S(O)_2-$.

The term "substituted" refers to moieties having substituents replacing a hydrogen on one or more carbons of the backbone. It will be understood that "substitution" or "substituted with" includes the implicit proviso that such substitution is in accordance with permitted valence of the substituted atom and the substituent, and that the substitution results in a stable compound, e.g., which does not spontaneously undergo transformation such as by rearrangement, cyclization, elimination, etc. As used herein, the term "substituted" is contemplated to include all permissible substituents of organic compounds. In a broad aspect, the permissible substituents include acyclic and cyclic, branched and unbranched, carbocyclic and heterocyclic, aromatic and non-aromatic substituents of organic compounds. The permissible substituents can be one or more and the same or different for appropriate organic compounds. For purposes of this invention, the heteroatoms such as nitrogen may have hydrogen substituents and/or any permissible substituents of organic compounds described herein which satisfy the valences of the heteroatoms. Substituents can include any substituents described herein, for example, a halogen, a hydroxyl, a carbonyl (such as a carboxyl, an alkoxycarbonyl, a formyl, or an acyl), a thiocarbonyl (such as a thioester, a thioacetate, or a thioformate), an alkoxyl, a phosphoryl, a phosphate, a phosphonate, a phosphinate, an amino, an amido, an amidine, an imine, a cyano, a nitro, an azido, a sulfhydryl, an alkylthio, a sulfate, a sulfonate, a sulfamoyl, a sulfonamido, a sulfonyl, a heterocyclyl, an aralkyl, or an aromatic or heteroaromatic moiety. It will be understood by those skilled in the art that the moieties substituted on the hydrocarbon chain can themselves be substituted, if appropriate.

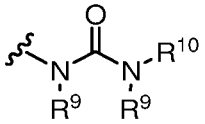
The term "thioalkyl", as used herein, refers to an alkyl group substituted with a thiol group.

The term "thioester", as used herein, refers to a group $-C(O)SR^9$ or $–SC(O)R^9$

wherein R^9 represents a hydrocarbyl.

The term "thioether", as used herein, is equivalent to an ether, wherein the oxygen is replaced with a sulfur.

The term "urea" is art-recognized and may be represented by the general formula



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wherein R^9 and R^{10} independently represent hydrogen or a hydrocarbyl.

Many of the compounds useful in the methods and compositions of this disclosure have at least one stereogenic center in their structure. This stereogenic center may be present in a R or a S configuration, said R and S notation is used in correspondence with the rules described in Pure Appl. Chem. (1976), 45, 11-30. The disclosure contemplates all stereoisomeric forms such as enantiomeric and diastereoisomeric forms of the compounds, salts.

Furthermore, certain compounds which contain alkenyl groups may exist as Z (zusammen) or E (entgegen) isomers. In each instance, the disclosure includes both mixture and separate individual isomers.

EXAMPLES

The invention now being generally described, it will be more readily understood by reference to the following examples which are included merely for purposes of illustration of certain aspects and embodiments of the present invention and are not intended to limit the invention.

Example 1: Synthesis of Exemplary Electrolytes

DMTMSA and THF were chosen for demonstration, since DMTMSA is a weakly solvating solvent with favorable molecular structure (*Nat. Energy* **6**, 495-505 (2021)), and THF can dissolve NaFSI to form ~7 m solution. By changing the molar ratio between DMTMSA and THF, the polarization curves of these electrolytes with 1 m NaFSI changed correspondingly (**FIG. 9**). The average CEs and cycling overpotentials at 1.0 mA cm^{-2} over 100 cycles were calculated to evaluate their electrochemical performance. As THF ratio increased within the HSEs, the average cycling overpotential firstly decreased from >600 mV to ~72 mV, and then increased to ~156 mV (**FIG. 8C**). Moreover, the average CE initially increased from ~92.60% to ~99.30%, followed by a decrease to ~64.02% (**FIG. 8D**), which was matched with the trend observed by using the Aurbach method at 1.0 mA cm^{-2} with areal capacity of 1.0 mAh cm^{-2} (**FIG. 10**). The non-monotonic dependence between the average CEs and cycling overpotentials guided our electrolyte HSE design, where the optimized molar ratio between DMTMSA and THF is 4:1 when NaFSI is used as the salt, and is called "1 m NaFSI DMTMSA/THF" afterwards.

Recent work has observed that precycling protocol optimization can facilitate the formation of a more stable SEI, which can also be applied for 1 m NaFSI DMTMSA/THF (*Adv. Mater.* **34**, 2108252 (2022)). Using this strategy, the average CE measured by the Aurbach

method can reach 99.72% at 1.0 mA cm^{-2} (**FIG. 11**). Weakly solvated fluorinated sulfonamide-based solvents cannot be replaced by the same amount of non-solvating diluent, such as 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE), as confirmed by the precipitation of salt and the large polarization curve.

Linear sweep voltammetry (LSV) measurements were conducted using Nallstainless steel (SS) cells at a scan rate of 1.0 mV s^{-1}. 1 m NaFSI THF exhibited onset of oxidation at ~4.0 V (**FIG. 12**), while 1 m NaFSI DMTMSA/THF was stable up to ~4.5 V, which is similar to the oxidative voltage of 1 m NaFSI DMTMSA at ~4.6 V. This enhanced stability suggests that THF molecules in our HSE are not "free" solvent molecules, but are coordinated to Na^+, increasing their stability toward oxidation.

Ionic conductivity was measured using electrochemical impedance spectroscopy (EIS) results. The ionic conductivity of 1 m NaFSI DMTMSA/THF is ~220% greater than for the DMTMSA only electrolyte at room temperature (**FIG. 13**). Activation energy was calculated using the Arrhenius fitting model; the value of 1 m NaFSI DMTMSA/THF was 14.90 kJ mol^{-1}, which is lower than common HCE and LHCE with only strong solvating solvents (*Angew. Chem. Int. Ed.* **63**, e202400406 (2024)).

The viscosity of 1 m NaFSI DMTMSA/THF is ~5.3 cP at room temperature (**FIG. 14**), which is close to the value of advanced electrolytes with similar concentrations (*ACS Energy Lett.* **3**, 315-321 (2018), *Nat. Energy* **6**, 495-505 (2021)), and the value remains consistent for more than 3 weeks. The observed greater ionic conductivity and stability are important factors to achieve fast cycling (≥3.0 mA cm^{-2}) and high cut-off voltage (~4.0 V) for sodium metal batteries (SMBs).

Complete plating and stripping of sodium metal were used to measure cycling reversibility. 1 m NaFSI THF is unstable as the CE fluctuates during long-term cycling using NallCu cells at 1.0 mA cm^{-2}, while the CE fluctuation is less pronounced for the DMTMSA-only electrolyte, with an average CE of ~96.1% over 100 cycles. Short-circuits happened in the subsequent cycles, as indicated by the voltage curves. By contrast, 1 m NaFSI DMTMSA/THF showed a higher initial CE of 95.8% and a rapid CE increase to >99.0% within the first 10 cycles, indicating activation for this HSE. The CE remained at ~99.50% over 250 cycles, and stable cycling over 500 cycles is seen for three nominally identical NallCu cells (**FIG. 15**), showing good reproducibility.

The fast activation was also observed when the current density increased to 3.0 mA cm^{-2} and when the areal capacity increases to 3.0 mAh cm^{-2}. After only 5 and 2 cycles, respectively, the cycling CE exceeded 99.0%, which is the fastest activation observed so far in this work and

in the literature (**Table 1**). The fast activation of this HSE suggested the rapid formation of a passivation layer and minimized dissolution of reduced electrolyte products (*Nat. Energy* **7**, 718-725 (2022)), which is one of the important electrolyte design principles. The average CE was ~99.3% over 100 cycles with stable cycling overpotential of ~80 mV using an areal capacity of 3.0 mAh cm^{-2}.

Rate performance was also conducted to evaluate this HSE. For 1 m NaFSI THF, poor cycling reversibility was observed for all current densities; however, there is a relatively high CE of ~97% with a low cycling overpotential of <100 mV using a current density of <0.5 mA cm^{-2} for the DMTMSA-only electrolyte. When the current density reached 1.5 mA cm^{-2}, a sharp voltage drop with a potential minimum of –2.4 V can be observed during the sodium-metal plating process and soft short-circuiting happened afterwards.

In contrast, 1 m NaFSI DMTMSA/THF shows stable cycling at 3.0 mA cm^{-2} without obvious buildup of concentration polarization. As a result, the CE remains at ~99.4% over 165 cycles at 3.0 mA cm^{-2} with stable cycling overpotential.

The cycling reversibility and oxidative stability makes this HSE promising when paired with common sodium cathodes such as $Na_3V_2(PO_4)_3$, and $Na_{0.44}MnO_2$. As shown in **FIG. 17**, sudden capacity loss and polarization buildup can be observed after 50 cycles for 1 m NaFSI THF in a Na||$Na_3V_2(PO_4)_3$ cell at 0.2 C rate (1 C = 120 mA g^{-1}) with areal capacity of ~1.5 mAh cm^{-2}. The cycle life was prolonged to ~200 cycles using the DMTMSA-only electrolyte, due to improved oxidative stability. By contrast, capacity retention was ~97.5 % over 400 cycles with an average CE of ~99.9% using 1 m NaFSI DMTMSA/THF. Similar stability was achieved using $Na_{0.44}MnO_2$ as the cathode with an areal capacity of ~1.0 mAh cm^{-2}. 1 m NaFSI DMTMSA/THF enabled a capacity retention of ~77.9 % over 600 cycles with an average CE of >99.9% (**FIG. 18**).

The improvement of rate performance was also observed for 1 m NaFSI DMTMSA/THF, which delivers a specific capacity of ~101.7 mAh g^{-1} at 1.6 C (~2.4 mA cm^{-2}) (**FIG. 19**). In contrast, 1 m NaFSI THF and DMTMSA-only electrolyte cannot cycle at this rate due to unstable charging and large polarization. When the current density was increased to ~3.2 mA cm^{-2}, corresponding to 3.2 C with an areal capacity of ~1.0 mAh cm^{-2}, with a higher charging cut-off voltage of 3.9 V, stable cycling is observed using 1 m NaFSI DMTMSA/THF, with an initial specific capacity of ~108.9 mAh g^{-1}. The capacity retention is ~98.1 % over 500 cycles with an average CE of >99.9%**.** Further increasing the cycling rate to 5.0 C (~5.0 mA cm^{-2}) and cut-off voltage to 4.0 V was achieved with an initial specific capacity of ~92.9 mAh g^{-1}. 1 m NaFSI DMTMSA/THF enables a capacity retention of ~70% over 1500 cycles with

an average CE of ~99.9% (**FIG. 20**). A pouch cell with the configuration of Na||$Na_3V_2(PO_4)_3$ was assembled to test 1 m NaFSI DMTMSA/THF. A uniaxial pressure of ~50 kPa was applied. After 125 cycles, capacity retention was ~95.8% and the average CE was ~99.9%. Compared with the other electrolytes, e.g., ether-based and carbonate-based, and electrolyte additives using the same cathode chemistry (**Table 2**), 1 m NaFSI DMTMSA/THF shows excellent reversibility under practical current density (≥3.0 mA cm^{-2}) and areal capacity (≥1.0 mAh cm^{-2}).

Na metal deposition morphology was studied for these different electrolytes. For the DMTMSA-only electrolyte, metal deposition is compact while the particle size is small (**FIG. 21A**). The average area and perimeter are 0.43 μm^2 and 3.11 μm, respectively, as calculated from ~1700 individual microparticles labeled using a computer vision method (**FIG. 22**). The high particle density can be attributed to the high nucleation density, as confirmed by the large nucleation overpotential at 1.0 mA cm^{-1}. The DMTMSA only electrolyte induces the formation of an inorganic-rich SEI, which can stabilize the electrode-electrolyte interface, leading to a compact deposition morphology. When 1 m NaFSI THF was applied, the morphology became loose, and the grain size is small with an average grain area of 8.7 μm^2 (**FIG. 21C**). By contrast, the deposition is compact, and the particle size is large using 1 m NaFSI DMTMSA/THF (**FIG. 21B),** contributing from the stable inorganic-rich SEI and larger ionic conductivity of the HSE. The ratio between the particle area and perimeter is defined as the structure factor, which is related to the size and shape for electrodeposited sodium. Most microparticles show larger values as shown in the distribution of structure factor using 1 m NaFSI DMTMSA/THF, and the average structure factor value is ~4× and ~15× larger than 1 m NaFSI THF and DMTMSA only electrolyte, respectively.

The improved deposition behavior can be explained by the optimized solvation structure of HSEs. As the molar ratio between DMTMSA and THF increases, the cation-dipole interaction becomes weaker. The downshift of ^{23}Na NMR peak from −6.8 ppm to −11.0 ppm can be observed (**FIG. 23A**), reflecting the shielding effect induced by the increase of electron density near the cation and suggesting greater anion–cation association. Moreover, the peak width for different HSEs is larger than 1 m NaFSI THF and DMTMSA-only electrolyte, which is consistent with a mix of cation solvation environments within the HSEs. The interaction between solvents, induced by the dipole-dipole interaction, can also be distinguished by the proton chemical shift for both THF and DMTMSA (**FIG. 23B**), together with the ^{19}F NMR chemical shift from DMTMSA (**FIG. 23C**). Raman spectroscopy was used to further show how the combination of ion-dipole and dipole-dipole interactions in HSEs can tune solvation

structures. The blueshift of Raman peaks can be seen when the molar ratio between DMTMSA and THF increases from ~1.35 to ~6.43. Meanwhile, the SSIP decreases from >60% to <10% and AGG increases from ~14% to ~55%, while the CIP slightly varies from ~25% to ~37%, as calculated using the deconvolution results (**FIG. 24**). The co-existence of solvated DMTMSA and THF was confirmed by Fourier-transform infrared spectroscopy (FTIR). The formation of ion pairs is essential for upshifting the electrode potentials (*Nat. Energy* **7**, 1217-1224 (2022)), which in turn weakens the reducing ability of the metal anode and therefore improves the CE. Compared with the intrinsic electrode potential, a large shift of >0.32 V can be seen for 1 m NaFSI DMTMSA/THF.

To shed light on the solvation structures and determine the distribution of Na^+ solvates for the HSEs, molecular dynamics (MD) simulations were employed (**FIG. 25**). The coordination structures of anions and different solvents were calculated. Since the molecular structure of DMTMSA solvent is similar to the FSI^- anion, both of them participate in Na^+ solvation in DMTMSA only electrolyte. The coordination number (CN) for DMTMSA and FSI^- are 2.08 and 2.86, respectively, in the primary solvation sheath, therefore mainly forming the Na^+-anion cluster, which is the typical molecular feature for the WSEs. Since THF shows a stronger interaction with Na^+ than DMTMSA and FSI^-, the partial replacement of FSI^- and modification of the primary solvation sheath can be achieved by controlling the THF amounts. The CN for DMTMSA, FSI^- and THF are 2.07, 2.46 and 0.66, respectively for 1 m NaFSI DMTMSA/THF. The reduction of Na^+-anion cluster and increasing Na^+-anion single pair can maintain the preferred anion decomposition at the metal anode to form stable SEI and increase the ionic conductivity simultaneously. On the other hand, extra THF can form the over solvated electrolytes and solvent surrounded Na^+ becomes dominant. Due to the unstable decomposition of THF solvent both at the cathode and anode, the CE decay and polarization buildup can be seen for THF only electrolyte. The spectroscopic analysis and MD simulation, along with the electrochemical performance, indicates that a balanced solvation structure can be a better choice for electrolyte design to achieve fast cycling, while still maintaining good stability against anode and cathode.

Subsequently, different sodium salts, including sodium bis(trifluoromethanesulfonyl)imide (NaTFSI), sodium (fluorosulfonyl)(trifluoromethanesulfonyl)imide (NaFTFSI), and NaFSI, and various fluorinated sulfonamide-based weakly coordinating solvents and common strongly solvating solvents have been used to prepare in total seventeen HSEs, including up to five hybrid solvents (**FIG . 26**). Their oxidative tolerance (**FIG. 27**), cycling stability against sodium metal anode

(**FIGs. 28-30**), and ionic conductivity are tested. As shown in **FIG. 31**, improved CE with good oxidative stability can be found, which indicates the design principle for HSEs is effective. Especially, seven of them reach CE of >99% with fast activation and 1 m NaFSI DMTMSA/diglyme achieves a high CE of ~99.64% at 1.0 mA cm^{-1} with the oxidative stability up to ~4.9 V. Besides, the introduction of ionic liquid 1-butyl-1-methylpyrrolidinium bis(fluorosulfonyl)imide ([Pyr14][FSI]) can further improve the ionic conductivity of 1 m NaFSI DMTMSA/THF by ~75% at room temperature, and increase the oxidative stability to ~4.6 V, and thus the onset oxidative potential becomes even higher than commercial carbonate electrolyte (~4.5 V). Therefore, compared with the advanced electrolytes proposed in recent work for sodium metal batteries (**Table 1**), the HSEs can achieve the fastest activation, maintain low overpotentials and high reversibility even when cycled with a practical current density (~3.0 mA cm^{-2}), owing to the favored solvation structures contributing from the fine-tuning between strong and weak solvating solvents.

Table 1 Electrochemical performance of Na||Cu cells

Electrolyte	**Current density (mA cm^{-2})**	**Areal capacity (mAh cm^{-2})**	**Activation cycle number (>99.0%)**	**CE**	**Cycling overpotential (mV)**	**Ref.**
1 m NaFSI DMTMSA/THF	1.0	1.0	10	99.72%	75	This work
	1.0	3.0	2	99.25%	75	This work
	3.0	1.0	5	99.40%	230	This work
1 m NaFSI DMTMSA/Diglyme	1.0	1.0	12	99.64%	110	This work
1.1 M NaFSI + 0.3 M $NaNO_3$ TMP	1.0	1.0	/	~99%	~20	*Nat. Energy* **9**, 446-456 (2024)
1.5 M NaFSI DME:BTFE=1:3 (mol)	1.0	1.0	>30	~99%	~170	*ACS Energy Lett.* **3**, 315-321 (2018)
2.1 M NaFSI DME:BTFE=1:2 (mol)	1.0	1.0	>30	98.95%	~145	

2.3 M NaFSI DME:TTE=1:1 (mol)	1.0	1.0	N/A	~98%	/	
5.2 M NaFSI DME	1.0	1.0	N/A	~98%	~230	
4.0 M NaFSI DME	1.0	1.0	>30	~99%	~130	*Nano Energy* **30**, 825-830 (2016)
NaFSI:THF=1:2 (mol)	0.5	0.5	>20	~99%	/	
1.0 M $NaPF_6$ Diglyme	0.5	1.0	/	99.9%	~15	*ACS Cent. Sci.* **1**, 449-455 (2015)
	1.0	1.0	N/A	91.22% (Cu)	~35 (Cu)	*Small* **18**, 2203409 (2022)
	1.0	1.0	N/A	98.66% (Sn)	~20 (Sn)	
	1.0	1.0	~10	99.41% (Au)	~20 (Au)	
	1.0	1.0	N/A	70% (Cu)	16 (Cu)	*Adv. Energy Mater.* **13**, 2204125 (2023)
	1.0	1.0	/	99.9% (SF-Cu)	20 (SF-Cu)	
	3.0	1.0	/	99.2% (COF-Cu)	/	*Sci. Adv.* **9**, eadh8060 (2023)
1.0 M $NaPF_6$ FEC:FEMC=1:1 (vol) 0.3 wt% LiDFOB	0.5	1.0	N/A	98.42%	~75	*Adv. Funct. Mater.* **34**, 2401868 (2024)

2.0 M NaOTf + 0.08 M $Bi(OTf)_3$ + 0.4 M DTD DME	0.5	0.5	~8	99.1%	~32	*ACS Energy Lett.* **8**, 2746-2752 (2023)
NaFSI:Diglyme:HFME =1:1.17:3.82 (mol)	0.5	0.5	N/A	97.1%	~104	*Angew. Chem. Int. Ed.* **63**, e202400406 (2024)
	0.5	1.0	N/A	95.9%	/	
1.0 M $NaPF_6$ Diglyme: Me-THF=1:1 (vol)	0.5	1.0	/	99.74%	~22	*Adv. Mater.* **36**, 2312508 (2024)

Notes:

1. "~" indicates that the values are estimated based on the graphs in the reference.
2. "/" indicates that the values are hard to distinguish.
3. "N/A" indicates that the CE never exceeds 99.0% and the activation cycle number is not applicable here.
4. The default working electrode is Cu foil unless otherwise specified.

Table 2 Electrochemical performance of sodium metal batteries

Electrode	**Electrolyte**	**Current density (mA cm^{-2})**	**Areal capacity (mAh cm^{-2})**	**Charging voltage (V)**	**Cell type**	**Capacity retention**	**Ref.**
NVP	1 m NaFSI DMTMSA/THF	0.3	1.5	3.8	Coin	~97.1% after 500 cycles	This work
	1 m NaFSI DMTMSA/THF	3.2	1.0	3.9	Coin	~98.1% after 500 cycles	This work
	1 m NaFSI DMTMSA/THF	5.0	1.0	4.0	Coin	~70% after 1500 cycles	This work
	1 m NaFSI DMTMSA/THF	0.3	1.2	3.8	Pouch	~96% after 125 cycles	This work
	5.2 M NaFSI DME	3.6	0.18	3.7	Coin	~48% after 40000 cycles	*ACS Energy Lett.* **3**, 315-321 (2018)
	2.1 M NaFSI DME:BTFE=1:2 (mol)	3.6	0.18	3.7	Coin	~91% after 40000 cycles	
	0.75 M $NaClO_4$ FEC:PC=1:1 (wt)	6.0	0.10	3.8	Coin	~48% after 8000 cycles	*J. Am. Chem. Soc.* **145**, 21661-

	0.75 M $NaClO_4$ + 0.01 M LiTFSI FEC:PC=1:1 (wt)	6.0	0.10	3.8	Coin	~89% after 10000 cycles	21671 (2023)
	NaTFSI:[Pyr13][FSI]: TFEE=1:3:1 (mol)	1.35	0.27	3.8	Coin	~95% after 2000 cycles	*Adv. Funct. Mater.* **34**, 2312295 (2024)
	1.0 M $NaPF_6$ FEC:DMC=1:1 (vol) TTE/DMTP additives	0.4	0.4	4.0	Coin	~89% after 1000 cycles	*Adv. Funct. Mater.* **32**, 2109378 (2022)
	1.0 M $NaPF_6$ Diglyme	2.2	1.1	3.9	Coin	~93% after 160 cycles	*Adv. Energy Mater.* **13**, 2204125 (2023)
	1.0 M $NaPF_6$ Diglyme	2.2	1.1	3.9	Coin	~96% after 800 cycles (SF-Na)	
NMO	1 m NaFSI DMTMSA/THF	0.3	1.0	3.8	Coin	~78% after 600 cycles	This work
	1.0 M $NaPF_6$ Diglyme: Me-THF=1:1 (vol)	0.23	0.45	3.6	Coin	~80% after 500 cycles	*Adv. Mater.* **36**, 2312508 (2024)
	1.0 M $NaPF_6$ Diglyme: THF=3:2 (vol)	0.23	0.45	3.6	Coin	~80% after 210 cycles	

	NaFSI:Diglyme:HFME =1:1.17:3.82 (mol)	0.6	0.3	4.2	Coin	~87% after 350 cycles	*Angew. Chem. Int. Ed.* **63**, e202400406 (2024)

INCORPORATION BY REFERENCE

All publications and patents mentioned herein are hereby incorporated by reference in their entirety as if each individual publication or patent was specifically and individually indicated to be incorporated by reference. In case of conflict, the present application, including any definitions herein, will control.

EQUIVALENTS

While specific embodiments of the subject invention have been discussed, the above specification is illustrative and not restrictive. Many variations of the invention will become apparent to those skilled in the art upon review of this specification and the claims below. The full scope of the invention should be determined by reference to the claims, along with their full scope of equivalents, and the specification, along with such variations.

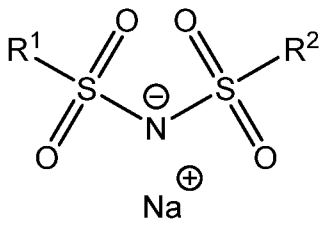
CLAIMS

We claim:

1. A composition, comprising:
a halogenated sodium salt; a halogenated sulfonate; and a co-solvent.

2. The composition of claim 1, wherein the halogenated sodium salt is a fluorinated sodium salt.

3. The composition of claim 2, wherein the fluorinated sodium salt has a structure represented by formula I:



I

wherein
R^1 and R^2 are each independently fluoro or fluoroalkyl.

4. The composition of claim 3, wherein R^1 is fluoro.

5. The composition of claim 3, wherein R^1 is fluoroalkyl.

6. The composition of any one of claims 3-5, wherein R^2 is fluoro.

7. The composition of any one of claims 3-5, wherein R^2 is fluoroalkyl.

8. The composition of claim 1, wherein the halogenated sodium salt is NFSI.

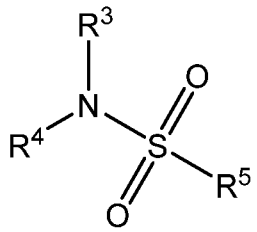
9. The composition of claim 1, wherein the halogenated sodium salt is NaFTFSI.

10. The composition of claim 1, wherein the halogenated sodium salt is NaTFSI.

11. The composition of claim 1, wherein the halogenated sodium salt is $NaPF_6$.

12. The composition of any one of claims 1-11, wherein the halogenated sulfonate is a fluorinated sulfonate.

13. The composition of any one of claims 1-11, wherein the halogenated sulfonate has a structure represented by formula II:



II

wherein

R^3 and R^4 are each independently alkyl, aryl, cycloalkyl, or arakyl; or R^3 and R^4 combine with the intervening nitrogen atom to form a heterocyclyl; and

R^5 is fluoroalkyl.

14. The composition of claim 13, wherein R^3 is alkyl (*e.g.,* methyl or ethyl).

15. The composition of claim 13 or 14, wherein R^4 is alkyl (*e.g.,* methyl or ethyl).

16. The composition of claim 13, wherein R^3 and R^4 combine with the intervening nitrogen atom to form a heterocyclyl (*e.g.,* pyrrolidinyl, piperidinyl, or morpholinyl).

17. The composition of any one of claims 1-16, wherein the co-solvent is an organic co-solvent.

18. The composition of claim 17, wherein the organic co-solvent is an ethereal solvent (*e.g.,* THF, diglyme, 1-methoxy-2-(2-methoxyethoxy)ethane, dimethyl ether, or Tetraethylene glycol dimethyl ether).

19. The composition of claim 17, wherein the organic co-solvent is THF.

20. The composition of any one of claims 1-16, wherein the co-solvent comprises THF, [Pyr14][FSI], FEC, or TM; or a mixture of any of the foregoing.

21. The composition of any one of claims 1-20, wherein the molar ratio of the halogenated sulfonate:co-solvent is about 1:1, about 2:1, about 3:1, about 4:1, about 5:1, about 6:1, about 7:1, or about 8:1.

22. The composition of any one of claims 1-21, wherein the molar ratio of the halogenated sulfonate:co-solvent is about 4:1.

23. An electrolyte comprising the composition of any one of claims 1-22.

24. An electrochemical cell comprising the electrolyte of claim 23.

25. The electrochemical cell of claim 24, wherein the electrochemical cell comprises sodium.

26. The electrochemical cell of claim 24 or 25, wherein the electrochemical cell comprises copper.

27. The electrochemical cell of any one of claims 24-26, wherein the coulombic efficiency (CE) of the electrochemical cell is greater than about 98%.

28. The electrochemical cell of any one of claims 24-26, wherein the coulombic efficiency (CE) of the electrochemical cell is greater than about 99%.

29. A battery, comprising the electrolyte of claim 23 or the electrochemical cell of any one of claims 24-28.

30. The battery of claim 29, wherein the battery is not a lithium battery.

31. The battery of claim 29 or 30, wherein the battery is a barium, calcium, sodium, magnesium, or aluminum battery.

32. The battery of claim 31, wherein the battery is a sodium battery.

33. The batter of any one of claims 29-32, wherein the battery comprises a sodium cathode (*e.g.,* $Na_3V_2(PO_4)_3$ or $Na_{0.44}MnO_2$).

34. A non-lithium battery, comprising $R^1–S(=O)_2–NR^2R^3$, wherein
R^1 is trifluoromethane and
R^2 and R^3 are the same or different and are selected from the group consisting of alkyl-, morpholinyl-, piperidinyl-, and pyrrolidinyl-.

35. The non-lithium battery of claim 34, further comprising a salt or a metal, wherein the salt or metal is selected from the group consisting of barium, calcium, sodium, magnesium, and aluminum.

36. The non-lithium battery of claim 34 or 35, wherein R^2 and R^3 are the same or different and comprise an alkyl selected from methyl, ethyl, propyl, or butyl.

37. The non-lithium battery of claim 34 or 35, comprising N,N-dimethyltrifluoromethane sulfonamide (DMTMSA).

38. The non-lithium battery of any one of claims 34-36, comprising sodium bis(fluorosulfonyl)imide (NaFSI).

39. The non-lithium battery of any one of claims 34-36, comprising sodium bis(trifluoromethylsulfonyl)imide (NaTFSI) salt.

40. The non-lithium battery of any one of claims 34-39, comprising a Na-Cu cell.

41. The non-lithium battery of any one of claims 34-40, wherein the Coulombic efficiency is greater than 80%, 85% 90%, 95%, or 99%.

FIG. 1A

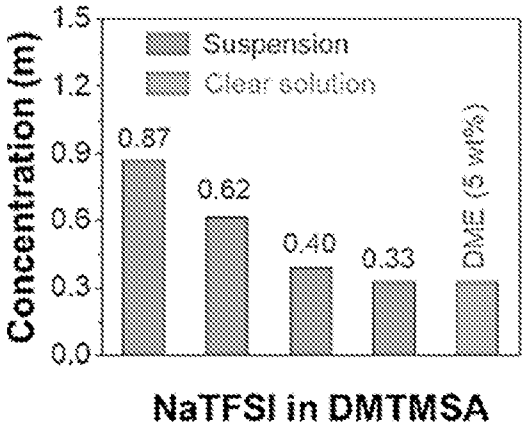


FIG. 1B

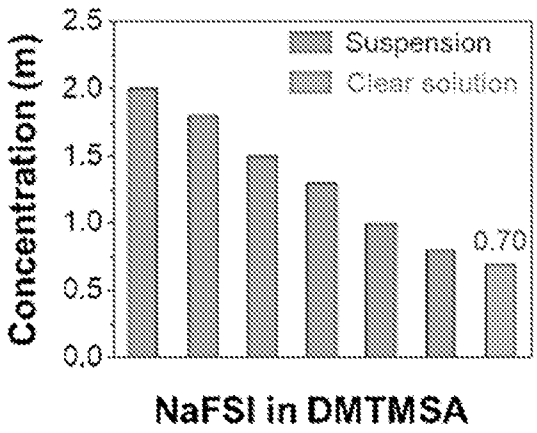


FIG. 2A

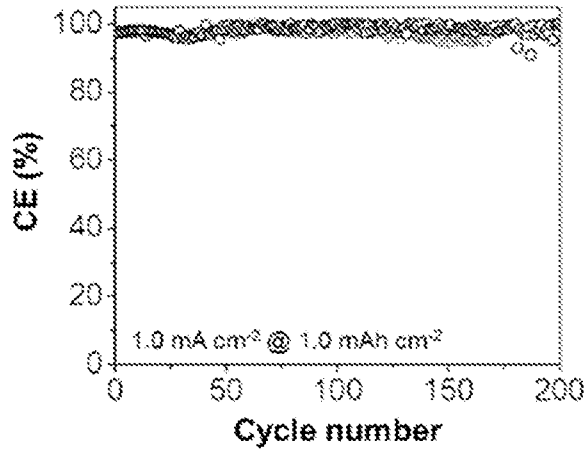


FIG. 2B

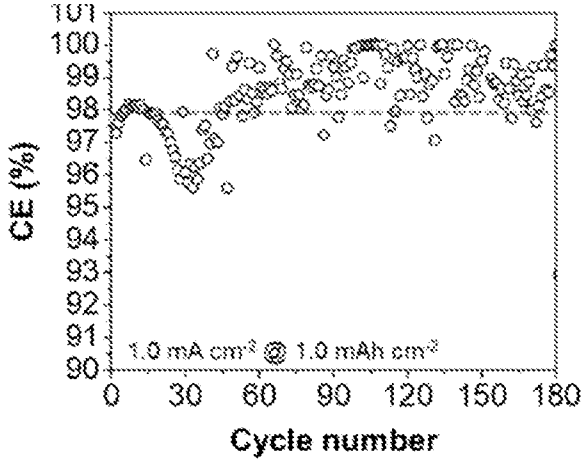

CE (%)
101
100
99
98
97
96
95
94
93
92
91
90
1.0 mA cm⁻² @ 1.0 mAh cm⁻²
0
30
60
90
120
150
180
Cycle number

FIG. 3A

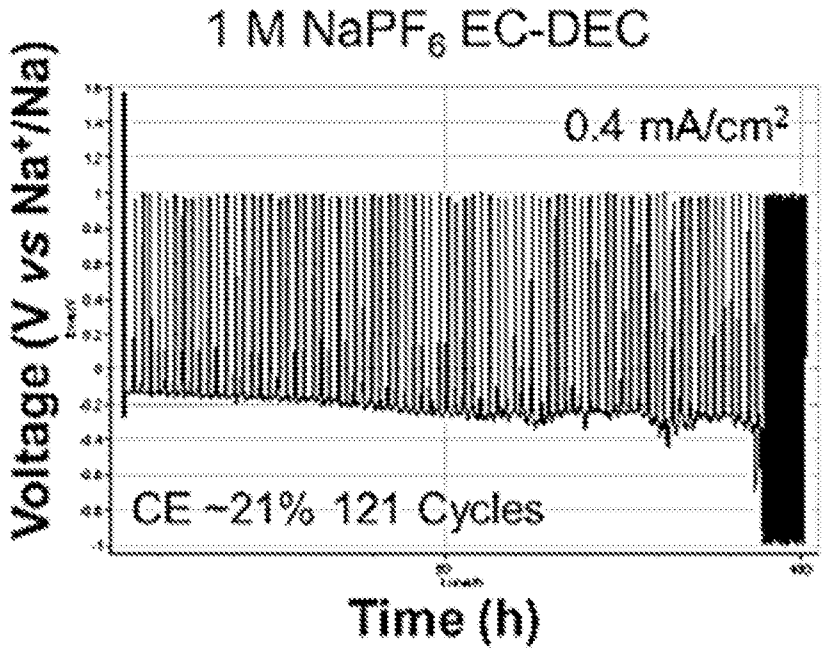

1 M NaPF6 EC-DEC
0.4 mA/cm²
CE ~21% 121 Cycles
Voltage (V vs Na⁺/Na)
Time (h)

FIG. 3B

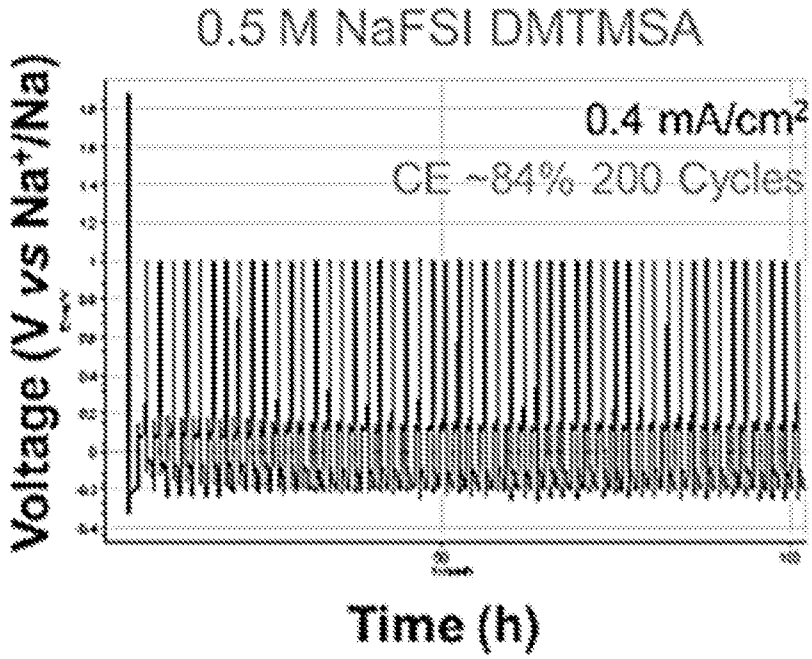

0.5 M NaFSI DMTMSA
0.4 mA/cm²
CE ~84% 200 Cycles
Voltage (V vs Na⁺/Na)
Time (h)

FIG. 3C

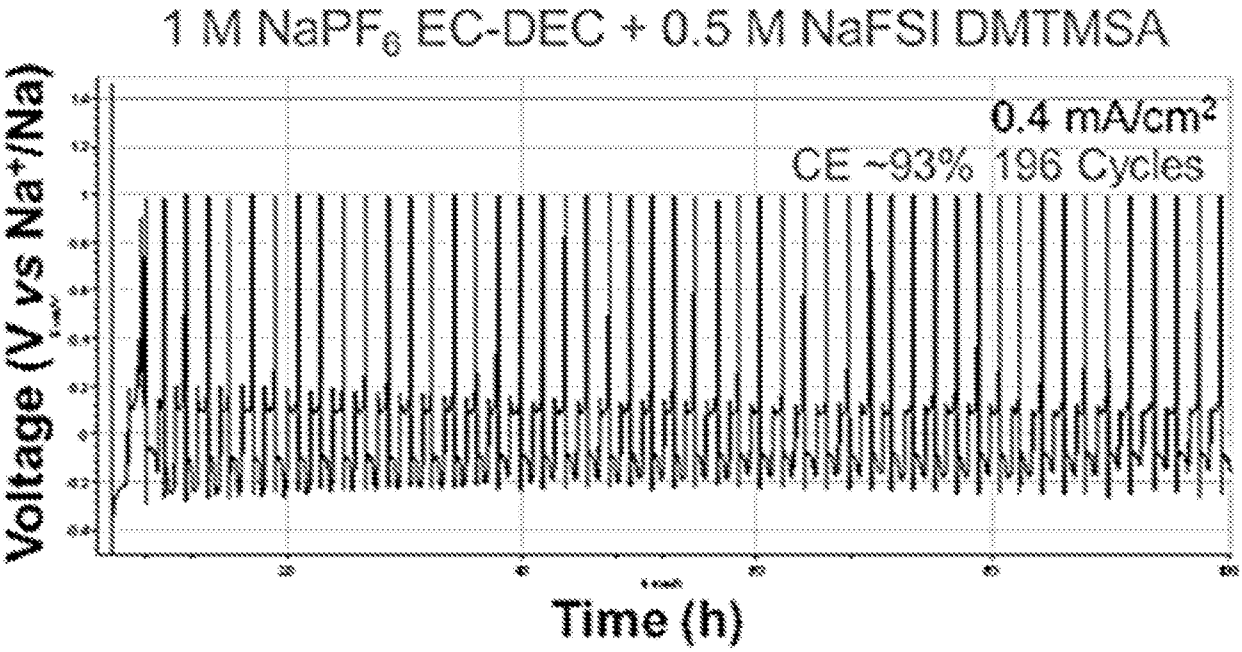

1 M NaPF6 EC-DEC + 0.5 M NaFSI DMTMSA
0.4 mA/cm²
CE ~93% 196 Cycles
Voltage (V vs Na⁺/Na)
Time (h)

FIG. 4A

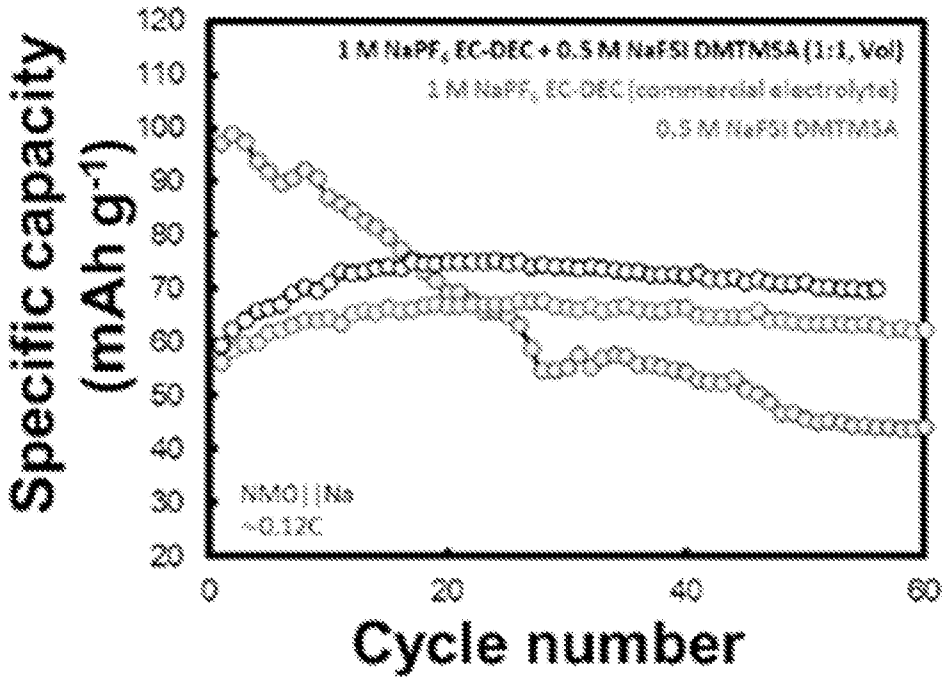

1 M NaPF6 EC-DEC + 0.5 M NaFSI DMTMSA (1:1, Vol)
1 M NaPF6 EC-DEC (commercial electrolyte)
0.5 M NaFSI DMTMSA
NMO | |Na
~0.12C
Specific capacity (mAh g-1)
Cycle number
120
110
100
90
80
70
60
50
40
30
20
0
20
40
60

FIG. 4B

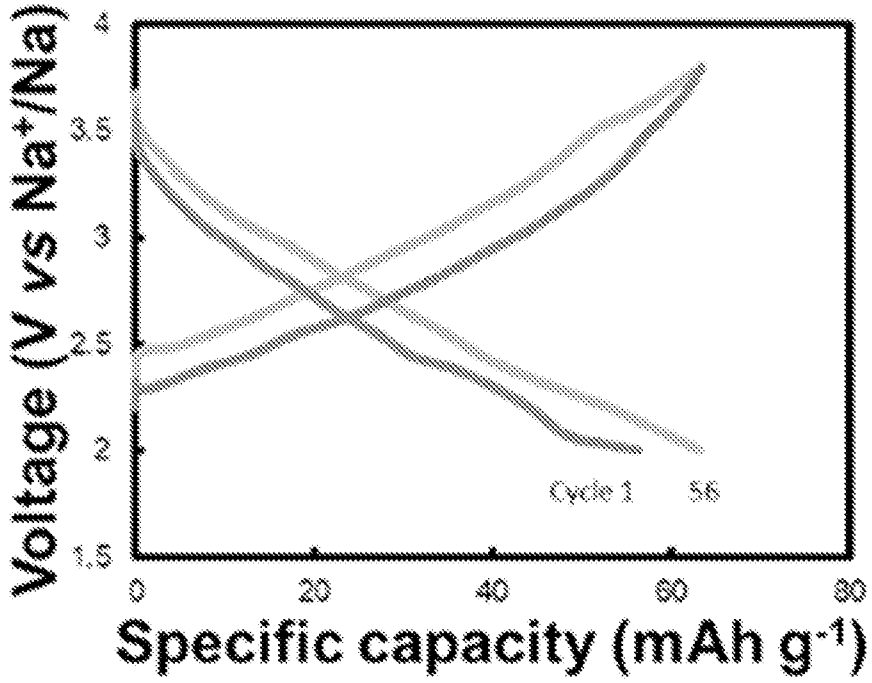

Voltage (V vs Na+/Na)
Specific capacity (mAh g-1)
Cycle 1
56
4
3.5
3
2.5
2
1.5
0
20
40
60
80

FIG. 4C

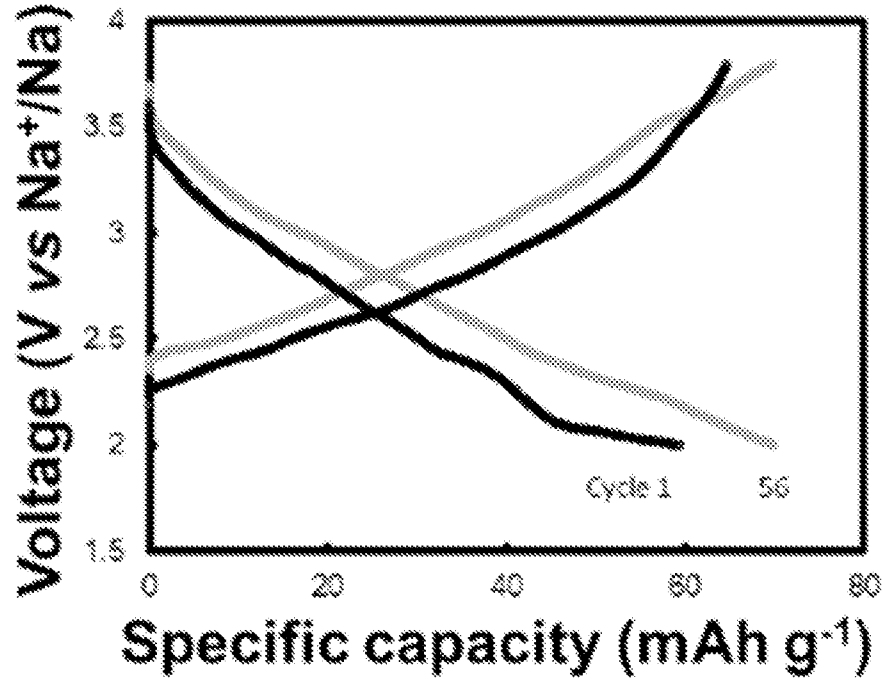

Voltage (V vs Na+/Na)
4
3.5
3
2.5
2
1.5
0
20
40
60
80
Specific capacity (mAh g-1)
Cycle 1
56

FIG. 4D

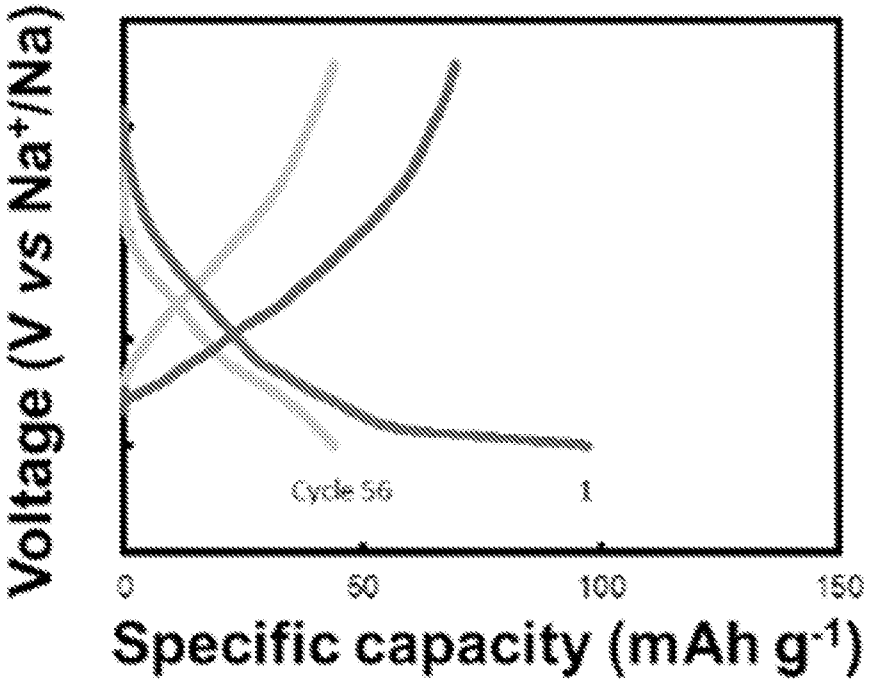

Voltage (V vs Na+/Na)
0
50
100
150
Specific capacity (mAh g-1)
Cycle 56
1

FIG. 5A

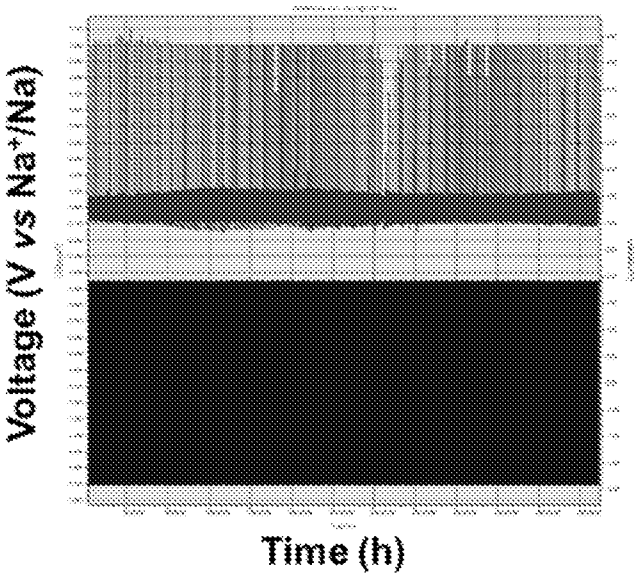


FIG. 5B

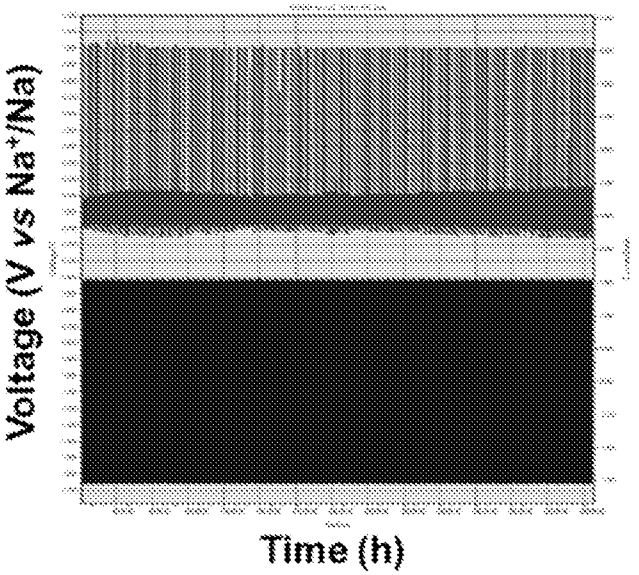


FIG. 6

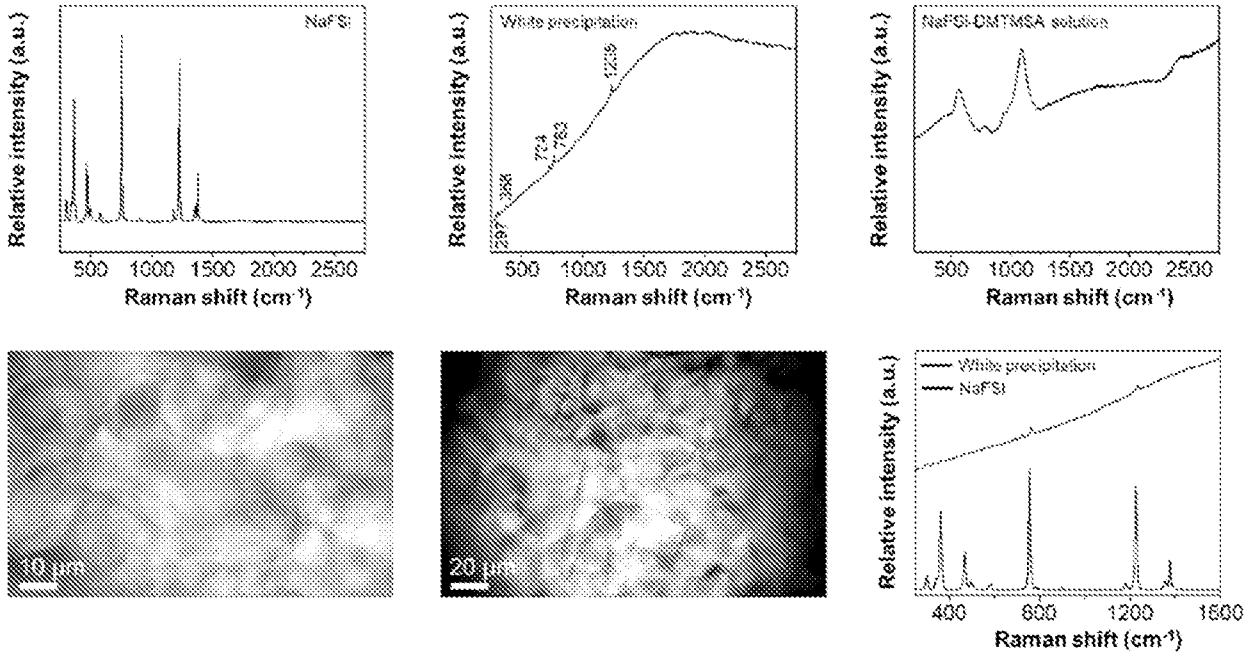


FIG. 7A

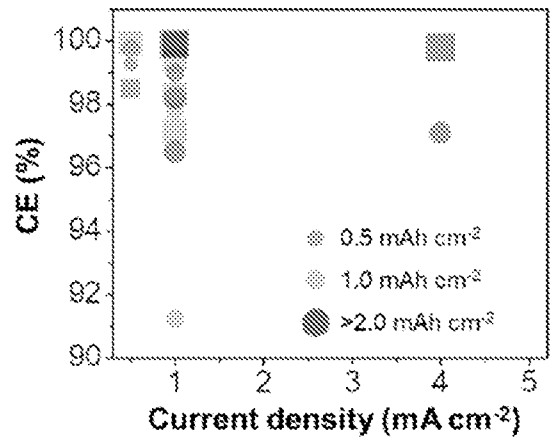


FIG. 7B

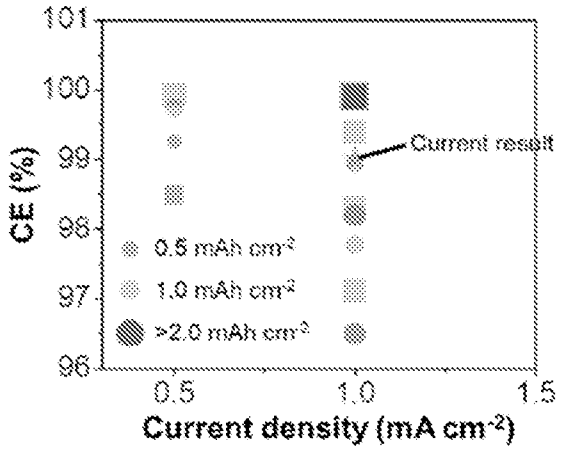


FIG. 8A

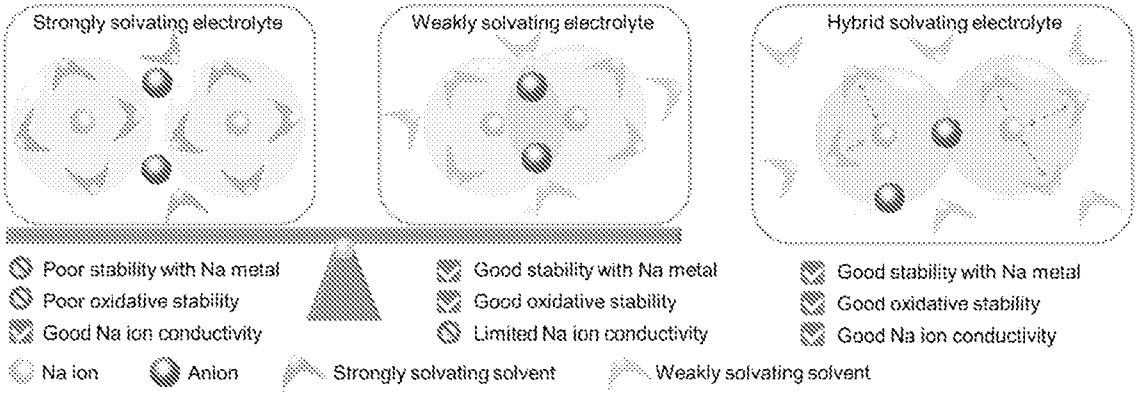


FIG. 8B

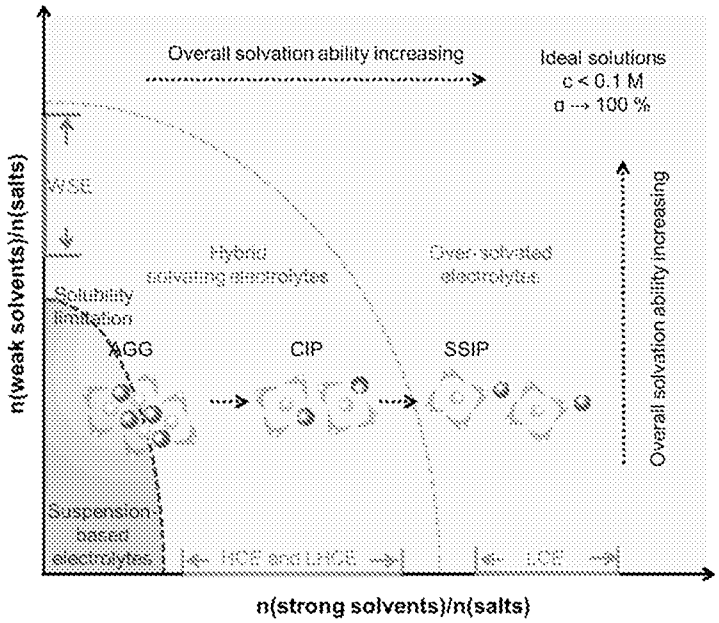


FIG. 8C

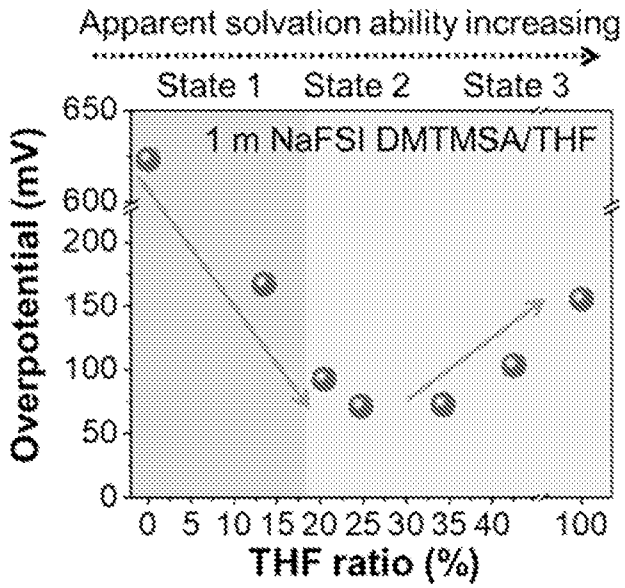


FIG. 8D

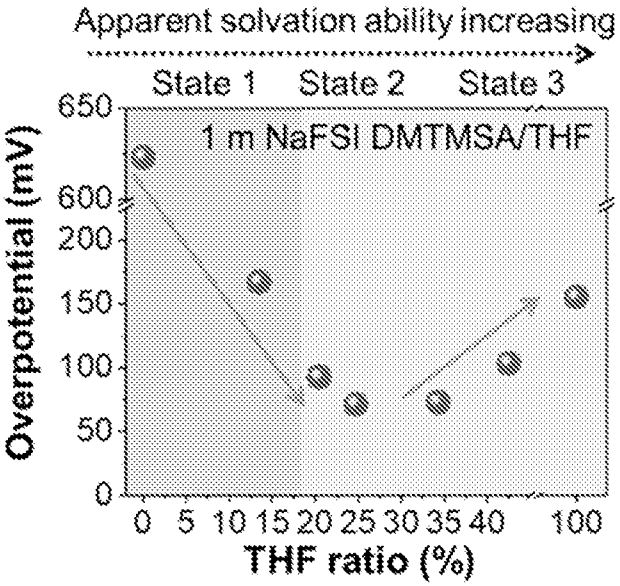

Apparent solvation ability increasing
State 1
State 2
State 3
1 m NaFSI DMTMSA/THF
Overpotential (mV)
650
600
200
150
100
50
0
0 5 10 15 20 25 30 35 40 100
THF ratio (%)

FIG. 9A

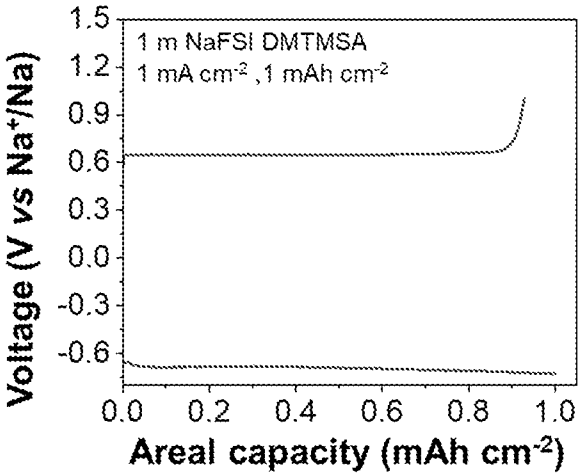


FIG. 9B

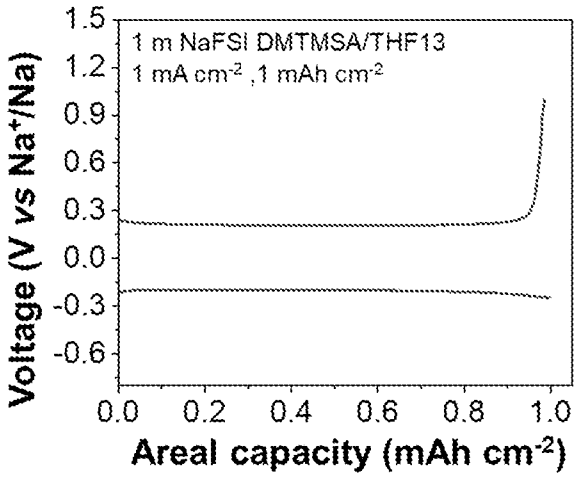


FIG. 9C

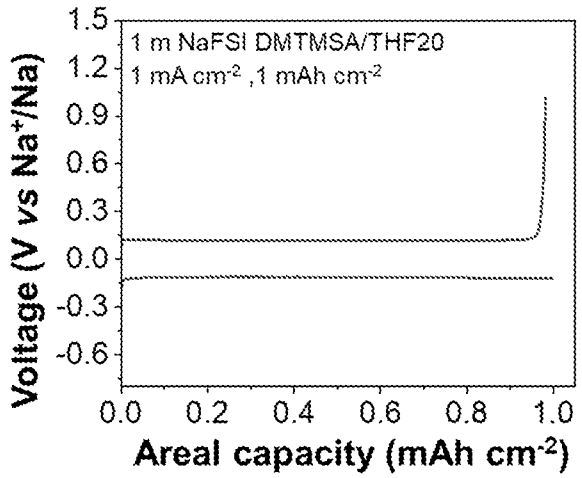


FIG. 9D

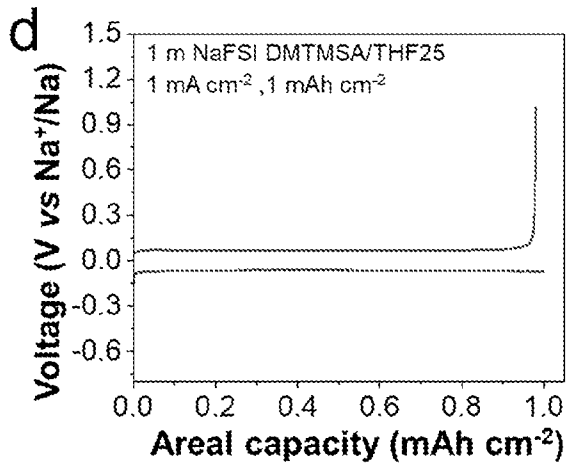


FIG. 9E

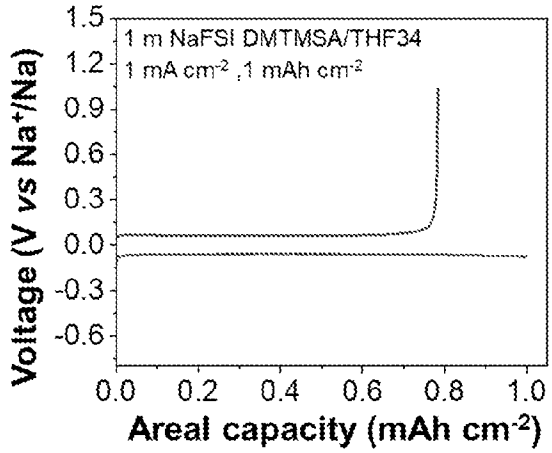


FIG. 9F

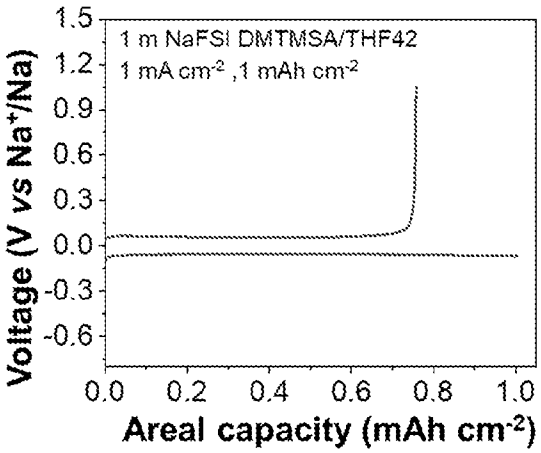


FIG. 9G

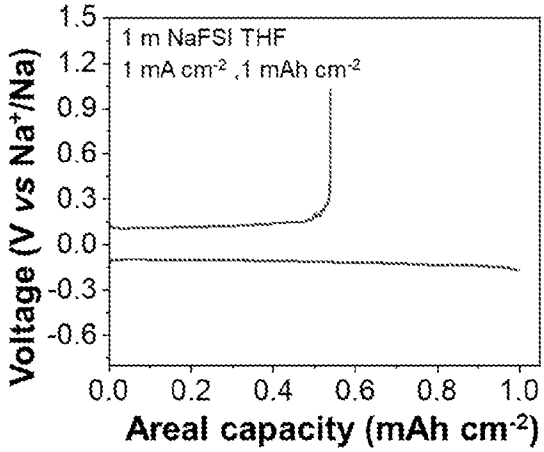


FIG. 10A

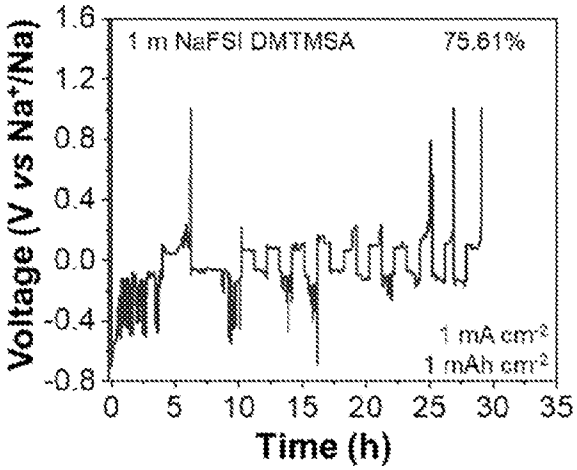


FIG. 10B

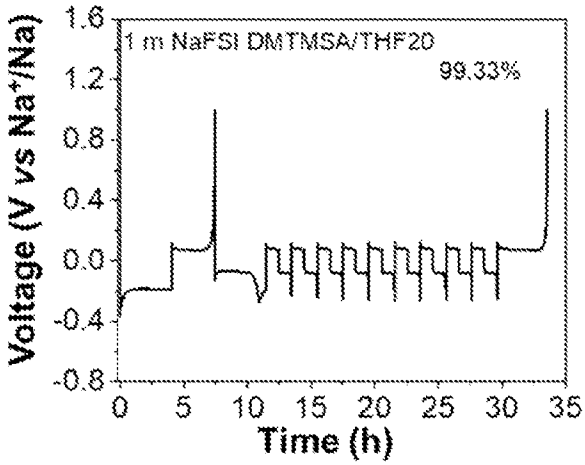


FIG. 10C

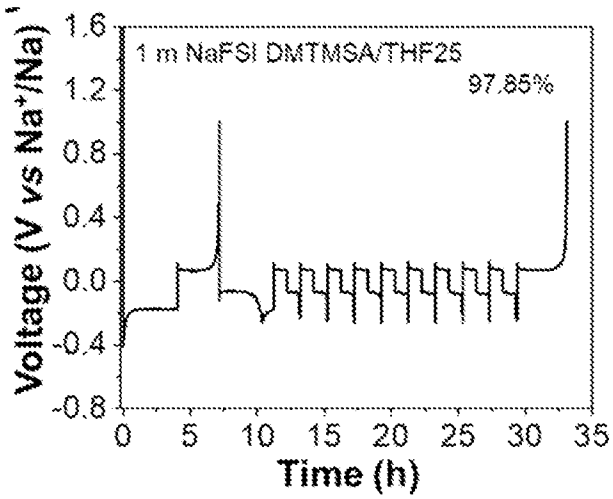


FIG. 10D

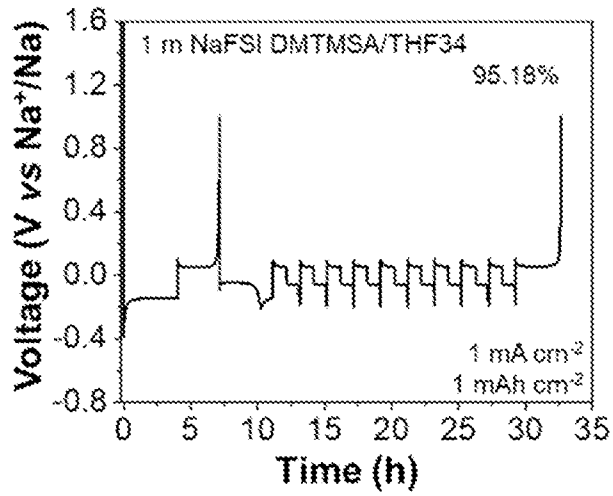


FIG. 10E

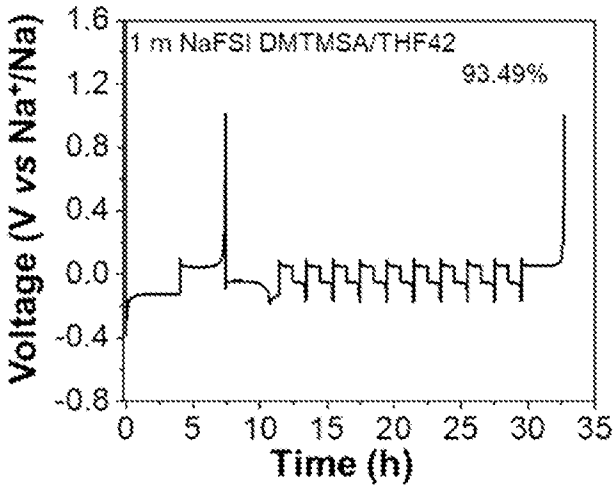


FIG. 10F

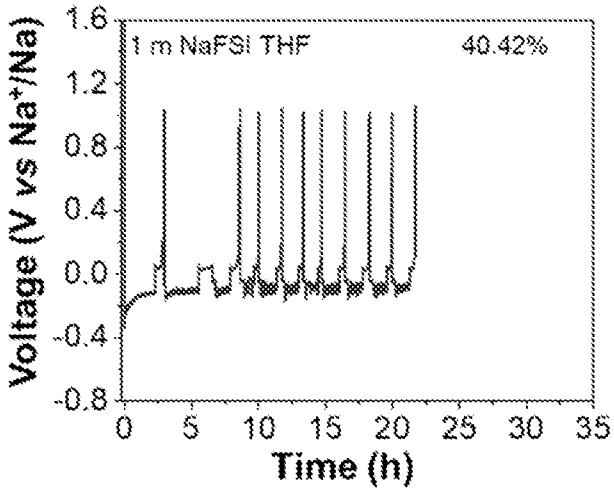


FIG. 10G

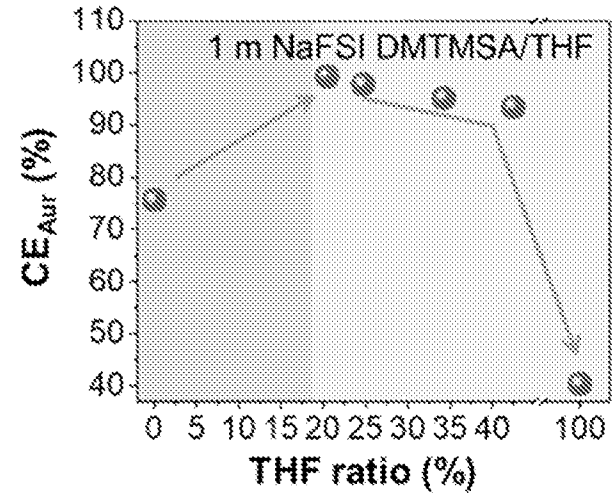


FIG. 10H

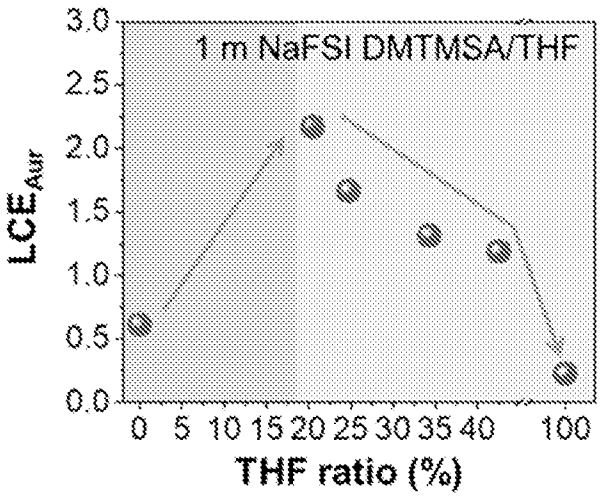


FIG. 11

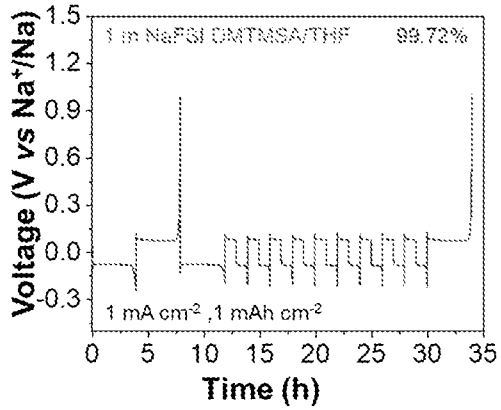


FIG. 12

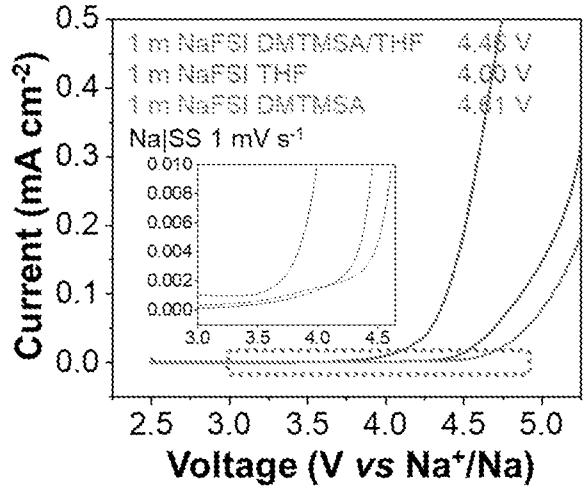


FIG. 13

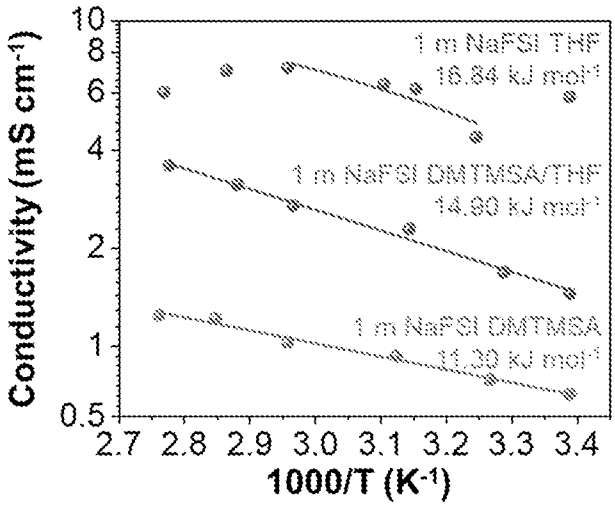


FIG. 14A

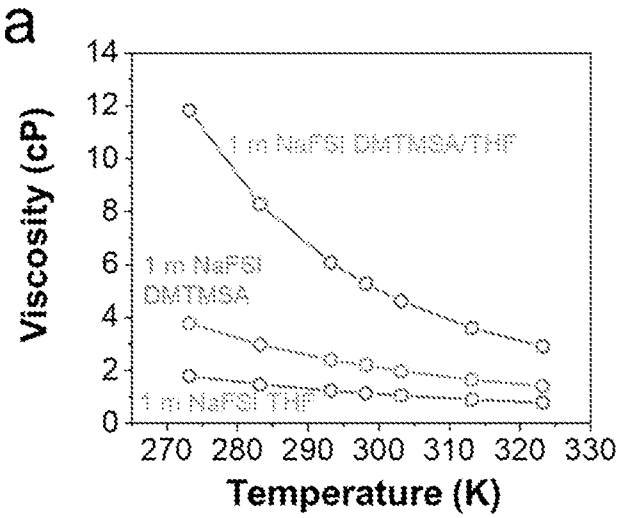


FIG. 14B

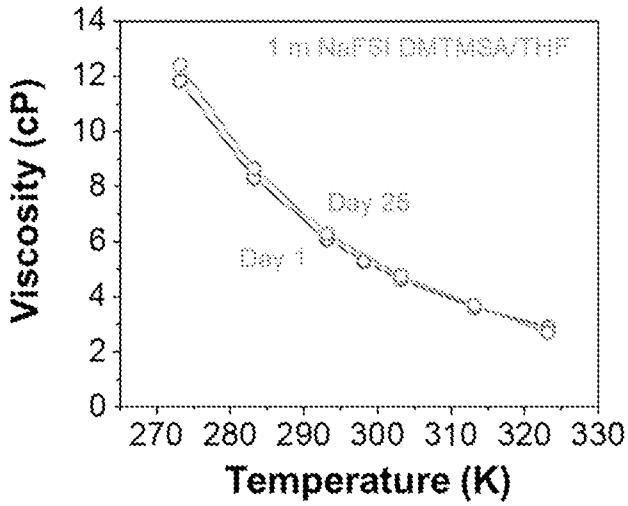


FIG. 15A

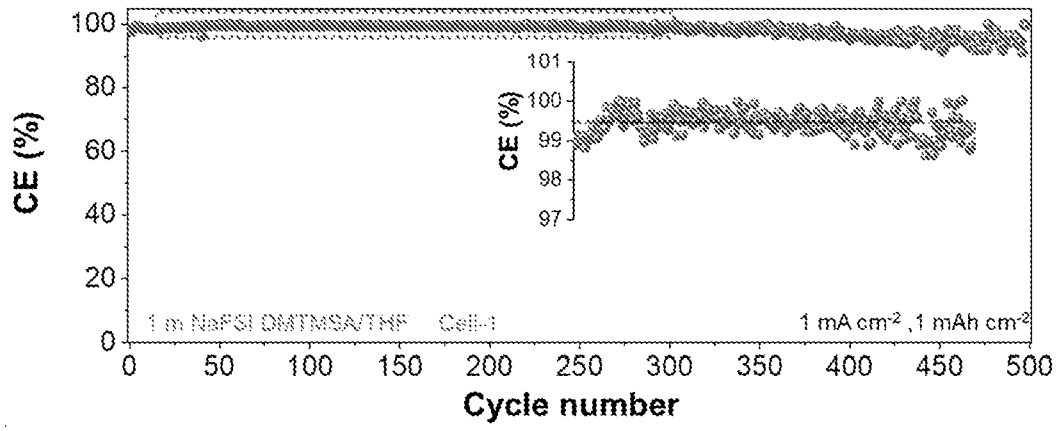


FIG. 15B

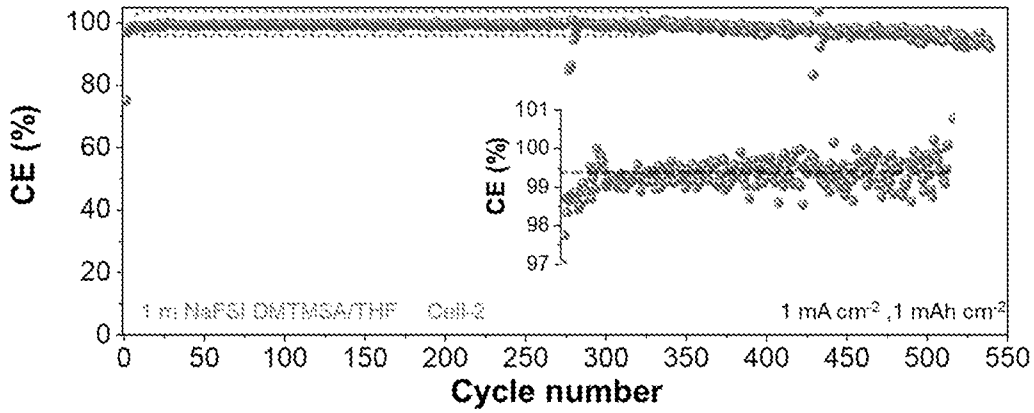


FIG. 15C

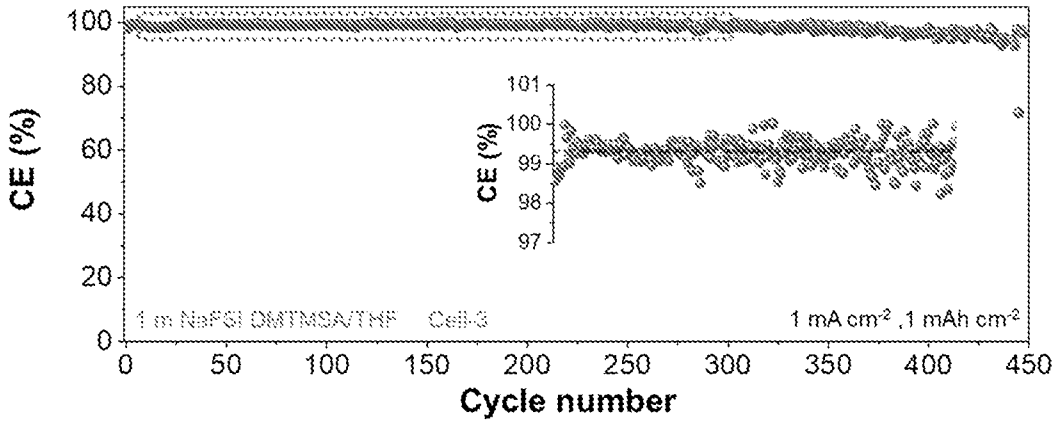


FIG. 16

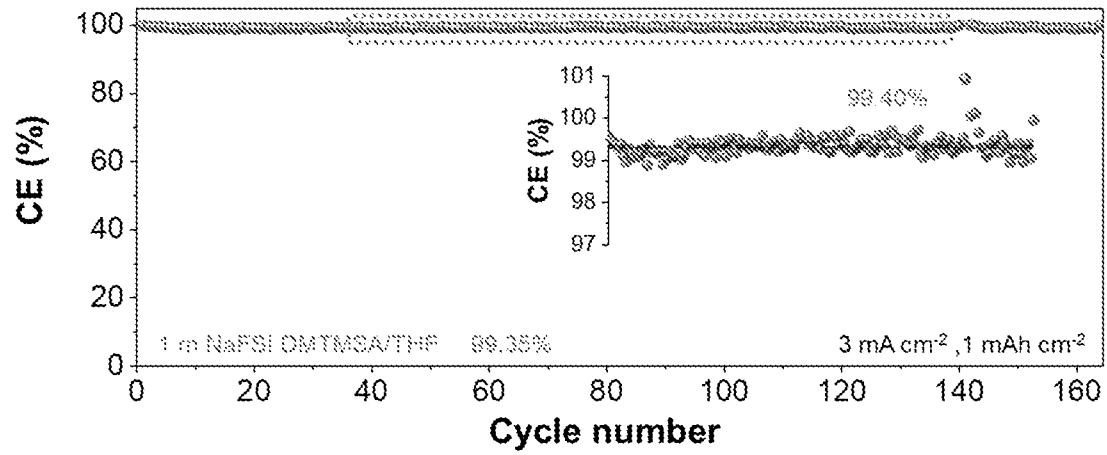


FIG. 17

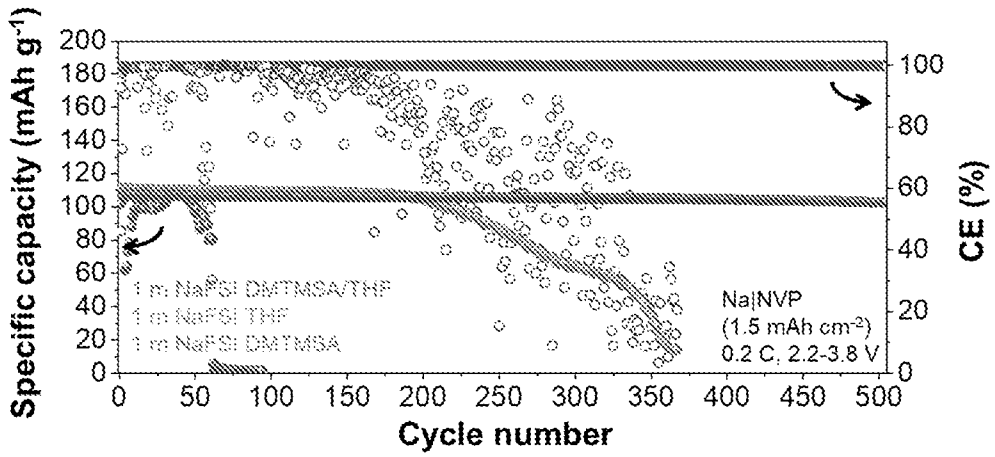


FIG. 18

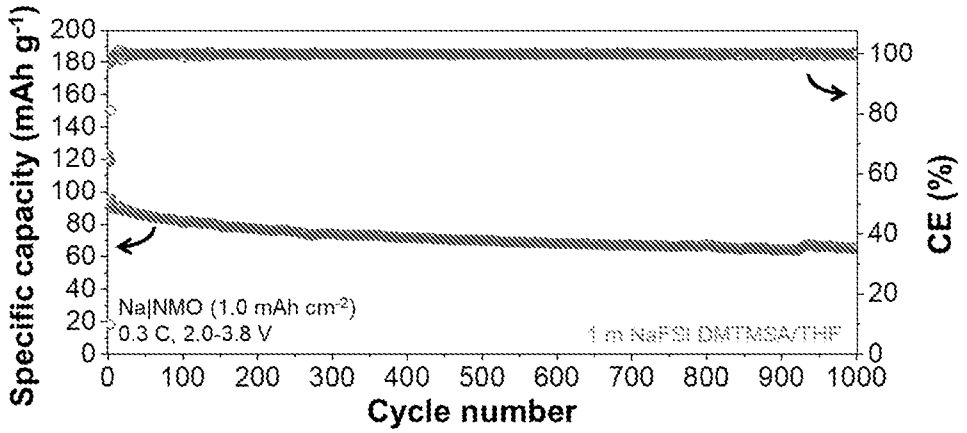


FIG. 19

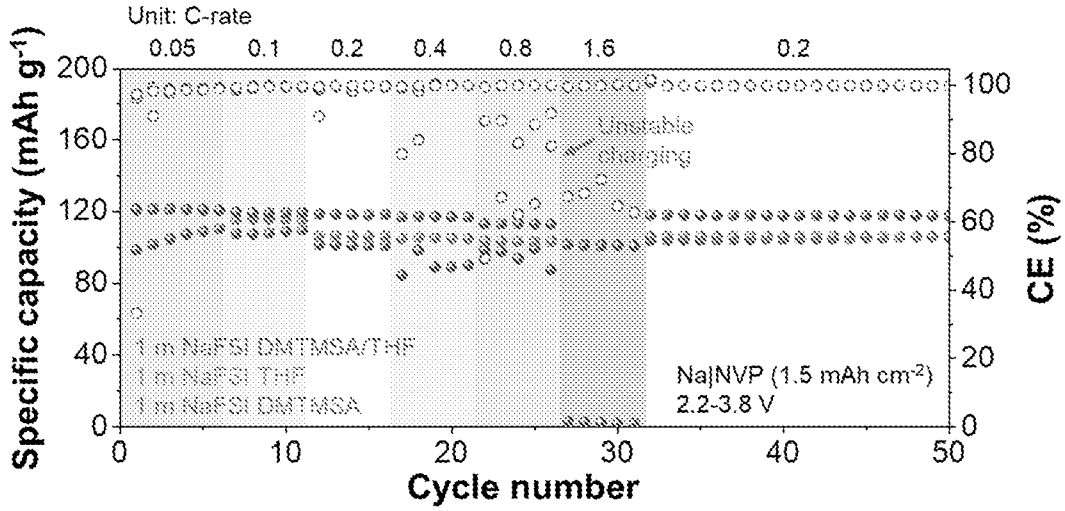


FIG. 20

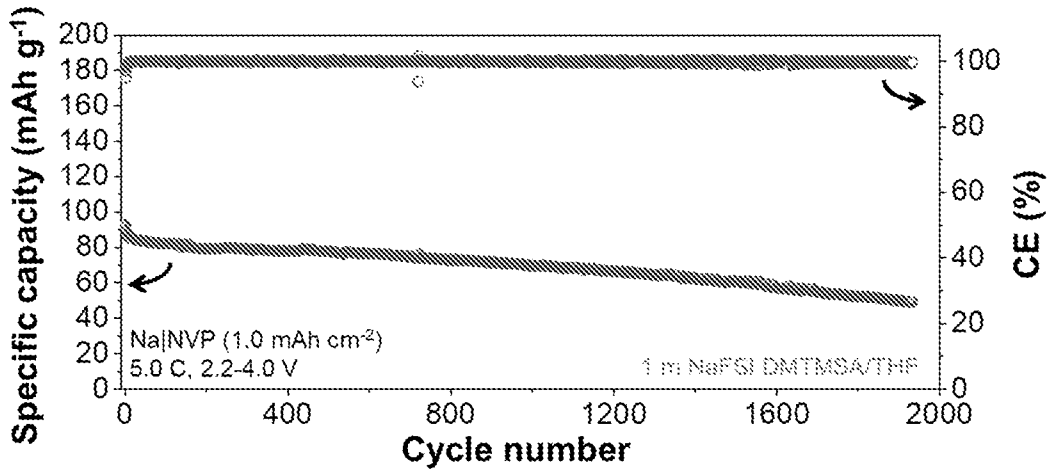


FIG. 21A

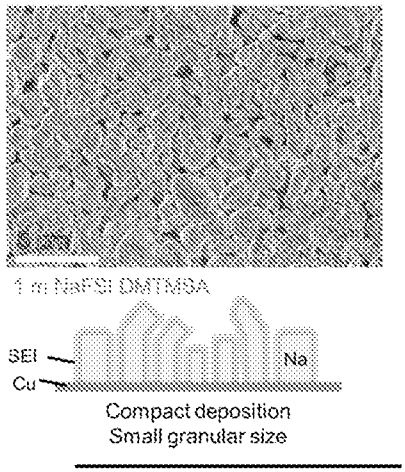


FIG. 21B

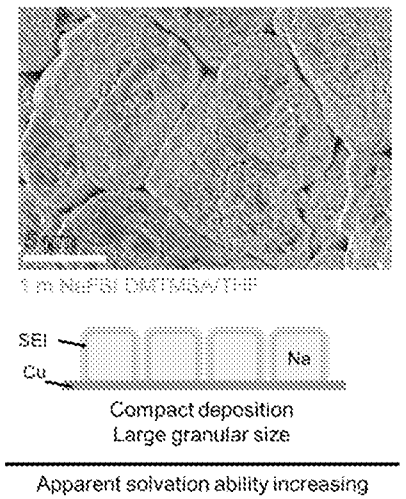


FIG. 21C

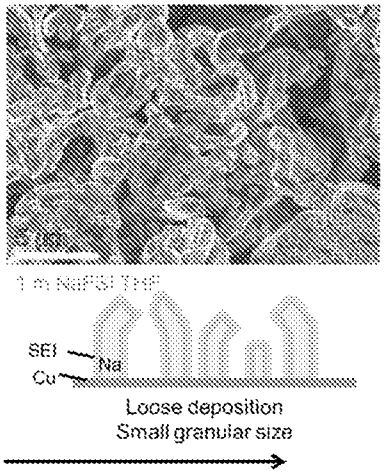


FIG. 22A

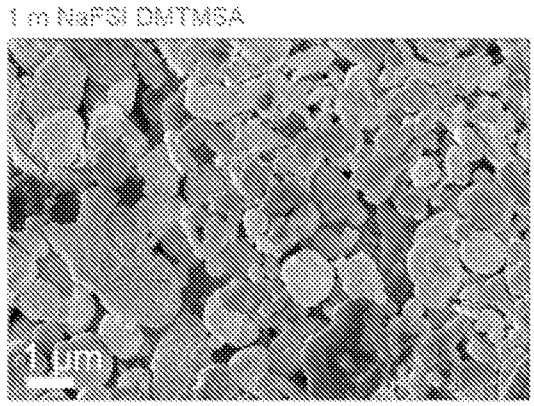


FIG. 22B

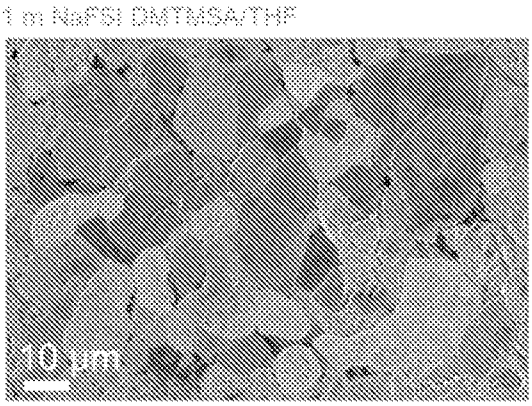


FIG. 22C

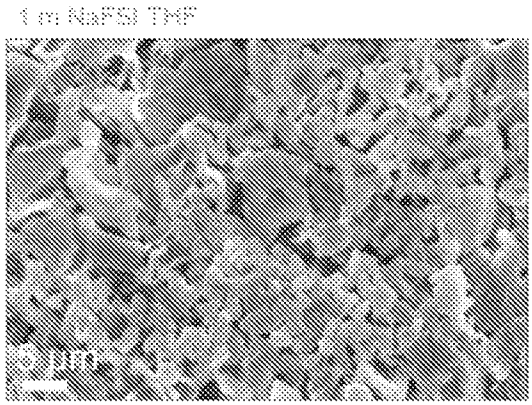


FIG. 22D

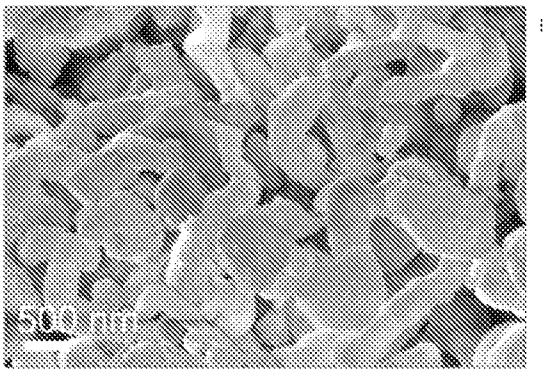


FIG. 22E

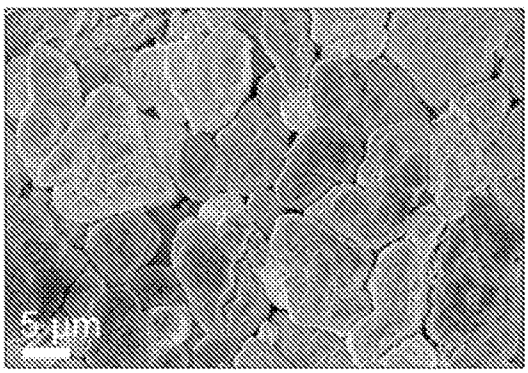


FIG. 22F

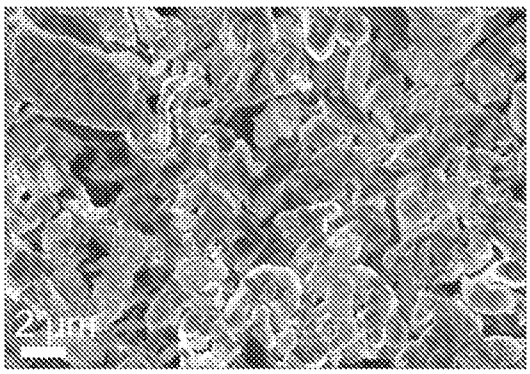


FIG. 22G

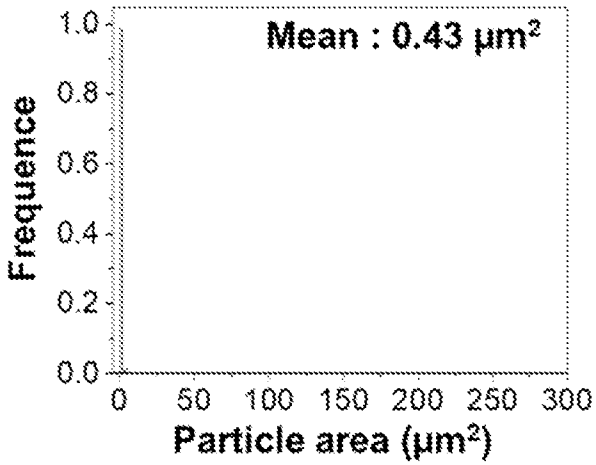


FIG. 22H

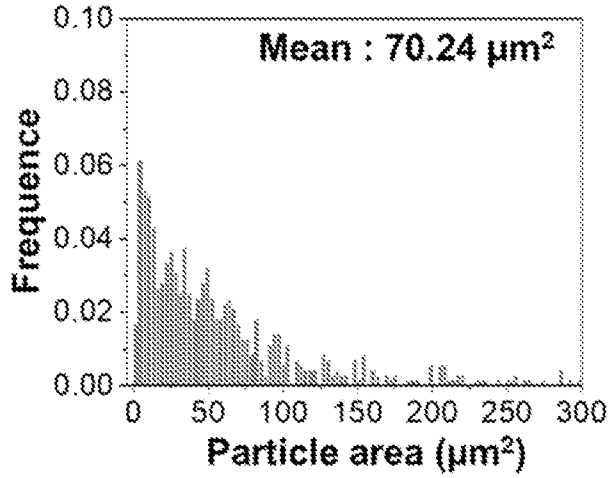


FIG. 22I

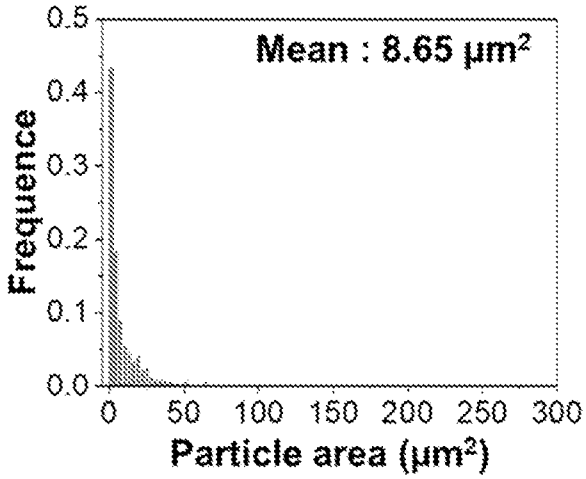


FIG. 22J

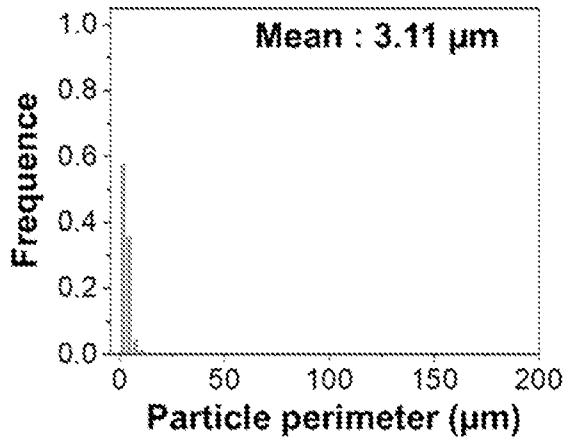


FIG. 22K

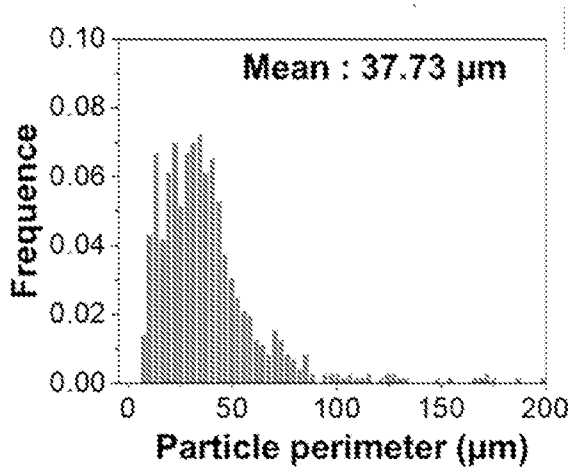


FIG. 22L

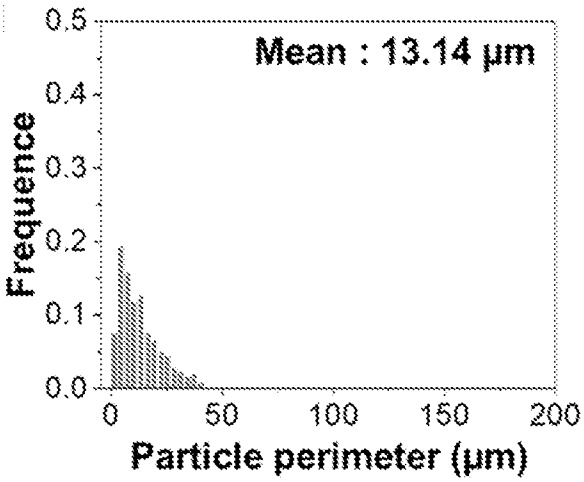


FIG. 23A

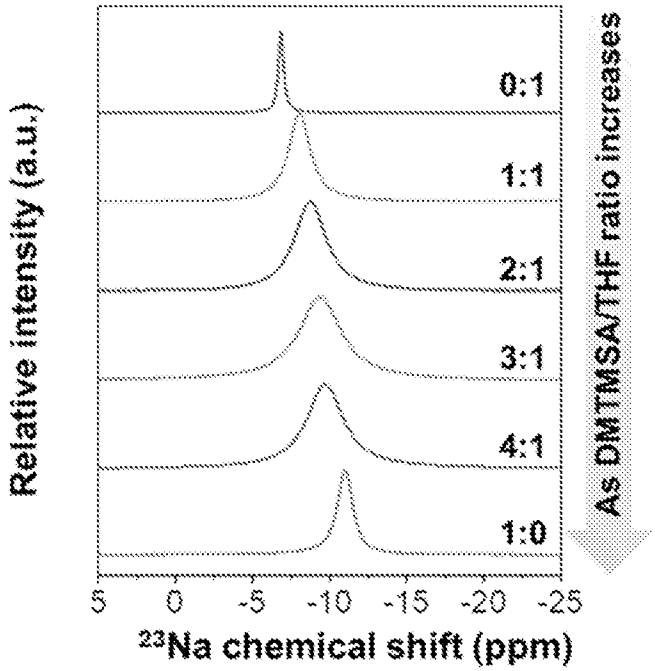


FIG. 23B

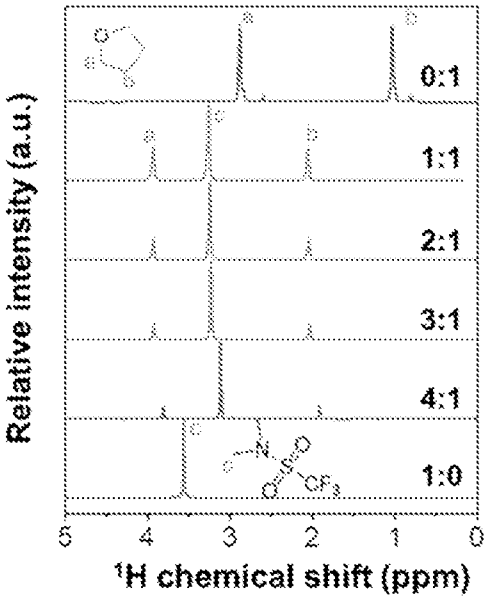


FIG. 23C

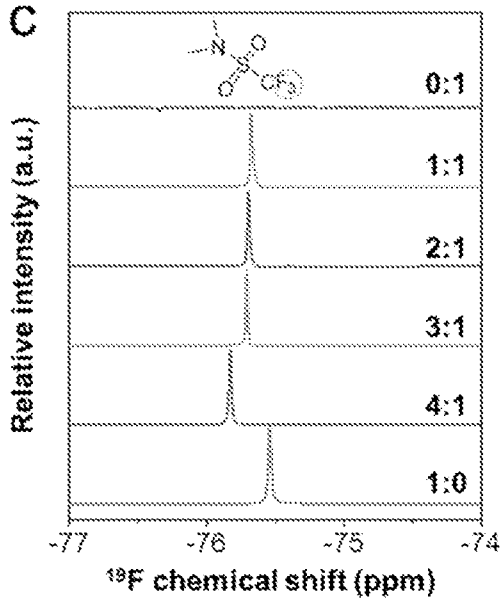


FIG. 24

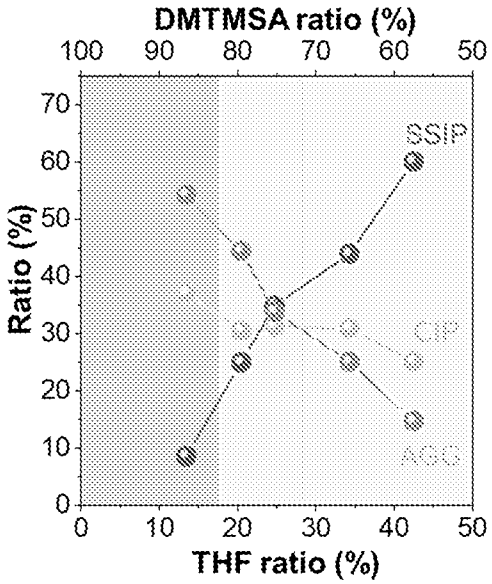

DMTMSA ratio (%)
100 90 80 70 60 50
70 60 50 40 30 20 10 0
Ratio (%)
SSIP
CIP
AGG
0 10 20 30 40 50
THF ratio (%)

FIG. 25

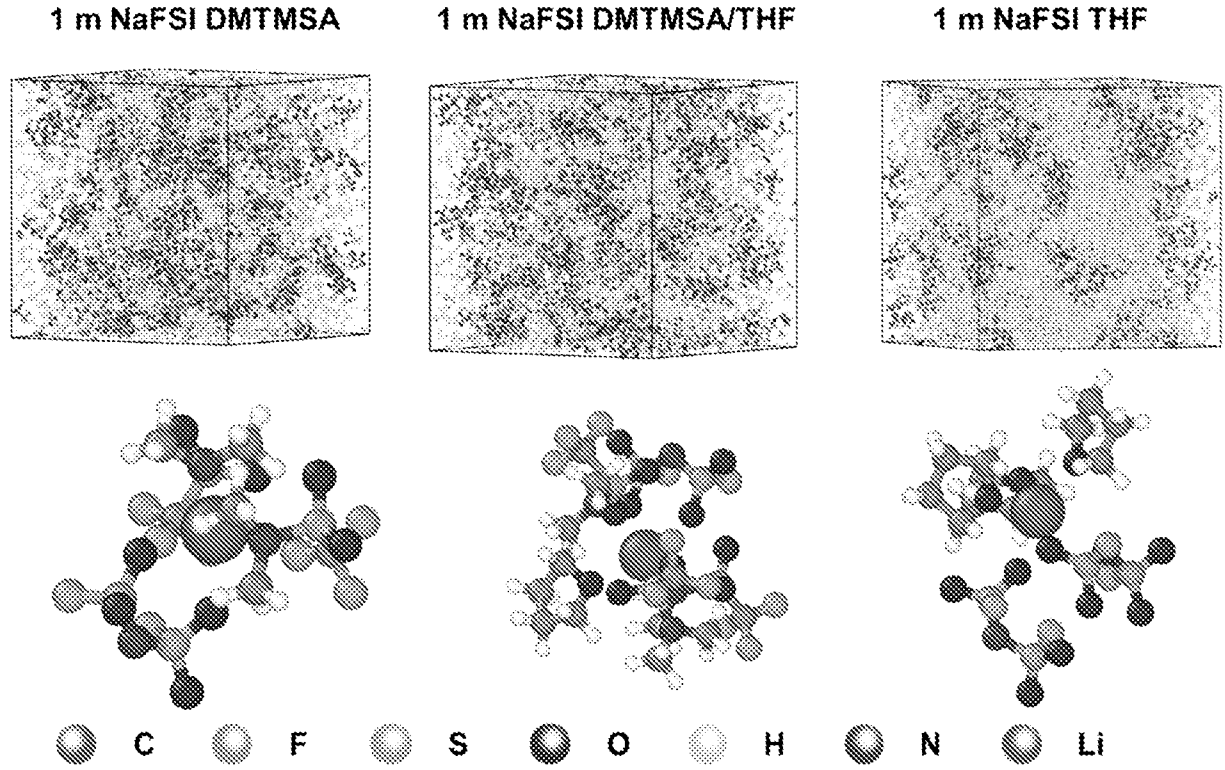

1 m NaFSI DMTMSA
1 m NaFSI DMTMSA/THF
1 m NaFSI THF
C
F
S
O
H
N
Li

FIG. 26A

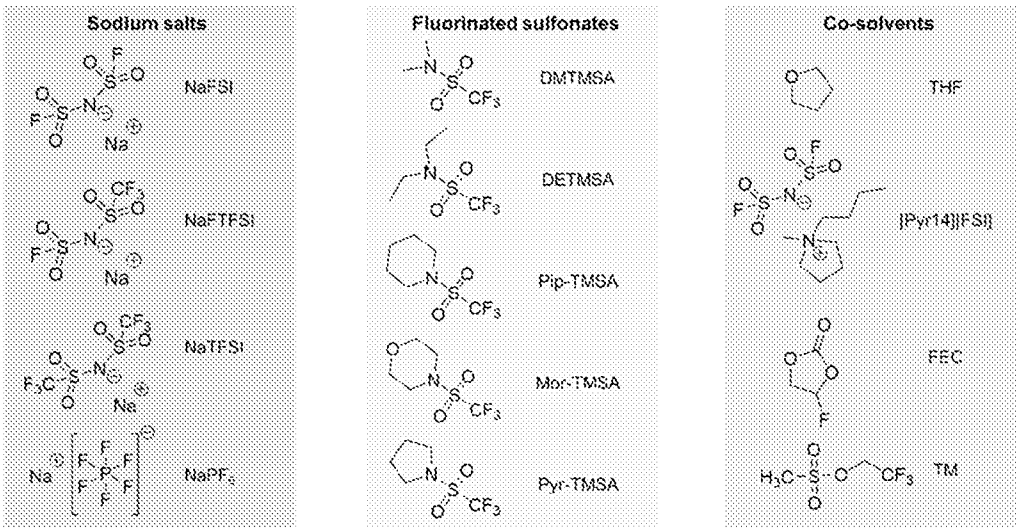


FIG. 26B

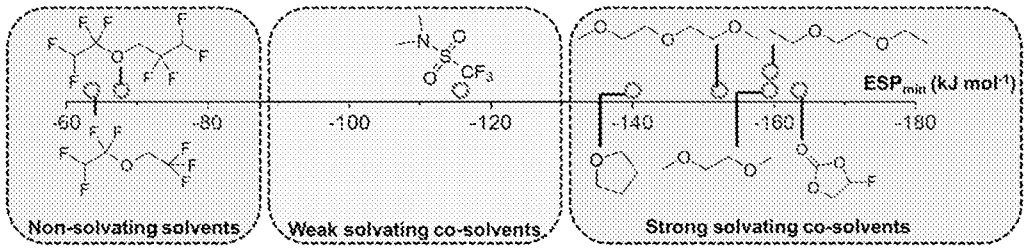


FIG. 27A

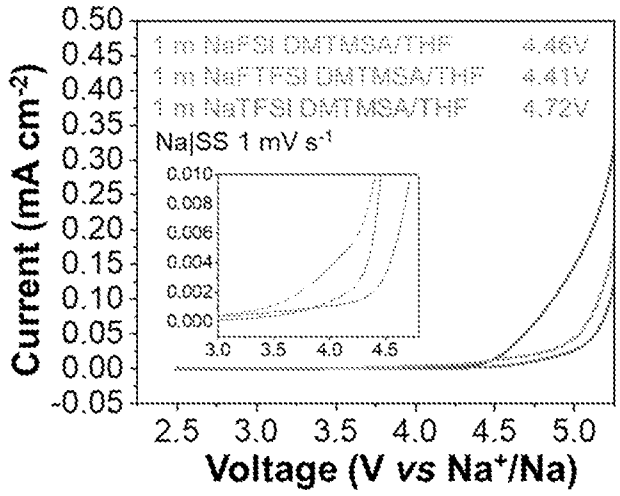


FIG. 27B

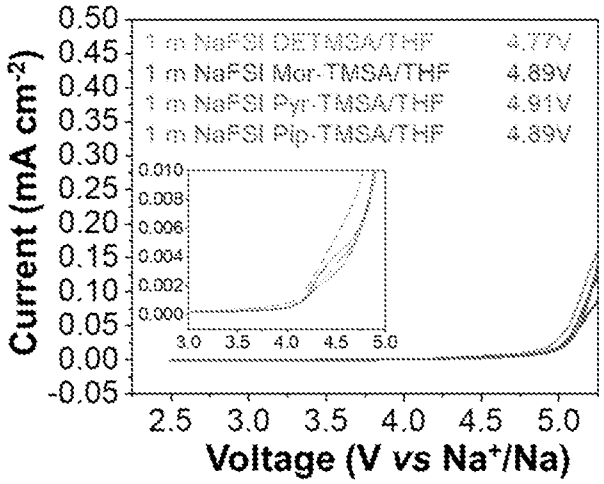


FIG. 27C

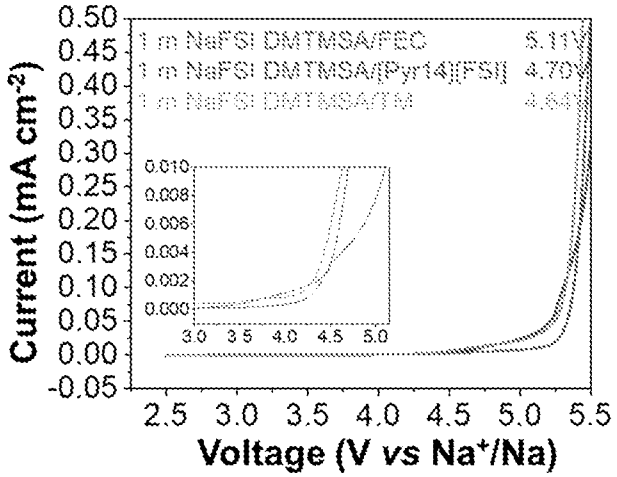


FIG. 27D

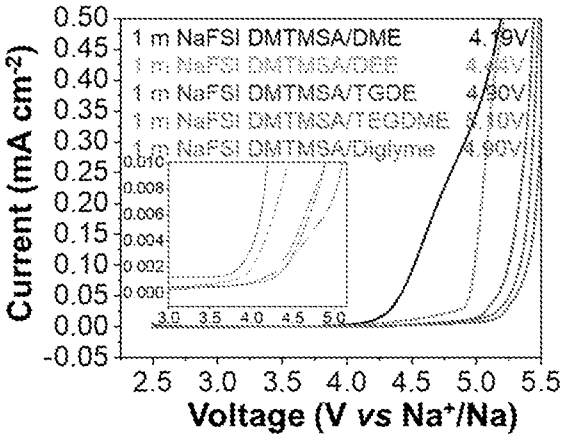


FIG. 27E

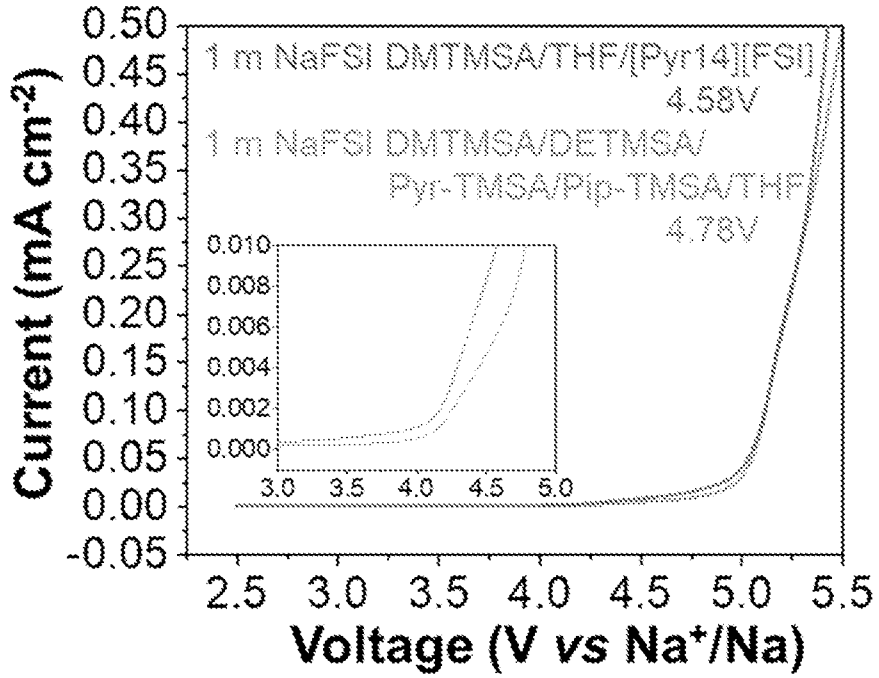


FIG. 27F

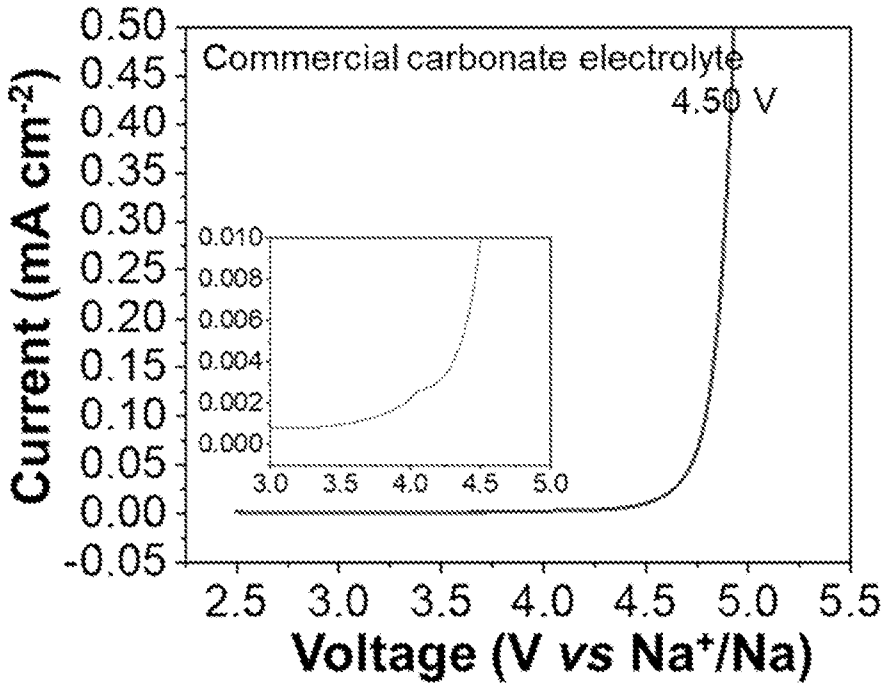


FIG. 28A

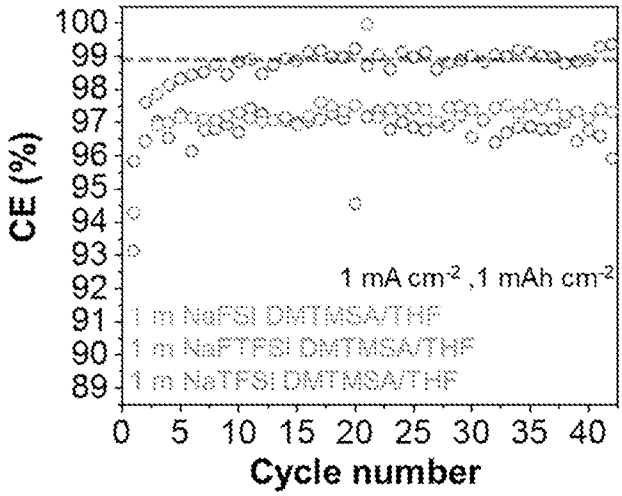


FIG. 28B

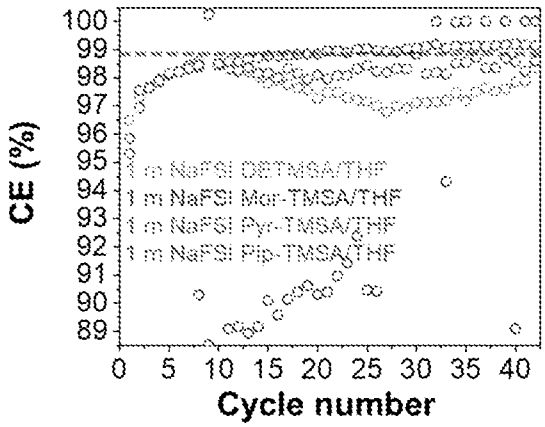


FIG. 28C

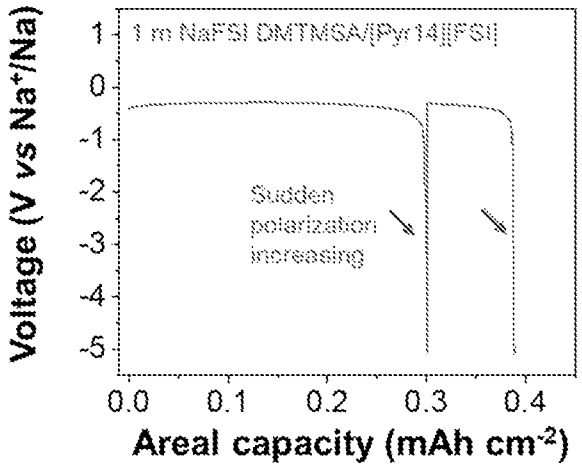


FIG. 28D

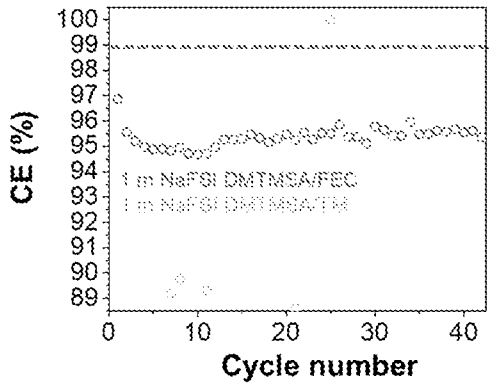


FIG. 28E

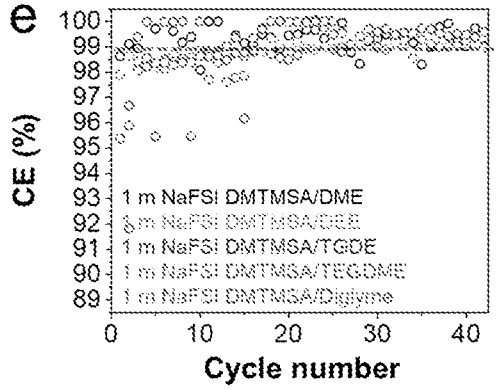


FIG. 28F

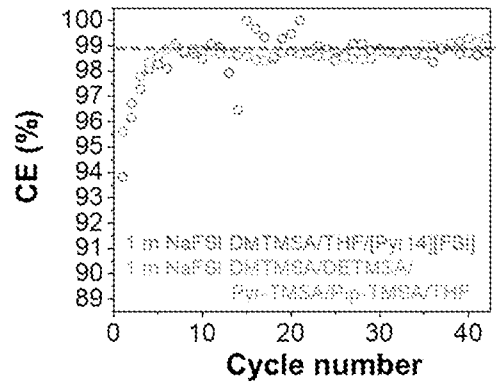


FIG. 29A

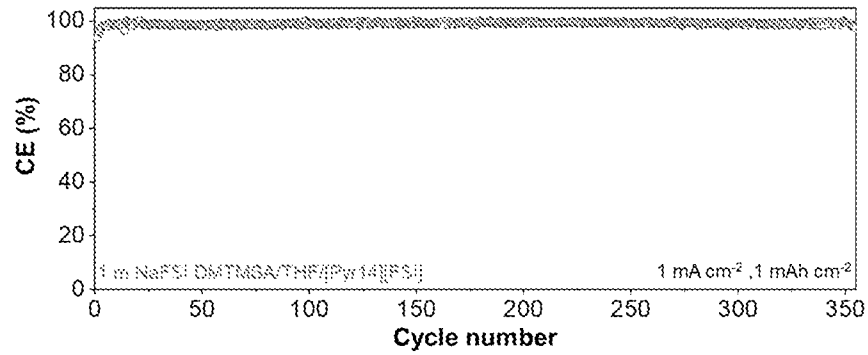


FIG. 29B

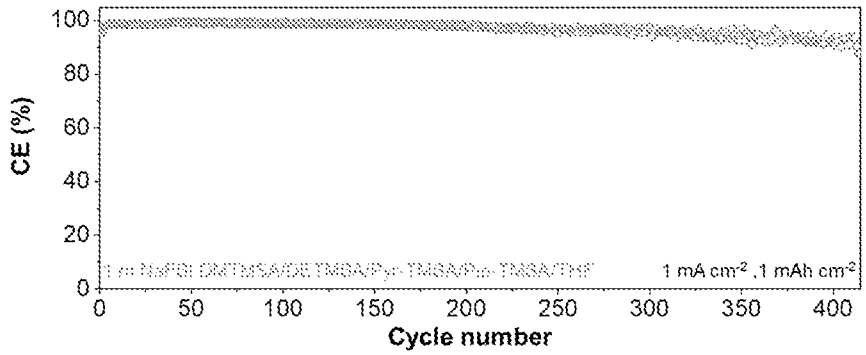


FIG. 29C

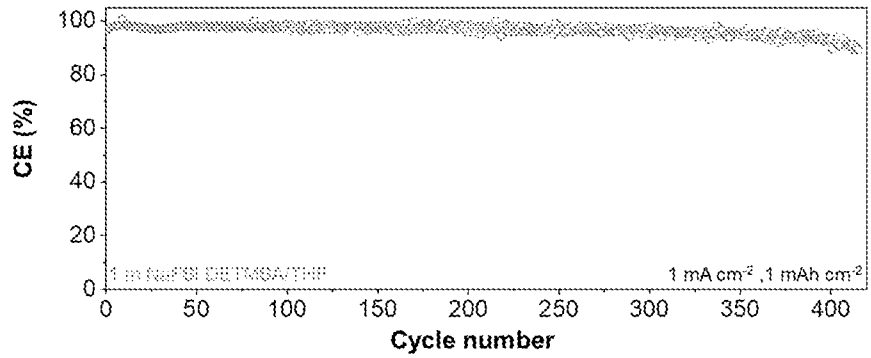


FIG. 29D

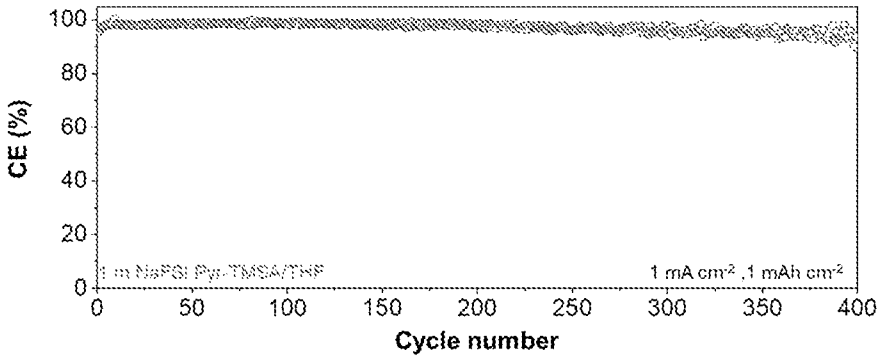


FIG. 29E

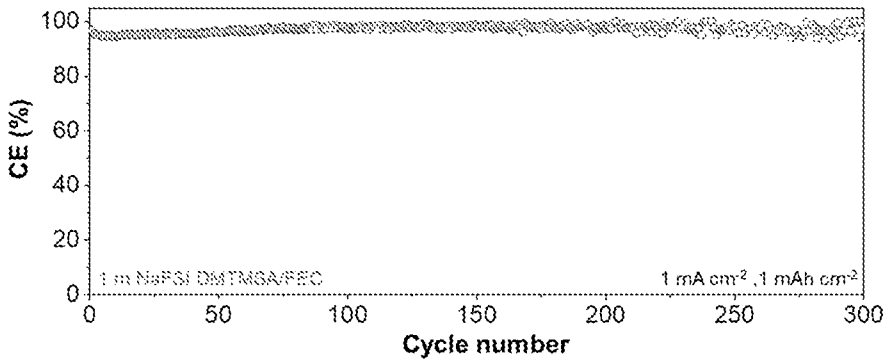


FIG. 29F

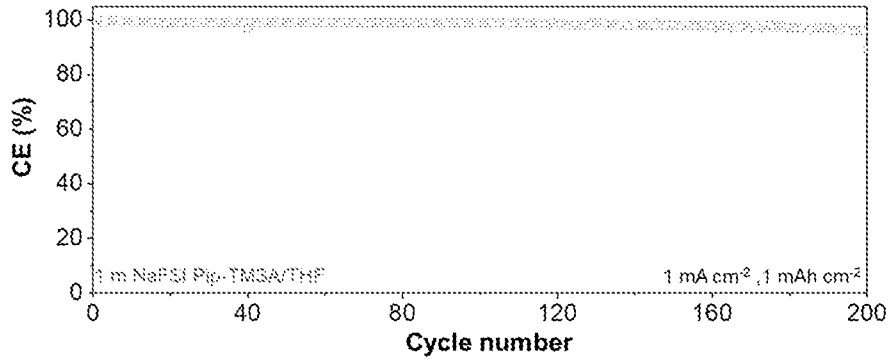


FIG. 29G

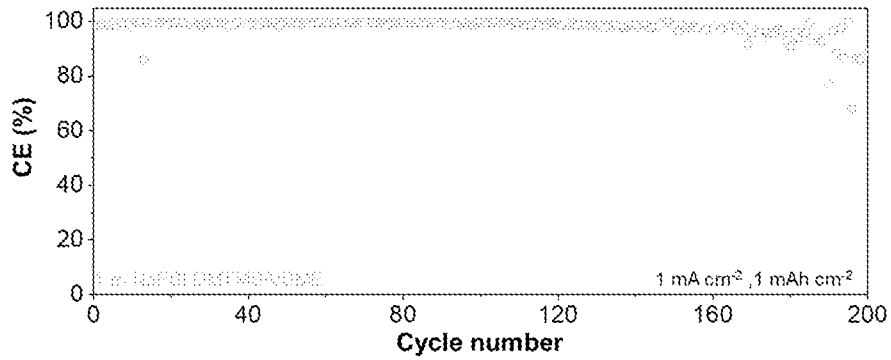


FIG. 29H

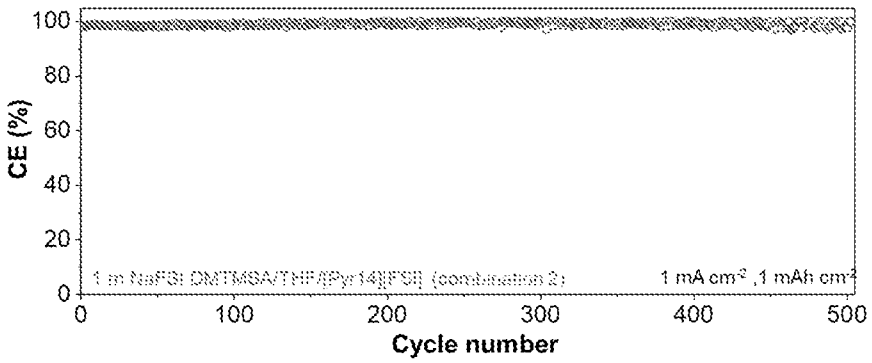


FIG. 29I

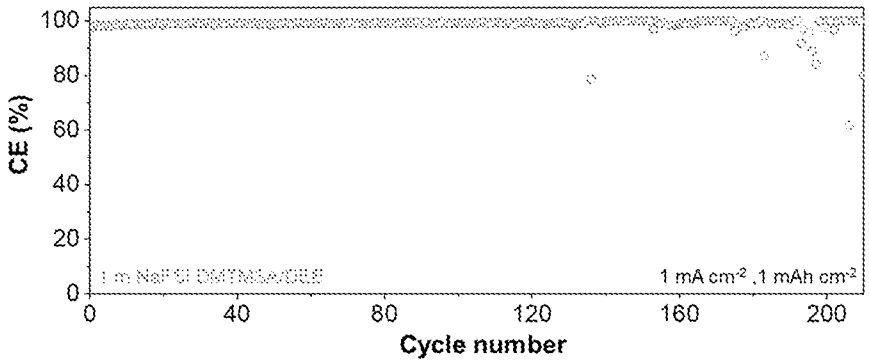


FIG. 30A

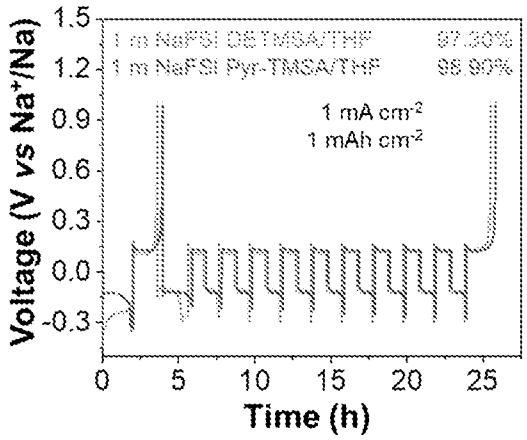


FIG. 30B

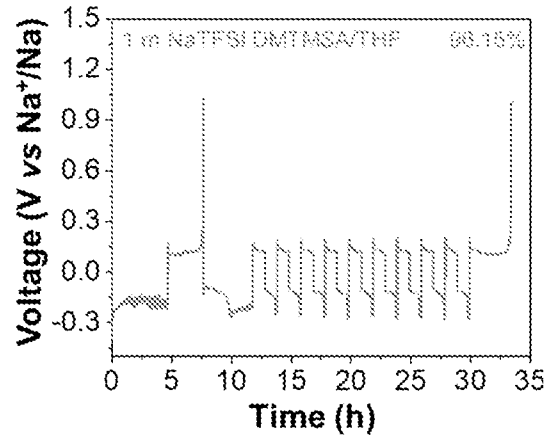


FIG. 30C

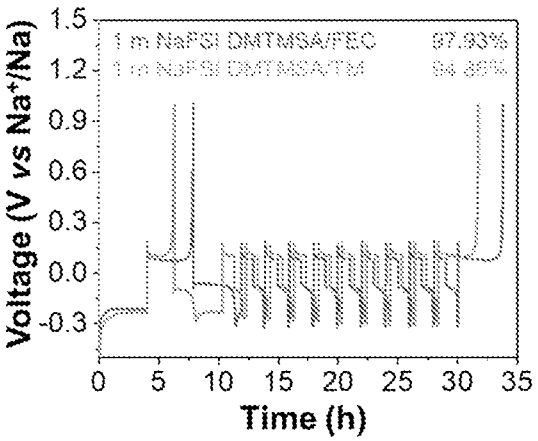


FIG. 30D

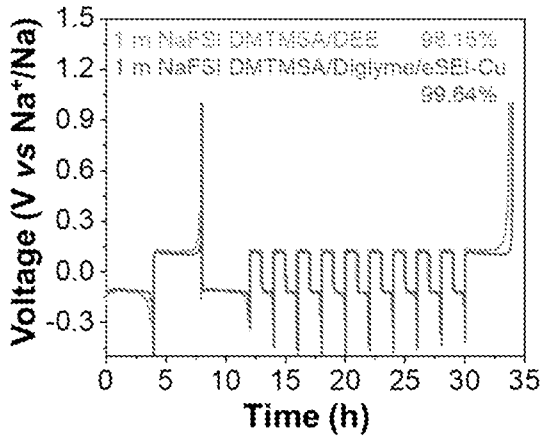


FIG. 30E

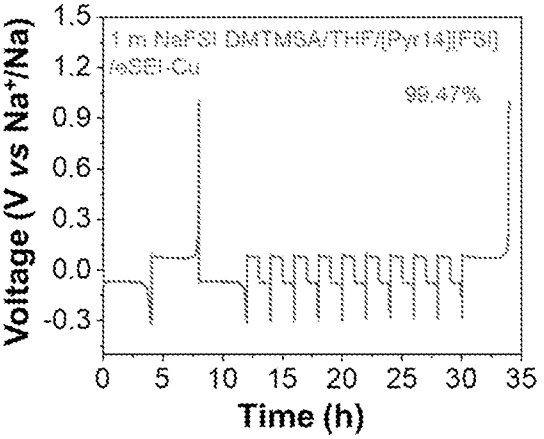


FIG. 30F

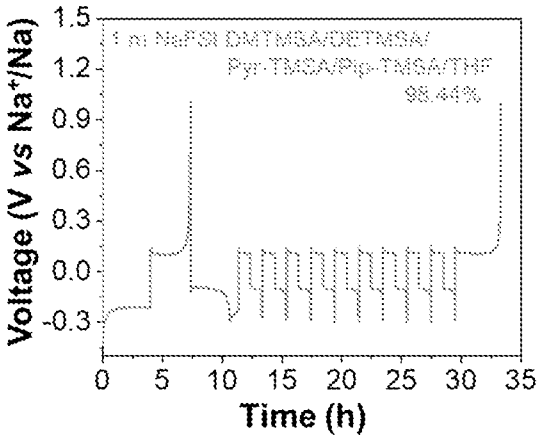
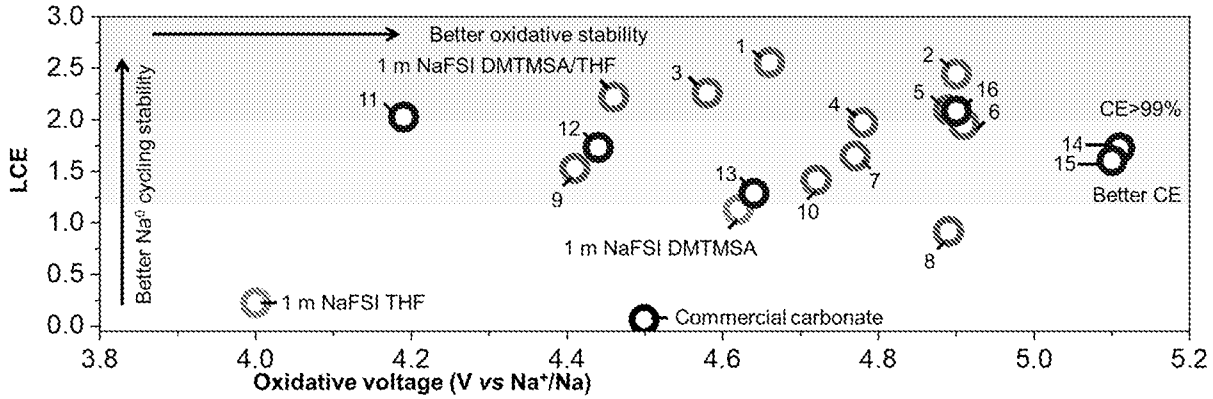


FIG. 31



1 1 m NaFSI DMTMSA/THF/eSEI-Cu
2 1 m NaFSI DMTMSA/Diglyme/eSEI-Cu
3 1 m NaFSI DMTMSA/THF/[Pyr14][FSI]
4 1 m NaFSI DMTMSA/DETMSA/Pyr-TMSA/Pip-TMSA/THF
5 1 m NaFSI Pip-TMSA/THF
6 1 m NaFSI Pyr-TMSA/THF
7 1 m NaFSI DETMSA/THF
8 1 m NaFSI Mor-TMSA/THF
9 1 m NaFTFSI DMTMSA/THF
10 1 m NaTFSI DMTMSA/THF
11 1 m NaFSI DMTMSA/DME
12 1 m NaFSI DMTMSA/DEE
13 1 m NaFSI DMTMSA/TM
14 1 m NaFSI DMTMSA/FEC
15 1 m NaFSI DMTMSA/TEGDME
16 1 m NaFSI DMTMSA/TGDE