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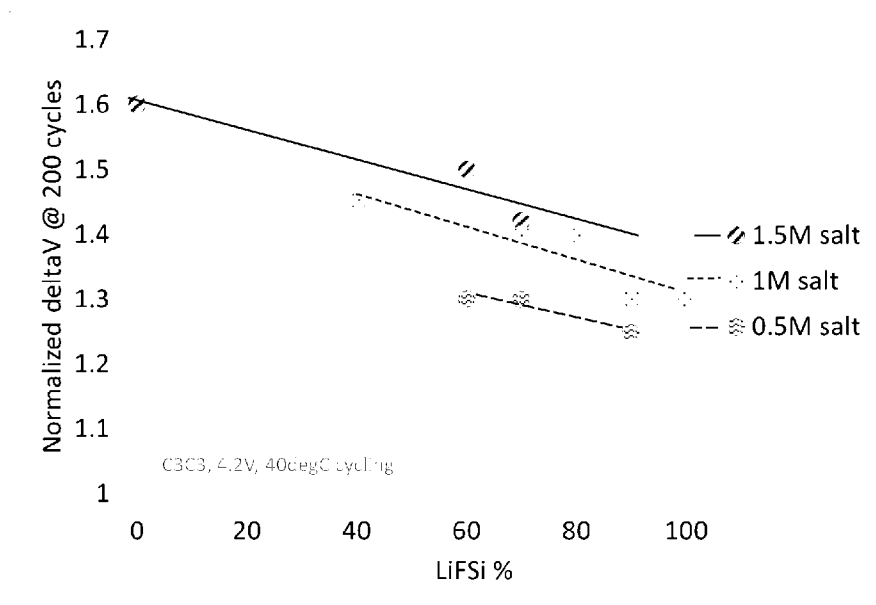


FIG. 1

(57) Abstract: A low salt electrolyte for an energy storage device, including a solvent an additive and a lithium salt at a low total concentration. Such low salt electrolytes may allow for improved energy storage device performances, such as improved internal resistance (e.g., reduced direct current internal resistance (DCR) growth) and improved dissolution properties (e.g., reduced Mn and/or Al dissolution).



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- *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))*

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LOW SALT ELECTROLYTE COMPOSITIONS FOR ENERGY STORAGE DEVICES, 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 U.S. Provisional Application No. 63/585,774, filed on September 27, 2023, which is incorporated by reference herein in its entirety for all purposes.

BACKGROUND

Field

[0002] The present disclosure relates generally to energy storage devices, and specifically to cathode active materials for lithium-ion batteries and processes for forming the same.

Description of the Related Art

[0003] 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 limits of electrochemical energy storage devices can result in increased energy density, increased power capability, and broadening the range of real-world use cases.

[0004] Some cathode electrodes in lithium-ion batteries are fabricated from first row transition metal oxides. Examples of such cathode active materials include lithium cobalt oxide (LCO), lithium nickel manganese cobalt oxide (NMC) and lithium manganese oxide (LMO). Some other cathode electrodes in lithium-ion batteries include transition metal phosphate, such as lithium iron phosphate (LFP). However, the performance of cathode active materials used in lithium-ion batteries can be responsible for inferior and undesirable battery performance, including the loss of charge storage capacity during repeated charge/discharge cycles.

SUMMARY

[0005] 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.

[0006] In one aspect, a low salt electrolyte energy storage device is described. The low salt electrolyte energy storage device includes a cathode electrode comprising an iron phosphate based active material; a separator; an anode electrode; a low salt electrolyte, comprising: a solvent in an amount of at least about 50 wt.%; an additive in an amount of at most about 10 wt.%; and a lithium salt, wherein a total concentration of the lithium salt is about 0.5-1.2 M; wherein the lithium salt comprises a primary salt selected from the group consisting of LiFSi, LiTFSi, and combinations thereof at a primary amount of about 60-95 mol%, and a co-salt selected from the group consisting of LiPF₆, LiBOB, LiDFOB, and combinations thereof at a co-amount of about 5-40 mol%; and a housing, wherein the cathode electrode, the separator, the anode electrode and low salt electrolyte are positioned within the housing.

[0007] In another aspect, a low salt electrolyte for an energy storage device is disclosed. The low salt electrolyte includes a solvent in an amount of at least about 50 wt.%; an additive in an amount of at most about 10 wt.%; and a lithium salt, wherein a total concentration of the lithium salt is at most about 1.1 M.

[0008] In some embodiments, the low salt electrolyte comprises a total concentration of the lithium salt of 0.5-1 M. In some embodiments, the lithium salt is selected from the group consisting of LiFSi, LiTFSi, and combinations thereof. In some embodiments, the lithium salt comprises LiFSi. In some embodiments, the lithium salt further comprises a co-salt. In some embodiments, the lithium salt comprises the co-salt in an amount below about 50 mol%. In some embodiments, the co-salt comprises a compound is selected from the group consisting of LiPF₆, LiBOB, LiDFOB, and combinations thereof. In some embodiments, the lithium salt comprises 60-97 mol% of LiFSi and 3-40 mol% of LiPF₆. In some embodiments,

the solvent comprises a compound is selected from the group consisting of a carbonate, an ether, an ester, and combinations thereof. In some embodiments, the solvent comprises a compound is selected from the group consisting of EC, PC, VEC, VC, FEC, DMC, DEC, EMC, MA, MP, EA, MB, and combinations thereof. In some embodiments, the solvent comprises a compound is selected from the group consisting of EC, DMC, EMC, and combinations thereof. In some embodiments, the solvent comprises EC and EMC. In some embodiments, the additive comprises a compound selected from the group consisting of DTD, VC, FEC, and combinations thereof.

[0009] In another aspect, an energy storage device is disclosed. The energy storage includes a cathode electrode; a separator; an anode electrode; a low salt electrolyte; and a housing, wherein the cathode electrode, the separator, the anode electrode and low salt electrolyte are positioned within the housing.

[0010] In some embodiments, the cathode electrode comprises lithium manganese iron phosphate (LMFP) active material. In some embodiments, the anode electrode comprises graphite. In some embodiments, the energy storage device is a battery. In some embodiments, the DCR growth is reduced by about 5-40% after 200 cycles relative to an energy storage device comprising a lithium salt at a higher total concentration. In some embodiments, the Mn loading on the negative electrode due to Mn deposition is reduced by a factor of about 2-3 relative to an energy storage device comprising a lithium salt at a higher total concentration.

[0011] In another aspect, a method of preparing an energy storage device is described. The method includes positioning a cathode electrode, a separator, an anode electrode and a low salt electrolyte within a housing.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] FIG. 1 is a plot showing the normalized (to the third charge-discharge cycle) voltage polarization measurement of energy storage devices at different salt conditions, according to some embodiments.

[0013] FIG. 2 is a bar chart showing the normalized (to the third charge-discharge cycle) voltage polarization measurement of energy storage devices, according to some embodiments.

[0014] FIG. 3A shows bar charts detailing the Mn loading and Mn deposition rate on the negative electrode of an energy storage device with 1.2M salt concentration operated at 40°C after 200 charge/discharge cycles versus the composition of the electrolyte, according to some embodiments.

[0015] FIG. 3B shows bar charts detailing the Mn loading and Mn deposition rate on the negative electrode of an energy storage device with 1.0M salt concentration operated at 40°C after 200 charge/discharge cycles versus the composition of the electrolyte, according to some embodiments.

[0016] FIG. 4A shows bar charts detailing the Mn loading and Mn deposition rate on the negative electrode of an energy storage device with 1.2M salt concentration operated at 70°C after 200 charge/discharge cycles versus the composition of the electrolyte, according to some embodiments.

[0017] FIG. 4B shows bar charts detailing the Mn loading and Mn deposition rate on the negative electrode of an energy storage device with 1.0M salt concentration operated at 70°C after 200 charge/discharge cycles versus the composition of the electrolyte, according to some embodiments.

[0018] FIG. 5A shows bar charts detailing the Al loading and Al deposition rate on the negative electrode of an energy storage device with 1.2M salt concentration operated at 40°C after 200 charge/discharge cycles versus the composition of the electrolyte, according to some embodiments.

[0019] FIG. 5B shows bar charts detailing the Al loading and Al deposition rate on the negative electrode of an energy storage device with 1.0M salt concentration operated at 40°C after 200 charge/discharge cycles versus the composition of the electrolyte, according to some embodiments.

[0020] FIG. 6A shows bar charts detailing the Al loading and Al deposition rate on the negative electrode of an energy storage device with 1.2M salt concentration operated at 70°C after 200 charge/discharge cycles versus the composition of the electrolyte, according to some embodiments.

[0021] FIG. 6B shows bar charts detailing the Al loading and Al deposition rate on the negative electrode of an energy storage device with 1.0M salt concentration operated at

70°C after 200 charge/discharge cycles versus the composition of the electrolyte, according to some embodiments.

[0022] FIG. 7A shows plots detailing the absolute discharge capacity, normalized discharge capacity and normalized voltage polarization ($\Delta V / \Delta V''$) measurements of energy storage devices of the electrolyte with 1.2 M salt concentration operated at 40°C, according to some embodiments.

[0023] FIG. 7B shows plots detailing the absolute discharge capacity, normalized discharge capacity and normalized voltage polarization ($\Delta V / \Delta V''$) measurements of energy storage devices of the electrolyte with 1.0 M salt concentration operated at 40°C, according to some embodiments.

[0024] FIG. 8A shows plots detailing the absolute discharge capacity, normalized discharge capacity and normalized voltage polarization ($\Delta V / \Delta V''$) measurements of energy storage devices of the electrolyte with 1.2 M salt concentration operated at 70°C, according to some embodiments.

[0025] FIG. 8B shows plots detailing the absolute discharge capacity, normalized discharge capacity and normalized voltage polarization ($\Delta V / \Delta V''$) measurements of energy storage devices of the electrolyte with 1.0 M salt concentration operated at 70°C, according to some embodiments.

[0026] FIG. 9A shows bar charts detailing the Mn loading (a) and Mn deposition rate (d) on the negative electrode of an energy storage device with 1.5M salt concentration operated at 40°C after 200 charge/discharge cycles versus the composition of the electrolyte, according to some embodiments.

[0027] FIG. 9B shows bar charts detailing the Mn loading (b) and Mn deposition rate (e) on the negative electrode of an energy storage device with 1.0M salt concentration operated at 40°C after 200 charge/discharge cycles versus the composition of the electrolyte, according to some embodiments.

[0028] FIG. 9C shows bar charts detailing the Mn loading (c) and Mn deposition rate (f) on the negative electrode of an energy storage device with 0.5M salt concentration operated at 40°C after 200 charge/discharge cycles versus the composition of the electrolyte, according to some embodiments.

[0029] FIG. 10A shows bar charts detailing the Mn loading (a) and Mn deposition rate (d) on the negative electrode of an energy storage device with 1.5M salt concentration operated at 70°C after 200 charge/discharge cycles versus the composition of the electrolyte, according to some embodiments.

[0030] FIG. 10B shows bar charts detailing the Mn loading (b) and Mn deposition rate (e) on the negative electrode of an energy storage device with 1.0M salt concentration operated at 70°C after 200 charge/discharge cycles versus the composition of the electrolyte, according to some embodiments.

[0031] FIG. 10C shows bar charts detailing the Mn loading (c) and Mn deposition rate (f) on the negative electrode of an energy storage device with 0.5M salt concentration operated at 70°C after 200 charge/discharge cycles versus the composition of the electrolyte, according to some embodiments.

[0032] FIG. 11A is a bar chart showing the Al loading on the negative electrode of an energy storage device with 1.5M salt concentration operated at 40°C after 200 charge/discharge cycles versus the composition of the electrolyte, according to some embodiments.

[0033] FIG. 11B is a bar chart showing the Al loading on the negative electrode of an energy storage device with 1.0M salt concentration operated at 40°C after 200 charge/discharge cycles versus the composition of the electrolyte, according to some embodiments.

[0034] FIG. 11C is a bar chart showing the Al loading on the negative electrode of an energy storage device with 0.5M salt concentration operated at 40°C after 200 charge/discharge cycles versus the composition of the electrolyte, according to some embodiments.

[0035] FIG. 12A is a bar chart showing the Al loading on the negative electrode of an energy storage device with 1.5M salt concentration operated at 70°C after 200 charge/discharge cycles versus the composition of the electrolyte, according to some embodiments.

[0036] FIG. 12B is a bar chart showing the Al loading on the negative electrode of an energy storage device with 1.0M salt concentration operated at 70°C after 200

charge/discharge cycles versus the composition of the electrolyte, according to some embodiments.

[0037] FIG. 12C is a bar chart showing the Al loading on the negative electrode of an energy storage device with 0.5M salt concentration operated at 70°C after 200 charge/discharge cycles versus the composition of the electrolyte, according to some embodiments.

[0038] FIG. 13A shows plots detailing (a) the discharge capacity, (d) normalized discharge capacity and (g) normalized voltage polarization (“Normalized ΔV ”) measurements of energy storage devices with 1.5 M salt concentration of the electrolyte at 40°C, according to some embodiments.

[0039] FIG. 13B shows plots detailing (b) the discharge capacity, (e) normalized discharge capacity and (h) normalized voltage polarization measurements (“Normalized ΔV ”) of energy storage devices with 1 M salt concentration of the electrolyte at 40°C, according to some embodiments.

[0040] FIG. 13C shows plots detailing (c) the discharge capacity, (f) normalized discharge capacity and (i) normalized voltage polarization measurements (“Normalized ΔV ”) of energy storage devices with 0.5 M salt concentration of the electrolyte at 40°C, according to some embodiments.

[0041] FIG. 14A shows plots detailing (a) the discharge capacity, (d) normalized discharge capacity and (g) normalized voltage polarization (“Normalized ΔV ”) measurements of energy storage devices with 1.5 M salt concentration of the electrolyte at 70°C, according to some embodiments.

[0042] FIG. 14B shows plots detailing (b) the discharge capacity, (e) normalized discharge capacity and (h) normalized voltage polarization (“Normalized ΔV ”) measurements of energy storage devices with 1.0 M salt concentration of the electrolyte at 70°C, according to some embodiments.

[0043] FIG. 14C shows plots detailing (c) the discharge capacity, (f) normalized discharge capacity and (i) normalized voltage polarization (“Normalized ΔV ”) measurements of energy storage devices with 0.5 M salt concentration of the electrolyte at 70°C, according to some embodiments.

DETAILED DESCRIPTION

[0044] The present disclosure may be understood by reference to the following detailed description. It is noted that, for purposes of illustrative clarity, certain elements in various drawings may not be drawn to scale, may be represented schematically or conceptually, or otherwise may not correspond exactly to certain physical configurations of embodiments.

[0045] Provided herein are various embodiments of low salt electrolytes for energy storage devices, and methods thereof. Such low salt electrolytes may allow for improved energy storage device performances, such as improved internal resistance (e.g., reduced direct current internal resistance (DCR) growth), improved dissolution properties (e.g., reduced Mn and/or Al dissolution), and improved capacity retention.

Low Salt Electrolytes

[0046] An energy storage device may be charged with an electrolyte (e.g., a lithium-containing electrolyte). In some embodiments, the electrolyte includes a lithium salt and a solvent. In some embodiments, the solvent is a non-aqueous or organic solvent.

[0047] In some embodiments, the lithium salt includes an anion that is relatively redox stable. In some embodiments, the anion can be monovalent. In some embodiments, a lithium salt (e.g., primary salt, co-salt) can be selected from lithium hexafluorophosphate (LiPF_6), lithium bis(trifluoromethanesulfonyl)imide or lithium bis(fluorosulfonyl)imide (LiFSi or $(\text{LiN}(\text{SO}_2\text{F})_2)$), lithium tetrafluoroborate (LiBF_4), lithium perchlorate (LiClO_4), lithium bis(trifluoromethanesulfonyl)imide ($\text{LiN}(\text{SO}_2\text{CF}_3)_2$), lithium trifluoromethanesulfonate (LiSO_3CF_3), lithium bis(oxalato)borate ($\text{LiB}(\text{C}_2\text{O}_4)_2$ or LiBOB), lithium bis(trifluoromethane)sulfonimide (LiTFSI), lithium difluoro(oxalato)borate ($\text{LiC}_2\text{BF}_2\text{O}_4$ or LiDFOB), lithium tetrafluoro oxalate phosphate (LiTFOP), lithium difluoro dioxalate phosphate (LiDFDOP), and combinations thereof. In some embodiments, the total lithium 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 or 1.8 M, or any range of values therebetween. For example, in some embodiments, the total lithium salt concentration is or is at most about 1.1 M, is or is at most about 1.1 M, is or is at most about 1.5 M, is or is about 0.5-1.1 M, is or is about 0.5-1.5 M, or is or is about 0.5-1 M.

[0048] In some embodiments, the lithium salt includes a primary salt (e.g., LiFSi) and a co-salt (e.g., one or more of LiPF₆, LiBOB, LiDOFOB). In some embodiments the lithium salt comprises the primary salt in, in about, in at least, or in at least about, 50 mol%, 55 mol%, 60 mol%, 65 mol%, 70 mol%, 75 mol%, 80 mol%, 85 mol%, 90 mol%, 92 mol%, 95 mol%, 97 mol%, 98 mol% or 99 mol%, or any range of values therebetween. In some embodiments, the lithium salt comprises the co-salt in less than or less than about 50 mol%. In some embodiments, the lithium salt comprises the co-salt in, in about, in less than, in less than about, in at most, or in at most about, 1 mol%, 2 mol%, 3 mol%, 5 mol%, 8 mol%, 10 mol%, 15 mol%, 20 mol%, 25 mol%, 30 mol%, 35 mol%, 40 mol%, 45 mol%, 50 mol%, or any range of values therebetween. In some embodiments, the primary salt comprises or is LiFSi and/or LiTFSI. In some embodiments, the co-salt comprises or is LiPF₆, LiBOB and/or LiDOFOB.

[0049] In some embodiments, an energy storage device can include a liquid solvent. The solvent need not dissolve every component, and need not completely dissolve any component, of the electrolyte. In further embodiments, the solvent can be 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), 1,3-propene sultone (PRS), 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. In some embodiments, the solvent may include a ratio of EC:DMC:EMC of 10-30:0-90:0-70.

[0050] In some embodiments, one or more solvents can be used at a concentration of, of about, of at least, or at least about, 30 wt. %, 35 wt. %, 40 wt. %, 45 wt. %, 50 wt. %, 55

wt. %, 60 wt. %, 65 wt. %, 70 wt. %, 75 wt. %, 80 wt. %, 85 wt. % or 90 wt. %, or any range of values therebetween.

[0051] In some embodiments, the electrolyte includes an additive. In some embodiments, the additive may include 1,3-propene sultone (PRS), 1,3,2-dioxathiolane-2,2-dioxide (“DTD”), EC, PC, VEC, VC, FEC, DMC, DEC, EMC, MA, MP, EA, MB, and combinations thereof. For example, in some embodiments the additive comprises VC, DTD, VC and FEC, or solvents described herein may be utilized as additives in the electrolyte system. In some embodiments, the additive can be used at a concentration of, of about, of at most, or at most about, 0.1 wt. %, 0.2 wt. %, 0.3 wt. %, 0.4 wt. %, 0.5 wt. %, 0.6 wt. %, 0.7 wt. %, 0.8 wt. %, 0.9 wt. %, 1 wt. %, 1.1 wt. %, 1.2 wt. %, 1.3 wt. %, 1.4 wt. %, 1.5 wt. %, 1.6 wt. %, 1.7 wt. %, 1.8 wt. %, 1.9 wt. %, 2 wt. %, 2.1 wt. %, 2.2 wt. %, 2.3 wt. %, 2.4 wt. %, 2.5 wt. %, 2.6 wt. %, 2.7 wt. %, 2.8 wt. %, 2.9 wt. %, 3 wt. %, 4 wt. %, 5 wt. %, 6 wt. %, 7 wt. %, 8 wt. %, 9 wt. % or 10 wt. %, or any range of values therebetween. In some embodiments, solvents described are utilized as additives in the electrolyte system, and can be used at a concentration of, of about, of at most, or at most about, 0.1 wt.%, 0.2 wt.%, 0.3 wt.%, 0.4 wt.%, 0.5 wt.%, 0.6 wt.%, 0.7 wt.%, 0.8 wt.%, 0.9 wt.%, 1 wt.%, 1.1 wt.%, 1.2 wt.%, 1.3 wt.%, 1.4 wt.%, 1.5 wt.%, 1.6 wt.%, 1.7 wt.%, 1.8 wt.%, 1.9 wt.%, 2 wt.%, 2.1 wt.%, 2.2 wt.%, 2.3 wt.%, 2.4 wt.%, 2.5 wt.%, 2.6 wt.%, 2.7 wt.%, 2.8 wt.%, 2.9 wt.%, 3 wt.%, 4 wt.%, 5 wt.%, 6 wt.%, 7 wt.%, 8 wt.%, 9 wt.% or 10 wt.%, or any range of values therebetween. For example, in some embodiments, the amount of an additive in the electrolyte is or is about in any one of the following ranges: 0.1-10 wt.%, 1-6 wt.%, 2-5 wt.%, 0.1-6 wt.%, 2-8 wt.%, 2-3 wt.%, or 1-4 wt.%.

Energy Storage Device

[0052] An active material (e.g., cathode active material, anode active material) may be used in the preparation of an electrode film and/or electrode for an energy storage device. In some embodiments, an electrode comprises a current collector and an electrode film.

[0053] 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 cathode active material is selected from lithium iron phosphate (i.e.,

LiFePO₄ or “LFP”), lithium manganese iron phosphate (e.g., LiMn_{0.6}Fe_{0.4}PO₄ or “LMFP”), lithium nickel manganese cobalt oxide (i.e., LiNi_xMn_yCo_{1-x-y}O₂ or “NMC”), lithium nickel cobalt aluminum oxide (i.e., LiNi_xCo_yAl_zO₂ or “NCA”), lithium manganese oxide (“LMO”), lithium nickel manganese oxide (“LNMO”), lithium cobalt oxide (“LCO”), lithium titanate (“LTO”), or combinations thereof. In some embodiments, the cathode active material includes at least two of LFP, LMFP, NMC, NCA, LMO, LNMO, LCO, LTO, and combinations thereof. In some embodiments, the cathode active material is an iron phosphate-based active material. In some embodiments, iron phosphate-based active materials include LiFePO₄ (i.e., “lithium iron phosphate” and “LFP”) and LiMn_{1-x}Fe_xPO₄ (i.e., “lithium manganese iron phosphate” and “LMFP”) (e.g., LiMn_{0.6}Fe_{0.4}PO₄ or LiMn_{0.8}Fe_{0.2}PO₄). 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.

[0054] In some embodiments, the active material is an anode active material. In some embodiments, anode active materials can include, for example, an insertion material (such as carbon, graphite, and/or graphene), 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, SiOx-C, SnOx-C, Si-Sn, Si-SiOx, Sn-SnOx, Si-SiOx-C, Sn-SnOx-C, Si-Sn-C, SiOx-SnOx-C, Si-SiOx-Sn, or Sn-SiOx-SnOx.). 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.

[0055] In some embodiments, the 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.

[0056] In some embodiments, an 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.

[0057] In some embodiments, an 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.

[0058] In some embodiments, the electrode film includes a 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.

[0059] 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.

[0060] In some embodiments, an electrode film is disposed on a current collector to form an 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.

[0061] In some embodiments, an electrode is a double-sided 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.

[0062] In some embodiments, the energy storage device comprises a separator, an anode electrode, the cathode electrode, an electrolyte, and a housing, wherein the electrolyte, separator, anode electrode and cathode electrode are disposed within the housing and the separator is positioned between the anode and cathode electrodes. In some embodiments, an energy storage device is formed by placing an electrolyte, a separator, an anode electrode and the cathode electrode described herein within a housing, wherein the separator is placed between the anode electrode and the cathode electrode.

[0063] In some embodiments, the energy storage device is a lithium-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, the energy storage system or energy storage device may be used for electromobility. In some embodiments, the energy storage device may be used in 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.

[0064] In some embodiments, the use of low salt concentrations reduces, prevents and/or aids in preventing Mn dissolution from the cathode and/or deposition onto the anode. In some embodiments, Mn deposition after 200 cycles, C3/C3, cycling up to 4.2V, and 40°C is, is about, is at most, or is at most about, 15 $\mu\text{g}/\text{cm}^2$, 12 $\mu\text{g}/\text{cm}^2$, 11 $\mu\text{g}/\text{cm}^2$, 10 $\mu\text{g}/\text{cm}^2$, 9 $\mu\text{g}/\text{cm}^2$, 8 $\mu\text{g}/\text{cm}^2$, 7 $\mu\text{g}/\text{cm}^2$, 6 $\mu\text{g}/\text{cm}^2$, 5 $\mu\text{g}/\text{cm}^2$, 4 $\mu\text{g}/\text{cm}^2$, 3 $\mu\text{g}/\text{cm}^2$, 2 $\mu\text{g}/\text{cm}^2$, 1 $\mu\text{g}/\text{cm}^2$ or 0.5 $\mu\text{g}/\text{cm}^2$, or any range of values therebetween. In some embodiments, Mn deposition rate at C3/C3, cycling up to 4.2V, and 40°C is, is about, is at most, or is at most about, 0.016 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.015 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.014 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.013 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.012 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.011 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.010 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.009 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.008 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.007 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.006 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.005 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.004 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.003 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.002 $\mu\text{g}/\text{cm}^2/\text{cycle}$ or 0.001 $\mu\text{g}/\text{cm}^2/\text{cycle}$, or any range of values therebetween. In some embodiments, Mn deposition after 200 cycles, C3/C3, cycling up to 4.2V, and 70°C is, is about, is at most, or is at most about, 80 $\mu\text{g}/\text{cm}^2$, 70 $\mu\text{g}/\text{cm}^2$, 65 $\mu\text{g}/\text{cm}^2$, 60 $\mu\text{g}/\text{cm}^2$, 55 $\mu\text{g}/\text{cm}^2$, 50 $\mu\text{g}/\text{cm}^2$, 45 $\mu\text{g}/\text{cm}^2$, 40 $\mu\text{g}/\text{cm}^2$, 35 $\mu\text{g}/\text{cm}^2$, 30 $\mu\text{g}/\text{cm}^2$, 25 $\mu\text{g}/\text{cm}^2$, 20 $\mu\text{g}/\text{cm}^2$, 15 $\mu\text{g}/\text{cm}^2$, 12 $\mu\text{g}/\text{cm}^2$, 11 $\mu\text{g}/\text{cm}^2$, 10 $\mu\text{g}/\text{cm}^2$, 9 $\mu\text{g}/\text{cm}^2$, 8 $\mu\text{g}/\text{cm}^2$, 7 $\mu\text{g}/\text{cm}^2$, 6 $\mu\text{g}/\text{cm}^2$, 5 $\mu\text{g}/\text{cm}^2$, 4 $\mu\text{g}/\text{cm}^2$, 3 $\mu\text{g}/\text{cm}^2$ or 2 $\mu\text{g}/\text{cm}^2$, or any range of values therebetween. In some embodiments, Mn deposition rate at C3/C3, cycling up to 4.2V, and 70°C is, is about, is at most, or is at most about, 0.6 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.5 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.4 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.3 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.2 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.1 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.05 $\mu\text{g}/\text{cm}^2/\text{cycle}$ or 0.01 $\mu\text{g}/\text{cm}^2/\text{cycle}$, or any range of values therebetween.

[0065] In some embodiments, the use of low salt concentrations does not increase, does not significantly increase, reduces, prevents and/or aids in preventing dissolution of a current collector (e.g., Al dissolution) and/or deposition onto the anode. In some embodiments, Al deposition after 200 cycles, C3/C3, cycling up to 4.2V, and 40°C is, is about, is at most, or is at most about, 1 $\mu\text{g}/\text{cm}^2$, 0.9 $\mu\text{g}/\text{cm}^2$, 0.8 $\mu\text{g}/\text{cm}^2$, 0.7 $\mu\text{g}/\text{cm}^2$, 0.6 $\mu\text{g}/\text{cm}^2$, 0.5 $\mu\text{g}/\text{cm}^2$, 0.4 $\mu\text{g}/\text{cm}^2$, 0.3 $\mu\text{g}/\text{cm}^2$, 0.2 $\mu\text{g}/\text{cm}^2$, 0.1 $\mu\text{g}/\text{cm}^2$ or 0.05 $\mu\text{g}/\text{cm}^2$, or any range of values therebetween. In some embodiments, Al deposition rate at C3/C3, cycling up to 4.2V, and 40°C is, is about, is at most, or is at most about, 0.016 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.015 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.014

$\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.013 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.012 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.011 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.010 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.009 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.008 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.007 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.006 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.005 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.004 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.003 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.002 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.001 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.0005 $\mu\text{g}/\text{cm}^2/\text{cycle}$ or 0.0001 $\mu\text{g}/\text{cm}^2/\text{cycle}$, or any range of values therebetween. In some embodiments, Al deposition after 200 cycles, C3/C3, cycling up to 4.2V, and 70°C is, is about, is at most, or is at most about, 2 $\mu\text{g}/\text{cm}^2$, 1.5 $\mu\text{g}/\text{cm}^2$, 1.3 $\mu\text{g}/\text{cm}^2$, 1.2 $\mu\text{g}/\text{cm}^2$, 1.1 $\mu\text{g}/\text{cm}^2$, 1 $\mu\text{g}/\text{cm}^2$, 0.9 $\mu\text{g}/\text{cm}^2$, 0.8 $\mu\text{g}/\text{cm}^2$, 0.7 $\mu\text{g}/\text{cm}^2$, 0.6 $\mu\text{g}/\text{cm}^2$, 0.5 $\mu\text{g}/\text{cm}^2$, 0.4 $\mu\text{g}/\text{cm}^2$, 0.3 $\mu\text{g}/\text{cm}^2$, 0.2 $\mu\text{g}/\text{cm}^2$, 0.1 $\mu\text{g}/\text{cm}^2$ or 0.05 $\mu\text{g}/\text{cm}^2$, or any range of values therebetween. In some embodiments, Al deposition rate at C3/C3, cycling up to 4.2V, and 70°C is, is about, is at most, or is at most about, 0.016 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.015 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.014 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.013 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.012 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.011 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.010 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.009 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.008 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.007 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.006 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.005 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.004 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.003 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.002 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.001 $\mu\text{g}/\text{cm}^2/\text{cycle}$, 0.0005 $\mu\text{g}/\text{cm}^2/\text{cycle}$ or 0.0001 $\mu\text{g}/\text{cm}^2/\text{cycle}$, or any range of values therebetween.

[0066] In some embodiments, the use of low salt concentrations does not hinder, does not significantly hinder, improves and/or aids in improving the performance of an energy storage device. In some embodiments, the use of a low salt electrolyte in an energy storage device after 200 cycles, 400 cycles or 1200 cycles, C3/C3, cycling up to 4.2V, and at 40°C or 70°C has a normalized discharge capacity of, of about, of at least, or of at least about, 1, 0.95, 0.9, 0.85, 0.8, 0.75 or 0.7, or any range of values therebetween. In some embodiments, the use of a low salt electrolyte in an energy storage device after 200 cycles, 400 cycles or 1200 cycles, C3/C3, cycling up to 4.2V, and at 40°C or 70°C has a normalized ΔV of, of about, of at most, or of at most about, 1, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, 3 or 3.5, or any range values therebetween. In some embodiments, the use of a low salt electrolyte in an energy storage device at C3/C3, cycling up to 4.2V, and at 40°C or 70°C has an end of life (EOL) time of, of about, of at least, or of at least about 200 cycles, 300 cycles, 400 cycles, 500 cycles, 600 cycles, 700 cycles, 800 cycles, 900 cycles, 1000 cycles, 1100 cycles, 1200 cycles, 1300 cycles, 1500 cycles, 2000 cycles, 2500 cycles or 3000 cycles, or any range of values therebetween. In some embodiments, the DCR growth after 200, 400 or 1200 cycles of an energy storage device with a low salt electrolyte is reduced relative to an energy

storage device comprising a lithium salt at a higher total concentration by, by about, by at least, or by at least about, 3%, 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40% or 50%, or any range of value therebetween.

EXAMPLES

[0067] Example embodiments of the present disclosure, including processes, materials and/or resultant products, are described in the following examples. In these examples, “delta V” or ΔV is the average charge voltage minus the average discharge voltage. This is also called the voltage polarization. The voltage polarization measured during testing of a Li-ion cell at a fixed current is proportional to the internal resistance or DC resistance (i.e., “DCR”) of the cell. Therefore, tracking the voltage polarization during cell charge-discharge cycling also tracks the cell internal resistance growth.

[0068] In these examples, $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ LMFP/artificial graphite pouch cells were filled with electrolyte and vacuum sealed before undergoing a 24 hour wetting period at 1.5V followed by formation at C/20 at 40°C.

Example 1

[0069] FIG. 1 shows the normalized ΔV (normalized to the value at cycle 3) of $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ LMFP/graphite battery cells tested with EC:DMC:EMC electrolytes including various mol% amounts of LiFSi and LiPF_6 , and total lithium concentrations. The batteries were run for 200 cycles at C3/C3, with cycling up to 4.2V at 40°C. As seen in FIG. 1, electrolytes with total salt concentrations of 1 M and 0.5 M showed about 1-40% improved ΔV relative to electrolytes with total salt concentrations of 1.5 M. For example, FIG. 1 shows that at 60 mol% LiFSi and 1.5 M salt concentration a ΔV of 1.5, and at 0.5 M salt concentration a ΔV of 1.3, which is a 20% reduction and a 40 % reduction in DCR growth respectively. Furthermore, FIG. 1 demonstrates that DCR growth is inversely proportional to LiFSi molar ratio in an LiPF_6 :LiFSi salt blend. Such a DCR growth finding differs from other cell chemistries (e.g., NMC, LFP) which do not show as strong of a sensitivity for LiFSi content. In addition, FIG. 1 demonstrates that DCR growth decreases as total salt content decreases, which also differs from other cell chemistries (e.g., NMC/graphite cells) that show an inverse sensitivity (i.e., where DCR grows decreases as salt content increases).

Example 2

[0070] FIG. 2 shows the normalized ΔV (normalized to the value at cycle 3) of $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ LMFP/graphite battery cells tested with EC:DMC:EMC electrolytes with 1.5M LiPF_6 and including various weight % amounts of VC and/or DTD additives. The batteries were run for 200 cycles at C3/C3, with cycling up to 4.2V at 40°C. As seen in FIG. 2, electrolytes with 2% VC and electrolytes with 4% VC showed improved ΔV (i.e., about 3% and about 8%, respectively) relative to electrolytes with 2% VC and 1% DTD. Furthermore, FIG. 2 demonstrates that DCR growth decreases through the removal of DTD from the additive blend and through increasing VC content, which is unexpected since this is contrary to other cells chemistries (e.g., NMC/graphite cells). As such, FIG. 2 demonstrates that different additive systems may be used to effectively reduce the voltage polarization growth of LMFP cells.

Example 3

[0071] FIGS. 3A and 3B shows the impact of salt and salt concentration on the amount of Mn deposited on the graphite electrode of $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ LMFP/graphite battery cells tested with EC:DMC:EMC electrolytes having 1.2 M or 1.0 M total salt concentration with 100 mol% LiFSi, 80 mol% LiFSi and 20 mol% LiPF_6 , 80 mol% LiFSi and 20 mol% LiBOB, or 80 mol% LiFSi and 20 mol% LiDFOB. Such manganese deposited on the negative electrode is dissolved from the positive electrode and is an undesired process in LMFP cells. The batteries were run at C3/C3, with cycling up to 4.2V at 40°C. As seen in FIGS. 3A and 3B, the cells have an average of about 10 $\mu\text{g}/\text{cm}^2$ Mn loading on the negative electrode, wherein the 1.0 M LiFSi + LiDFOB cell demonstrates the least Mn loading and the lowest deposition rate.

[0072] FIGS. 4A and 4B shows the impact of salt and salt concentration on the amount of Mn deposited on the graphite electrode of $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ LMFP/graphite battery cells tested with EC:DMC:EMC electrolytes having 1.2 M or 1.0 M total salt concentration with 100 mol% LiFSi, 80 mol% LiFSi and 20 mol% LiPF_6 , 80 mol% LiFSi and 20 mol% LiBOB, or 80 mol% LiFSi and 20 mol% LiDFOB. Such manganese deposited on the negative electrode is dissolved from the positive electrode and is an undesired process in LMFP cells.

The batteries were run at C3/C3, with cycling up to 4.2V at 70°C. As seen in FIGS. 4A and 4B, electrolytes with including 1.0 M total salt concentration showed reduced Mn loading relative to electrolytes with including 1.2 M total salt concentration (e.g., a reduction in the Mn dissolution rate by up to about 20-30%). Specifically, LiFSi showed about a factor of 10 improvement, LiFSi + LiPF₆ showed about a factor of 1.2 improvement, LiFSi + LiBOB showed about a factor of 1.8 times, and LiFSi + LiDFOB showed about a factor of 1.2 improvement. In addition, electrolytes with 80 mol% LiFSi and 20 mol% LiPF₆ shows an increase in Mn dissolution by a factor of 3 compared to a 100 mol% LiFSi electrolyte, which is different from other cell chemistries (e.g., NMC, LFP) that do not show such a strong sensitivity for LiFSi content. FIGS. 4A and 4B show high Mn loading on the negative electrode relative to those shown in FIGS. 3A and 3B due to the accelerated 70 °C cycling temperature. As seen in FIGS. 4A and 4B, LiFSi + LiDFOB cells in both salt concentrations demonstrate the least Mn loading and the lowest deposition rate.

[0073] FIGS. 5A and 5B show the impact of salt and salt concentration on the amount of Al deposited on the same battery cells prepared and tested in FIGS. 3A and 3B at 40°C. FIGS. 5A and 5B demonstrate cells with minimal Al deposition on the negative electrode.

[0074] FIGS. 6A and 6B show the impact of salt and salt concentration on the amount of Al deposited on the same battery cells prepared and tested in FIGS. 4A and 4B at 70°C. FIGS. 6A and 6B demonstrate that cells with LiFSi + LiPF₆ and LiFSi + LiBOB show an absolute amount decrease in the amount of Al deposition on the negative electrode when total salt concentration is reduced to 1.0M, and the rate of Al deposition is relatively minimal.

[0075] FIGS. 7A and 7B show the absolute discharge capacity, normalized discharge capacity and normalized voltage polarization ($\Delta V / \Delta V''$) measurements on the same battery cells prepared and tested in FIGS. 3A and 3B at 40°C. FIGS. 7A and 7B demonstrate that cells with lower total salt showed improved 40 °C cycling, wherein the cell with 1.0 M LiFSi + LiPF₆ showed the best performance with a cycle life of about 1100 cycles to EOL at 40 °C cycling.

[0076] FIGS. 8A and 8B show the absolute discharge capacity, normalized discharge capacity and normalized voltage polarization ($\Delta V / \Delta V''$) measurements on the same battery cells prepared and tested in FIGS. 4A and 4B at 70°C. FIGS. 8A and 8B demonstrate

that cells with LiFSI+LiBOB and LiFSI+LiDFOB with 1.2 M total salt concentration outperformed the other cells, and the cell with 1.2 M LiFSI + LiBOB showed the best performance with a cycle life of about 280 cycles to EOL at 70 °C cycling.

Example 4

[0077] FIGS. 9A-9C shows the impact of salt and salt concentration on the loading of Mn deposited on the negative electrode of $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ LMFP/graphite battery cells tested with EC:DMC:EMC electrolytes having 1.5 M, 1.0 M or 0.5 M total salt concentration with various amounts of primary salt LiFSi and co-salt LiPF_6 , including 95 mol.% LiFSi + 5 mol.% LiPF_6 , 70 mol.% LiFSi + 30 mol.% LiPF_6 , and 60 mol.% LiFSi + 40 mol.% LiPF_6 . The batteries were run at C3/C3, with cycling up to 4.2V at 40°C. As seen in FIG. 9A-9C, the use of LiPF_6 /LiFSI blends lowers the rate of Mn deposition below the rate of Mn deposition for cells using 1.5 M LiPF_6 , and Mn deposition rate is lower for the 0.5 M salt cells relative to the 1.5 M salt cells.

[0078] FIGS. 10A-10C shows the impact of salt and salt concentration on the loading of Mn deposited on the negative electrode of $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ LMFP/graphite battery cells tested with EC:DMC:EMC electrolytes having 1.5 M, 1.0 M or 0.5 M total salt concentration with various amounts of primary salt LiFSi and co-salt LiPF_6 , including 95 mol.% LiFSi + 5 mol.% LiPF_6 , 70 mol.% LiFSi + 30 mol.% LiPF_6 , and 60 mol.% LiFSi + 40 mol.% LiPF_6 . The batteries were run at C3/C3, with cycling up to 4.2V at 70°C. As seen in FIG. 10A-10C, cells with some electrolytes showed reduced amounts of Mn loading on the negative electrode. Furthermore, electrolytes including 0.5 M total salt concentration showed reduced Mn loading relative to electrolytes with including 1.0 M total salt concentration. Specifically, 5 mol% LiPF_6 + 95 mol% showed about a 3 times improvement, 30 mol% LiPF_6 + 70 mol% showed about a 4 times improvement, and 40 mol% LiPF_6 + 60 mol% showed about a 1.6 times improvement. In addition, electrolytes with 0.5M total salt concentrations showed a reduction in the Mn dissolution rate by up to a factor of 3 relative to 1 M total salt concentrations. As such, FIGS. 10A-10C demonstrate that using LiPF_6 /LiFSI blends lowers the rate of Mn deposition below the rate of Mn deposition for cells using 1.5 M LiPF_6 , and Mn deposition rate is lower for the 0.5 M salt cells relative to the 1.5 M salt cells.

[0079] FIGS. 11A-11C show the impact of salt and salt concentration on the amount of Al deposited on the same battery cells prepared and tested in FIGS. 9A-9C at 40°C. FIGS. 12A-17C show the impact of salt and salt concentration on the amount of Al deposited on the same battery cells prepared and tested in FIGS. 10A-10C at 70°C. FIGS. 11A-11C and 12A-12C demonstrate that none of the cells exhibit Al dissolution above the instrumental noise (“Al baseline”).

[0080] FIGS. 13A-13C show the discharge capacity, normalized discharge capacity and normalized ΔV measurements of $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ LMFP/graphite battery cells tested with electrolytes with 1.5M, 1 M and 0.5 M total salt concentrations, respectively. Each of FIGS. 13A-13C show data for the batteries tested with 5 mol% LiPF_6 + 95 mol% LiFSi , 30 mol% LiPF_6 + 70 mol% LiFSi , and 40 mol% LiPF_6 + 60 mol% LiFSi . The batteries were run for about 1200 cycles at 40°C. As seen in FIGS. 13A-13C, low total salt concentration and mixed salt electrolytes generally show improved capacity retentions and/or DCR growths, wherein the 0.5 M cells unexpectedly demonstrate improved capacity retention and generally lower DCR growths relative to the higher molarity cells.

[0081] FIGS. 14A-14C show the discharge capacity, normalized discharge capacity and normalized ΔV measurements of $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ LMFP/graphite battery cells tested with electrolytes with 1.5M, 1 M and 0.5 M total salt concentrations, respectively. Each of FIGS. 13A-13C show data for the batteries tested with 5 mol% LiPF_6 + 95 mol% LiFSi , 30 mol% LiPF_6 + 70 mol% LiFSi , and 40 mol% LiPF_6 + 60 mol% LiFSi . The batteries were run for about 1200 cycles at 70°C. FIGS. 13A-13C and FIGS. 14A-14C demonstrate improved cycling lifetime and lower voltage polarization when salt quantity is lowered.

[0082] While certain embodiments 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.

[0083] 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.

[0084] 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.

[0085] 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.

[0086] 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.

[0087] 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.

[0088] 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.

[0089] 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.

[0090] 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.

[0091] The headings provided herein, if any, are for convenience only and do not necessarily affect the scope or meaning of the devices and methods disclosed herein.

WHAT IS CLAIMED IS:

1. A low salt electrolyte energy storage device, comprising:
 - a cathode electrode comprising an iron phosphate based active material;
 - a separator;
 - an anode electrode;
 - a low salt electrolyte, comprising:
 - a solvent in an amount of at least about 50 wt.%;
 - an additive in an amount of at most about 10 wt.%; and
 - a lithium salt, wherein a total concentration of the lithium salt is about 0.5-1.2 M;
 - wherein the lithium salt comprises a primary salt selected from the group consisting of LiFSi, LiTFSi, and combinations thereof at a primary amount of about 60-95 mol%, and a co-salt selected from the group consisting of LiPF₆, LiBOB, LiDFOB, and combinations thereof at a co-amount of about 5-40 mol%; and
 - a housing, wherein the cathode electrode, the separator, the anode electrode and low salt electrolyte are positioned within the housing.
2. A low salt electrolyte for an energy storage device, comprising:
 - a solvent in an amount of at least about 50 wt.%;
 - an additive in an amount of at most about 10 wt.%; and
 - a lithium salt, wherein a total concentration of the lithium salt is at most about 1.2 M.
3. The low salt electrolyte of Claim 2, comprising a total concentration of the lithium salt of 0.5-1 M.
4. The low salt electrolyte of Claim 2 or 3, wherein the lithium salt is selected from the group consisting of LiFSi, LiTFSi, and combinations thereof.
5. The low salt electrolyte of any one of Claims 2-4, wherein the lithium salt further comprises a co-salt.
6. The low salt electrolyte of Claim 5, wherein the lithium salt comprises the co-salt in an amount below about 50 mol%.

7. The low salt electrolyte of Claims 5 or 6, wherein the co-salt comprises a compound is selected from the group consisting of LiPF_6 , LiBOB, LiDOFOB, and combinations thereof.

8. The low salt electrolyte of any one of Claims 2-7, wherein the lithium salt comprises 60-97 mol% of LiFSi and 3-40 mol% of LiPF_6 .

9. The low salt electrolyte of any one of Claims 2-8, wherein the solvent comprises a compound is selected from the group consisting of a carbonate, an ether, an ester, and combinations thereof.

10. The low salt electrolyte of any one of Claims 2-9, wherein the solvent comprises a compound is selected from the group consisting of ethylene carbonate (EC), propylene carbonate (PC), vinyl ethylene carbonate (VEC), vinylene carbonate (VC), fluoroethylene carbonate (FEC), dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC), methyl acetate (MA), methyl propionate (MP), ethyl acetate (EA), methyl butyrate (MB), and combinations thereof.

11. The low salt electrolyte of any one of Claims 2-10, wherein the solvent comprises a compound is selected from the group consisting of EC, DMC, EMC, and combinations thereof.

12. The low salt electrolyte of any one of Claims 2-11, wherein the solvent comprises EC and EMC.

13. The low salt electrolyte of any one of Claims 2-12, wherein the additive comprises a compound selected from the group consisting of DTD, VC, FEC, and combinations thereof.

14. An energy storage device, comprising:

a cathode electrode;

a separator;

an anode electrode;

the low salt electrolyte of any one of Claims 2-13; and

a housing, wherein the cathode electrode, the separator, the anode electrode and low salt electrolyte are positioned within the housing.

15. The energy storage device of Claim 14, wherein the cathode electrode comprises a lithium manganese iron phosphate (LMFP) active material.

16. The energy storage device of Claim 14 or 15, wherein the anode electrode comprises graphite.

17. The energy storage device of any one of Claims 14-16, wherein the energy storage device is a battery.

18. The energy storage device of Claim 17, wherein the battery is an electric vehicle battery.

19. The energy storage device of any one of Claims 14-18, wherein the direct current internal resistance (DCR) growth is reduced by about 5-40% after 200 cycles relative to an energy storage device comprising a lithium salt at a higher total concentration.

20. The energy storage device of any one of Claims 14-19, wherein the Mn loading on the negative electrode due to Mn deposition is reduced by a factor of about 2-3 relative to an energy storage device comprising a lithium salt at a higher total concentration.

21. A method of preparing an energy storage device, comprising:

positioning a cathode electrode, a separator, an anode electrode and the low salt electrolyte of any one of Claims 2-13 within a housing.

1/13

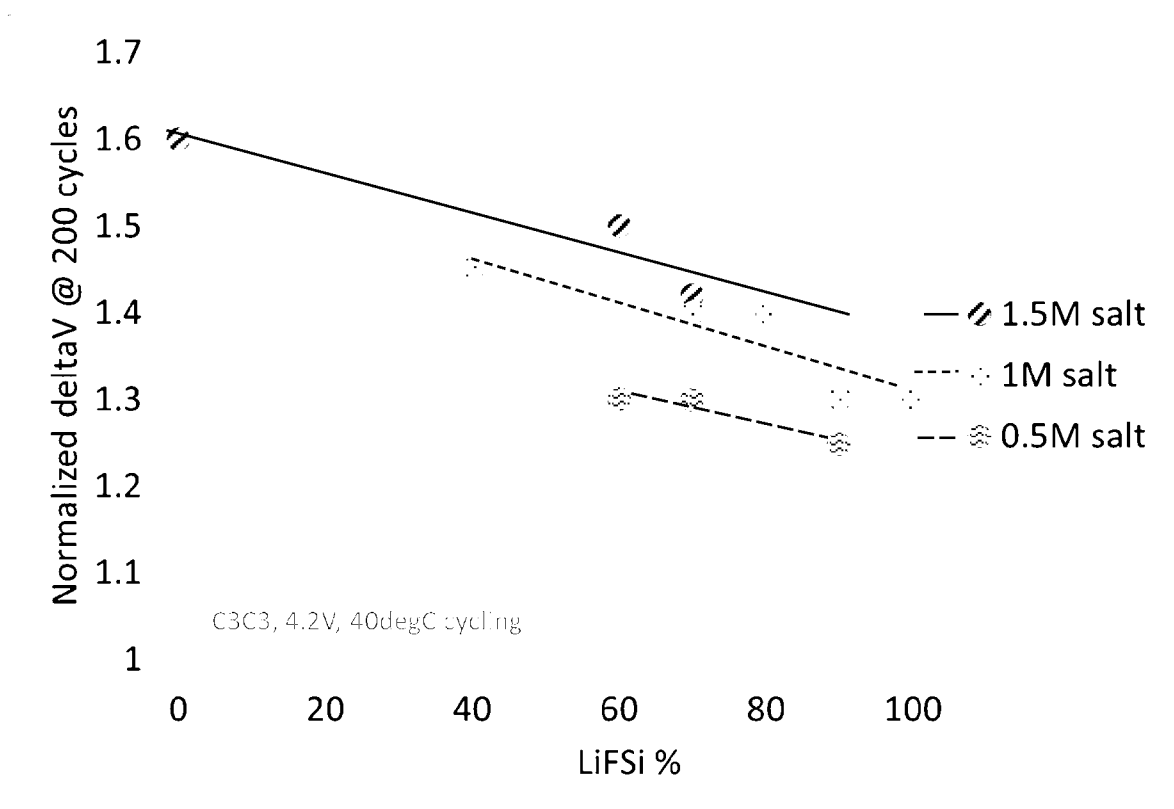


FIG. 1

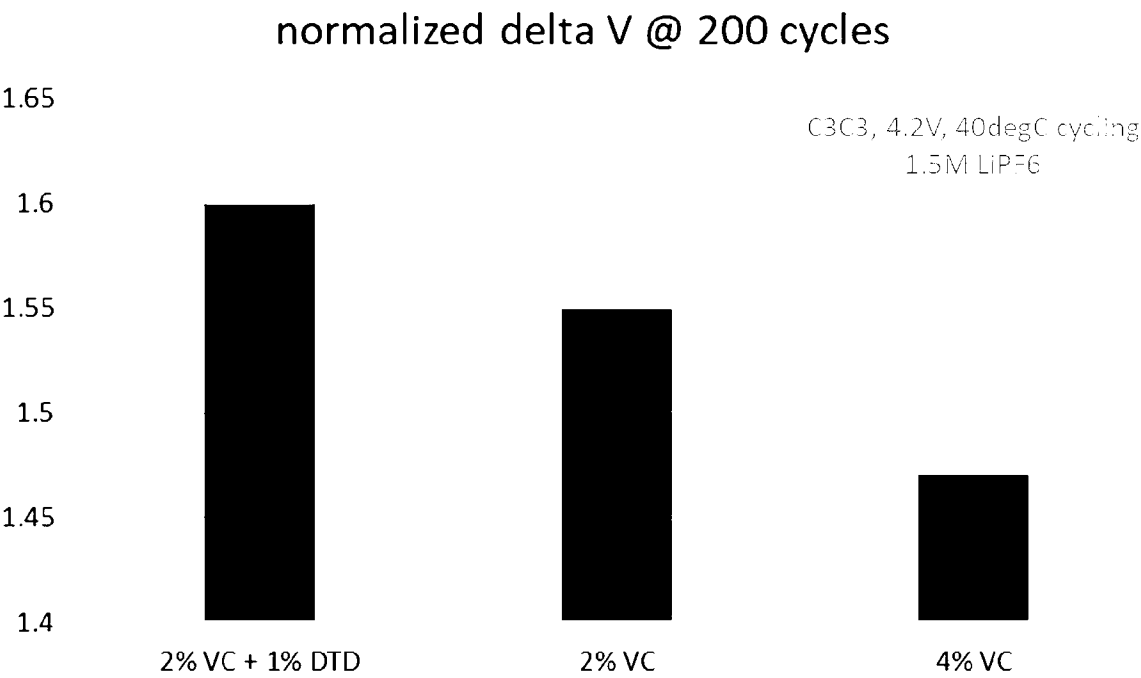


FIG. 2

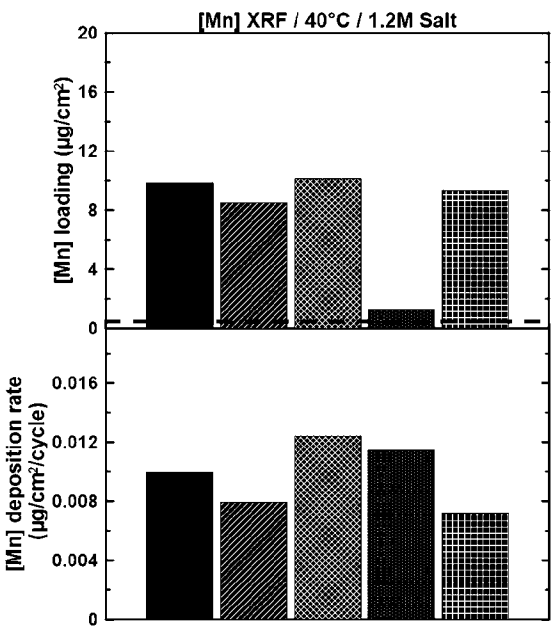


FIG. 3A

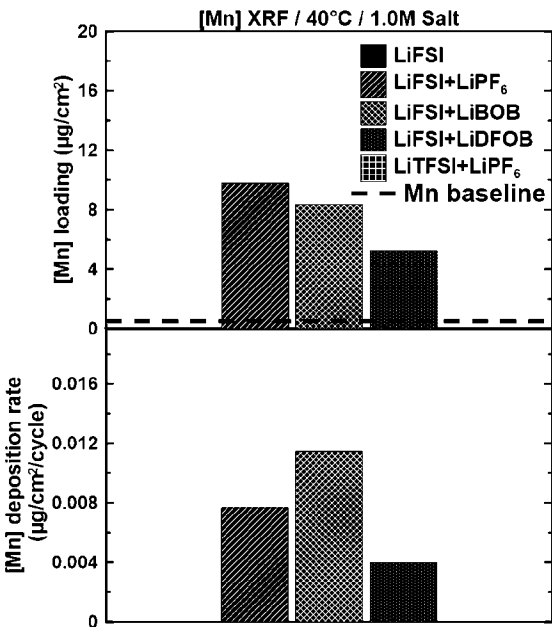


FIG. 3B

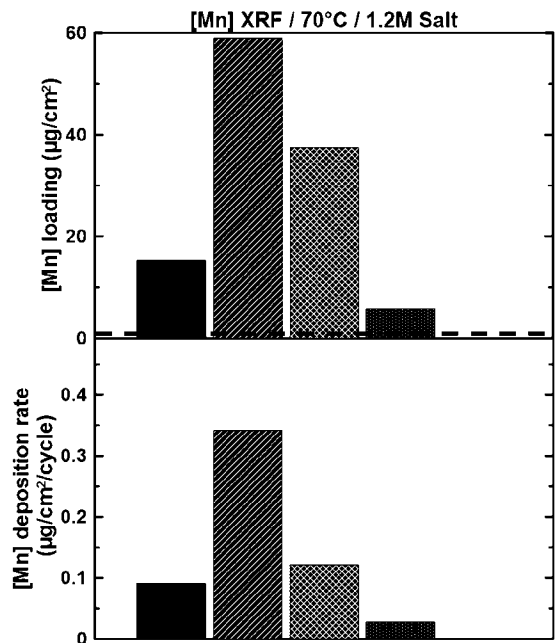


FIG. 4A

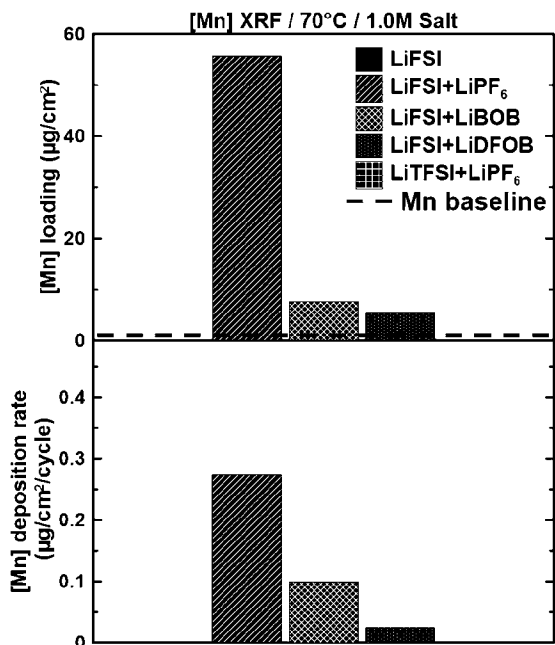


FIG. 4B

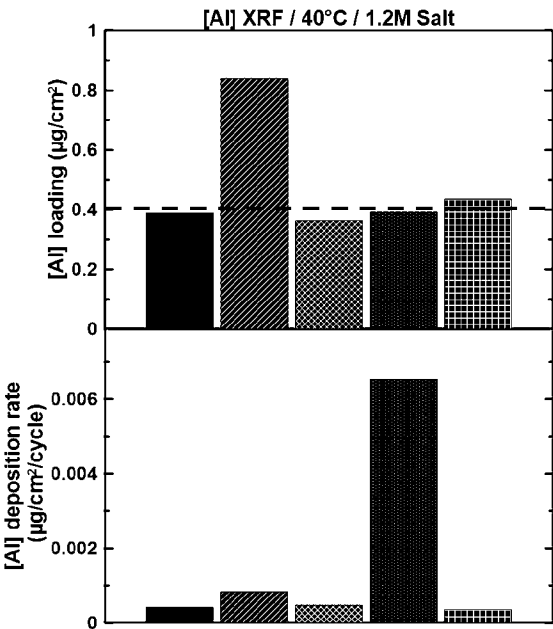


FIG. 5A

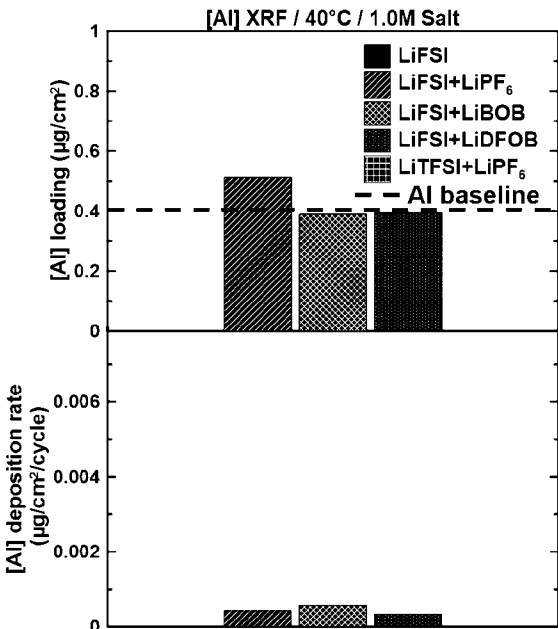


FIG. 5B

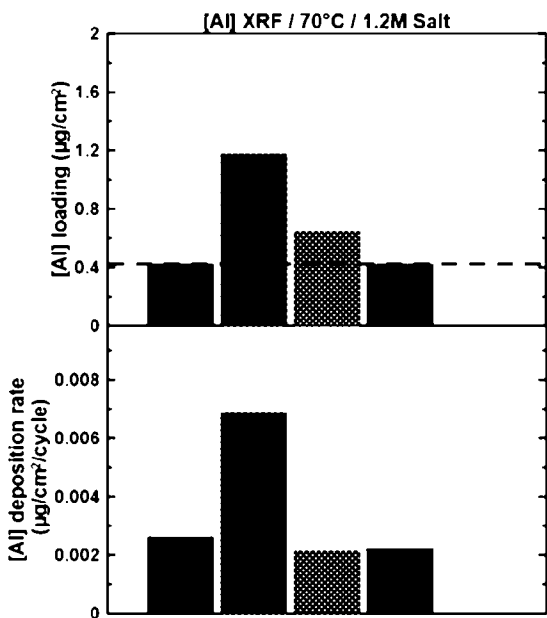


FIG. 6A

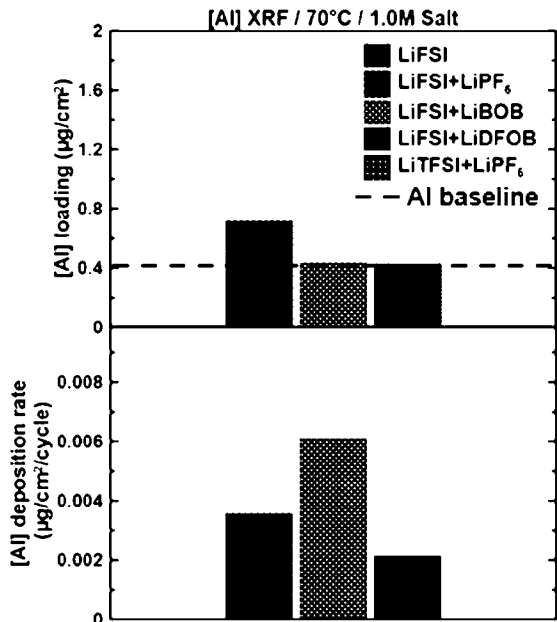


FIG. 6B

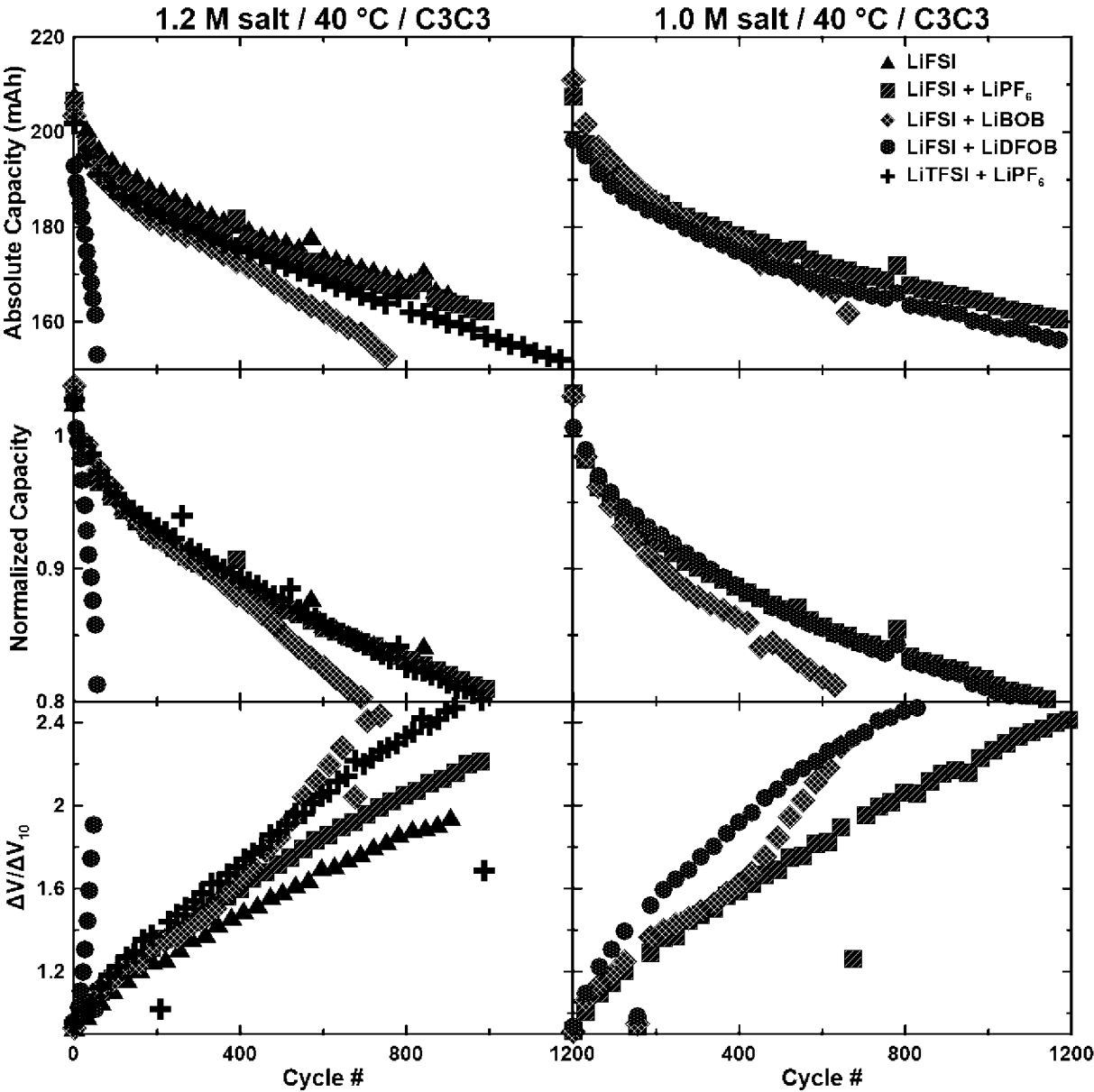


FIG. 7A

FIG. 7B

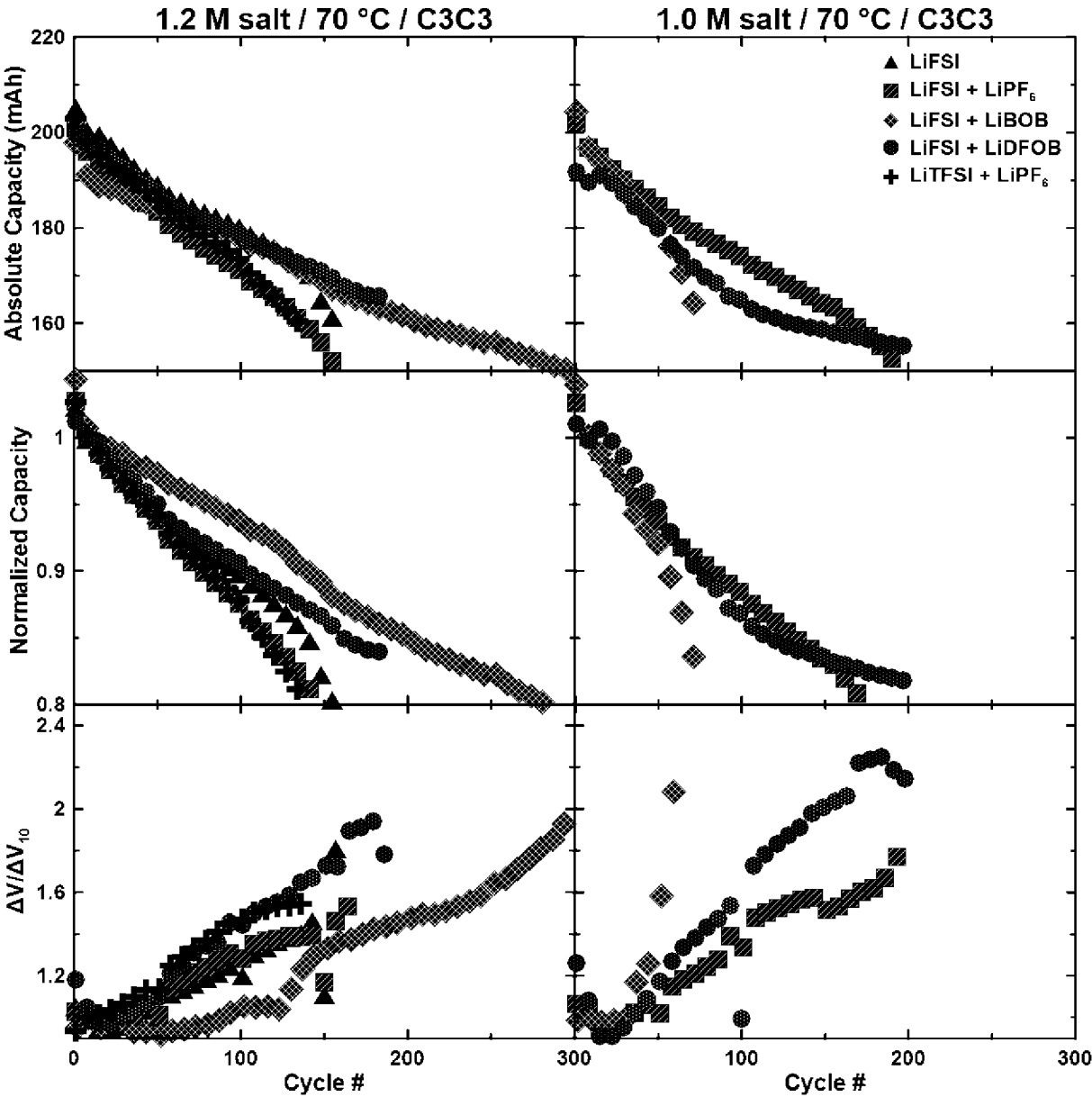


FIG. 8A

FIG. 8B

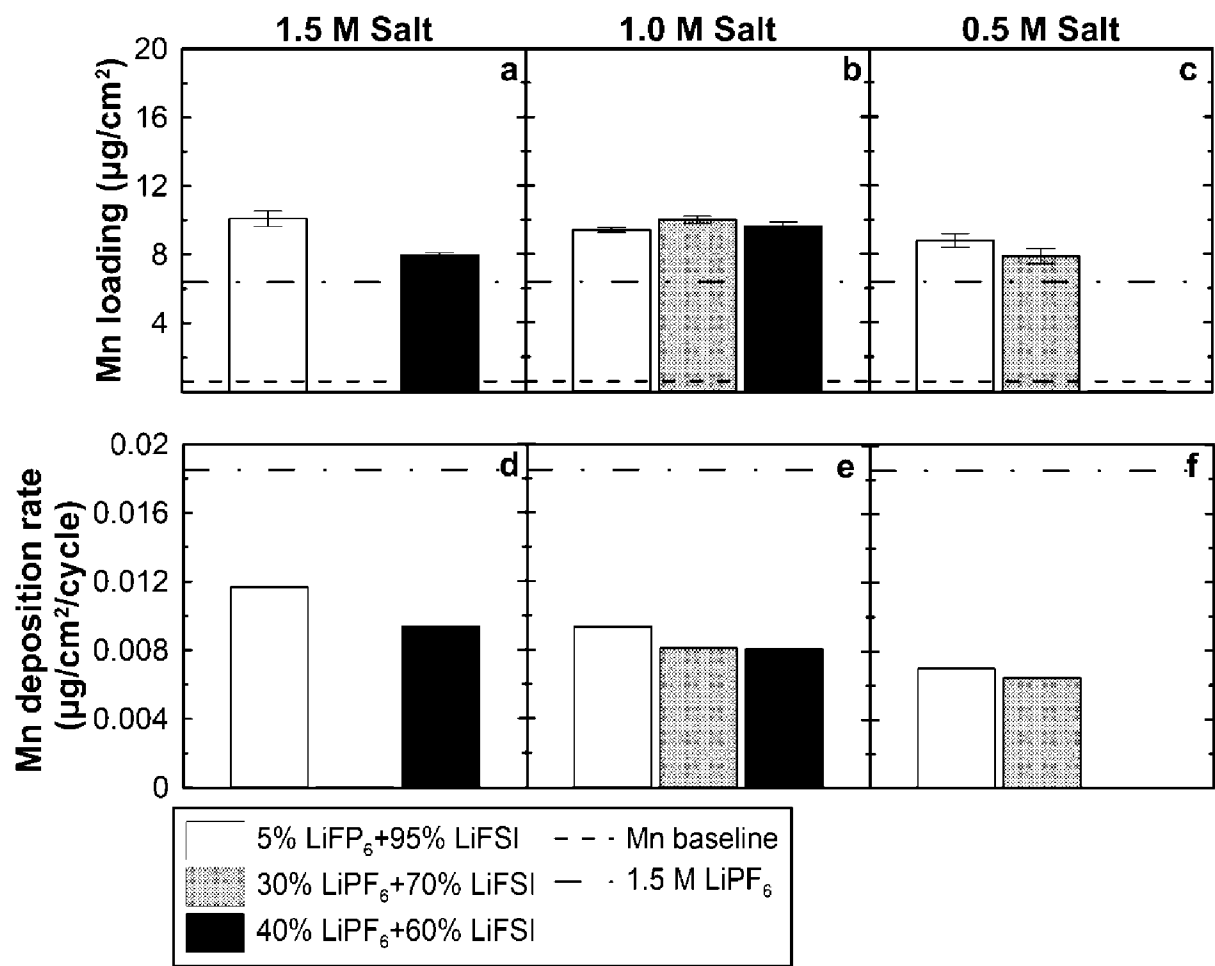
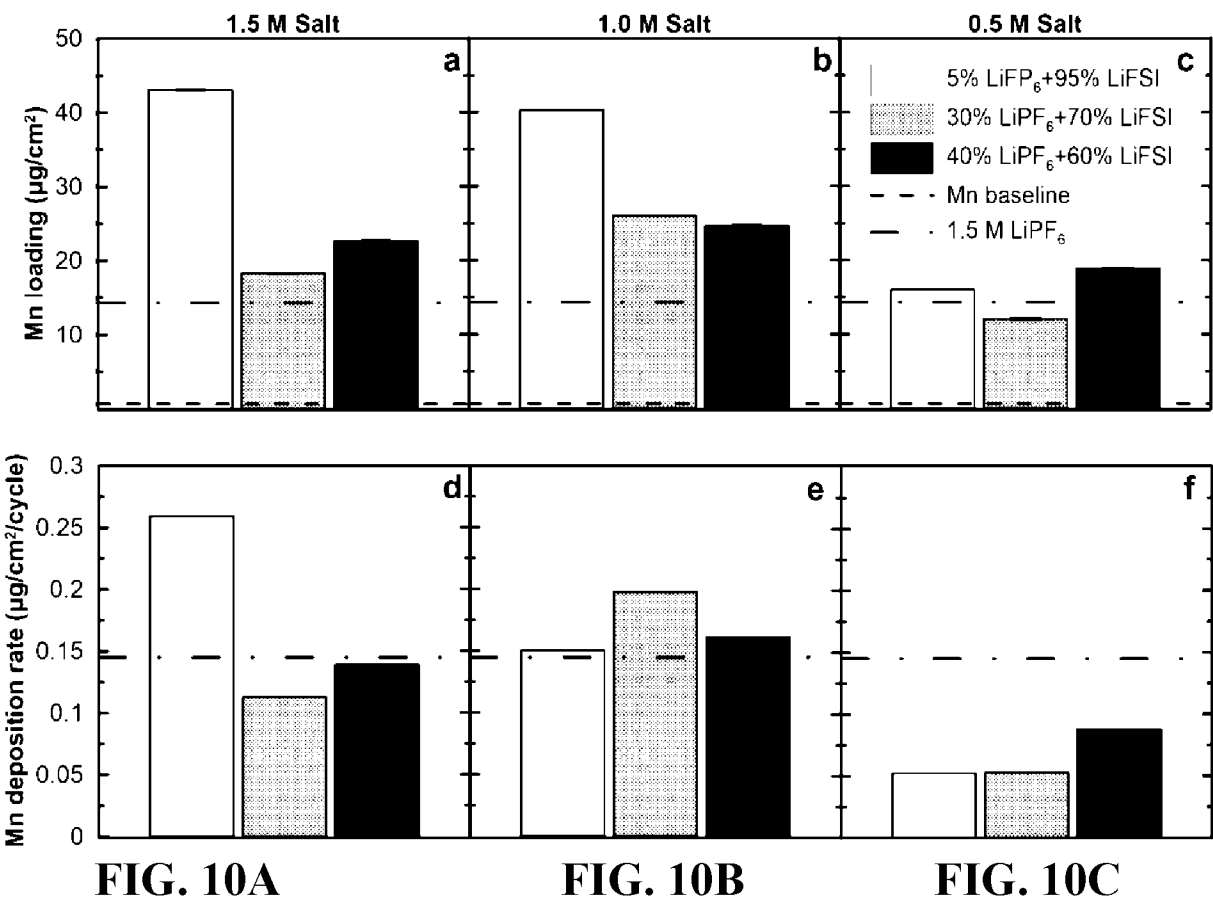
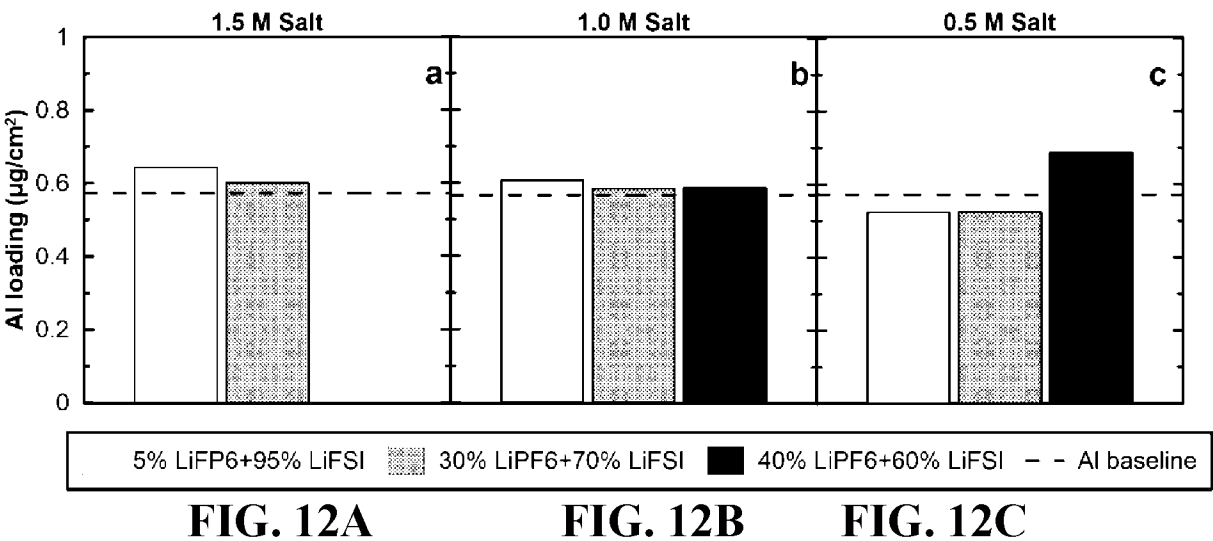
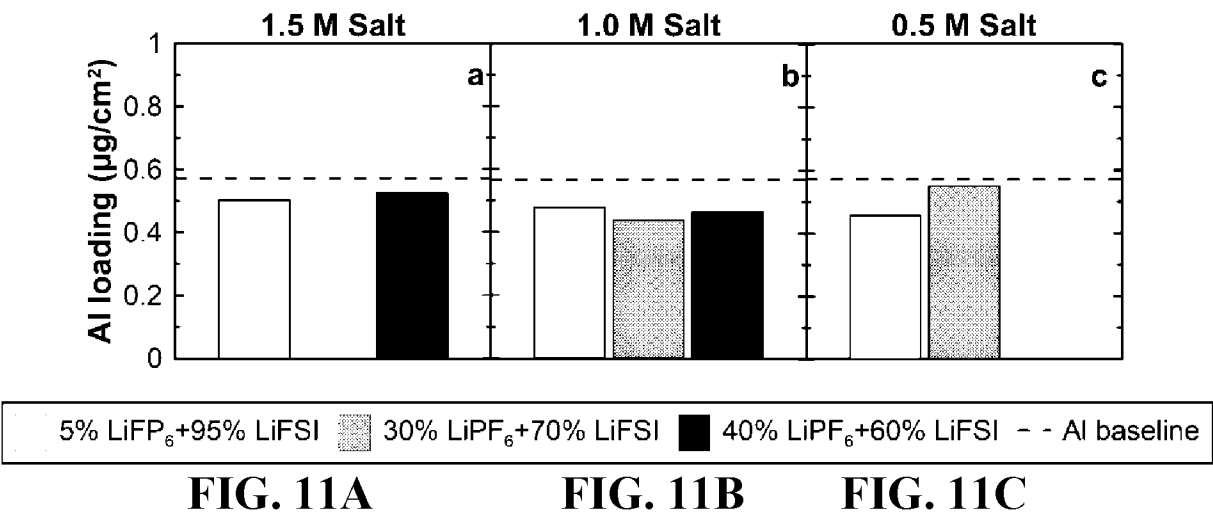


FIG. 9A

FIG. 9B

FIG. 9C





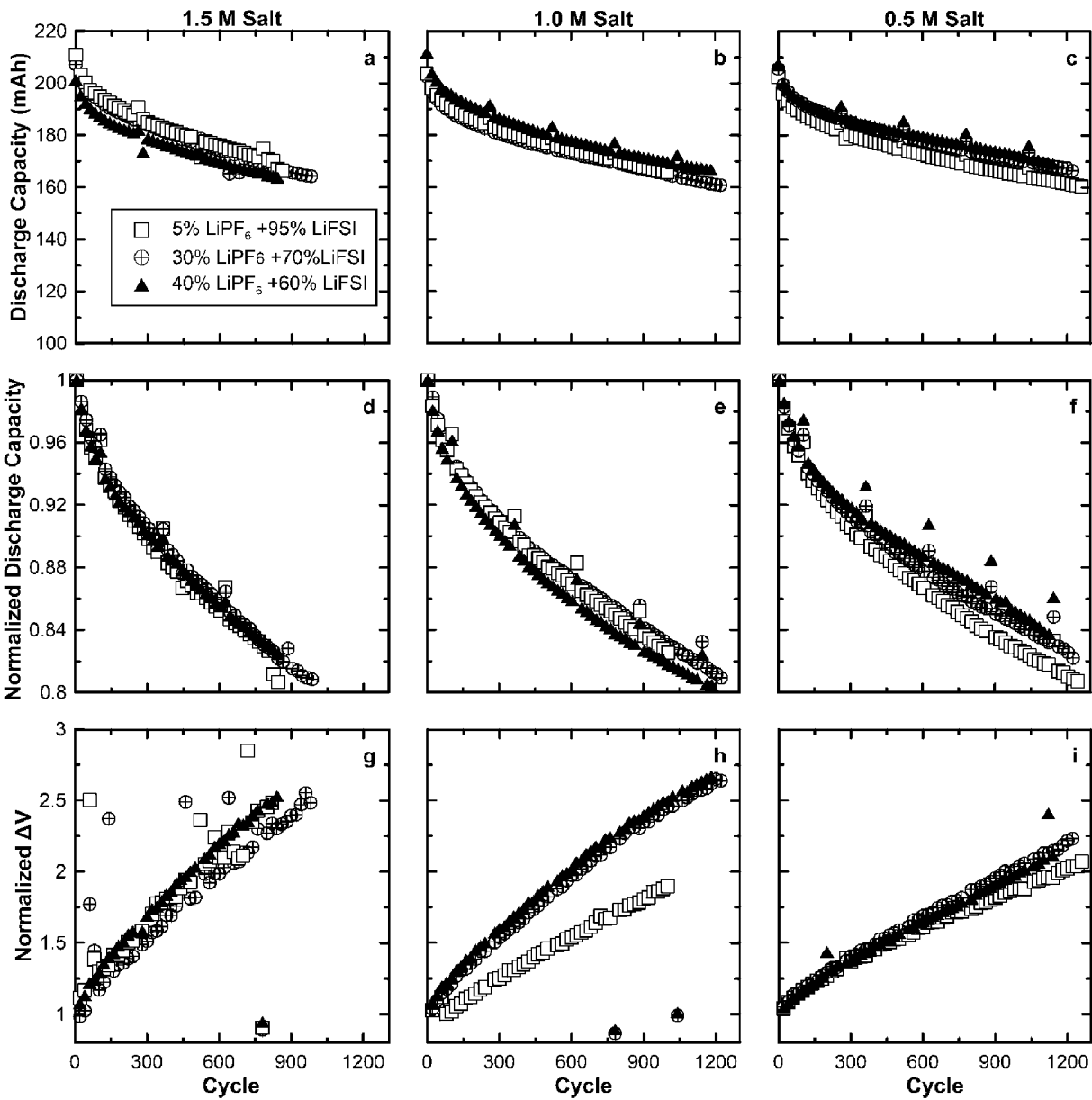


FIG. 13A

FIG. 13B

FIG. 13C

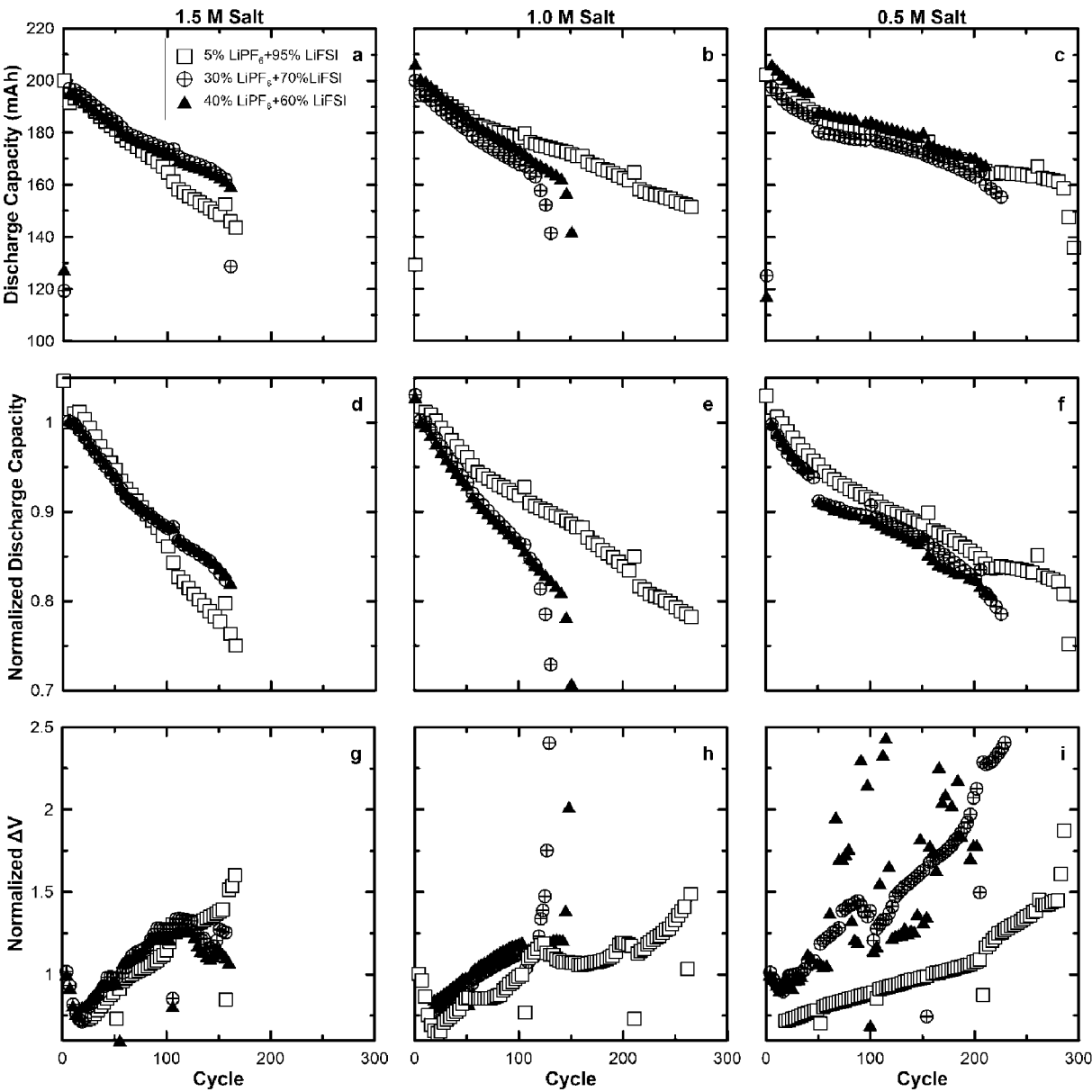


FIG. 14A

FIG. 14B

FIG. 14C

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2024/047227

A. CLASSIFICATION OF SUBJECT MATTER

INV. H01M4/58 H01M10/0525 H01M10/0567 H01M10/0568 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**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2021/226207 A1 (CHENG QIAN [JP]) 22 July 2021 (2021-07-22) paragraphs [0022], [0042], [0043], [0045], [0047] -----	1 - 12, 14, 16 - 21
X	US 2022/109190 A1 (LIANG CHENGDU [CN] ET AL) 7 April 2022 (2022-04-07) paragraphs [0022], [0037], [0039], [0043], [0045], [0046], [0049], [0061]; table 1 -----	1 - 21



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"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

10 February 2025

Date of mailing of the international search report

20/02/2025

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Möller, Claudia

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2024/047227

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