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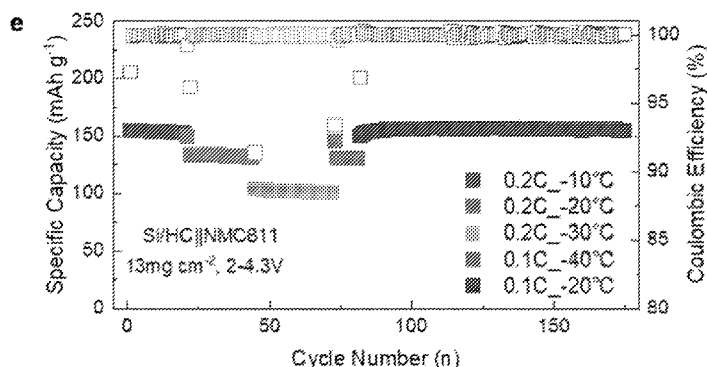


FIG. 27

(57) Abstract: Provided are electrochemical devices comprising an anode, cathode, and liquid electrolyte for providing ultrafast charging. Further, electrochemical devices efficiently operate under harsh conditions, such as at low temperatures. The electrolytes used within the electrochemical devices comprise a salt and a C₄-C₈ ether solvent, wherein the C₄-C₈ ether solvates the cation of the salt to form a solvate. The solvate may reversibly co-intercalate in the anode, or the solvate desolvates and the cation of the salt intercalates in the anode.

**ADVANCED LITHIUM-ION ELECTROLYTES FOR ULTRA-FAST CHARGING
AND WIDE-TEMPERATURE BATTERIES**

GOVERNMENT SUPPORT CLAUSE

[0001] This invention was made with government support under 2020-67021-31139 awarded by the United States Department of Agriculture – National Institute of Food and Agriculture, and under 2019-38502-30120 awarded by the United States Department of Agriculture – University of Tennessee; with government support through the Advanced Research Projects Agency-Energy (ARPA-E), U.S. Department of Energy, under Award Number DE-AR0001725; and the Sun Grant program of the National Institute of Food and Agriculture (NIFA), USDA, USA. The government has certain rights in the invention.

CROSS-REFERENCE TO RELATED APPLICATION(S)

[0002] This application claims the benefit under 35 U.S.C. § 119(e) to U.S. Provisional Application 63/592,395, filed October 23, 2023 and entitled “ADVANCED LITHIUM-ION ELECTROLYTES FOR ULTRA-FAST CHARGING AND WIDE-TEMPERATURE BATTERIES,” which is hereby incorporated herein by reference in its entirety.

TECHNICAL FIELD

[0003] This disclosure relates to electrolytes for use in batteries, and more particularly to electrochemical devices containing electrolytes having a combination of a salt and ether solvent for providing ultra-fast charging and low-temperature performance properties in addition to optimal performance under normal conditions.

BACKGROUND

[0004] Graphite is widely employed as an anode in commercial lithium (Li)-ion batteries, cycled in ethylene carbonate (EC)-based electrolytes. EC contributes to the stable solid-electrolyte interphase (SEI) on graphite and the suitable solvation structure that enables highly reversible desolvation-based Li-ion intercalation chemistry. However, the strong affinity of EC with Li ions and high electrolyte viscosity lead to inferior Li-ion battery performance under harsh conditions such as low temperatures and high charge rates.

[0005] Prior to the discovery of EC, researchers had investigated other solvents for graphite anode, including ether, yet limited reversibility was documented. Cycling graphite anodes can

be challenging for ether electrolytes. For example, the broadly studied dilute ether electrolyte formulation, 1M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in 1,3-dioxolane (DOL)/1,2-dimethoxyethane (DME), is commonly used for Li metal batteries. However, it delivers an ultralow Coulombic efficiency (CE) in graphite anodes and a voltage profile signifying irreversible reactions rather than forming Li_xC_6 . It has been believed that ethers are linked to detrimental Li-solvent co-intercalation and cell failure. To date, dilute ether electrolytes have been believed to be incompatible with graphite in Li-ion batteries due to the detrimental solvent co-intercalation and graphite exfoliation.

SUMMARY

[0006] Described herein are embodiments of electrochemical devices (e.g., batteries) that include dilute ether electrolytes used with a graphite anode. Different dilute ether electrolytes may be used with the ether solvents for the electrolytes including, but not limited to, tetrahydrofuran (THF), 2-methyltetrahydrofuran (2MeTHF), 2,5-methyltetrahydrofuran (2,5-MeTHF), tetrahydropyran (THP), 4-methyltetrahydropyran (4MeTHP), 2-methyloxetane, 3-methyloxetane, 1,3-dioxalane (DOL), and 1,2-dimethoxyethane (DME or glyme). Different salts may be used within the dilute ether electrolytes, including those comprising Li^+ , Na^+ , and K^+ , Mg^{2+} , Ca^{2+} , and Al^{3+} . Some such salts include, but are not limited to, lithium hexafluorophosphate (LiPF_6), lithium bis(fluorosulfonyl)imide (LiFSI), and lithium tetrafluoroborate (LiBF_4). While the dilute ether electrolytes are primarily combined with a graphite anode, other types of anodes are explored including those based on silicon, hard carbon, a combination of silicon and hard carbon, and a combination of graphite and silicon. Various types of cathodes may also be used. The electrochemical devices described herein, which use a dilute ether solvent, are reversible, can provide fast-charging capabilities, and have desirable capacity retention, especially under low-temperature conditions.

[0007] Provided herein are dilute ether electrolytes for use with a graphite anode and that enable reversibility (e.g., recharging). The dilute ether electrolytes are based on tailoring the solvation structures and thermodynamic properties of the ether electrolytes. As described herein, ether solvents can support graphite reversibly by modulating the anion. In some embodiments, a redesigned electrolyte consisting of a single-solvent 1,3-dioxolane (DOL) and single-salt lithium bis(fluorosulfonyl)imide (LiFSI) provides weakened Li-solvent interaction and results in an inorganic-rich solid-electrolyte interphase (SEI) formed on the anode surface. Consequently, the electrolyte may result in a battery cell having about a 99.9%

Coulombic efficiency with >96% capacity retention (approximately 350 mAh/g) after 300 cycles at C/5 using natural graphite as an anode. The weakly solvating electrolyte maintains desirable transport properties, enabling better charging rate capability than carbonate electrolytes (e.g., ethylene carbonate (EC)) and with an areal capacity of 2 to 4 mAh/cm². The electrochemical devices of the disclosure provide the potential of dilute ether electrolytes for easy desolvation-based intercalation chemistry in graphite, creating a viable path toward fast-charging batteries.

[0008] Also described herein are reductive-stable electrolytes (RSEs) that resolve the issue of the irreversibility of Li-ether co-intercalation in a graphite anode. The RSEs are effective for graphite anodes operated under extreme conditions and provide reversibility of Li-ether co-intercalation. Traditionally, a solid- electrolyte interphase (SEI), which forms between the anode and the electrolyte, needs to be thin and homogenous to facilitate reversibility (e.g., rechargeability) in the electrodes. Such a thin and homogenous SEI enables intercalation chemistry. However, the RSEs described herein use a heterogeneous interphase based on grainy lithium fluoride (LiF) for operating Li-solvent co-intercalation chemistry, thereby enabling remarkable reversibility.

[0009] Further described herein is the *in-situ* synthesis of ternary graphite intercalation compounds (t-GICs) in RSEs. In some embodiments, the *in-situ* synthesis of t-GICs in a tetrahydrofuran (THF) electrolyte is provided. Such a synthesis can be achieved via a spontaneous, controllable reaction between binary-GICs and THF molecules during initial graphite lithiation. This synthesis may be characterized and quantified via *operando* X-ray and electrochemical analyses. The resulting t-GIC chemistry can obviate the necessity for complete Li-ion desolvation, which facilitates rapid kinetics and synchronous charge/discharge of graphite particles even under high current densities. Consequently, the graphite anode demonstrates unprecedented fast charging (1 min), dendrite-free, low-temperature performance, and ultralong lifetimes exceeding 10,000 cycles. In some embodiments, full cells coupled with layered cathode may provide remarkable cycling stability upon a 15-minute charge and excellent rate capability even at -40 °C. Additionally explored in this disclosure are full cells that are tested with THF-based electrolytes to determine optimal performance in low-temperature applications.

[0010] The chemical strategies provided within the disclosure extend beyond Li-ion batteries to encompass additional metal-ion batteries, including, but not limited to, sodium (Na)-ion, potassium (K)-ion, aluminum (Al)-ion, calcium (Ca)-ion and magnesium (Mg)-ion batteries,

as well as alloys such as lithium-aluminum alloy, underscoring their broad applicability. The present disclosure contributes to the advancement of intercalation chemistry such as graphite, silicon and carbon chemistry, as well as alloy anodes (e.g., aluminum, tin, magnesium, silver and antimony) and presents a low-cost, adaptable approach to achieving fast-charging and low-temperature batteries.

[0011] While multiple embodiments are disclosed, still other embodiments of the present disclosure will become apparent to those skilled in the art from the following detailed description, which shows and describes illustrative embodiments of the disclosure. Accordingly, the figures and detailed descriptions are to be regarded as illustrative in nature and not restrictive.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] Fig. 1a is an example diagram of Li^+ -O radial distribution function (RDF) results for the electrolyte 1M LiTFSI DOL/DME.

[0013] Fig. 1b is an example diagram of Li^+ -O radial distribution function (RDF) results for the electrolyte 1M LiTFSI DOL.

[0014] Fig. 1c is an example diagram of Li^+ -O radial distribution function (RDF) results for the electrolyte 1M LiFSI DOL.

[0015] Fig. 1d is an example diagram of oxygen coordination numbers (CNs) by solvent/anion.

[0016] Fig. 1e is an example diagram of Raman spectra of different salts and electrolytes.

[0017] Fig. 1f is another example diagram of Raman spectra of different salts and electrolytes.

[0018] Fig. 1g is an example diagram of a population analysis of specific solvation structures based on a molecular dynamic (MD) simulation of the electrolyte 1M LiTFSI DOL/DME.

[0019] Fig. 1h is an example diagram of a population analysis of specific solvation structures based on an MD simulation of the electrolyte 1M LiTFSI DOL.

[0020] Fig. 1i is an example diagram of a population analysis of specific solvation structures based on an MD simulation of the electrolyte 1M LiFSI DOL.

[0021] Fig. 1j is an example diagram of a spin density of the Li-4DOL-TFSI and Li-4DOL-FSI.

[0022] Fig. 1k is an example diagram of the lowest unoccupied molecular orbital (LUMO) analysis of DOL, Li-4DOL-TFSI, and Li-4DOL-FSI.

[0023] Fig. 2a is an example diagram of cyclic voltammetry (CV) scan results of the electrolyte 1M LiTFSI DOL/DME.

[0024] Fig. 2b is an example diagram of CV scan results of the electrolyte 1M LiTFSI DOL.

[0025] Fig. 2c is an example diagram of CV scan results of the electrolyte 1M LiFSI DOL.

[0026] Fig. 2d is an example diagram of three initial charge/discharge profiles of the electrolyte 1M LiTFSI DOL/DME and a picture of the electrode used.

[0027] Fig. 2e is an example diagram of three initial charge/discharge profiles of the electrolyte 1M LiTFSI DOL a picture of the electrode used.

[0028] Fig. 2f is an example diagram of three initial charge/discharge profiles of the electrolyte 1M LiFSI DOL a picture of the electrode used.

[0029] Fig. 2g is an example diagram of results of X-ray diffraction (XRD) patterns of the graphite in DOL-based electrolytes after a first discharge.

[0030] Fig. 2h is an example diagram of an average CE of graphite electrodes from a second to a tenth cycle of the electrolytes LiFSI-DOL and LiOTF-DME.

[0031] Fig. 2i is an example schematic illustrating reductive stability of ether electrolytes.

[0032] Fig. 3a is an example diagram of X-ray photoelectron spectroscopy (XPS) results of the solid-electrolyte interphase (SEI) of different electrolytes.

[0033] Fig. 3b is an example diagram of soft X-ray absorption spectroscopy results of different electrolytes.

[0034] Fig. 3c is an example image of cryogenic transmission electron microscopy (cryo-TEM) of the SEI of the electrolyte Li-4DOL-FSI.

[0035] Fig. 3d are example images of high-angle annular dark field (HAADF) and EDS elemental mappings of the dashed region in Fig. 3c.

[0036] Fig. 3e are example high-resolution TEM images in the F-rich domain of the amorphous region.

[0037] Fig. 4a is an example diagram of cycling capacity of graphite cells in the electrolyte 1M LiFSI DOL.

[0038] Fig. 4b is an example diagram of charge/discharge profiles of the electrolytes LP57 and LiFSI DOL after a number of cycles.

[0039] Fig. 4c is an example diagram of cycling capacity of mesocarbon microbeads (MCMB) in various electrolytes.

[0040] Fig. 4d is an example diagram of charge/discharge profiles at different C-rates of the electrolyte 1M LiFSI DOL.

[0041] Fig. 4e is an example diagram of activation energy of the electrolytes 1M LiTFSI DOL and LP57.

[0042] Fig. 4f is an example diagram of solvation energy of different solvents with different coordination numbers.

[0043] Fig. 4g is an example schematic of the desolvation process in CIP-dominating electrolytes.

[0044] Fig. 4h is an example diagram of a summary of the graphite intercalation chemistry operated in different solvent-dependent electrolyte chemistries.

[0045] Fig. 5a is an example diagram of the areal capacity of various electrolytes at room temperature (RT), low temperature (LT), and at different C-rates.

[0046] Fig. 5b is an example diagram of a voltage profile of various electrolytes at LT and at different C-rates.

[0047] Fig. 5c is an example diagram of the specific capacity of graphite-based half cells vs. C-rate with the electrolyte 1M LiFSI DOL compared to other half cells.

[0048] Fig. 5d is an example diagram of the cycling capacity of half-cells using the electrolytes LP57 and 1M LiFSI DOL.

[0049] Fig. 6 is an example schematic diagram of a quadrant-based selection of salts and solvents to generate an electrolyte.

[0050] Fig. 7A is an example diagram of CV results of graphite-Li cells using the electrolyte 1M LiBF₄ G1.

[0051] Fig. 7B is an example diagram of cycling performances of the electrolytes 1M LiBF₄ G1 and 1M LiFSI G1.

[0052] Fig. 7C is an example diagram of charge/discharge voltage profiles of graphite cells in the electrolyte 1M LiFSI G1.

[0053] Fig. 7D is an example diagram of charge/discharge voltage profiles of graphite cells in the electrolyte 1M LiBF₄ G1.

[0054] Fig. 7E is an example diagram of initial coulombic efficiency (ICE) in different electrode composition and cycling conditions.

[0055] Fig. 7F is an example diagram of cycling performance of graphite-Li cells using a 901SA electrode composition.

[0056] Fig. 7G is an example diagram of cycling performance of existing electrolytes vs. the electrolyte 1M LiBF₄ G1.

[0057] Fig. 8A is an example of scanning electron microscope (SEM) images of graphite cycled in 1M LiBF₄ G1 and 1M LiFSI G1.

[0058] Fig. 8B is an example diagram of XRD patterns of graphite cycled in different electrolytes.

[0059] Fig. 8C is an example of Raman spectra of charged graphite cycled in different electrolytes.

[0060] Fig. 8D is an example of atomic concentrations of elements of the electrolytes 1M LiFSI G1 and 1M LiBF₄ G1.

[0061] Fig. 8E is an example of high-resolution F spectra results of the electrolytes 1M LiFSI G1 and 1M LiBF₄ G1.

[0062] Fig. 8F is an example of C K-edge soft XAS spectra results of the electrolytes 1M LiFSI G1 and 1M LiBF₄ G1.

[0063] Fig. 9A is an example of high-resolution TEM (HRTEM) images of graphite cycled in 1M LiBF₄ G1.

[0064] Fig. 9B is another example of HRTEM images of graphite cycled in 1M LiBF₄ G1.

[0065] Fig. 9C is an example of HRTEM images of graphite cycled in 1M LiFSI G1.

[0066] Fig. 9D is another example of HRTEM images of graphite cycled in 1M LiFSI G1.

[0067] Fig. 9E is an example of high-angle annular dark-field (HAADF) images of graphite cycled in 1M LiFSI G1.

[0068] Fig. 9F is an example of HAADF images of graphite cycled in 1M LiBF₄ G1 (RSE).

[0069] Fig. 9G is an example of HAADF images of graphite cycled in RSE taken along a plane different than in Fig. 9F.

[0070] Fig. 9H is an example of red-channel only EDS maps of graphite cycled in 1M LiFSI G1 and in RSE.

[0071] Fig. 9I is an example diagram of intensity distribution for the EDS map of Fig. 9H.

[0072] Fig. 10A is an example diagram of potentiostatic intermittent titration technique (PITT) results of the electrolytes RSE and 1M LiFSI G1.

[0073] Fig. 10B is an example diagram of simulation results of LUMO analysis of LiBF₄ and LiFSI with different numbers of solvents.

[0074] Fig. 10C is an example of ab initio molecular dynamics (AIMD) simulations of the electrolyte LiBF₄ G1 in an SSIP configuration on a -1 charged basal plane.

[0075] Fig. 10D is an example of charge transfer plots of the simulation results of Fig. 10C.

[0076] Fig. 10E is an example of AIMD simulations of the electrolyte LiBF_4 in an SSIP configuration on a neutral edge plane.

[0077] Fig. 10F is an example of charge transfer plots of the simulation results of Fig. 10E.

[0078] Fig. 10G is an example of AIMD simulations of the electrolyte LiBF_4 in an SSIP configuration on a -1 charged edge plane.

[0079] Fig. 10H is an example of charge transfer plots of the simulation results of FIG. 10G.

[0080] Fig. 11A is an example contour plot of synchrotron XRD measurements of a graphite-Li cell cycled in RSE.

[0081] Fig. 11B is an example voltage profile of a graphite-Li cell cycled in RSE.

[0082] Fig. 11C is an example diagram of XRD patterns extracted from in-operation measurements of a graphite-Li cell cycled in RSE at specific potentials.

[0083] Fig. 11D is an example diagram of coherent X-ray multocrystal diffraction (CMCD) results for two cycles of graphite-Li cells cycled in RSE.

[0084] Fig. 11E is an example schematic diagram of structure change and interphase design based on the electrolyte RSE.

[0085] Fig. 12A is an example diagram of cycling performance of graphite anodes cycled in RSE (e.g., 1M LiBF_4 G1) and in LP57.

[0086] Fig. 12B is an example diagram of a voltage profile for a graphite anode cycled in RSE at different mass loading rates.

[0087] Fig. 12C is an example diagram of a voltage profile for a graphite anode cycled in LP57 at different mass loading rates.

[0088] Fig. 12D is an example diagram of the kinetics of different metals with co-intercalation and desolvation.

[0089] Fig. 12E is an example diagram of CV data of natural graphite cycled in 1M LiBF_4 G1 at different scan rates.

[0090] Fig. 12F is an example diagram of the peak current dependence on scan rate derived from CV data.

[0091] Fig. 12G is an example diagram of Nyquist plots of graphite cells cycled in different electrolytes.

[0092] Fig. 12H is an example diagram of the areal capacity of graphite cells cycled in RSE at different mass loading rates.

[0093] Fig. 12I is an example schematic showing co-intercalation for graphite cycled in RSE.

[0094] Fig. 13a is an example diagram of charge/discharge voltage profiles of three different electrolytes.

[0095] Fig. 13b is an example diagram of charge/discharge voltage profiles of the electrolyte 1M LiPF₆-THF with different rest periods after the first lithiation.

[0096] Fig. 13c is an example of images of lithiated graphite soaked in the electrolytes THF and EMC initially and after 24 hours of soaking.

[0097] Fig. 13d is an example diagram of discharge curves for full battery cells at different C-rates using the electrolyte 1M LiPF₆-THF.

[0098] Fig. 13e is an example diagram of XRD patterns for full battery cells at different C-rates using the electrolyte 1M LiPF₆-THF.

[0099] Fig. 13f is an example diagram of Fourier transform infrared spectroscopy (FTIR) of graphite in full battery cells after different charge/discharge cycles.

[0100] Fig. 14a is an example diagram of synchrotron XRD results of a full cell using the electrolyte 1M LiPF₆-THF during a first cycle.

[0101] Fig. 14b is an example diagram of synchrotron XRD results of a full cell using the electrolyte 1M LiPF₆-THF during a second cycle.

[0102] Fig. 14c is an example diagram of delineated synchrotron XRD results of a full cell using the electrolyte 1M LiPF₆-THF.

[0103] Fig. 14d is an example of CMCD images of a cell using the electrolyte 1M LiPF₆-THF.

[0104] Fig. 14e is an example diagram of a mass charge of graphite at different states of discharge for a G||Li cell using the electrolyte 1M LiPF₆-THF.

[0105] Fig. 14f is an example schematic diagram of the *in-situ* transformation of b-GICs to t-GICs under battery operating conditions.

[0106] Fig. 15a is an example diagram of Raman spectra of the 1M LiPF₆-THF electrolyte taken at different temperatures.

[0107] Fig. 15b is an example diagram of the FTIR spectrum of the 1M LiPF₆-THF electrolyte.

[0108] Fig. 15c is an example diagram of classical molecular dynamics (cMD) simulations for three different electrolytes sandwiched between two electrodes.

[0109] Fig. 15d is an example diagram of a radial distribution of three different electrolytes.

[0110] Fig. 15e is an example diagram of the solvation energy between Li⁺ and three different solvent molecules.

[0111] Fig. 15f is an example diagram of the binding energy between Li^+ and three different solvent molecules.

[0112] Fig. 16a is an example diagram of cycling performance of a G||Li cell at different C-rates using the electrolyte 1M LiPF_6 -THF.

[0113] Fig. 16b is an example diagram of long-term cycling performance of a G||Li cell at a 10 C-rate using the electrolyte 1M LiPF_6 -THF.

[0114] Fig. 16c is an example diagram of long-term cycling performance of a G||Li cell at a 20 C-rate using the electrolyte 1M LiPF_6 -THF.

[0115] Fig. 16d is an example diagram of long-term cycling performance of a G||Li cell at a 50 C-rate using the electrolyte 1M LiPF_6 -THF.

[0116] Fig. 16e is an example diagram of cycling performance of a G||Li cell at a different C-rates and at a temperature of -20°C using the electrolyte 1M LiPF_6 -THF.

[0117] Fig. 16f is an example diagram of long-term cycling performance of a G||Li cell at a 10 C-rate and at a temperature of -20°C using the electrolyte 1M LiPF_6 -THF.

[0118] Fig. 16g is an example diagram of cycling performance of a G||Li cell at a different C-rates and at a temperature of -40°C using the electrolyte 1M LiPF_6 -THF.

[0119] Fig. 16h is an example diagram of long-term cycling performance of a G||Li cell at a 2 C-rate and at a temperature of -40°C using the electrolyte 1M LiPF_6 -THF.

[0120] Fig. 17a is an example diagram of voltage profiles of a G||NMC811 full cell at different C-rates.

[0121] Fig. 17b is an example diagram of full cell capacities for various full cells including a G||NMC811 full cell that uses the electrolyte 1M LiPF_6 -THF.

[0122] Fig. 17c is an example diagram of the G||NMC811 full cell's long-term cycling performance at 4C.

[0123] Fig. 17d is an example diagram of the G||NMC811 full cell's cycling performance at different C-rates.

[0124] Fig. 17e is an example diagram of the power and energy density of various full cells including the G||NMC811 full cell.

[0125] Fig. 17f is an example diagram of the G||NMC811 full cell's cycling performance at different C-rates at a temperature of -20°C .

[0126] Fig. 17g is an example diagram of the G||NMC811 full cell's cycling performance at different C-rates at a temperature of -40°C .

[0127] Fig. 18a is a diagram of the cycling performance of a graphite anode cycled in different electrolytes at different C-rates and at a temperature of 23 °C.

[0128] Fig. 18b is a diagram of the cycling performance of a graphite anode cycled in different electrolytes at a temperature range of 23 to -20 °C.

[0129] Fig. 19a is an example diagram of the cycling performance of a graphite anode cycled in different electrolytes at a 0.2 C rate and at a temperature of -20 °C.

[0130] Fig. 19b is an example diagram of the long-term cycling performance of a graphite anode cycled in the 1M LiPF₆-2MeTHF electrolyte at a 2 C rate and at a temperature of -20 °C.

[0131] Fig. 20a is an example diagram of the cycling performance of a graphite anode cycled in the 1M LiPF₆-2MeTHF electrolyte at different C-rates and at a temperature of -20 °C, along with the corresponding voltage profiles.

[0132] Fig. 20b is an example diagram of the cycling performance of a μ Si/Graphite anode cycled in the 1M LiPF₆-2MeTHF electrolyte at different C-rates and at a temperature of -20 °C, along with the corresponding voltage profiles.

[0133] Fig. 20c is an example diagram of the cycling performance of a Si anode cycled in the electrolyte 1M LiPF₆-2MeTHF at different C-rates and at a temperature of -20 °C, along with the corresponding voltage profiles.

[0134] Fig. 20d is an example diagram of the cycling performance of a Graphite||NMC622 full cell cycled in the 1M LiPF₆-2MeTHF electrolyte at different C-rates and at a temperature of -20 °C.

[0135] Fig. 20e is an example diagram of the long-term cycling performance of Graphite||NMC622 pouch cells cycled in the 1M LiPF₆-2MeTHF electrolyte at 0.2 C and at a temperature of -20 °C.

[0136] Fig. 21a is an example diagram of the cycling performance of a Si/HC anode cycled in the electrolyte 1.5M LiPF₆-2MeTHF at different C-rates, along with a corresponding voltage profile.

[0137] Fig. 21b is an example diagram of the long-term cycling performance of a Si/HC anode cycled in the electrolyte 1.5M LiPF₆-2MeTHF at a 2 C rate, along with a corresponding voltage profile.

[0138] Fig. 22a is an example diagram of a voltage profile of a hard carbon (HC) anode cycled in the 1M LiPF₆-2MeTHF and 1M LiPF₆-EC/EMC electrolytes.

[0139] Fig. 22b is an example diagram of the cycling performance of an HC anode cycled in the 1M LiPF₆-2MeTHF and 1M LiPF₆-EC/EMC electrolytes.

[0140] Fig. 22c is an example diagram of the long-term cycling performance of an HC anode cycled in the 1M LiPF₆-2MeTHF and 1M LiPF₆-EC/EMC electrolytes.

[0141] Fig. 23a is a voltage profile illustrating the low-temperature performance of an HC anode cycled in the 1M LiPF₆-THF electrolyte.

[0142] Fig. 23b is a rate capability illustrating the low-temperature performance of an HC anode cycled in the 1M LiPF₆-THF electrolyte.

[0143] Fig. 23c is the long-term cycling/stability illustrating the low-temperature performance of an HC anode cycled in the 1M LiPF₆-THF electrolyte.

[0144] Fig. 24a shows the LSV curve of the Li||Al cell to test the oxidation stability of the 1M LiFSI-4MeTHP electrolyte, which only begins to decompose around 4.8V.

[0145] Fig. 24b shows the rate capability of the Li||NMC811 cell in the 1M LiFSI-4MeTHP electrolyte within the voltage range of 2.8-4.5V.

[0146] Fig. 24c shows the corresponding voltage profiles of the Li||NMC811 cell in the 1M LiFSI-4MeTHP electrolyte. The constant voltage charge (CVC) is added to match standard rate performance at 5.0 and 10.0 C. At 0.2, 0.5, 1.0, 2.0, 5.0, and 10.0 C, the Li||NMC811 cell delivers specific capacities of 217, 211, 203, 194, 183, and 153 mAh g⁻¹, respectively.

[0147] Fig. 24d shows a fresh Li||NMC811 cell tested at 3C for long-term cycling, achieving 80% capacity retention after 550 cycles, with an average Coulombic efficiency of up to 99.9%.

[0148] Fig. 24e shows the corresponding voltage profiles of the Li||NMC811 cell at 3C in the 1M LiFSI-4MeTHP electrolyte.

[0149] Fig. 25a shows the rate performance of the Gr||NMC811 full cell in the 1M LiPF₆-4MeTHP+2wt% FEC electrolyte within the voltage range of 2.8-4.5V, delivering specific capacities of 209, 205, 193, 182 and 147 mAh g⁻¹ at 0.1, 0.2, 0.5, 1.0, and 2.0 C, respectively.

[0150] Fig. 25b shows the corresponding voltage profiles of the Gr||NMC811 full cell in the 1M LiPF₆-4MeTHP+2wt% FEC.

[0151] Fig. 25c shows the long-term cycling performance of the Gr||NMC811 full cell at 1C within the voltage range of 3 to 4.4V, achieving 88% capacity retention after 400 cycles, with an average Coulombic efficiency of up to 99.9%.

[0152] Fig. 25d shows the corresponding voltage profiles of the Gr||NMC811 full cell in the 1M LiPF₆-4MeTHP+2wt% FEC.

[0153] Fig. 26a shows the CV curves of the Si/HC||Li cell in the 1M LiPF₆-4MeTHP electrolyte.

[0154] Fig. 26b shows the voltage profiles of the Si/HC||Li cell in the 1M LiPF₆-4MeTHP electrolyte at current densities of 0.2, 0.5, 1.0, 1.5, 2.0, 2.5C (1C=1.2 A/g).

[0155] Fig. 26c shows the rate performance of the Si/HC||Li cell in the 1M LiPF₆-4MeTHP electrolyte.

[0156] Fig. 26d shows the voltage profiles of the Si/HC||Li cell in the 1M LiPF₆-4MeTHP electrolyte at 2C (specific capacity with varying voltage).

[0157] Fig. 26e shows the long-term cycling of the Si/HC||Li in the 1M LiPF₆-4MeTHP electrolyte at 2C (areal capacity variance over cycle number).

[0158] Fig. 26f shows the voltage profiles of the Si/HC||Li cell at low temperatures (specific capacity with varying voltage).

[0159] Fig. 26g shows the rate capability of the Si/HC||Li anode at low temperatures (specific capacity over cycle number).

[0160] Fig. 27a shows the LSV curve of the Li||Al cell to test the oxidation stability of the 1M LiPF₆-4MeTHP electrolyte, which only begins to decompose around 4.8V.

[0161] Fig. 27b shows the voltage profiles of the Si/HC||NMC811 full cell in the 1M LiPF₆-MTHP electrolyte at current densities of 0.1, 0.2, 0.5, 1.0, 2.0, 4.0C (1C=0.2 A/g). The voltage range is 2-4.3V (specific capacity with varying voltage).

[0162] Fig. 27c shows the rate performance for the Si/HC||NMC811 full cell in the 1M LiPF₆-MTHP electrolyte (specific capacity with cycle number).

[0163] Fig. 27d shows the long-term cycling performance of the Si/HC||NMC811 full cell in the 1M LiPF₆-MTHP electrolyte at 2C. The voltage range is 2-4.2V.

[0164] Fig. 27e shows the low temperatures cycling performance of the Si/HC||NMC811 full cell in the 1M LiPF₆-MTHP electrolyte. The voltage range is 2-4.3V.

DETAILED DESCRIPTION

[0165] The embodiments of this disclosure are not limited to particular electrochemical devices, which can vary and are understood by skilled artisans. It is further to be understood that all terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting in any manner or scope. So that the present disclosure may be more readily understood, certain terms are first defined. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood

by one of ordinary skill in the art to which embodiments of the disclosure pertain. Many methods and materials similar, modified, or equivalent to those described herein can be used in the practice of the embodiments of the present disclosure without undue experimentation, the preferred materials and methods are described herein. In describing and claiming the embodiments of the present disclosure, the following terminology will be used in accordance with the definitions set out below.

[0166] Numeric ranges recited within the specification are inclusive of the numbers defining the range and include each integer within the defined range. Throughout this disclosure, various aspects of this disclosure are presented in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosure. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges, fractions, and individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6, and decimals and fractions, for example, 1.2, 3.8, $1\frac{1}{2}$, and $4\frac{3}{4}$. This applies regardless of the breadth of the range.

[0167] The term “about,” as used herein, refers to variation in the numerical quantity that can occur, for example, through typical measuring techniques and equipment, with respect to any quantifiable variable, including, but not limited to, mass, volume, temperature, and time. Further, given solid and liquid handling procedures used in the real world, there is certain inadvertent error and variation that is likely through differences in the manufacture, source, or purity of the ingredients used to make the compositions or carry out the methods and the like. Whether or not modified by the term “about,” the claims include equivalents to the quantities.

[0168] The term "actives" or "percent actives" or "percent by weight actives" or "actives concentration" are used interchangeably herein and refers to the concentration of those ingredients involved in cleaning expressed as a percentage minus inert ingredients such as water or salts. It is also sometimes indicated by a percentage in parentheses, for example, “chemical (10%).”

[0169] The term "weight percent," "wt.%, " "wt-%," "percent by weight," "% by weight," and variations thereof, as used herein, refer to the concentration of a substance as the weight of that substance divided by the total weight of the composition and multiplied by 100.

[0170] Graphite has excellent structural tunability and is an intriguing material for studying guest-host interactions. For example, reversible Li-ion intercalation in graphite has spurred the rapid development of Li-ion batteries (LIBs). The early success of LIBs cannot be garnered without a protective solid-electrolyte interphase (SEI) layer formed on graphite cycled in ethylene carbonate (EC)-based electrolytes. However, a difficulty with electrode materials, including graphite, is that an operating voltage window of electrode materials can be beyond the stability window of electrolytes. Accordingly, a uniform, thin, and dense SEI is needed in commercial LIBs.

[0171] Graphite intercalation compounds (GICs) are compounds formed by the insertion of guest species into the layers of graphite. GICs have shown programmable physiochemical properties for applications such as electrical conductors, catalysis, hydrogen storage, and energy storage. Among these, alkali-ion based GICs are particularly attractive as electrodes for rechargeable batteries. GICs exhibit adjustable guest-host interactions with anions, cations, and solvated cations, enabling different battery chemistries. One of the most extensively studied GICs is lithiated graphite (LiC_6), a binary GIC (b-GIC) serving as the anode in commercial Li-ion batteries (LIBs). Electrochemical synthesis of LiC_6 can be intricate, governed by factors including the solvation structure, the thermodynamic properties of electrolytes, and the graphite-electrolyte electrochemical interphase. In conventional graphite intercalation chemistry, the interphase between the graphite anode and the electrolyte allows cations to be transported while blocking other electrolyte components, such as solvent molecules.

[0172] In addition to binary GICs, ternary-GICs (t-GICs) form another category of GICs. While b-GICs have one type of guest species (e.g., lithium ions) intercalated into the graphite, t-GICs have two types of species that are both intercalated (i.e., are co-intercalated) into the graphite. For example, t-GICs can include both ions (e.g., lithium ions) and ether solvent molecules that are co-intercalated within the graphite. Typically, a single reaction can only lead to either b-GICs or t-GICs, and the co-existence of and interconversion between b-GICs and t-GICs is rare because they need distinct interactions between cation and anion/solvent.

[0173] Although Li-ether co-intercalation has been reported since the 1990s, its reversibility remains a long-lasting challenge. Li-t-GICs have been shown to be unstable, suffering from more severe degradation at large current densities. Therefore, most efforts on exploring the co-intercalation mechanism and understanding interphase formation have been focused on beyond-Li chemistries.

[0174] Despite the extensive attempts to utilize the co-intercalation mechanism for rechargeable Li-ion batteries, several issues have been encountered. For example, previous studies have proposed the reversibility and kinetics of Na-ion and K-ion are superior to Li-ion co-intercalation. Additionally, it has been difficult to study the nature of the SEI and its formation in a co-intercalative system, which is crucial to understanding the properties of a corresponding battery. Further, it is unknown how electrochemically stable electrolytes encounter reduction in the presence of the electrode surface.

[0175] Unidentate cyclic ether ligands, such as the solvent tetrahydrofuran (THF), can have unique electrochemical and chemical interactions with graphite, which can enable dynamic interconversion between b-GICs and t-GICs even under battery operating conditions. Hybrid intercalation and co-intercalation reactions are possible, which can offer dynamic interconversion between b-GICs and t-GICs. Dynamic interconversion between b-GICs and t-GICs can be used in designing extreme-condition batteries because t-GICs offer excellent chemical and structural tunability and have outstanding electrical conductivity and fast diffusion of solvated ions between graphene layers. Additionally, the energy barrier of the charge transfer process is lowered in t-GICs relative to b-GICs due to their co-intercalation mechanism rather than the intercalation mechanism of b-GICs.

[0176] Solvents, including propylene carbonate (PC), 1,2-dimethoxyethane (DME, also referred to as G1), and tetrahydrofuran (THF) were tested and were found to induce solvent co-intercalation due to a limited SEI formation. Such a co-intercalation process produces ternary graphite-intercalation compounds (t-GICs), which can be structurally stable depending on the type of solvents. Compared to PC, which suffers from runaway reduction, ethers are more reductively stable and are suitable to realize reversible co-intercalation. An electrolyte catering to co-intercalation comprises a reductive-stable anion and a reductive-stable solvent.

[0177] Previous attempts of using glyme solvents (e.g., DME) with lithium-t-GICs have had cycling stability issues. However, as discussed further herein, by using THF solvents instead of glyme solvents, the cycling stability issues can be resolved due to the dynamic

interconversion between b-GICs and t-GICs with THF solvents. Further, an extreme-condition battery with fast-charging capabilities in low-temperature applications can be made using THF solvents. Additionally, by synthesizing the t-GICs *in-situ* (e.g., in a battery cell during cycling), asynchronous reactions can be avoided, thereby enabling graphite particles to charge/discharge synchronously. Further, as THF is relatively inexpensive compared to commercial electrolyte solvents, creating a battery using THF as a solvent in the electrolyte leads to cost savings over other batteries.

[0178] Described herein are examples of electrochemical devices, such as batteries, which have advantageous properties over existing electrochemical devices. The properties include, but are not limited to, low-temperature operation, fast charging, long lasting cyclability, and low-cost construction. The electrochemical devices disclosed herein comprise an anode, a cathode, and an electrolyte that includes a salt and a solvent.

[0179] In embodiments of the electrochemical devices disclosed herein, the anode can comprise a variety of elements and/or compounds such as graphite, silicon, hard carbons, and combinations thereof. If the anode comprises graphite or hard carbon, the anode can have a local graphitic structure determined by graphitic peaks measured by x-ray diffraction and Raman spectroscopy. The anode can comprise a synthetic graphite, a natural graphite, or a combination thereof. Further the anode can comprise a hard carbon derived from a biomass, coal, and/or petroleum byproduct (e.g., waste).

[0180] In similarity with the anode, the cathode can comprise a variety of compounds. For instance, the cathode can comprise $M_n-X_q-R-F_y$, where M is selected from Li, Na, and K; X comprises one or more transition metals; R is O_2 or PO_4 ; n is one or greater; q is greater than zero for each individual X; and y is zero or greater. In some examples, the cathode comprises $M-CoO_2$, $M-FeSO_4F$, $M-FePO_4$, or $M-Ni_xMn_yCo_zO_2$, where $x + y + z = 1$. In further examples, the cathode compounds can include $LiCoO_2$, $LiNiO_2$, $LiFePO_4$, $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$, or $Li_{1.75}Mn_{0.45}Ti_{0.45}Fe_{0.1}O_2F_{0.75}$.

[0181] The electrochemical devices disclosed herein can comprise liquid electrolytes comprising a salt and a solvent. For example, in some embodiments, the electrochemical devices can include a liquid electrolyte including a salt $M^+ A^-$ and a C_4-C_8 ether solvent, where M^+ is selected from the cations Li^+ , Na^+ , and K^+ and where A^- is an anion. In some embodiments, the anion comprises hexafluorophosphate (PF_6^-), tetrafluoroborate (BF_4^-), triflate ($CF_3SO_3^-$), bis(fluorosulfonyl)imide (FSI), or a combination thereof. Further, the salt

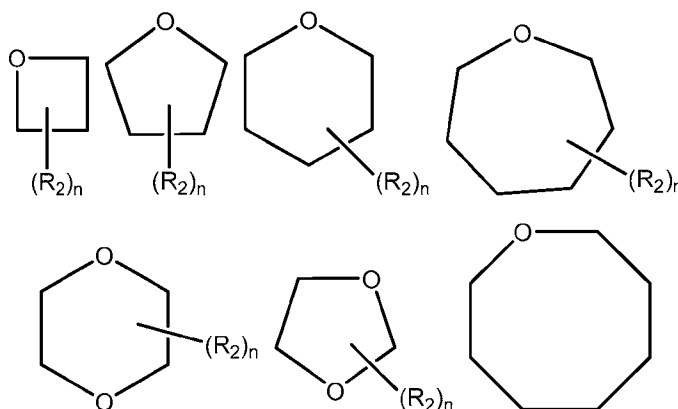
$M^+ A^-$ can have an initial concentration in the ether solvent of approximately 0.5 M to 2.5 M (e.g., +/- 15%).

[0182] The C₄-C₈ ether solvent (also referred to as “C₄-C₈ ether”) that makes up the liquid electrolyte of the electrochemical devices disclosed herein can comprise a variety of compounds. For instance, the C₄-C₈ ether can comprise a cyclic C₄-C₈ ether or a non-cyclic C₄-C₈ ether. In examples where the C₄-C₈ ether is a cyclic ether, it can comprise a compound of formula (I), where R₁ is a C₄-C₈ divalent alkylene radical that can optionally be interrupted by one or more oxygen or sulfur atoms. Further, the compound can optionally be substituted with one or more R₂ selected from the group of a C₁-C₂ alkyl and a halogen, where the C₁-C₂ alkyl can also optionally be substituted with one or more halogen.



(I)

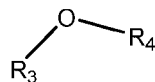
[0183] In some examples, the C₄-C₈ ether can comprise a compound selected from the group of:



[0184] In the above group, each R₂ can be independently selected from the group of methyl, ethyl, or fluoro with the corresponding n value being 0, 1, or 2. Further, each methyl and ethyl group can be independently substituted by one, two, or three fluorine atoms. In some specific examples, the C₄-C₈ ether can include, but is not limited to, tetrahydrofuran (THF), 2-methyltetrahydrofuran (2MeTHF), 2,5-methyltetrahydrofuran (2,5-MeTHF),

tetrahydropyran (THP), 4-methyltetrahydropyran (4MeTHP), 2-methyloxetane, 3-methyloxetane, 1,3-dioxalane, or combinations thereof.

[0185] In some embodiments where the C₄-C₈ ether is a non-cyclic C₄-C₈ ether, it can comprise a compound of formula (II), where R₃ and R₄ are independently selected from the group of methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, and tert-butyl, all of which can optionally be substituted with one or more fluorine atoms.



(II)

[0186] The C₄-C₈ ether can have a variety of properties that can be a result of its chemical structure. In aspects, the C₄-C₈ ether can have a melting point of between about -120°C to about -10°C with some examples having a melting point of from about -90°C to about -10°C, about -80°C to about -10°C, about -70°C to about -10°C, about -60°C to about -10°C, about -50°C to about -10°C, or about -40°C to about -10°C. The melting point can be dependent on temperature and pressure of the C₄-C₈ ether, however, the specified range of melting point between about -120°C to about -10°C can be at approximately room temperature (e.g., 273°K) and pressure (e.g., atmospheric pressure). In addition to melting point, the C₄-C₈ ether can have other properties. For example, the C₄-C₈ ether can have a dynamic viscosity of between about 0.4 mPa to about 0.6 mPa at 273°K and atmospheric pressure.

[0187] The C₄-C₈ ether can act in different ways when incorporated into example electrochemical devices (e.g., batteries). For instance, when using the C₄-C₈ ether in example electrochemical devices, the C₄-C₈ ether solvates the cation M⁺ of the salt M⁺ A⁻ and forms a solvate. In some examples, the solvate can reversibly co-intercalate in the anode. Additionally or alternatively, in some examples, the solvate desolvates and the cation M⁺ of the salt intercalates in the anode. The reactions of co-intercalation and intercalation can provide certain advantages to electrochemical devices using the C₄-C₈ ether.

[0188] Embodiments of electrochemical devices (e.g., batteries) that use an anode comprising graphite, silicon, hard carbon, or a combination thereof, a cathode, and a liquid electrolyte comprising a salt M⁺ A⁻ and a C₄-C₈ ether, where the salt cation M⁺ of the salt is one of Li⁺, Na⁺, or K⁺, can have specific properties. The properties of such electrochemical devices can include an original specific capacity and a specific capacity after a number of

cycles. For instance, in some embodiments, electrochemical devices of the above specified type can have a specific capacity of about 60% to 99% of their original specific capacity after a number of cycles ranging from about 200 to 10,000 cycles. In examples, the electrochemical devices may have a specific capacity measured after a number of cycles that is from 70% to 99%, from 80% to 99%, 90% to 99%, 95% to 99%, or 97% to 99% of the original specific capacity. In further examples, the specific capacity as described above is measured after from 200 to 1000 cycles, from 1000 to 10,000 cycles, from 2000 to 10,000 cycles, from 3000 cycles to 10,000 cycles, from 4000 to 10,000 cycles, from 5000 to 10,000 cycles, from 6000 to 10,000 cycles, 7000 to 10,000 cycles, 8000 to 10,000 cycles, or from 9000 to 10,000 cycles.

[0189] In some such embodiments, the electrochemical devices can have a specific capacity of about 60% to 99% of their original specific capacity after 9,000 or more cycles.

Additionally or alternatively, in some such embodiments, the electrochemical devices can have a specific capacity that is above 97% of the original specific capacity after a number of cycles. Embodiments of electrochemical devices described herein can have specific capacities that are dependent on the number of cycles. For example, an electrochemical device as described herein can have a specific capacity of 99% of its original specific capacity after 9,000 cycles. In another example, an electrochemical device as described herein can have a specific capacity of 60% of its original specific capacity after 200 cycles.

[0190] In some examples, the specific capacity after a number of cycles of an electrochemical device can be dependent on an operating temperature that ranges from 0°C to -120°C. In some examples, the specific capacity after a number of cycles of an electrochemical device can be dependent on a charge/discharge rate C that ranges from 0.1C to 50C. In some examples, the specific capacity of an electrochemical device is dependent on one or more of an operating temperature, a charge/discharge rate, or a number of cycles, each of which having a range as specified herein.

[0191] The properties of electrochemical devices described herein can also include a cell average discharge voltage at which an electrochemical device operates. For instance, in some embodiments, an electrochemical device can operate at a cell average discharge voltage from about 1.0V to about 4.3V.

[0192] In some embodiments, an anode of an electrochemical device comprises an anode stack including an anodic current collector, with the anode formed over at least a portion of the anodic current collector. In such embodiments, a cathode of the electrochemical device

comprises a cathode stack including a cathodic current collector, with the cathode formed over at least a portion of the cathode stack. Further, in such embodiments, a separator material can be disposed between the cathode stack and the anode stack of the electrochemical device. The separator material can comprise one or more of a nonwoven fiber, a cotton fiber, a nylon, a polyester, a glass, a polymer film, a polyethylene, a polypropylene, a poly(tetrafluoroethylene), a polyvinyl chloride, a ceramic, a rubber, or an asbestos. Electrochemical devices that comprise the anode stack, the cathode stack, and the separator material can also include an electrolyte such as the electrolytes described elsewhere herein (e.g., an electrolyte having a cation of Li^+ , Na^+ , or K^+ , an anion, and a $\text{C}_4\text{-C}_8$ ether solvent) and can form a battery.

[0193] All publications and patent applications in this specification are indicative of the level of ordinary skill in the art to which this disclosure pertains. All publications and patent applications are herein incorporated by reference to the same extent as if each individual publication or patent application was specifically and individually indicated as incorporated by reference.

Examples

[0194] Embodiments of the present disclosure are further defined in the following non-limiting Examples. It should be understood that these Examples, while indicating certain embodiments of the disclosure, are given by way of illustration only. From the above discussion and these Examples, one skilled in the art can ascertain the essential characteristics of this disclosure, and without departing from the spirit and scope thereof, can make various changes and modifications of the embodiments of the disclosure to adapt it to various usages and conditions. Thus, various modifications of the embodiments of the disclosure, in addition to those shown and described herein, will be apparent to those skilled in the art from the foregoing description. Such modifications are also intended to fall within the scope of the appended claims.

Example 1

Analysis of Solvation Structures and Thermodynamic Properties

[0195] A redesign of conventional dilute ether electrolytes, (1M LiTFSI DOL/DME, volume ratio of DOL to DME of 1:1) is provided by tuning the local Li-ion solvation environment (e.g., removing a solvent, changing the salt used) and thermodynamic properties. The conventional dilute electrolyte 1M LiTFSI DOL/DME, ratio 1:1 has a low Coulomb efficiency

(CE) and is generally irreversible. However, by using a singular solvent (e.g., DOL or DME) rather than a combination of solvents, both the solvent DOL and DME can lead to a >99% CE with excellent capacity retention via the desolvation mechanism and co-intercalation, respectively. In particular, the following example demonstrates that using the ether solvent (DOL) and salt (LiFSI) at a low concentration (1M) delivered high reversibility (approximately 99.9% CE regardless of the graphite type) and outperformed carbonate electrolytes (ECs) for fast-charging graphite-based Li-ion batteries. The solvation structures and thermodynamic properties were analyzed to establish a structure-performance relationship for dilute ether electrolytes used in graphite-based batteries.

[0196] Tuning the solvation structure by removing DME from DOL/DME. Molecular dynamics (MD) simulations were performed to determine the solvation structures of the electrolytes 1M LiTFSI DOL/DME (e.g., conventional), 1M LiTFSI DOL, and 1M LiFSI DOL. Illustrated in **Figs. 1a-c** are the Li^+ -O radial distribution function (RDF) results between the different electrolytes in solid lines with the integrated RDF in dashed lines. The RDF results of **Fig. 1a** indicate that DME dominates the first solvation shell in 1M LiTFSI DOL/DME electrolyte and the dominant ionic association of Li^+ is solvent-separated ion pair (SSIP). In contrast, the results of **Figs. 1b-c** indicate that 1M LiTFSI DOL and 1M LiFSI DOL both demonstrate a characteristic contact-ion pair (CIP) structure where the anion participates closely in the first solvation shell. The binding enthalpy ΔH of single-solvent binding for DOL and DME solvated with Li^+ is -1.56 eV and -2.63 eV, respectively, which indicates a stronger binding and solvation power of DME over DOL. This is also reflected by the Gibbs free energy ΔG of -1.29 eV vs. -2.25 eV (DOL vs. DME), which shows that both solvation processes are thermodynamically favorable to occur, but DME is more favorable in comparison to DOL. From Li-3DOL to Li-4DOL, ΔG increases from -0.43 eV to -0.03 eV, suggesting that after four DOL molecules are added to the solvation shell it becomes almost thermodynamically unfavorable. This behavior can be referred to as the “steric effect” of cyclic ether. Such a steric effect typically allows for more anion existence in the first solvation shell. The oxygen coordination numbers (CN) by solvent or anion is quantified in **Fig. 1d** for each electrolyte with the data being averaged throughout a 50 ns simulation time for each electrolyte. The average CN of DME oxygen chelating with Li^+ is around five and there is negligible coordination contribution from the anion. In 1M LiTFSI DOL and 1M LiFSI DOL, the anion provides a 0.8 CN and 1.3 CN, respectively. More FSI⁻ coordination in the latter may be due to less steric hindrance of this anion compared to bulky TFSI⁻.

[0197] As illustrated in **Figs. 1e-f**, which include the Raman spectra of different salts, solvents, and electrolytes, the Raman spectra illustrate the impact of removing DME from conventional DOL/DME-based electrolytes on the solvation structure. The free DOL peak is prominent in all electrolytes. In contrast, when DME exists in the electrolyte, the feature of free DME becomes less remarkable due to the strong Li-DME coordination. The peaks related to the anion undergo a redshift (e.g., leftward in the figure) from the salt to the solvated state due to a reduced coordination between the cation and anion. The redshift is less apparent in 1M LiTFSI DOL (745 cm^{-1}) than 1M LiTFSI DOL/DME (739 cm^{-1}), which indicates a stronger Li-anion interaction in 1M LiTFSI DOL. In the spectra of LiFSI-based electrolyte, the S–N–S bending peak has a more notable redshift in 1M LiFSI DOL/DME (2:8 in volume) than 1M LiFSI DOL. This further supports that eliminating DME contributes to strengthened cation-anion interaction.

[0198] MD simulations were used to quantify the populations of specific solvation structures, namely SSIP, CIP, free anion (FA), and aggregate (AGG). **Fig. 1g** is an illustration of a population analysis of specific solvation structures based on an MD simulation of the conventional electrolyte 1M LiTFSI DOL/DME. **Fig. 1h** is an illustration of a population analysis of specific solvation structures based on an MD simulation of the electrolyte 1M LiTFSI DOL. **Fig. 1i** is an illustration of a population analysis of specific solvation structures based on an MD simulation of the electrolyte 1M LiFSI DOL. By removing DME from the electrolyte (1M LiTFSI DOL vs. 1M LiTFSI DOL/DME), the CIP population increases from 4% to 42% as illustrated in **Fig. 1h** compared to **Fig. 1g**. However, the CIP population stays nearly unchanged after switching the anion from TFSI⁻ (**Fig. 1h**) to FSI⁻ (**Fig. 1i**). The main difference between 1M LiTFSI DOL and 1M LiFSI DOL is the increased fraction of AGG, from 18% into 36%.

[0199] **Tailoring the thermodynamic properties from 1M LiTFSI DOL to 1M LiFSI DOL.** The graphite/electrolyte interface (e.g., SEI) is key to retaining stable cycling performance. The reductive stability of electrolyte species, which fundamentally dictates the formation of the SEI, was investigated. The reduction of the most common primary solvated complex with anion coordination in each DOL system (the Li-4DOL-anion) is highlighted in **Fig. 1j-k**. **Fig. 1j-k** illustrate the spin density and lowest unoccupied molecular orbital (LUMO) analysis of the Li-4DOL-anion (e.g., TFSI and FSI). The frontier orbital is delocalized on DOL for Li-4DOL-TFSI, with a LUMO energy of -0.24 eV . In contrast, the LUMO of Li-4DOL-FSI is on FSI⁻ with a lower LUMO energy of -0.42 eV . The LUMO level

between the AGG and the CIP structure are quite similar which indicates that the reduction would occur in a similar fashion. Though there is no surface in these simulations, LiF is expected to be formed with CIP electrolyte and based on the LUMO results, the AGG should also favor the same. In general, the LUMO of solvation species in 1M LiFSI DOL is lower than that of 1M LiTFSI DOL. This is also observed from density functional theory (DFT) reduction calculations where coordinated FSI⁻ tends to be decomposed at a higher voltage, predicted to be approximately 1.8 V vs. Li/Li⁺, which is higher than that of a coordinated TFSI⁻. From both the reduction potential calculations and relative LUMO levels, the FSI⁻ is more likely to be reduced than a TFSI⁻ species.

[0200] Bulk physicochemical properties. When utilizing a weak-binding solvent, it is likely that the ionic conductivity will be significantly hampered due to the lack of Li salt dissociation. For example, this is the case in both the solvents diethyl ether and 1,4-dioxane. DOL should have a moderate interaction with Li-ion, given its intermediate dielectric constant (7.3) and 5M solubility for LiTFSI. From 1M LiTFSI DOL/DME to 1M LiTFSI DOL, the ion conductivity decreases while the transference number (t_+) slightly increases, which originates from a stronger Li-anion interaction. When LiTFSI is replaced by LiFSI, the ion conductivity is improved. Meanwhile, 1M LiFSI DOL shows a high t_+ of approximately 0.6, superior to the most widely used commercial electrolyte 1M LiPF₆, ethylene carbonate (EC)/ethyl methyl carbonate (EMC) 3:7 in volume (LP57).

[0201] Improved compatibility between ether and graphite based on structural and compositional redesign. To experimentally study the graphite intercalation chemistry in dilute ether electrolytes, cyclic voltammetry (CV) was performed using natural graphite (hereinafter referred to as “graphite”) as the working electrode. The graphite was flake-shaped to provide easy observation of morphological changes (e.g., expansion). **Figs. 2a-c** illustrate CV scans of three electrolytes in graphite/Li cells from 0.01 V to 1.5 V at a rate of 0.2 mV/s. As shown in **Fig. 2a**, the conventional DOL/DME-based electrolyte leads to notable irreversibility. In comparison, in **Fig. 2c**, 1M LiFSI DOL exhibits a reduction through coordinated FSI⁻ at approximately 1.2 V, which is higher than that of 1M LiTFSI DOL (approximately 0.5 V, **Fig. 2b**), consistent with the trend predicted by the LUMO analysis (**Fig. 1k**). Though several other weak coordinating ethers, for example, 2-methyltetrahydrofuran (2-MeTHF), also enables limited co-intercalation, only DOL exhibits such high reduction potential. **Figs. 2d-f** illustrate the initial three charge/discharge voltage profiles of graphite/Li half-cells using the three different electrolytes. The inset

images of each of **Figs. 2d-f** show the corresponding lithiated graphite after the first discharge. The charge/discharge curves of each graphite half-cell at a rate of C/5 illustrated in **Fig. 2d-f** show that 1M LiTFSI DOL/DME yields the lowest initial coulombic efficiency (ICE) of 21%, followed by 1M LiTFSI DOL at 65% and 1M LiFSI DOL at 84%. In the 1M LiTFSI DOL/DME electrolyte, the Li-DME co-intercalation expands the graphite and increases the surface area, making reductive-unstable solvated DOL readily decompose and result in irreversibility. In contrast, both DOL-based electrolytes showed no discernible expansion. Clear 3-stage plateaus and high capacities support the reversible phase change of graphite by removing DME. Despite negligible co-intercalation, the remarkable capacity during the first discharge using 1M LiTFSI DOL can be attributed to the electrolyte reduction and the carbon black contribute to partial irreversibility. The golden color of the electrode shown at the inset of **Fig. 2f** suggests the formation of LiC_6 in 1M LiFSI DOL after the first lithiation. **Fig. 2g** provides x-ray diffraction (XRD) patterns of the graphite in the DOL-based electrolytes after the first discharge. These patterns provide direct evidence for the Stage I LiC_6 when cycled in 1M LiFSI. In contrast, graphite only formed the Stage II compound (LiC_{12}) when cycled in 1M LiTFSI DOL. In conclusion, 1M LiTFSI DOL is still operational for graphite, with good capacity retention and decent CE (approximately 99.0%) compared to other solvents that co-intercalate (e.g., propylene carbonate). The redesigned electrolyte 1M LiFSI DOL contributes to less electrolyte reduction, yielding a very high ICE and a very low impedance compared to others.

[0202] Overcriticized co-intercalation and overlooked anions. To determine if co-intercalation is reversible, single-solvent DME electrolytes were also evaluated. Existing electrolytes that combine electrochemically stable anions and glyme-based solvents provide stable cycling using co-intercalation, such as those based on Na-ions and K-ions. In other terms, a system using co-intercalation requires no SEI. By using a reductive-stable anion triflate (OTF^-) instead of TFSI⁻, a better capacity retention and approximately 99% CE in CB-free electrodes with DME electrolytes can be achieved. By using a singular solvent in an electrolyte, such as DOL or DME, rather than the existing electrolytes that use both DOL and DME together, high reversibility is achievable when cycling a graphite anode through the desolvation mechanism for DOL and the co-intercalation mechanism for DME. **Fig. 2h** illustrates the average CE of graphite electrodes from the second to the tenth cycle at a C rate of C/5 using the electrolytes LiFSI-DOL and LiOTF-DME, either with carbon black (CB) or without CB.

[0203] Li-solvent intercalation is not the root cause for the low reversibility in ether/graphite operation. Instead, the anion is the dictating factor. As illustrated in **Fig. 2i**, for example, for ether electrolytes, the reductive stability of anions (or their solvated complex) and the decomposition products (e.g., SEI) govern the reversibility of graphite anode. For example, the reductive stability of DME is greater than DOL, while the reductive stability of LiOTF is greater than LiTFSI, which is in turn greater than LiFSI. Solvated DME (or other glyme) is reductively stable among expanded graphite layers and can be paired with reductive-stable lithium salts. Since the desolvation-based mechanism offers much higher capacity, the examples described herein are focused on a DOL-based electrolyte, in which a reductive-unstable anion can provide abundant inorganic species in the SEI and can ensure good battery performance.

[0204] **Anion-derived SEI in the dilute DOL-based electrolytes.** Based on the peak intensity (e.g., **Fig. 3a**) in X-ray photoelectron spectroscopy (XPS) of the SEI (e.g., with F 1s), the fraction of LiF follows the trend where 1M LiFSI DOL is greater than LiTFSI DOL which is greater than LP57. The fluorinated interface was further confirmed by using the soft XAS spectra of the F K-edge of graphite electrodes after 5 cycles at a rate of C/5, with total electron yield (TEY) and fluorescence yield (FY) modes. The TEY mode was taken at approximately a five nanometer (nm) probing depth and the FY mode was made at approximately a 50 nm probing depth, as shown in **Fig. 3b**. The F K-edge of cycled graphite from DOL-based electrolytes shifts to a higher energy compared to that of LP57, which indicates formation of more LiF in DOL electrolytes. The low electronic conductivity of LiF in the SEI effectively decreases the electrolyte reduction, especially in 1M LiFSI DOL. Depth-dependent composition information was also used to further understand the architecture of the SEI derived from the electrolyte 1M LiFSI DOL. The electrode cycled in 1M LiFSI DOL corresponds to a lower carbon concentration because Li_2CO_3 is not a decomposition product, in contrast to LP57, which is a decomposition product. The fluorine (F) concentration for 1M LiFSI DOL is systematically higher than that for LP57. Because the carbon (C) and oxygen (O) concentrations decrease with increasing sputtering time, inorganic species dominate in the inner SEI while organic species dominate the outer SEI in both electrolytes. In some examples, the organic component is poly-DOL generated by the ring-opening polymerization (ROP).

[0205] While XPS and soft XAS represent ensemble-averaged characterizations, further investigation into the spatial distribution of SEI was performed. As illustrated in **Fig. 3c**,

cryogenic transmission electron microscopy (cryo-TEM) was used to investigate the SEI of graphite electrodes after 50 cycles at a rate of C/5. The dashed lines of **Fig. 3c** highlight the SEI region, which has a thickness of 30 nm to 50 nm and is based on the corresponding scanning transmission electron microscopy (STEM) with energy dispersive X-ray spectrometry (EDS). The corresponding high-angle annular dark field (HAADF) and EDS elemental mappings of the dashed region in **Fig. 3c** are illustrated in **Fig. 3d**. **Fig. 3d** shows enriched inorganic species at the graphite interface, both individually and combined, and again shows the SEI thickness. Large fluorine-rich (F-rich) nanoparticles (about 50nm-70 nm) can also be seen. **Fig. 3e** provides high-resolution TEM images for the F-rich domain in which a mixture of crystalline and amorphous domains can be revealed. By using fast Fourier transform (FFT) and inverse FFT (IFFT), crystalline LiF was found to be present in the SEI (e.g., bottom left highlighted region of **Fig. 3e**) along with the presence of crystalline Li₂O and Li₂SO₄.

[0206] SEI formation mechanism. Three reasons can collectively lead to the inorganic-rich SEI and prohibited co-intercalation. Firstly, 1M LiFSI DOL has Li-4DOL-FSI, Li-3DOL-2FSI, and Li-3DOL-FSI as its favorable solvation structures. Secondly, the frontier orbital is on FSI⁻ rather than DOL by using LiFSI instead of LiTFSI. Thirdly, the cleavage of the S-F bond cleavage occurs easily, leading to a more thorough reduction of FSI⁻ compared to TFSI⁻. Further, the potential of SEI formation should be higher than the potential where the co-intercalation takes place. To probe the formation process, potentiostatic intermittent titration technique (PITT) was performed. The data from PITT indicated a higher reduction potential is found in CIP-dominated 1M LiFSI DOL compared to the SSIP-dominated 1M LiFSI DME. In 1M LiFSI DOL, the fresh cell was held at 1.18 V and a peak suggestive of SEI nucleation and growth by FSI⁻ reduction was observed. This data is consistent with the observations during CV, the constant current tests, and the cryo-TEM/STEM results. The comparison also represents direct experimental evidence exemplifying the reduction potential of an anion regulated by the solvation structure.

[0207] Long-term cycling of graphite in 1M LiFSI DOL. **Fig. 4a** illustrates the reversible capacity of natural graphite cells in 1M LiFSI DOL at C/5 and 1C with the corresponding CE. Using the natural graphite cells, a reversible capacity of 350 mAh/g after 300 cycles using a C/5 rate was achieved with the cells having a high average CE of approximately 99.9% after the formation cycle. As illustrated in **Fig. 4b**, increasing the C-rate to 1C, the reversible capacity was 330 mAh/g with outstanding retention and CE. These results are

enabled by the preferential reduction of FSI-DOL complexes and the inorganic-rich SEI. In contrast, commercial carbonate electrolytes may only deliver 150 to 200 mAh/g at 1C, which is much lower. Although natural graphite represents a good model material for understanding electrolyte-dependent electrochemical behaviors, artificial graphite is of greater practical value due to the reduced surface area and faster Li-ion diffusion. When exploiting mesocarbon microbeads (MCMB) as an anode, for example, a much-improved ICE was found in 1M LiTFSI DOL due to mitigated runaway electrolyte reduction. This can help in establishing a standard for a fast-charging graphite-based LIB with weakly-solvated ether electrolytes. There was also good reversibility of MCMB when cycled in 1M LiFSI DOL. The cyclability found in this experiment represents the best performances of dilute ether electrolytes in graphite without any co-solvent or additive.

[0208] Outstanding interphase kinetics in DOL-based electrolytes. Fast-charge behavior is influenced by many parameters, including ionic conductivity, transference number, and desolvation energy. In the present example, an MCMB electrode with a low mass loading (1.3 to 1.8 mg/cm²) was used to minimize the interference of mass transport and further ameliorate the retention in 1M LiTFSI DOL. As seen in **Fig. 4c**, MCMB cells in 1M LiFSI DOL demonstrate almost no capacity decay from C/5 to 1C. At 2C the capacity is 310 mAh/g, while in the electrolyte LP57, the value is merely 150 mAh/g. Even in 1M LiTFSI DOL, the reversible capacities are still higher than those in commercial carbonate electrolytes. The excellent power density enabled by 1M LiFSI DOL can also be supported by the voltage profiles. The voltage profiles at different C-rates comparing 1M LiFSI DOL with LP 57 are illustrated in **Fig. 4d**. The voltage profiles illustrate smaller overpotentials with better capacity retention. Similar conclusions can be made when the natural graphite is used for rate capabilities.

[0209] The activation energy during the charge transfer process in both 1M LiTFSI DOL and LP57 electrolytes is illustrated in **Fig. 4e**, which shows that LP57 has a higher activation energy of 67 kJ/mol than 1M LiFSI DOL, which has a value of 42 kJ/mol. Through DFT calculations, DOL indeed has the lowest desolvation energy compared with DME, EC, and EMC. For example, **Fig. 4f** illustrates the solvation energy of the different solvents with different coordination numbers. In **Fib. 4f**, for Li-1DOL, the $\Delta G_{\text{solvation}}$ is -1.38 eV while the value for Li-1EC is -1.81 eV. This suggests that there is weaker binding in DOL. Based on an existing proposed desolvation model, anions will be repulsed by the electric field (E-field). Accordingly, a low coordination number (CN) from weakly binding solvent in the solvation

shell is highly desired for an easier desolvation process. **Fig. 4g** illustrates a schematic of the desolvation process in both CIP-dominating electrolytes after the initial cycles. 1M LiTFSI DOL (CN=3.97, total number of solvents) has a binding free energy of -2.68 eV and 1M LiFSI DOL (CN=3.50) has a binding free energy of -2.67 eV. The higher capacity in 1M LiFSI DOL can possibly be attributed to a more conductive SEI. Regarding LP57, the $\text{Li}(\text{EC})_2(\text{EMC})_2$ complex represents the most likely coordination in the primary solvation shell. As calculated, the complex (CN=4.00) suffers from much higher binding energy (-5.68 eV) due to the strong binding of the carbonyl oxygens in the species. Therefore, DOL-based electrolytes, such as those presented in this disclosure, can simultaneously provide high capacity, easier desolvation, and can outperforming EC-based electrolytes and glyme-based electrolytes. **Fig. 4h** is a summary of the graphite intercalation chemistry operated in different solvent-dependent electrolyte chemistries.

[0210] Superior mass transport of 1M LiFSI DOL in graphite anode of moderate-to-high mass loading. DOL shows the potential for operating LIBs under harsh conditions since it has a wide temperature window for remaining a liquid state and a low viscosity. The mass loading of an MCMB electrode was increased to approximately 5.7 mg/cm² in order to evaluate impacts of the weakened Li-solvent interaction on the Li-ion mass transport. The cyclability of DOL-based electrolytes is confirmed first. The ICE (85 to 92%) and subsequent CE (close to 99.9%) are comparable to that in carbonate electrolytes. In 1M LiFSI DOL, the capacity is much higher than LP57 counterpart at a C rate of C/2.

[0211] Despite higher t_+ and lower desolvation energy, LiTFSI DOL behaves slightly inferior to LP57 when using electrodes of higher mass loading with a C-rate higher than C/2. This can be due to the important role of ionic conductivity for the graphite application under fast charging. On the other hand, in 1M LiFSI DOL, as seen in **Fig. 5a**, the balanced bulk transport and desolvation processes contribute to a superior rate capability at room temperature (RT) and low temperature (LT) (e.g., 0 °C). At RT, approximately 1 mAh/cm² can be maintained at 2C, whereas LP57 has severe capacity loss starting at C/2. Voltage profiles at LT are illustrated in **Fig. 5b** and support the kinetic differences associated with concentration polarization. 1M LiFSI DOL has smaller overpotentials and more clear plateaus. **Fig. 5c** illustrates that graphite-based half cells adopting 1M LiFSI DOL outperform many existing cells that relied on material optimization, SEI design, electrode engineering, or other new electrolytes. In **Fig. 5c**, the shaded area of means a high C-rate (e.g., greater than

C/2) region of graphite, LP30 means 1M LiPF₆ in EC/Dimethyl carbonate (DMC) 1:1 wt.%, and the graphite electrode for 1M LiFSI DOL was approximately 9.2 mg/cm².

[0212] After rate tests at LT, the small charge transfer resistance (R_{ct}) in 1M LiFSI DOL was confirmed. An areal capacity of approximately 1.5 mAh/cm² at C/2 at LT can be delivered using the identical cell without microstructural degradation of mesocarbon microbeads (MCMB). Full cells using a lithium iron phosphate cathode (LFP) and an MCMB anode were created for further testing. A DOL-based electrolyte reaches a maximum oxidation limit of 4.0 V, lower than the DME-based electrolyte. As such, LiFePO₄ and sulfur cathodes can be compatible with DOL-based electrolytes. During the rate capability measurement in 1M LiFSI DOL based cell, the capacity of the full cell, starting from 3C, is much better than that in the LP57-based cell. Further, stable cycling was found at 1C. To support the superior kinetics and less possibility to plate Li metal in 1M LiFSI DOL, fast-charging full cells at 4C were measured. Li metal plating, which causes resistance buildup and electrolyte consumption, is severe in LP57. However, there no dead Li was observed in 1M LiFSI DOL. The cycling performance of full cells (approximately 2.4 mAh/cm²) at a rate of C/3 (2.5 V to 3.9 V) can be seen in **Fig. 5d**, where the N/P ratio is about 1.2 and the specific capacity is calculated based on LFP. The electrolyte 1M LiFSI DOL contributes to a high capacity retention (approximately 84% after 200 cycles at C/3) and excellent CE. Cycling in LP57 leads to more capacity decay due to less fluorinated SEI and thus unsuppressed electrolyte consumption as well as SEI thickening.

[0213] Finally, DOL-based electrolytes can be used for Li and Si anodes and be superior to commercial carbonate electrolytes. A reversible graphite/Li composite anode is feasible when employing LiFSI-DOL based electrolytes. Additionally, the fast kinetics can be universally beneficial for operating other anodes under harsh conditions (e.g., low temperature and fast charging).

[0214] In this example, a redesigned dilute ether electrolyte (e.g., 1M LiFSI DOL) with a graphite anode uses intercalation, thereby simultaneously enabling high capacity and fast interfacial kinetics. By removing the solvent DME from the DME/DOL solvent combination, more CIP and AGG solvation structures are generated as well as abundant solvated anions in single-DOL electrolytes. When using the salt LiFSI instead of LiTFSI, the frontier orbital is shifted from the solvent to the anion. The resulting SEI is enriched with LiF, Li₃N, Li₂SO₄ and Li₂O, which supports the reversibility of a graphite anode by inhibiting co-intercalation and excessive electrolyte decomposition. Consequently, the excellent cyclability of graphite

in 1M LiFSI DOL was proven. Further, the electrolyte 1M LiFSI DOL has a balanced ionic conductivity, Li ion transference number, and interphase kinetics. Accordingly, the resulting fast-charge performances under moderate-to-high mass loading conditions are consistently better than existing EC-based electrolytes. Besides graphite, high-capacity anodes such as Li metal and Si deliver excellent reversibility in 1M LiFSI DOL. The described example provides that the anion species can dictate the electrochemical mechanism and reversibility of dilute ether electrolytes with graphite anodes. For instance, DOL and DME can be individually compatible with graphite anode in LIBs based on the desolvation and the co-intercalation mechanism using 1M lithium salts.

Example 2

Analysis of Reductive-Stable Electrolyte LiBF₄ DME (G1)

[0215] In this example, a new reductive-stable electrolyte (RSE), 1M LiBF₄ 1,2-dimethoxyethane (DME, herein referred to as “G1”), is formulated and tested. Testing the RSE in a battery cell using natural graphite provided a cell with high capacity retention (approximately 90%) after 400 cycles and excellent Coulomb efficiency (CE) that approaches 100%. The RSE can provide a heterogeneous interphase that enables the long-cycling ability of the graphite anode via the co-intercalation mechanism. In comparison, the electrolyte 1M lithium bis(trifluoromethanesulfonyl)imide (LiFSI) G1 gives rise to rapid cell degradation, which is reductively unstable (i.e., not an RSE). The distinct electrochemical behaviors between the two electrolytes can originate from the different compositions and geometries of their respective SEIs. The SEIs of both were measured by spectroscopic and imaging techniques and confirm this distinction. For example, the interphase in RSE exhibits a heterogeneous spatial distribution: large LiF particles (50 to 150 nm) occupy the edge plane and small LiF particles (<5 nm) are distributed sparsely on the basal plane. Computational testing provided that the edge plane possesses catalytic effects, which allows for decomposition of anion and solvent molecules. Once the catalytic sites are covered by decomposed products, the reaction is self-terminated.

[0216] Besides the favorable interphase formation, RSE also enables an excellent structural reversibility of graphite during Li-ether co-intercalation, as shown by in-operation synchrotron X-ray diffraction (XRD) and coherent X-ray multocrystal diffraction (CMCD). The graphite anode also showed no capacity difference with increasing current density, likely due to the negligible desolvation and almost non-existent SEI. This example demonstrates reversibility and kinetics of Li-ether co-intercalation chemistry, which have been

underestimated. The co-intercalated graphite is used to investigate the nature, role, and origin of SEIs formed by reductive-stable electrolytes.

[0217] Quadrant scheme to down-select solvent and salt for reversible Li-ether

co-intercalation in graphite: To formulate an electrolyte with the desired properties, the quadrant scheme illustrated in **Fig. 6** was used to choose a solvent and a corresponding salt. In formulating an RSE, a solvent on the vertical axis is chosen that is stable with Li metal to minimize the influence of the counter electrode (e.g., Li metal). In Na-ion batteries where reversible co-intercalation is widely reported, diglyme (G2) and tetraglyme (G4) based electrolytes are stable against Na metal. However, Li-ion electrolytes using these two solvents are not stable against Li metal, leading to dendritic growth and rapid dead Li accumulation. Accordingly, the electrolytes in Quadrant IV of **Fig. 6** fail to provide good cycling when using a Li metal anode. Compared to the solvents G2 and G4, G1 can minimize the interference of the counter electrode for excellent compatibility with Li metal.

[0218] Further, in formulating an RSE, a salt is chosen that does not form a continuous, uniform SEI. PF_6^- , OTF^- , and BF_4^- are reductive stable anions and enable excellent CE (approximately 99.9%) and cyclability in Na-ion and K-ion systems, including Na/K-solvent co-intercalation in graphite. In contrast, due to the reductive decomposition, DFOB^- , TFSI^- , and FSI^- are good film-forming anions and the resulting SEIs of these anions may impede the Li-solvent co-intercalation. Thus, these anions are incompatible with the co-intercalation mechanism (Quadrants II and III in **Fig. 6**). In **Fig. 6**, the fading mechanisms of the co-intercalation chemistry are highlighted by the “X” signs.

[0219] Ethylene carbonate (EC)-based electrolytes that use LiBF_4 as a main salt form a discontinuous SEI with grainy LiF particles, thereby failing to suppress carbonate reduction on the graphite anode surface. The grainy SEI is desired for Li-ether co-intercalation and accordingly, a combination of LiBF_4 and G1 (Quadrant I) is an ideal electrolyte to test Li-ether co-intercalation in graphite.

[0220] Cyclic voltammetry (CV) was performed for graphite-Li cells (between 0.01 V to 2 V at 0.2 mV/s) using the Quadrant I electrolyte 1M LiBF_4 G1 (i.e., RSE) which is illustrated in **Fig. 7A** and the Quadrant II electrolyte 1M LiFSI G1. Both electrolytes exhibited clear co-intercalation behaviors. Further, when examining the cycling performance of these electrolytes, as illustrated in **Fig. 7B**, RSE contributes to stable cycling of a graphite anode with an approximately 93% capacity retention after 200 cycles at 1 A/g between 0.01 V and 2 V. In contrast, 1M LiFSI G1 triggers rapid capacity fading and a low CE (<90%) at initial

cycles. These two electrolytes provide distinct voltage profiles as illustrated in **Fig. 7C-D**, which depicts the charge/discharge voltage profiles of graphite-Li cells in the respective electrolytes. The potential-rebounding phenomenon when LiFSI is used signifies an SEI nucleation process, discussed elsewhere herein. When RSE is employed, the co-intercalation in graphite is highly reversible, with the exception of the first cycle. To address the low ICE in RSE, the influence of electrode composition and discharge cut-off voltage on ICE was investigated as partially illustrated in **Fig. 7E**. **Fig. 7E** illustrates the initial coulombic efficiency (ICE) in different electrode composition and cycling conditions with the XYZ representing the mass ratio between the active material, carbon black, and the binder, followed by the name of the binder. By removing carbon black, replacing polyvinylidene fluoride (PVDF) with sodium alginate (SA), and increasing the lower cut-off voltage from 0.01 V to 0.1 V, the ICE is enhanced to >90%. Such an ICE is among the highest reported for graphite-Li cells. Carbon black can trigger more electrolyte reduction and function as an additional co-intercalation host. The use of a fluorine-free SA binder allows for fewer physically trapped Li-ions, and no fluorine interference during the surface analyses. Accordingly, 901SA is used in subsequent experiments in this example.

[0221] The cycling performance of graphite-Li cells using a 901SA electrode composition is illustrated in **Fig. 7F** with the first cycle omitted. As can be seen, in RSE, the capacity retention reached about 92%, about 88%, and about 96% after 400 cycles at 0.5 A/g, 1 A/g, and 2 A/g, respectively. Also, the average CE after the first cycle approached 100%. In brief, Li-G1 co-intercalation can provide excellent cyclability at larger current densities, demonstrating the effectiveness of the Quadrant I electrolytes in comparison to existing electrolytes (**Fig. 7G**). In comparison, 1M LiFSI G1 leads to rapid capacity decay due to larger interfacial resistance. To eliminate the influence of Li metal in the results, the CE was measured for Li-Cu cells in both electrolytes. 1M LiFSI G1 delivers high CE of >97% on average throughout 400 cycles at 0.5 mA/cm² and 0.5 mAh/cm². In contrast, RSE provides much lower CE and rapid cell shorting before reaching 150 cycles. These results show that Li metal is not responsible for the drastic capacity decay of graphite-Li cells in 1M LiFSI G1.

[0222] To further evaluate the effectiveness of the quadrant scheme, G2 and G4 electrolytes using LiBF₄ (Quadrant IV of **Fig. 6**) were measured. Using these electrolytes, there was continuous capacity degradation due to the counter electrode failure. Li metal in G2 electrolytes exhibits extreme instability. Li-Li cells cycled in 1M LiBF₄ G2 quickly short. The average CE in Li-Cu cells is lower than 20% with a limited cycle life. Though 1M LiFSI

G2 has a higher CE, its behavior toward graphite anode is similar to that of LiFSI G1 because of the reductive instability of FSI⁻.

[0223] The Quadrant scheme illustrates why the reversibility of co-intercalation in graphite was previously underestimated and offers new insights into using co-intercalation for fast-charging Li batteries.

[0224] **Structural and Compositional Understanding of Li-ether Co-Intercalation in Graphite:** The morphological change of cycled graphite was further tested and is illustrated in **Fig. 8A**, which includes scanning electron microscope (SEM) images of cycled graphite in 1M LiBF₄ G1 and 1M LiFSI G1 at different states with a scale of 10 μ m. After the first cycle, exfoliation happens because of the Li-G1 co-intercalation. Cycled in 1M LiFSI G1, graphite is still heavily expanded at the 10th de-lithiation despite the low capacity. The expansion is unrecoverable at the full de-lithiated state. **Fig. 8B** includes XRD patterns of cycled graphite at the charged state with the * signifying using Kapton tape and the # signifying using Cu foil. The XRD patterns illustrated in **Fig. 8B** confirm that the Li-G1 co-intercalation generally reduces graphite crystallinity, as reflected by the broadened and weakened (002) peak. **Fig. 8C** includes Raman spectra of the charged graphite cycled in 1M LiBF₄ G1 and 1M LiFSI G1. The D-band/G-band ratio in Raman spectra, reflected in **Fig. 8C**, provides that RSE leads to higher disorder than 1M LiFSI G1. Such irreversible structural and morphological changes are not observed in graphite with the Li co-intercalation-free chemistry. LiBF₄ G1 increases the bulk structural disorder in graphite but can still enable long cycle life and high CE, which suggests that solid-electrolyte interphase governs the Li-G1 co-intercalation.

[0225] X-ray photoelectron spectroscopy (XPS) was used to investigate the chemical compositions of the SEIs on a graphite anode using different salts. Atomic concentration, which is illustrated in **Fig. 8D**, demonstrates a higher F content ($11.6 \pm 0.9\%$ over $2.3\% \pm 0.2\%$) in the SEI derived from 1M LiFSI G1 over the SEI derived from 1M LiBF₄ G1. This corroborates the strong reduction tendency of FSI⁻. Since BF₄⁻ is oxygen-free, the higher O content in the as-formed SEI can be attributed to the co-intercalated G1 close to the surface. Using high-resolution F spectra (F 1s), the results of which are illustrated in **Fig. 8E**, a strong Li-F peak is located at 684.5 eV as is a feature from B-F and S-F. F K-edge soft X-ray absorption (soft XAS) spectra had characteristic peaks at approximately 690 eV and 700 eV and the edge shift to higher energy, which indicates the existence of LiF. Both XPS and soft

XAS data show an interphase enriched with inorganic species when using the RSE. This can explain the approximately 10% irreversible capacity in the first cycle.

[0226] Additional data was collected using C K-edge soft XAS spectra, with a 5-10nm probing depth in the total electron yield (TEY) mode. This data is identified in **Fig. 8F**, where the graphite was cycled in 1M LiBF₄ G1 and 1M LiFSI G1 with 901SA cycled at 0.2 A/g between 0.1 V and 2.0 V for ten cycles. The peak at 285.5 eV signifies the transition of C 1s to π^* (sp^2 bond) and the edge at 292.3 eV stems from the transition of C 1s to σ^* (sp^3 bond). The π^* and σ^* intensities follow the trend of pristine anode having a greater normalized intensity than the anode cycled with 1M LiBF₄ G1, which has a greater normalized intensity than the anode cycled in 1M LiFSI G1. This illustrates that graphite cycled in 1M LiFSI G1 is covered by a thicker SEI. A σ^* resonance at 287.2 eV, highlighted in the blue region of **Fig. 8F**, can be attributed to the C–O states originating from solvated ether between graphene layers. Trace electrolyte decomposition in RSE renders good Li-ether co-intercalation capacity and stability. However, XPS and soft XAS are ensemble-average techniques and as such, the spatial distribution of reduction products is unclear. Transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS) mapping can help probe nanoscale morphology and distribution of LiF.

[0227] Spatial distribution of the fluorinated interphase at different length scales:

High-resolution TEM (HRTEM) images of graphite cycled in 1M LiBF₄ G1 (i.e., RSE) were collected after the graphite was cycled ten times (i.e., ten cycles). As illustrated in **Fig. 9A**, the RSE endows the co-intercalative graphite with a clean surface and the noticeable lattice fringe of exfoliated graphite. In some regions, as seen in **Fig. 9B**, trace ultrasmall LiF particles (<5 nm) can be seen. In contrast, as seen in **Fig. 9C-D**, the graphite cycled in 1M LiFSI G1 is covered by a thick SEI. These results are consistent with the XPS and soft XAS data. Further, from the fast Fourier transform (FFT) image of the graphite domain, no clear lattice fringe is observed in the graphite cycled in 1M LiFSI G1. This corroborates that SEI vastly covers the surface of graphene layers. In some other regions, graphite (002) can be detected in FFT. At the 10th cycle, there is still 30% to 50% capacity retention in 1M LiFSI G1 cells because the SEI has not covered the entire surface. A TEM measurement for graphite cycled in 1M LiFSI G1 for one cycle was also collected, however, the surface is still not as clean as the graphite surface cycled for 10 cycles in 1M LiBF₄ G1. From these results, it is clear that the nature of SEI is critical for co-intercalated graphite.

[0228] Scanning-TEM (STEM)-EDS for the cycled graphite particles along the *ab* (basal) plane was also collected for graphite cycled in 1M LiFSI G1 (**Fig. 9E**) and 1M LiBF₄ G1 (e.g., RSE) (**Fig. 9F**). Expanded graphite features can be seen from the high-angle annular dark-field (HAADF) images of **Fig. 9E-F**. The F signal (in yellow) is widely dispersed throughout the graphite cycled in 1M LiFSI G1 (**Fig. 9E**). In stark contrast, the F signal is highly heterogeneous in graphite cycled in RSE (**Fig. 9F**). LiF nanoparticles (50 to 150 nm) distribute heterogeneously on graphite. When observing along the *c* axis (e.g., near perpendicular to the *ab* plane), as illustrated in **Fig. 9G**, LiF nanoparticles mostly locate at the edge plane. This can explain a large quantity of clean graphite surfaces cycled in RSE were observed. A set of further processed EDS maps (Red channel only) is presented in **Fig. 9H**, which more clearly demonstrates the distribution of LiF. To quantitatively understand the LiF distribution, the intensity distribution for the EDS map is plotted in **Fig. 9I**. The distribution of F on graphite cycled in RSE is much narrower than that cycled in 1M LiFSI G1, which confirms the heterogeneity of LiF distribution of RSE at the micron length scale. The statistical parameter Kurtosis (Kurt) value was also calculated and is illustrated in the inset in **Fig. 9I**. A higher Kurt value corresponds to larger deviations (i.e., more extreme values). The Kurt value of RSE is much higher than the Kurt value of 1M LiFSI G1 (11.7 vs. 0.3), which further confirms the heterogeneity of the SEI. The LiF signals found in XPS and soft XAS originate primarily from these heterogeneously distributed LiF nanoparticles. In some examples, it may be more appropriate to describe the protective layer formed on graphite cycled in 1M LiBF₄ G1 as a “pseudo-SEI” because of the heterogeneity.

[0229] **Pseudo-SEI formation mechanisms and implications:** Discussed herein is an investigation into the mechanism of forming the pseudo-SEI. A potentiostatic intermittent titration technique (PITT) was applied to study the electrochemical reduction of different anions with the PITT curves of graphite-Li cells in the electrolyte 1M LiBF₄ G1 using between 0.1 V to 0.5 V and the electrolyte 1M LiFSI G1 using between 0.6 V and 1.0 V held for two hours. The results of the PITT are illustrated in **FIG. 10A**. In 1M LiFSI G1, the anion reduction (SEI nucleation) is found when the potential decreases from 0.5 V to 0.4 V. During anion reduction, each nucleus experiences two-dimensional growth and finally overlaps with others. In contrast, RSE is free of these characteristics from 1.0 V to 0.1 V. To further investigate the reductive stability of the electrolytes, the lowest unoccupied molecular orbital (LUMO) level of solvation complexes of LiBF₄ and LiFSI were calculated with different numbers of solvents by using density functional theory (DFT). The simulation results are

illustrated in **Fig. 10B**. With one G1 solvent, the contact ion pair (CIP) structure is more stable than the solvent-separated ion pair (SSIP) configuration. With two or three G1 solvents, the SSIP is more stable. The LUMO level of LiBF₄ in different structures is higher than LiFSI counterparts, which suggests a higher intrinsic reductive stability of LiBF₄.

[0230] Ab initio molecular dynamics (AIMD) simulations of the electrolytes were carried out in both CIP and SSIP configurations on basal and edge planes, and in neutral and charged conditions, to investigate the molecular origin for the observed heterogeneous distribution of LiF. The AIMD simulations at different time periods (e.g., 0 ps, 1 ps, 2 ps, and 10 ps) of LiBF₄ G1 in an SSIP configuration on a -1 charged basal plane is illustrated in **Fig. 10C** with the corresponding charge transfer plot illustrated in **Fig. 10D**. The AIMD simulations at different time periods of LiBF₄ in an SSIP configuration on a neutral edge plane is illustrated in **Fig. 10E** with the corresponding charge transfer plot illustrated in **Fig. 10F**. Finally, the AIMD simulations at different time periods of LiBF₄ in an SSIP configuration on a -1 charged edge plane is illustrated in **Fig. 10G** with the corresponding charge transfer plot illustrated in **Fig. 10H**.

[0231] The edge plane model that is used in the simulations is terminated with ketonic groups, which is the dominant termination for graphite edge surface. In the charged surface, an additional electron (-1 charge) was introduced to represent a higher discharge state or a lower potential. The electrolyte with salt (e.g., LiBF₄ G1) in the CIP configuration is stable on both the basal and edge planes in both the neutral and charged states, as there is no reaction observed within 10 ps of simulations of these systems. When the initial electrolyte (e.g., LiBF₄ G1) configuration is SSIP, no reaction was observed on the basal planes under either neutral (not pictured) or charged (**Fig. 10C-D**) conditions within the 10 ps simulation time. In contrast, interface reactions of the SSIP electrolyte (e.g., LiBF₄ G1) on the edge planes under both neutral (**Fig. 10E-F**) and charged (**Fig. 10G-H**) conditions. On the neutral edge plane, the anion goes through cleavage of the B-F bond (Fig. 10E-F, BF₄⁻ breaks into BF₃ + F⁻) and the charge transfers from the graphite surface to the electrolyte species during the simulation time of 0-1 ps. Between 1-2 ps, the decomposed BF₃ absorbs on the oxygen site of the graphite surface. Subsequently, a proton (H⁺) dissociates from one of the G1 solvents and combines with F⁻ to form HF species. After 2 ps, the formed BF₃ and HF molecules remain on the graphite surface without further reactions. On the charged edge plane, as shown in **Fig. 10G-H**, G1 loses a proton that binds to the oxygen site of the graphite

surface during the simulation time of 0-1 ps. After 1 ps, no further reactions were observed at the interface.

[0232] The relative reductive stability of the electrolyte LiBF₄ G1 calculated by DFT and the surface-specific reactivity simulated by AIMD are consistent with the experimental findings that LiFSI is more reactive than LiBF₄, and the edge surface is more active towards RSE decomposition than the basal plane. When the catalytic site on the edge is passivated by pseudo-SEI, the reduction can be attenuated. Such a self-terminated mechanism explains the EDS mapping data and high CE (>99.5%) after a few cycles.

[0233] Structural transformations and reversibility of graphite during co-intercalation:

To further clarify the reversibility of co-intercalative graphite cycled in RSE and provide detailed phase transformation mechanisms, synchrotron XRD measurements (e.g., wavelength of 0.024 nm) were conducted on operating graphite-Li cells cycled in RSE with a voltage range of 0 to about 3 V at a rate of 1C (1C = 100mAh/g). The contour plot and the voltage profile are displayed in **Fig. 11A** and **Fig. 11B**, respectively. The structural change of co-intercalative graphite in Li chemistry is complex but indicates similarity to Na systems. Initially, (002) fades away, corresponding to the irreversible exfoliation process (a). In section (b), a stage-3 graphite intercalation compound (GIC) formation is observed supported by peak splitting of (002) to (005) and (006). Then stage-3 GIC gradually changes to stage-2 GIC (c) based on the formation of (004) and (005). The plateau at approximately 0.75 V in the electrochemical profiles is associated with the transformation of stage-2 GIC to stage-1 GIC (d) containing more peaks. **Fig. 11C**, which includes XRD patterns extracted from the in-operating measurements at specific potentials (e.g., the first lithiation), demonstrates the two-phase transition clearly. Referencing both **Fig. 11B** and **Fig. 11C**, stage-1 GIC with high lithiation extent is featured by the (001) and (002) peaks at lower angle as well as a very intense (003) peak. Next, further lithiation into Stage-1 GIC happens (e). At the end of lithiation when the voltage is approaching 0 V (f), more weak peaks are found between (001) and (002) as well as (002) and (003). Though the fine structure has not been achieved, it is likely a result of in-plane reconstruction. During de-lithiation, the reversible phase transition can be observed, finally resulting in the single (002) peak at the original location.

[0234] While XRD provides ensemble-averaged characterization for the electrode, CMCD probes crystal structure changes for a small number of particles, with each particle contributing to a bright spot on each diffraction ring. Therefore, the technique helps determine whether these particles have concurrent charging/discharging reactions. CMCD

was obtained for the first two cycles of graphite-Li cells while in operation at a wavelength of 0.103 nm (**Fig. 11D**). As illustrated in **Fig. 11D**, the initial CMCD pattern displays bright diffraction spots, corresponding to the (002) planes of graphite particles. The bright spots gradually disappear when the voltage reduces to below 1.0 V, indicating an exfoliation process. Upon both lithiation and de-lithiation, the evolution of CMCD rings is consistent with the observations in XRD patterns. Since all bright spots evolve in the same fashion, the co-intercalation reaction is determined to be concurrent between different graphite particles.

[0235] The in operation XRD and CMCD data illustrates the structural reversibility of Li-G1 co-intercalation in graphite and the homogenous reaction among primary particles. The structural change and interphase design based on RSE are demonstrated in **Fig. 11E**, which provides a possible path to full utilization of co-intercalation capacity.

[0236] **Rapid interphase kinetics based on reversible Li-ether co-intercalation:** The rate performance of co-intercalative graphite was also tested using a graphite cell. As illustrated in **Fig. 12A**, as the current density increases from 0.1 A/g to 4 A/g, there is almost no capacity fading when using RSE. However, when the cell is cycled in LP57 (e.g., 1M LiPF₆ ethylene carbonate (EC)/ethyl methyl carbonate (EMC) 3:7 in volume) the specific capacity drops notably and becomes lower than that in RSE cells starting from 0.5 A/g. According to the corresponding voltage profiles, which are illustrated in **Fig. 12B-C**, co-intercalative graphite shows minimal overpotentials, which is consistent with outstanding capacity retention. Furthermore, the kinetic of Li-ether co-intercalation is comparable to that of the Na-ether co-intercalation as illustrated in **Fig. 12D**, where the representative Na-based electrolyte is 1M NaPF₆ G2.

[0237] To understand the diffusion behavior of solvated-Li at different potentials, CV data was collected for natural graphite cycled in 1M LiBF₄ G1 with multiple scan rates from 0.2 to 2 mV/s, as seen in **Fig. 12E**. There are three stages for the co-intercalation (e.g., i-iii, illustrated in **Fig. 12F**), consistent with the voltage profile. **Fig. 12F** shows the peak current dependence on the scan rate derived from the CV profiles. The scan rate and peak current follow a power-law equation $i = a v^b$, where i is the measured peak current, v is the voltage sweep rate, and a and b are adjustable parameters. A b value of 0.5 typically indicates a diffusion-controlled reaction while a b value of 1 suggests a capacitive reaction. A high b value of 0.94 is reported for 1.2 V to 0.8 V (iii), which is indicative of the capacitive behavior and is consistent with the slope shape in the voltage profile found in **Fig. 12B**. Stages (i) and (ii) have b values of 0.61 and 0.68, respectively, which means they have mixed behaviors of

adsorption and diffusion. Such pseudocapacitive characteristics contribute to the observed excellent fast-charge capability. **Fig. 12G** shows Nyquist plots of cycled cells in different electrolytes after the first lithiation. The Nyquist plots show a 90-degree curve symbolizing the pseudocapacitive nature of co-intercalation.

[0238] The mass loading of graphite (e.g., SA901) was increased to determine whether the RSE co-intercalation maintains its excellent kinetics. LiBF₄ has a lower dissociation extent, and the ionic conductivity of as-formed electrolytes can be poor. However, the graphite electrodes with higher loading (>7 mg/cm²) still exhibit excellent capacity at high current density (98 mAh/h at 0.5 A/g and 90 mAh/g at 0.1 A/g) as seen in **Fig. 12H**. The co-intercalation has outstanding rate capability because it only needs to remove 0.5 G1 molecules from the first coordination shell (Li-2.5G1 to Li-2G1). The co-intercalation process is depicted in **Fig. 12I**. This process corresponds to a low activation energy of 25 kJ/mol, which is much lower than that of EC-based electrolytes (60-70 kJ/mol). These results support that Li-ether co-intercalation chemistry can be reversibly operated at large current densities.

[0239] This example provides an effective electrolyte and interphase design which enables reversible, fast Li-ether co-intercalation in graphite. The nature, function, and formation of the interphase on graphite when cycled in 1M LiBF₄ G1 was explored. 1M LiBF₄ G1 enables excellent cycling stability of co-intercalative graphite anode, which complements the electrolyte 1M LiFSI DOL, which was explored in Example 1. Together, this example and Example 1 demonstrate that ether electrolytes using 1M salts can operate the graphite anode in Li-ion batteries by matching the reductive stability of electrolyte ingredients. The pseudo-SEI generated in RSE can play an important role in suppressing continuous electrolyte reductions. The pseudo-SEI can be extended to other systems using electrochemically stable electrolytes, for example, hard carbon in Na-ion batteries. This example provides experimental and theoretical proof that the electrolyte components are stable on the basal plane but become destabilized on the catalytic edge plane. The corresponding reduction is unlikely to form a continuous, thin, or uniform film, instead forming a heterogeneously SEI, because of the intrinsic stability of electrolyte components.

Example 3

Analysis of t-THF-GIC with Ultralong Lifespan and Low-Temperature Performance

[0240] In this example, cells were formulated using the solvent tetrahydrofuran (THF) in an electrolyte. When tested, the cells had an ultralong lifespan of over 10,000 cycles with high

Coulombic efficiency (CE) and negligible capacity decay of the lifespan. The cells also had one-minute fast charging (100% retention) and unprecedented low-temperature performance without detrimental Li plating. The outstanding stability and kinetics of the cells is due to the use of a simple, scalable, low-cost 1M LiPF₆ -THF electrolyte, which transforms b-GICs to t-GICs *in-situ* (e.g., during the initial cycle). The *in-situ* chemical synthesis of t-THF-GIC can proceed through uptaking THF molecules from the electrolyte in the absence of a dense and continuous SEI. The extent of the *in-situ* b-GICs to t-GICs transformation can be highly programmable by modulating various parameters including current density, temperature, and SEI properties. Paired with a nickel manganese cobalt (NMC) cathode, a full cell displays outstanding cycling stability with a 15-minute charging. The excellent rate capability is present even at -40 °C. Using a graphite anode with this innovative operation mechanism enables extremely well performing co-intercalation based batteries that excel over others, especially when operated in low temperatures.

[0241] A natural graphite anode was used in this example. A graphite anode has traditionally been understood to reversibly store mobile ions in a single storage mechanism, either intercalation or co-intercalation. **Fig. 13a** depicts discharge-charge curves which show intercalation in a graphite anode cycled in 1M LiPF₆ - EC/EMC electrolyte (EC/EMC based) and co-intercalation in a graphite anode cycled in 1M LiBF₄ - DME electrolyte (DME based electrolyte). The voltage profiles and the corresponding dQ/dV curves illustrated in **Fig. 13a** show common intercalation or co-intercalation plateaus. When using the 1M LiPF₆-THF electrolyte, though, interesting phenomena are found. For example, as seen in **Fig. 13a**, the first lithiation (e.g., charging) shows a co-intercalation-free mode, while the first delithiation (e.g., discharging) is a combination of co-intercalation and intercalation. The corresponding dQ/dV curves are asymmetrical. Further, the second lithiation is a predominantly co-intercalation mode and is highly reversible. The co-intercalation-free mode can be explained by the weak Li⁺-THF binding, especially compared to glyme (e.g., DME) counterparts. The co-intercalation contribution during the first delithiation can arise from the chemical reaction between b-GIC and THF molecules in the electrolyte. The underlying dynamic transformation from b-GICs to t-GICs is discussed elsewhere herein.

Electrochemical analyses were performed to provide further information into the *in-situ* formation of t-GICs in operating batteries. First, the adjustability of the Li storage mechanism in the 1st cycle is explored. As shown in **Fig. 13b**, the capacity contribution from deintercalating Li ions decreases if the cell using the 1M LiPF₆-THF electrolyte is rested after

the first lithiation. Especially after a 48h rest, the capacity contribution from deintercalating Li ions disappears, and the charging curve overlaps with the 2nd charge. These results show that the *in-situ* b-GICs to t-GICs transformation is not completed immediately following the formation of b-GIC.

[0242] How the *in-situ* transformation is governed by the reaction environment was also investigated. The pure chemical reaction was tested (e.g., without the influence of the electrical field) by soaking lithiated graphite (i.e., LiC₆) in THF and EMC solvents. A golden-to-black color change was present only in the THF solvent after 24h, as seen in the photographs of **Fig. 13c**. In full battery cells, the discharge capacity anomalously increases as the current density increases from 0.2 to 5 C, as is illustrated in the discharge curves of **Fig. 13d**. Specifically, in **Fig. 13d**, the stage II (e.g., in blue) to stage I (e.g., in green) conversion of lithiated graphite is less pronounced when a low current density is used. When the cells are rested after the initial discharge, there is a decrease in the following charge capacity, especially for the cells cycled at high current densities. At low current densities or during the rest, there is ample time for THF to react with b-GICs to increase the transformation to t-GICs.

[0243] The X-ray diffraction (XRD) patterns illustrated in **Fig. 13e** further show that the LiC₆ characteristic peaks weaken after soaking the graphite anodes in THF or cycling at low current densities. This is because the b-GIC can have two phase transformation pathways: (1) further lithiation to form lower-stage b-GIC, and (2) a chemical reaction with free THF molecules in the electrolyte. At a low current density, the reactions are more concurrent, leading to more formation of t-GICs. The same chemical reaction also occurs in a similar G||Na (i.e., graphite-sodium) system and in a G||K system (i.e., graphite-potassium) system, which is surprising as it was traditionally thought that a cyclic ether (e.g., THF) cannot reversibly co-intercalate into graphite.

[0244] The *in-situ* formation of t-GIC can be affected by the SEI formation process, which is associated with the stability of salts and solvents. When the salt is switched from LiPF₆ to LiFSI, more LiC₆ is formed during the first lithiation, but the b-GICs to t-GICs transformation is less pronounced. The co-intercalation behavior still occurs, but it is irreversible and leads to rapid capacity decay of the G||Li (i.e., graphite-lithium) cell. Thicker SEIs were found when the graphite anode was cycled in the 1M LiFSI-THF electrolyte, which hampers the interaction between b-GIC and free THF molecules. In comparison, the graphite anode cycled in 1M LiPF₆-THF exhibited clean surfaces without SEI formation or

alternatively, with an ultrathin SEI sporadically distributed, which is consistent with its high ICE. The clean graphite surface can explain the high reversibility of the Li^+ -THF co-intercalation. Differences in SEI properties can lead to drastically different kinetics. The desolvation energy and the energy for Li^+ transport through the SEI was tested. The desolvation energies of the two electrolytes, 1M LiPF_6 -THF and 1M LiFSI -THF, remained at almost the same value (e.g., 34 kJ mol^{-1} vs. 32 kJ mol^{-1} , respectively). This is consistent with the voltage profile of the G||Li cell which indicates incomplete desolvation leads to solvent co-intercalation into graphite. However, the activation energy for Li^+ transport through SEI in the LiPF_6 -THF electrolyte is significantly lower than that in the LiFSI -THF electrolyte (e.g., 10 kJ mol^{-1} vs. 36 kJ mol^{-1} , respectively)

[0245] The structural changes of graphite due to the b-GICs to t-GICs transformation were examined using *ex situ* Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy. Compared with pristine graphite, the Li^+ -THF characteristic FTIR peaks emerge after full discharge (i.e., including the first discharge), and then disappear after full charge, as seen in **Fig. 13f**. This directly demonstrates the uptake of free THF molecules and the b-GICs to t-GICs transformation. Meanwhile, the Li^+ -THF co-intercalation is highly reversible. The *ex situ* Raman spectroscopy of the pristine graphite exhibits a weak D band (1350 cm^{-1}) and a strong G band (1600 cm^{-1}), with an I_D/I_G ratio of 0.25. During the 1st discharge, the intensity of the D band increases significantly. This implies that the well-ordered graphitic interlayers become disordered due to structural changes caused by the THF uptake. During the 1st charge, the intensity of the D and G bands cannot return to their original state. The same phenomenon is present in the 2nd and 3rd cycles, while the I_D/I_G ratio increases from 0.25 to 0.28, which suggests an increase in structural disorder attributable to repeated Li^+ -THF co-intercalation. In operation optical microscopy of graphite during cycling was taken. Only a slight yellowish change occurred during the first discharge, which indicates the presence of LiC_6 , while in subsequent cycles, the graphite remained black with volume expansion, confirming the co-intercalation behavior.

[0246] The structural evolution of graphite was further investigated in operation (e.g., *operando*) using synchrotron XRD, illustrated in **Fig. 14a-b** (e.g., first cycle and second cycle). The pristine graphite displayed a strong (002) diffraction peak at 7.7° . During the 1st discharge (e.g., **Fig. 14a**), graphite undergoes lithiation to form b-GIC LiC_{18} and LiC_{12} , as evidenced by the shift of (002) peak towards low angles. At stage II (approximately 0.12 V), Li^+ -THF t-GIC gradually emerges as illustrated by the three new peaks at lower angles and

one new peak at higher angles, corresponding to the (001), (002), (003), and (004) planes of graphite, respectively. Since the lithiation voltage profile shows no co-intercalation feature between 0.4 to 0.7 V, the emergence of Li⁺-THF t-GIC is caused by the chemical reaction between b-GIC and free THF molecules. Upon the subsequent charge, these new peaks shift back reversibly and appear at the end of the charge. However, the (002) peak is weakened due to the increasing structural disorder. Such a reversible evolution of the (002) peak is observed in the subsequent cycles, like the 2nd cycle illustrated in **Fig. 14b**, but the LiC₆ peak no longer appears. This suggests a pure Li⁺-THF co-intercalation behavior with excellent reversibility. **Fig. 14c** delineates the position of the t-GIC (003) peak along with cycling time. The t-GIC (003) peak at 5.87° emerged at 52.7 min during discharging due to the b-GIC to t-GIC transformation. The asymmetric behavior of structural evolution in the first cycle agrees with the asymmetric voltage profile and the *in-situ* b-GICs to t-GICs transformation. After the 2nd and 3rd cycles, the peak shift is highly symmetric, consistent with excellent reversibility of Li⁺-THF co-intercalation. *Ex-situ* XRD patterns further characterized the evolution of graphite diffraction peak after the 10th and 100th cycles, where the (002) peak of both showed similar intensities. These results demonstrate that the Li⁺-THF co-intercalation in the graphite is highly reversible, and the interlayer structure of graphite is highly stable during extended cycling.

[0247] The in operation coherent X-ray multocrystal diffraction (CMCD) technique can capture the structural transformation of graphite particles, with each diffraction spot representing a particle. CMCD was used to monitor if these particles have synchronous reactions. In **Fig. 14d**, the CMCD image captured at the open circuit voltage (OCV) shows a single ring composed of sequential bright diffraction spots, which correspond to c-axis reflections of tens of graphite particles. As seen in **Fig. 14d**, during the 1st discharge, the bright spots shift synchronously, then gradually weaken, and finally disappear completely. This indicates that the probed graphite particles exhibit synchronous lithiation first and subsequently exhibit synchronous co-intercalation behavior at the low voltage. Such a synchronous behavior allows graphite particles to contribute to capacity delivery concurrently, thereby achieving a fast-charging electrode. In subsequent cycles, the weak ring moved reversibly, which indicates that the co-intercalation is highly reversible. The stoichiometry of t-GIC was investigated based on the following equation:



[0248] According to the voltage profile of the G||Li cell (e.g., illustrated in **Fig. 13b**), the measured reversible capacity of graphite after fully discharging is approximately 120 mAh g⁻¹, which indicates that one $\text{Li}^+(\text{THF})_y$ complex contains 18 carbon atoms. The y value is then estimated based on the mass change of graphite at different states of discharge, as illustrated in **Fig. 14e**. From the mass change of graphite at different states of discharge, the estimated value is $y = 1$, or in other terms, one THF molecule is co-intercalated with one Li^+ .

[0249] The *in-situ* b-GICs to t-GICs transformation under battery operating conditions (e.g., during the first lithiation) is schematically described in **Fig. 14f**. The as-formed t-GICs are highly reversible upon continuous electrochemical cycling, which informs the operation of Li^+ -THF co-intercalation chemistry for extreme-condition batteries.

[0250] The physicochemical properties and solvation structure of the 1M LiPF_6 -THF electrolyte were investigated. The electrolyte presented excellent ion conductivity in the range of 20 °C to -40 °C, much higher than that of the commercial carbonate electrolyte (e.g., EC/EMC based), especially in the low-temperature region. Moreover, the electrolyte remained clear with no salt precipitation and had good fluidity at -40 °C. Differential scanning calorimetry (DSC) further measured that the electrolyte maintained a liquid phase even at -103°C, which provides a basis for sub-zero temperature applications. Besides the ion conductivity and viscosity, the solvation effect is also crucial for ion transport in batteries as it determines the desolvation kinetics and interphase properties. Accordingly, Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR) were performed on the electrolyte. The electrolyte of interest, 1M LiFSI -THF, was compared to the electrolyte 1M LiPF_6 -EC/EMC. **Fig. 15a** shows the Raman spectra of the 1M LiPF_6 -THF electrolyte at different temperatures. Pure LiPF_6 salt displays one peak at 771 cm⁻¹, corresponding to the P-F stretching vibration. After dissolving in THF, the P-F peak shifts to 742 cm⁻¹, which indicates the strong dissociation between Li^+ and PF_6^- . After adding LiPF_6 , the THF ring breathing shifts from 913 cm⁻¹ to 916 cm⁻¹, which indicates a weak interaction between THF and Li^+ . These shifted peaks remain at the same position after the temperature is decreased from 20 to -40 °C, which confirms the low-temperature stability of the electrolyte. For the LiFSI -THF electrolyte, the vibration band of THF remained at 913 cm⁻¹, which indicates a weaker interaction between THF and Li^+ . In comparison, the vibration band of the coordinated EC/EMC solvent indicated a strong interaction between Li^+ and EC/EMC. **Fig. 15b** illustrates the FTIR spectrum of the 1M LiPF_6 -THF electrolyte. A clear contact ion pair (CIP) peak is found at 864 cm⁻¹. Further, the C-O-C in the THF solvent is coordinated with

Li^+ after introducing the salt LiPF_6 . Further fitting the peak ratio, the Li^+ -THF content accounts for 46.8%.

[0251] Classical molecular dynamics (cMD) simulations were conducted to understand the dominating solvation structure at the anode surface in the electrolyte. Simulation boxes in cMD were constructed by sandwiching the electrolyte between two electrodes with a surface charge of $\pm 0.1 \text{ C m}^{-2}$. The double-layer structure near the anode in these the electrolytes 1 M LiPF_6 -THF (left), 1 M LiFSI -THF (middle), and 1M LiPF_6 -EC/EMC (right) is shown in **Fig. 15c**. The solvent|cation|anion layered structure is a result of the surface adsorption of the polar solvent molecules and the repelling Coulombic force to the anions. Li^+ -O radial distribution function $g(r)$ analysis was performed by taking the first Li^+ layer adjacent to the anode as the central ion to study the interfacial solvation structures. The radial distribution is illustrated in **Fig. 15d**. According to the solvation number from the solvent molecules, which are illustrated in **Fig. 15e**, THF-based electrolytes present interfacial solvation structures dominated by a mixture of CIP and the solvent-separated ion pair (SSIP). In comparison, in the EC/EMC-based electrolyte, the interfacial solvation structures are majorly SSIP. **Fig. 15f** illustrates the solvation energy between the Li^+ and different solvent molecules. As seen in **Fig. 15f**, as a result of this difference, the binding energy of Li^+ -THF is smaller than that of Li^+ -EC and Li^+ -EMC. Thus, Li^+ can be readily desolvated from THF, decreasing the coordination number from $\text{Li}^+-(\text{THF})_{3.5}$ to $\text{Li}^+-(\text{THF})_1$ prior to co-intercalation.

[0252] Kinetics analyses was performed and demonstrated that $D_{\text{Li}^+}^{\text{THF}}$ of graphite is almost the same during cycling at 23°C and -40°C , and further demonstrated that the Li^+ -THF storage process in graphite is similar to surface-limited capacitive reaction, which allows for fast charging. The electrochemical performance of G||Li cell in the 1 M LiPF_6 -THF electrolyte was also tested at different current densities and temperatures. The rate capability of an example G||Li cell is shown in **Fig. 16a**, where the average reversible capacities are 110, 105, 100, 98, and 97 mAh g^{-1} at the C-rates of 1, 10, 20, 30, and 40 C, respectively. Even at 50 C, the reversible capacity reaches 93 mAh g^{-1} , which is approximately 85% of the capacity at 1 C, which demonstrates the ultrafast kinetics of the Li^+ -THF co-intercalation. After these cycles, and returning to a 1 C rate, the reversible capacity maintains its original value and can be further cycled 1,000 times at 10 C without capacity fading, as seen in **Fig. 16a**. As illustrated in **Fig. 16b**, the G||Li cell can also be cycled 10,000 times at 10 C with a capacity retention of 93%, which indicates the superior stability of the Li^+ -THF co-intercalation.

[0253] **Fig. 16c-d** exhibit the ultralong cycling stability of the G||Li cell under ultrafast charging. For example, at 20 °C (3 mins discharge/charge), the G||Li cell delivered a reversible capacity of 100 mAh g⁻¹ and is cycled stably 10,000 times with 96% capacity retention (**Fig. 16c**). Further increasing to 50 °C (1 min discharge/charge), the G||Li cell still maintained a high reversible capacity of 92 mAh g⁻¹ after 10,000 cycles, with no capacity decay compared to the initial capacity (**Fig. 16d**). Further, the low-temperature fast charging is demonstrated in **Fig. 16e-h**. As illustrated in **Fig. 16e**, when cycled at -20 °C, the G||Li cell delivered reversible capacities of 111, 101, 95, and 91 mAh g⁻¹ at C rates of 1, 10, 20, and 30 C, respectively, which is only slightly different from the room-temperature capacity. Similarly, as illustrated in **Fig. 16f**, when cycled at 10 °C, the G||Li cell maintained superior cycling stability with a reversible capacity of 100 mAh g⁻¹ for 3,700 cycles at -20 °C, consistent with the initial capacity. Further cooling down to -40 °C, the reversible capacity at the C rates of 1, 2, 5, and 10 C were 110, 102, 75, and 40 mAh g⁻¹, respectively (**Fig. 16g**). Although the rate capability decreases, the reversible capacities at 1 and 2 C are almost the same as room temperature, which highlights the excellent low-temperature charging performance. Moreover, as seen in **Fig. 16h**, the G||Li cell shows excellent cycling stability for 1,000 cycles at 2 C at -40 °C with 100% capacity retention. The charging performance of the G||Li cell tested at room temperatures and low temperatures is surprising as traditional graphite anode-based cells have not been close to achieving such performances. The morphological evolution of the cycled graphite was characterized by scanning electron microscope (SEM) images. After 100 cycles, a severe expansion of the graphite layer was observed, but the overall structure was well preserved without obvious exfoliation, illustrating the high mechanical stability of the graphite anode. Moreover, there was no Li plating or “dead Li” formation on the graphite surface or in the separator. Energy dispersive X-ray spectroscopy (EDS) mapping of the cycled graphite showed that C, F, P, and O elements were well distributed on the surface of the graphite with the C content accounting for 91.7%. This indicates that the electrolyte (e.g., 1M LiPF₆-THF) is stable without excessive decomposition.

[0254] The cathode material NMC811 (lithium nickel manganese cobalt oxide) was used with the graphite anode and electrolyte 1M LiPF₆-THF to evaluate the fast-charging and low-temperature performance in Li-ion full cells. No pre-cycled process was required since the graphite anode has high ICEs in the 1M LiPF₆-THF electrolyte. Three formation cycles were performed with one cycle at 0.2 C, then two cycles at 0.5 C (1C = 0.2 A g⁻¹). The corresponding voltage profiles of the G||NMC811 full cell at 0.2C and 0.5C are

illustrated in **Fig. 17a**. The full cell delivered a capacity of 163 mA g^{-1} based on the mass of the cathode, with an average voltage of approximately 2.7 V at 0.5 C. As shown in **Fig. 17b**, which illustrates average voltage and capacity of the G||NMC811 and existing cells, the capacity of the G||NMC811 cell is much higher than existing Na-based or K-based cells. The full cell also delivered an initial capacity of 133 mAh g^{-1} at 4 C (e.g., at room temperature) when only constant current charging (CCC) was performed (**Fig. 17c**). After 800 cycles, the full cell maintained a reversible capacity of 123 mAh g^{-1} with an extremely low capacity decay rate of 0.009% per cycle. This result confirms the high stability of NMC811 and graphite in the 1M LiPF₆-THF electrolyte. A constant voltage charging (CVC) procedure was added to the CCC step for a complete charging process of 15 minutes. With this addition, the full cell delivered a high initial capacity of 146 mAh g^{-1} at 4 C with a capacity retention of 97% after 400 cycles, as seen in **Fig. 17c**. Further, **Fig. 17d** illustrates the rate capability of the G||NMC811 full cell at current densities ranging from 1 to 20 C (60 minutes to 1.5 mins charging process). For the C rates of 1, 2, 4, 6, 8, 10, 12, 14, 16, 18, and 20, the reversible capacities were 167, 163, 157, 151, 145, 139, 134, 129, 125, 120, and 114 mAh g^{-1} , respectively. Approximately 68% of the reversible capacity is retained even with a 20-fold increase in current density from 1 to 20 C. The high rate capability provides a remarkably high-power density of $4,180 \text{ W kg}^{-1}$ with an energy density of 106 Wh kg^{-1} (based on the total mass of the cathode and anode). This result is much higher than existing Na-based and K-based cells, as illustrated in the comparison of energy density and power density of **Fig. 17e**.

[0255] The low temperature (and fast charging) performance of the full cell was also tested. The full cell had excellent rate performance at -20 °C, delivering 142, 131, 120, 113, and 105 mAh g^{-1} at C rates of 0.2, 0.5, 1.0, 1.5, and 2.0 C, respectively (**Fig. 17f**). An impressive capacity (134 mA g^{-1}) and stability (approximately 92%) were also obtained after 150 cycles at 1 C. Even at -40 °C, the full cell using the 1M LiPF₆-THF electrolyte exhibited excellent rate performance. For example, as illustrated in **Fig. 17g**, the reversible capacities were determined to be 101, 91, 80, 69, and 61 mAh g^{-1} at 0.2, 0.333, 0.5, 0.75, and 1 C, respectively. Further cycling the full cell at 0.2 C, the full cell maintained 83% of its initial capacity after 150 cycles. Switching cycling the full cell to 0.5 C, the full cell retained 84% capacity retention after 300 cycles (**Fig. 17g**). Such low-temperature performance has not been found in existing Li-ion full cells.

[0256] In this example, t-GICs were *in situ* synthesized in the 1M LiPF₆-THF electrolyte via a controllable chemical reaction between b-GIC and THF during battery cycling. The transformation enabled reversible, rapid Li⁺-THF co-intercalation into graphite. The in-operation X-ray and electrochemical analyses confirmed the synthesis of t-GICs. Compared to a linear ether, a cyclic ether has a weak interaction with Li⁺ due to steric hindrance, which allows for easier partial desolvation of Li⁺-(THF)_{3.5} to yield Li⁺-(THF)₁ for rapid co-intercalation. The electrolyte 1M LiPF₆-THF made battery reactions in individual graphite particles proceed synchronously even during fast charging. As a result, the graphite anode displayed an ultralong lifespan of over 10,000 cycles with negligible capacity decay, 1-minute fast charging, and unprecedented low-temperature performance (including fast charging) with no lithium dendrite formation. Coupled with an NMC cathode, the full cell displayed an excellent balance between energy and power (e.g., as illustrated in the Ragone plot) and outstanding cycling stability for 800 cycles within 15 mins charging. Even at the low temperature of -40 °C, the excellent rate capability was achieved, with 100 mAh g⁻¹ at 0.1 C, 90 mAh g⁻¹ at 0.33 C, 80 mAh g⁻¹ at 0.5 C, and 60 mAh g⁻¹ at 1 C, respectively.

[0257] A full cell Li-ion battery using the graphite anode and the 1M LiPF₆-THF electrolyte has surprisingly high-power capability, especially at low temperatures. Additionally, using the solvent THF in the electrolyte has further advantages as THF is a low-cost, mass-produced chemical, making 1M LiPF₆-THF an attractive electrolyte for commercialization.

Example 4

Assessment of Specific Capacity and Coulombic Efficiency

[0258] Building off the performance of 1M LiPF₆-THF electrolyte, other electrolytes were also tested. For example, the electrolytes 1M LiPF₆-2MeTHF, 1M LiPF₆-2MeTHF-2vol.% fluoroethylene carbonate (FEC), and 1M LiFSI-2MeTHF were tested. Other commercial electrolytes were also tested for comparison purposes. From the testing, the electrolyte 1M LiPF₆-2MeTHF had the most favorable properties. The tests and the results of the tests are discussed in this example.

[0259] The electrolyte 1M LiPF₆-2MeTHF reduces the energy barriers for Li-ion transport and improves the capacity retention of anodes (Graphite, μ Si/Graphite, and Si), even during fast charging and low temperatures. For example, using a graphite anode with the 1M LiPF₆-2MeTHF electrolyte at room temperature provided excellent rate capabilities. As seen

in **Fig. 18a**, which illustrates the cycling performance of a graphite anode with different electrolytes, the specific capacity of the graphite anode using 1M LiPF₆-2MeTHF was 372, 357, 336, 252, 142, and 63 mAh g⁻¹ at the C rates of 0.2, 0.5, 1, 2, 3, and 5 C, respectively. Further, as seen in **Fig. 18b**, which illustrates the cycling performance of a graphite anode with different electrolytes at a temperature range of 23 to -20°C, the graphite anode cycled in the 1M LiPF₆-2MeTHF electrolyte showed the highest capacity. **Fig. 19a** compares the low-temperature performance of a graphite anode in the 1M LiPF₆-2MeTHF and 1M LiPF₆-EC/EMC+2vol.% VC electrolytes. The graphite anode cycled in the 1M LiPF₆-2MeTHF electrolyte showed a high capacity of 342 mAh g⁻¹ at 0.2 C (1C=0.37A g⁻¹) and maintained a capacity retention of 97% after 160 cycles. In contrast, a capacity of only 13 mAh g⁻¹ was obtained with the commercial electrolyte 1M LiPF₆-EC/EMC+2vol.% vinylene carbonate (VC). This result is likely due to the sluggish Li-ion transport and high barriers in the SEI layer. To demonstrate high cycling stability, a fresh graphite anode was tested at a high C rate. As illustrated in **Fig. 19b**, which shows the long-term cycling performance of the fresh graphite anode, the anode maintained a specific capacity of 170 mAh g⁻¹ after 1000 cycles at 2.0 C, with a capacity retention of 96%. The excellent cycling stability and high capacity at low temperatures are well beyond existing graphite anode batteries.

[0260] The rate capability of the graphite anode in the 1M LiPF₆-2MeTHF at -20°C was also tested. As seen in **Fig. 20a**, which illustrates the cycling performance and corresponding voltage profiles, the graphite anode had a specific capacity of 340, 318, 266, 151, and 80 mAh g⁻¹ at the rates of 0.2, 0.5, 1.0, 2.0, and 3.0 C, respectively. After returning to 1.0 C, the graphite anode still maintained the same value and with no further capacity fading after 500 cycles.

[0261] The electrolyte 1M LiPF₆-2MeTHF was also tested with anode materials other than graphite (e.g., μSi/Graphite and Si anode) at low temperatures (e.g., -20°C). As shown in **Fig. 20b**, which illustrates the cycling performance and voltage profile of the μSi/G anode, the μSi/G anode exhibited high specific capacities of 767, 742, 697, 614, and 521 mAh g⁻¹ when cycled at 0.2, 0.5, 1.0, 2.0 and 3.0 C (1C=0.37A g⁻¹), respectively. The cell retained the same specific capacity after returning to 0.2 and 1.0 C, thereby demonstrating cycling stability. For the pure Si anode, impressive low-temperature cycling performance was also achieved when cycling in the 1M LiPF₆-2MeTHF electrolyte. The cycling performance and voltage profile of the Si anode are illustrated in **Fig. 20c**. The specific capacities for the Si anode were 2182, 2072, 1985, 1847, and 1690 mAh g⁻¹ at the rates of 0.2, 0.4, 0.6, 0.8, and 1.0 C (1C=4.2A

g^{-1}). When using a rate of 0.2 C, the Si anode still has a capacity of 2116 mAh g^{-1} and was able to be cycled stably 250 times without capacity fading.

[0262] A single-layer pouch cell configuration with Gr anode and NMC622 cathode is cycled at -20°C . **Fig. 20d** shows the good rate performance of the Gr||NMC622 cell with specific capacities of 125, 120, 105, 100, and 90 mAh g^{-1} at 0.1, 0.2, 0.3, 0.5, and 1.0 C ($1\text{C}=0.18\text{A g}^{-1}$) at -20°C , respectively. At 0.2 C, the pouch cell can cycle stably for more than 365 days, achieving capacity retention of 90% after 500 cycles and 87% after 1000 cycles, respectively (**Fig. 20e**). Another pouch cell had a two-week rest after 500 cycles and then continued to cycle, which ultimately maintained the capacity retention after 1000 cycles (**Fig. 20e**), demonstrating good calendar life during the rest period. Overall, the 1M LiPF₆-2MeTHF electrolyte derives a low energy barrier SEI layer that enhances Li ions transport, and this SEI layer is exceptionally stable, improving the cycling stability of the anode.

[0263] Additionally, as shown in the cycling performance and voltage profiles in **Fig. 21a**, a SiHC (silicon-hard carbon, with 52% silicon content) anode with an areal capacity of 4.2 mAh/ cm^2 was tested with the electrolyte 1.5M LiPF₆-2MeTHF. It had specific capacities of 1564, 1441, 1227, 969, 795, and 626 mAh g^{-1} at rates of 0.2, 0.5, 1.0, 1.5, 2.0, and 2.5 C ($1\text{C}=1.2\text{A g}^{-1}$), respectively. After returning to 0.2 C, the Si/HC anode maintained the same value with no capacity fading. To demonstrate long-term cycling stability, a fresh Si/HC anode was tested, and the results are illustrated in **Fig. 21b**. The fresh Si/HC anode maintained a specific capacity of 800 mAh g^{-1} after 550 cycles at 2.0 C, with a capacity retention of 94%. As demonstrated, the electrolyte 1.5M LiPF₆-2MeTHF enables Si/HC anode to exhibit excellent electrochemical performance during fast charging conditions.

[0264] **Fig. 22a** illustrates the voltage profile of the HC anode cycled in the electrolyte 1M LiPF₆-THF and in the commercial carbonate electrolyte 1 M LiPF₆-EC/EMC+2vol.%VC. **Fig. 22b** illustrates the corresponding rate capability and **Fig. 22c** illustrates the corresponding long-term cycling performance. When compared with commercial carbonate electrolytes (e.g., 1 M LiPF₆-EC/EMC+2vol.%VC), the HC anode shows a higher specific capacity and longer plateau capacity in the 1M LiPF₆-THF electrolyte. Accordingly, the electrolyte is more conducive to insertion reaction in the low voltage range. The electrolyte (e.g., 1.0 M LiPF₆-THF) increases the electrochemical performance of hard carbon in lithium-ion batteries, which is evidenced by its high specific capacity (**Fig. 22a**), rate capability (**Fig. 22b**), and cycling stability (**Fig. 22c**). **Fig. 23a-c** illustrate the low-temperature performance of HC anode in the electrolyte with the voltage profile shown in

Fig. 23a, the rate capability shown in **Fig. 23b**, and the long-term cycling/stability shown in **Fig. 23c**.

Example 5

High Voltage Layered Cathode and Various Anodes in 4MeTHP-based Electrolytes

[0265] **Fig. 24** demonstrates the electrochemical performance of Li||NMC811 cells cycled in the 1M LiFSI-4MeTHP electrolytes. The LSV curve shows the high voltage stability of the electrolyte, which only begins to decompose around 4.8V (**Fig. 24a**). The cell undergoes two formation cycles at 0.2C ($1C=0.2A\ g^{-1}$) within the voltage range of 2.8 to 4.5V. The initial Coulombic efficiency of the cell is 89% (**Fig. 24c**). Then, the rate performance is performed at 23°C. Noticeably, the constant voltage charge (CVC) is added to match standard rate performance at 5.0 and 10.0 C. At 0.2, 0.5, 1.0, 2.0, 5.0, and 10.0 C, the Li||NMC811 cell delivers specific capacities of 217, 211, 203, 194, 183, and 153 mAh g^{-1} , respectively (**Fig. 24b, 24c**). After rate performance, the cell continues cycling at 2C and has no capacity fading after 90 cycles. A fresh Li||NMC811 cell is tested at 3C for long-term cycling (**Fig. 24d, 24e**). The cell delivers a specific capacity of 187 mAh g^{-1} , and achieves 80% capacity retention after 550 cycles, with an average Coulombic efficiency of up to 99.9% (**Fig. 24d, 24e**).

[0266] Additionally, the full cell configuration with Gr anode and NMC811 cathode is tested in the 1M LiPF₆-4MeTHP+2wt% FEC electrolyte for improved practical applications (**Fig. 25**). Neither the cathode nor the anode requires the prelithiation process. The full cell undergoes two formation cycles at 0.1C ($1C=0.2A\ g^{-1}$) within the voltage range of 2.8 to 4.5V. Then, the rate performance is performed at 23°C (**Fig. 25a**). At 0.1, 0.2, 0.5, 1.0, and 2.0 C, the full cell delivers specific capacities of 209, 205, 193, 182 and 147 mAh g^{-1} , respectively (**Fig. 25a, 25b**). A fresh full cell with a cathode mass loading of 9.2 mg cm^{-2} is tested at 1C within the voltage range of 3 to 4.4V for long-term cycling (**Fig. 25c**). The full cell delivers a specific capacity of 183 mAh g^{-1} , and achieves 88% capacity retention after 400 cycles, with an average Coulombic efficiency of up to 99.9% (**Fig. 25c, 25d**).

[0267] Further, the electrochemical performance of the Si/HC (Silicon-hard carbon, with 52% silicon content) anode was systematically tested under extreme conditions (e.g., fast charging and low temperatures) using the 1.0M LiPF₆-4MeTHP electrolyte (**Fig. 26**). The CV curve shows two dominant peaks at 0.2 and 0.01 V at the cathodic scan, corresponding to the Si alloying process, which has no excess solvent and salt decomposition peaks, showing the reduction stability of the electrolyte (**Fig. 26a**). In the anodic scan, two peaks at 0.33 and 0.51V represent the reversible conversion from Li_xSi back to Si, indicating the identical

lithiation/delithiation mechanism. The rate performance of the Si/HC anode at room temperature is shown in **Fig. 26b, 26c**. The mass loading is 2.5 mg cm^{-2} . The Si/HC anode delivers specific capacities of 1559, 1465, 1307, 1094, 907, and 765 mAh g^{-1} at 0.2, 0.5, 1, 1.5, 2.0, and 2.5 C ($1\text{C}=1.2 \text{ A g}^{-1}$), respectively. After returning to 0.2 C, the Si/HC anode maintains the same capacity without fading (**Fig. 26b, 26c**). Even under 2C high-rate cycling, the Si/HC anode still maintains a reversible capacity of 848 mAh g^{-1} after 1000 cycles, with a capacity retention of 91% and an average Coulombic efficiency of 99.9%, further highlighting the fast-charging capability of the electrolyte (**Fig. 26d, 26e**). **Fig. 26f, 26g** shows the incredible rate capability of the Si/HC anode at low temperatures. At 0.1, 0.2, 0.3, and 0.5C, the Si/HC anode delivers high specific capacities of 1427, 1413, 1392, and 1320 mAh g^{-1} , respectively. Further cycling at 0.5 C, the Si/HC anode achieves a capacity retention of 94% after 290 cycles. The average Coulombic efficiency is 99.9%.

[0268] The full cell configuration with Si/HC anode and NMC811 cathode is tested under fast charging and low-temperature conditions for better practical applications. Neither the cathode nor the anode requires the prelithiation process. The LSV curve shows the high voltage stability of the electrolyte, which only begins to decompose around 4.8V (**Fig. 27a**). The full cell undergoes two formation cycles at 0.1C ($1\text{C}=0.2 \text{ A g}^{-1}$) within the voltage range of 2 to 4.3V. The initial Coulombic efficiency of the full cell is 83% (**Fig. 27b**). Then, the rate performance is performed at 23°C. Noticeably, to match standard rate performance, the constant voltage charge (CVC) is added at 4.0 C. At 0.1, 0.2, 0.5, 1.0, 2.0, and 4.0 C, the full cell delivers specific capacities of 192, 185, 179, 170, 148, and 137 mAh g^{-1} , respectively (**Fig. 27b, 27c**). After rate performance, the full cell continues cycling at 2C and no capacity fading after 100 cycles. A fresh full cell with an areal capacity of 2.5 mAh cm^{-2} is tested at 2C for long-term cycling. The full cell delivers an areal capacity of 1.7 mAh cm^{-2} , and achieves 82% capacity retention after 550 cycles, with an average Coulombic efficiency of up to 99.9% (**Fig. 27d**). The full cell also demonstrates superior low-temperature cycling performance (both charge and discharge are at low temperatures). As shown in **Fig. 27e**, the full cell exhibits a specific capacity of 154 mAh g^{-1} at -10°C at 0.2C, 133 mAh g^{-1} at -20°C at 0.2C, 100 mAh g^{-1} at -30°C at 0.2C, 130 mAh g^{-1} at -40°C at 0.1C, and then 156 mAh g^{-1} at -20°C at 0.1C for 100 cycles without capacity fading. All these results demonstrate that 4MeTHP-based electrolytes are compatible with both cathodes and anodes, achieving excellent battery performance during fast charging and low temperatures.

[0269] The above specification provides a description of the manufacture and use of the disclosed compositions and methods. Since many embodiments can be made without departing from the spirit and scope of the disclosure, the disclosure resides in the claims.

CLAIMS

What is claimed is:

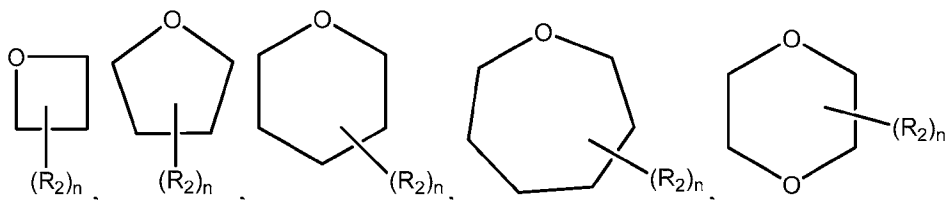
1. An electrochemical device comprising:
an anode comprising a graphite, a silicon, a hard carbon, or a combination thereof;
a cathode; and
a liquid electrolyte comprising a salt $M^{n+} (A^-)_n$ and a C₄-C₈ ether solvent, wherein M^{n+} is selected from Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , and Al^{3+} and wherein A^- is an anion, wherein the C₄-C₈ ether solvates the M^{n+} to form a solvate, and wherein the solvate reversibly co-intercalates in the anode, or wherein the solvate desolvates and the M^{n+} intercalates in the anode.
2. The electrochemical device of claim 1, wherein the C₄-C₈ ether is a cyclic C₄-C₈ ether.
3. The electrochemical device of claim 1 or claim 2 wherein the C₄-C₈ ether is a compound of formula (I)

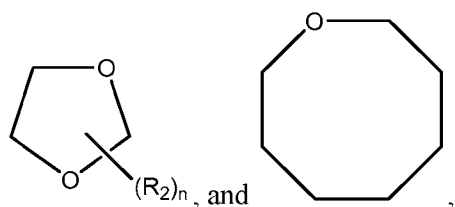


(I)

wherein R_1 is a C₄-C₈ divalent alkylene radical optionally interrupted by one or more oxygen or sulfur atoms, wherein the compound is optionally substituted with one or more R_2 selected from the group consisting of a C₁-C₂ alkyl and a halogen, and wherein the C₁-C₂ alkyl may be optionally substituted with one or more halogen.

4. The electrochemical device of claim 1 or 2 wherein the C₄-C₈ ether is a compound selected from the group consisting of





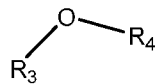
wherein each R_2 is independently selected from the group consisting of methyl, ethyl and fluoro;

wherein n is 0, 1, or 2; and

wherein each methyl and ethyl group is independently substituted by one, two, or three fluorine atoms.

5. The electrochemical device of claim 4 wherein n is 0 or 1.
6. The electrochemical device of claim 4 wherein n is 0.
7. The electrochemical device of claim 4 wherein R_2 is methyl.
8. The electrochemical device of claim 4 wherein R_2 is ethyl.
9. The electrochemical device of any one of claims 1-4 wherein the ether is tetrahydrofuran (THF), 2-methyltetrahydrofuran (2MeTHF), or 2,5-methyltetrahydrofuran (2,5-MeTHF).
10. The electrochemical device of any one of claims 1-4 wherein the ether is tetrahydropyran (THP) or 4-methyltetrahydropyran (4MeTHP).
11. The electrochemical device of any one of claims 1-4 wherein the ether is 2-methyloxetane or 3-methyloxetane.
12. The electrochemical device of any one of claims 1-4 wherein the ether is 1,3-dioxalane.
13. The electrochemical device of claim 1, wherein the ether is a non-cyclic C_4 - C_8 ether.
14. The electrochemical device of claim 13 wherein the non-cyclic C_4 - C_8 ether is a compound

of formula (II):



(II)

wherein R₃ and R₄ are independently selected from the group consisting of methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, and tert-butyl, all of which are optionally substituted with one or more fluorine atoms.

15. The electrochemical device of claim 14 wherein R₃ and R₄ are independently selected from the group consisting of methyl, ethyl, and n-propyl.

16. A battery comprising:

an anode comprising a graphite, a silicon, a hard carbon, or a combination thereof;

a cathode; and

a liquid electrolyte comprising a salt Mⁿ⁺ (A⁻)_n and a C₄-C₈ ether solvent, wherein Mⁿ⁺ is

selected from Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, and Al³⁺, wherein A⁻ is an anion, and wherein the C₄-C₈ ether solvates the Mⁿ⁺ to form a solvate,

wherein the solvate reversibly co-intercalates in the anode or wherein the solvate desolvates and the Mⁿ⁺ intercalates in the anode.

17. The electrochemical device of claim 1 or battery of claim 16 wherein the C₄-C₈ ether has a melting point of from about -120°C to about -10°C.

18. The electrochemical device or battery of claim 17 wherein the C₄-C₈ ether has a melting point of from about -100°C to about -10°C.

19. The electrochemical device or battery of claim 17 wherein the C₄-C₈ ether has a melting point of from about -90°C to about -10°C.

20. The electrochemical device or battery of claim 17 wherein the C₄-C₈ ether has a melting point of from about -80°C to about -10°C.

21. The electrochemical device or battery of claim 17 wherein the C₄-C₈ ether has a melting point of from about -70°C to about -10°C.
22. The electrochemical device or battery of claim 17 wherein the C₄-C₈ ether has a melting point of from about -60°C to about -10°C.
23. The electrochemical device or battery of claim 17 wherein the C₄-C₈ ether has a melting point of from about -50°C to about -10°C.
24. The electrochemical device or battery of claim 17 wherein the C₄-C₈ ether has a melting point of from about -40°C to about -10°C.
25. The battery of claim 16, wherein the C₄-C₈ ether has a dynamic viscosity of from 0.4 to 0.6 mPa at 273°K at atmospheric pressure.
26. The electrochemical device of claim 1 wherein the anion is hexafluorophosphate (PF₆⁻), tetrafluoroborate (BF₄⁻), triflate (CF₃SO₃⁻), bis(fluorosulfonyl)imide (FSI), or a combination thereof.
27. The electrochemical device of claim 1 wherein the anode is the graphite or a hard carbon with local graphitic structure as determined by graphitic peaks as measured by x-ray diffraction and Raman spectroscopy.
28. The electrochemical device of claim 27 wherein the graphite is synthetic or natural graphite, and wherein the hard carbon is derived from a biomass, coal, or petroleum byproduct.
29. The electrochemical device of claim 1 wherein the cathode comprises M_n-X_q-R-F_y, wherein M is selected from Li, Na, and K; X is one or more transition metals; R is O₂ or PO₄; n is one or greater; for each individual X, q is greater than zero; and y is zero or greater.
30. The electrochemical device of claim 29, wherein the cathode comprises M-CoO₂, M-FeSO₄F, M-FePO₄, or M-Ni_xMn_yCo_zO₂, wherein x + y + z = 1.

31. The electrochemical device of claim 29, wherein the cathode comprises LiCoO_2 , LiNiO_2 , LiFePO_4 , $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$, or $\text{Li}_{1.75}\text{Mn}_{0.45}\text{Ti}_{0.45}\text{Fe}_{0.1}\text{O}_2\text{F}_{0.75}$.

32. The electrochemical device of claim 1 which has a specific capacity measured after a number of cycles that is from 60% to 99% of an original specific capacity and wherein the number of cycles is from 200 to 10,000 cycles.

33. The electrochemical device of claim 32 which has a specific capacity measured after a number of cycles that is from 70% to 99% of the original specific capacity.

34. The electrochemical device of claim 32 which has a specific capacity measured after a number of cycles that is from 80% to 99% of the original specific capacity.

35. The electrochemical device of claim 32 which has a specific capacity measured after a number of cycles that is from 90% to 99% of the original specific capacity.

36. The electrochemical device of claim 32 which has a specific capacity measured after a number of cycles that is from 95% to 99% of the original specific capacity.

37. The electrochemical device of claim 32 which has a specific capacity measured after a number of cycles that is from 97% to 99% of the original specific capacity.

38. The electrochemical device of claim 32 wherein the number of cycles is from 200 to 1000 cycles.

39. The electrochemical device of claim 32 wherein the number of cycles is from 1000 to 10,000 cycles.

40. The electrochemical device of claim 32 wherein the number of cycles is from 2000 to 10,000 cycles.

41. The electrochemical device of claim 32 wherein the number of cycles is from 3000 to 10,000 cycles.

42. The electrochemical device of claim 32 wherein the number of cycles is from 4000 to 10,000 cycles.
43. The electrochemical device of claim 32 wherein the number of cycles is from 5000 to 10,000 cycles.
44. The electrochemical device of claim 32 wherein the number of cycles is from 6000 to 10,000 cycles.
45. The electrochemical device of claim 32 wherein the number of cycles is from 7000 to 10,000 cycles.
46. The electrochemical device of claim 32 wherein the number of cycles is from 8000 to 10,000 cycles.
47. The electrochemical device of claim 32 wherein the number of cycles is from 9000 to 10,000 cycles.
48. The electrochemical device of claim 1 wherein the initial concentration of the salt $M^n^+(A^-)_n$ in the C₄-C₈ cyclic ether solvent is from about 0.5 to 2.5M.
49. The electrochemical device of claim 1 further comprising: an anode stack comprising an anodic current collector and the anode formed over at least a portion of the anodic current collector; a cathode stack comprising a cathodic current collector and the cathode formed over at least a portion of the cathode stack, a separator material between the cathode stack and the anode stack; and the electrolyte, wherein the electrochemical device is a battery.
50. The electrochemical device of claim 49 wherein the separator material is selected from the group consisting of a nonwoven fiber, a cotton fiber, a nylon, a polyester, a glass, a polymer film, a polyethylene, a polypropylene, a poly(tetrafluoroethylene), a polyvinyl chloride, a ceramic, a rubber, and an asbestos.

51. A use of the solvate according to claim 1 as an electrolyte in an electrochemical device.
52. The use of claim 51 wherein the electrochemical device operates at a cell average discharge voltage of from about 1 V to about 4.6 V.

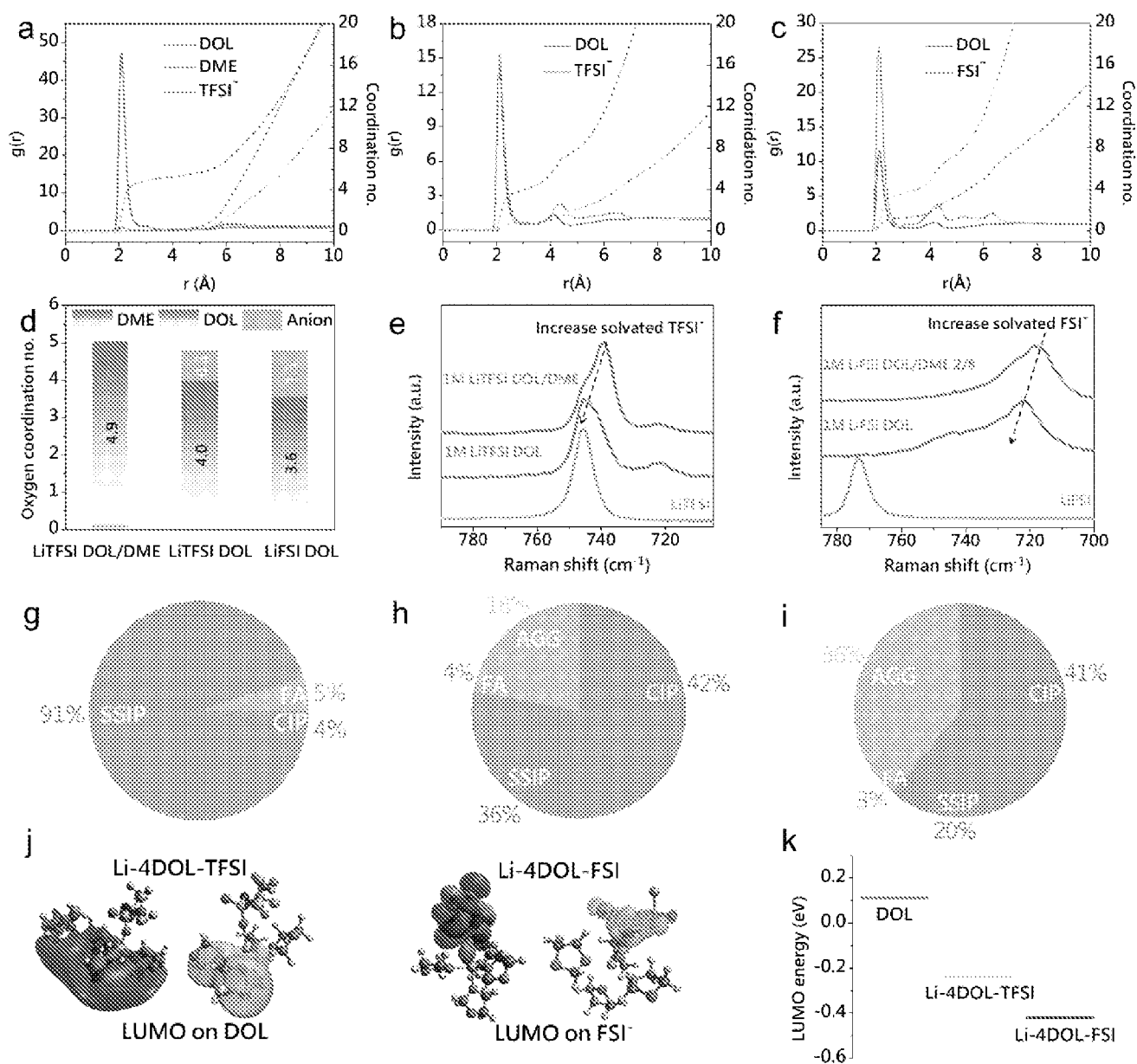


FIG. 1

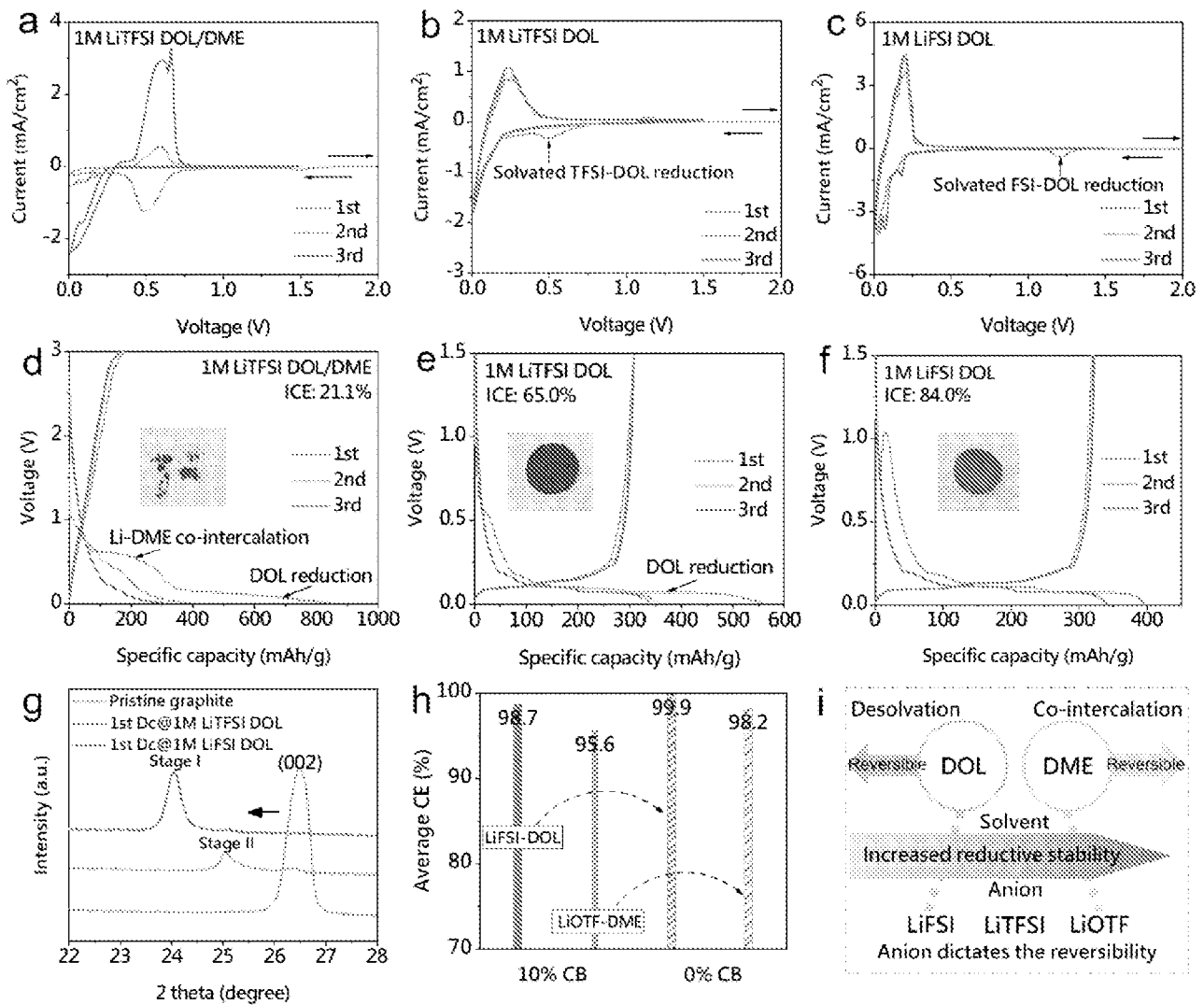


FIG. 2

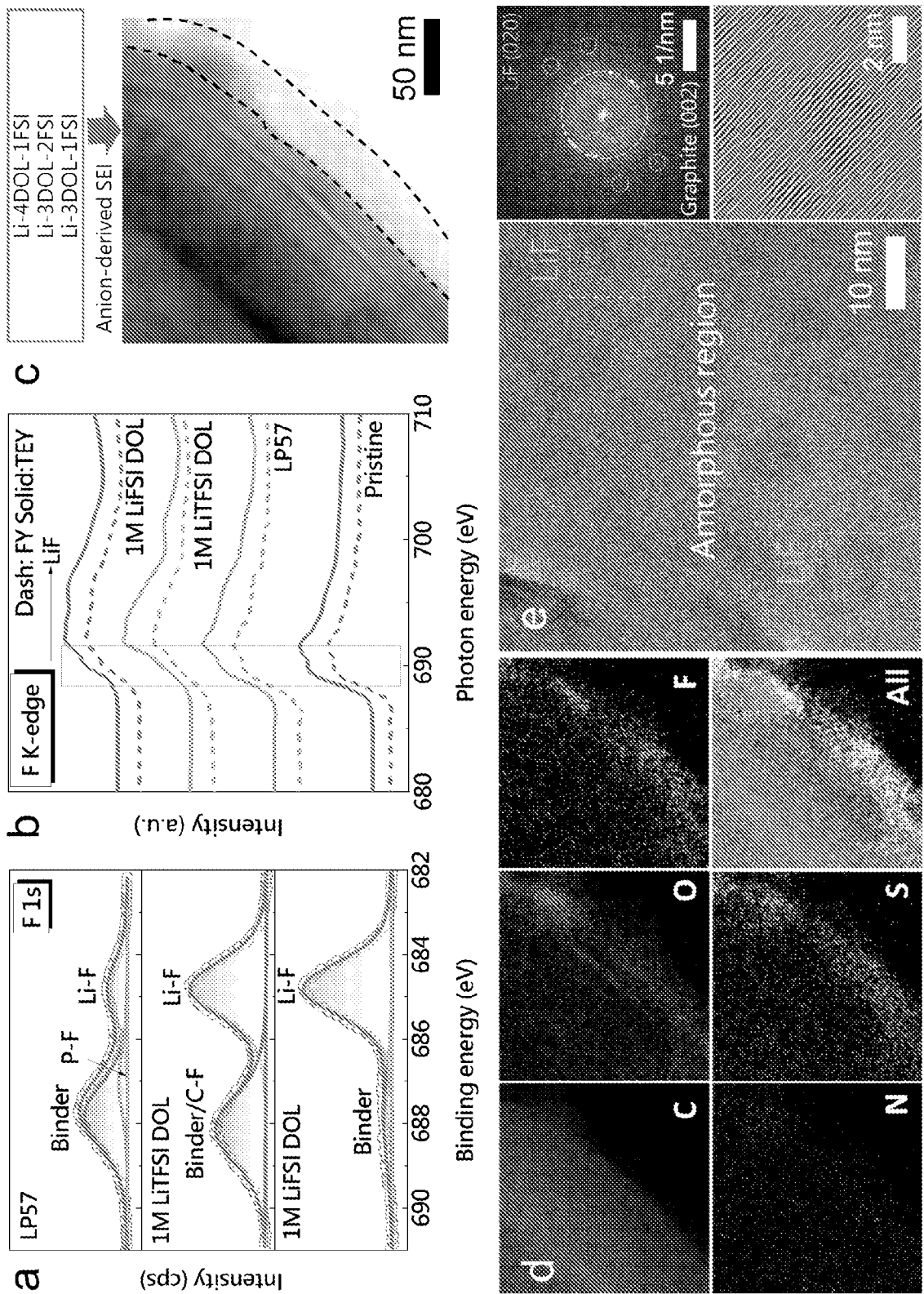


FIG. 3

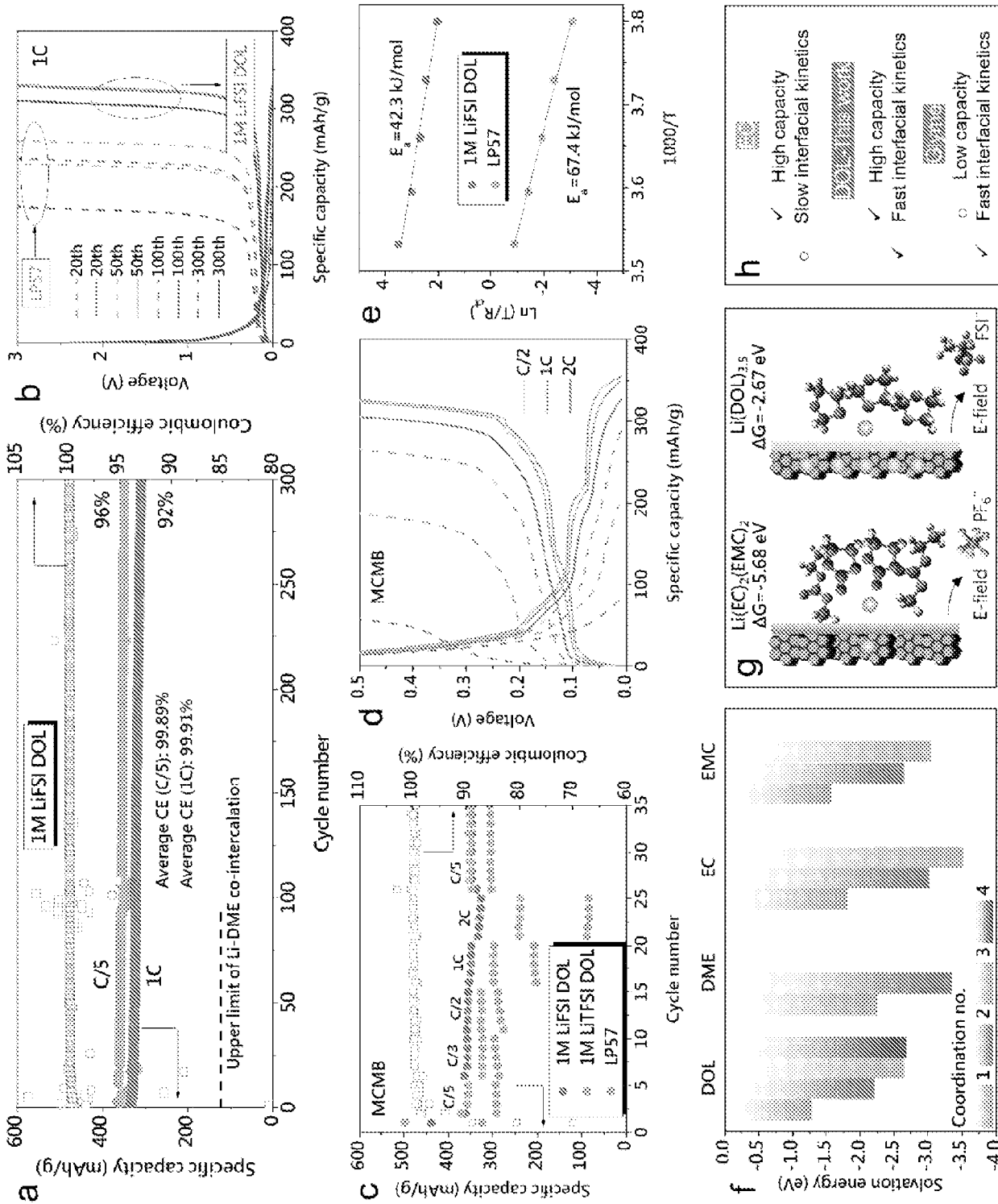


FIG. 4

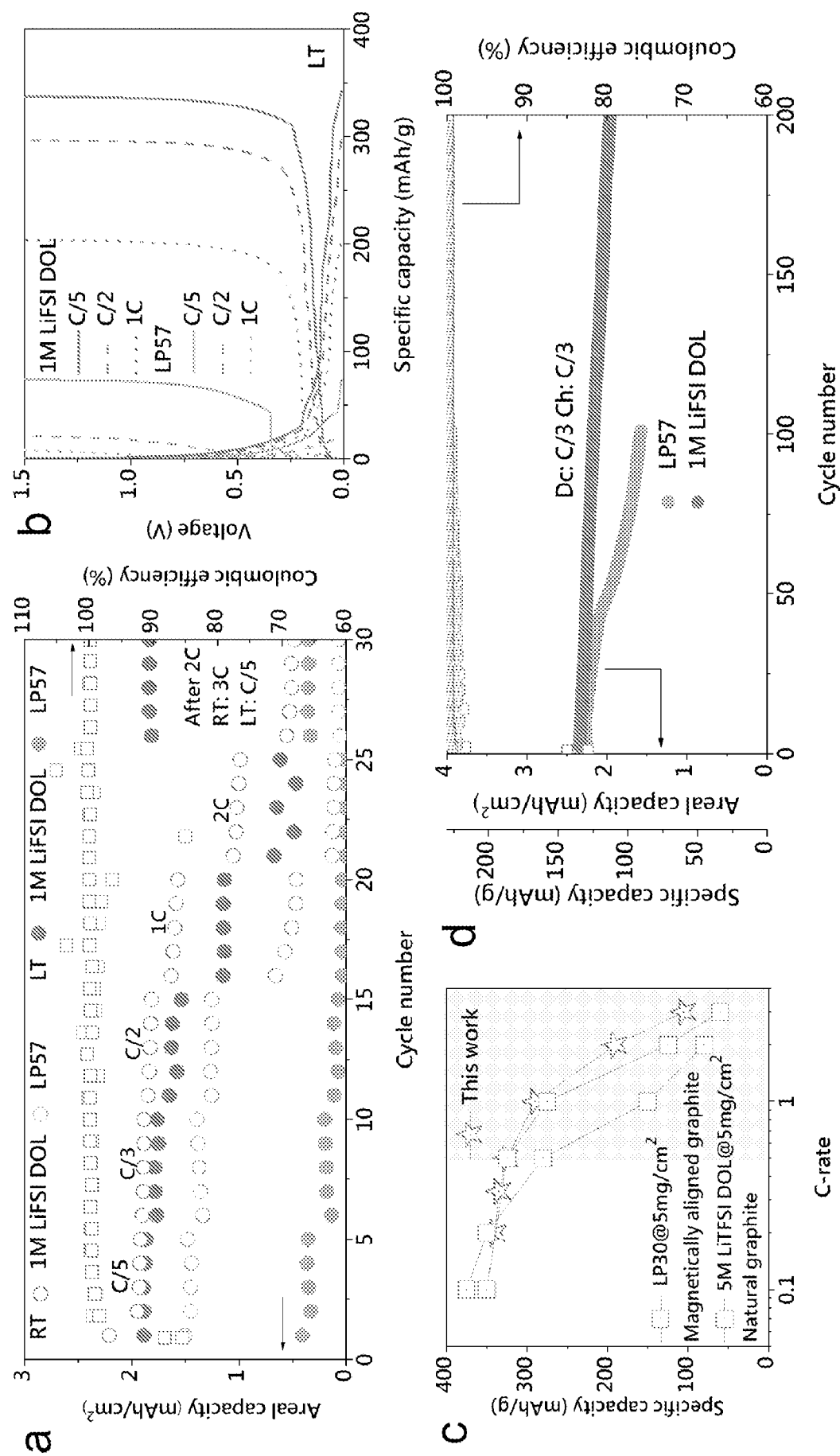


FIG. 5

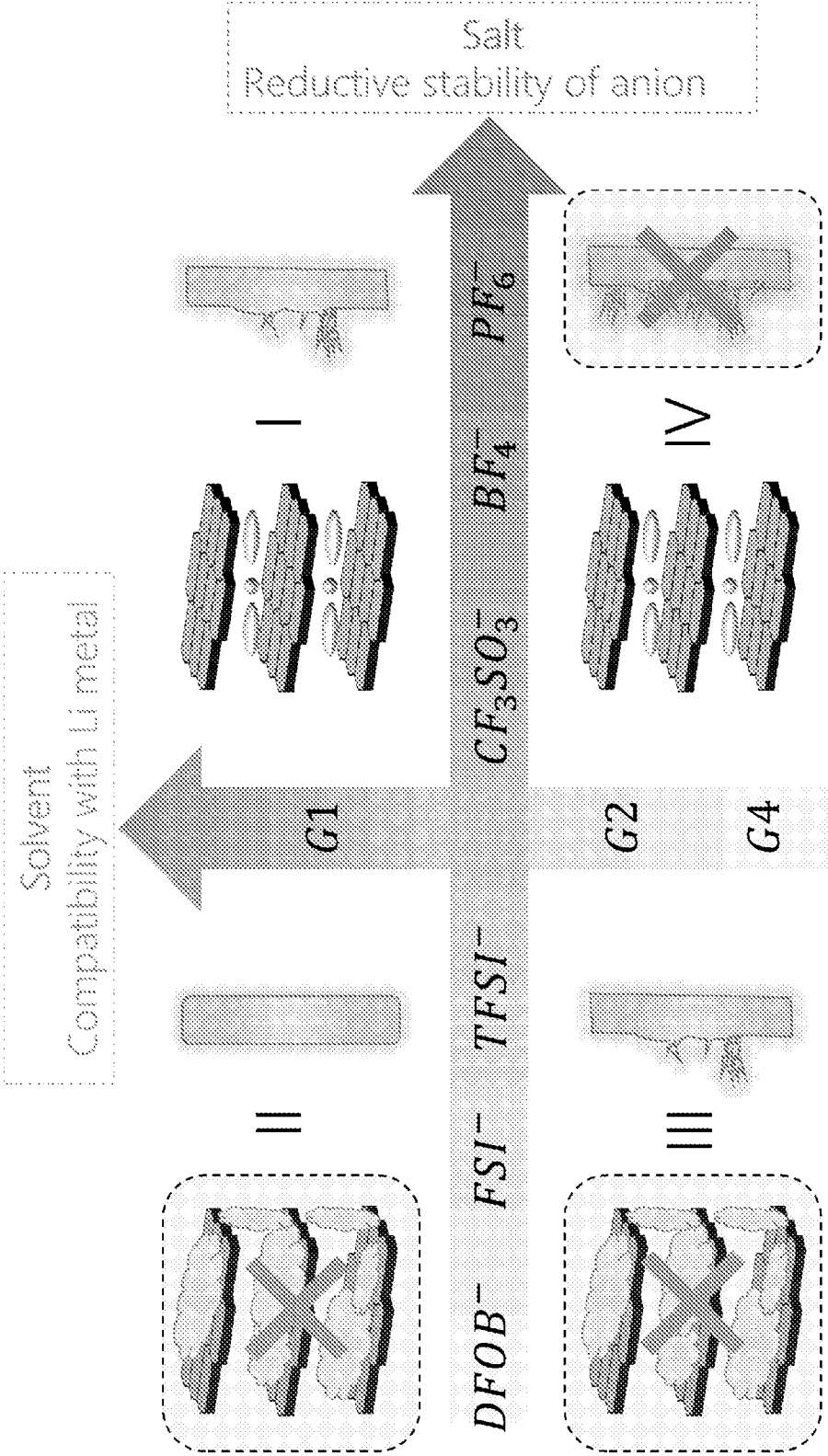


FIG. 6

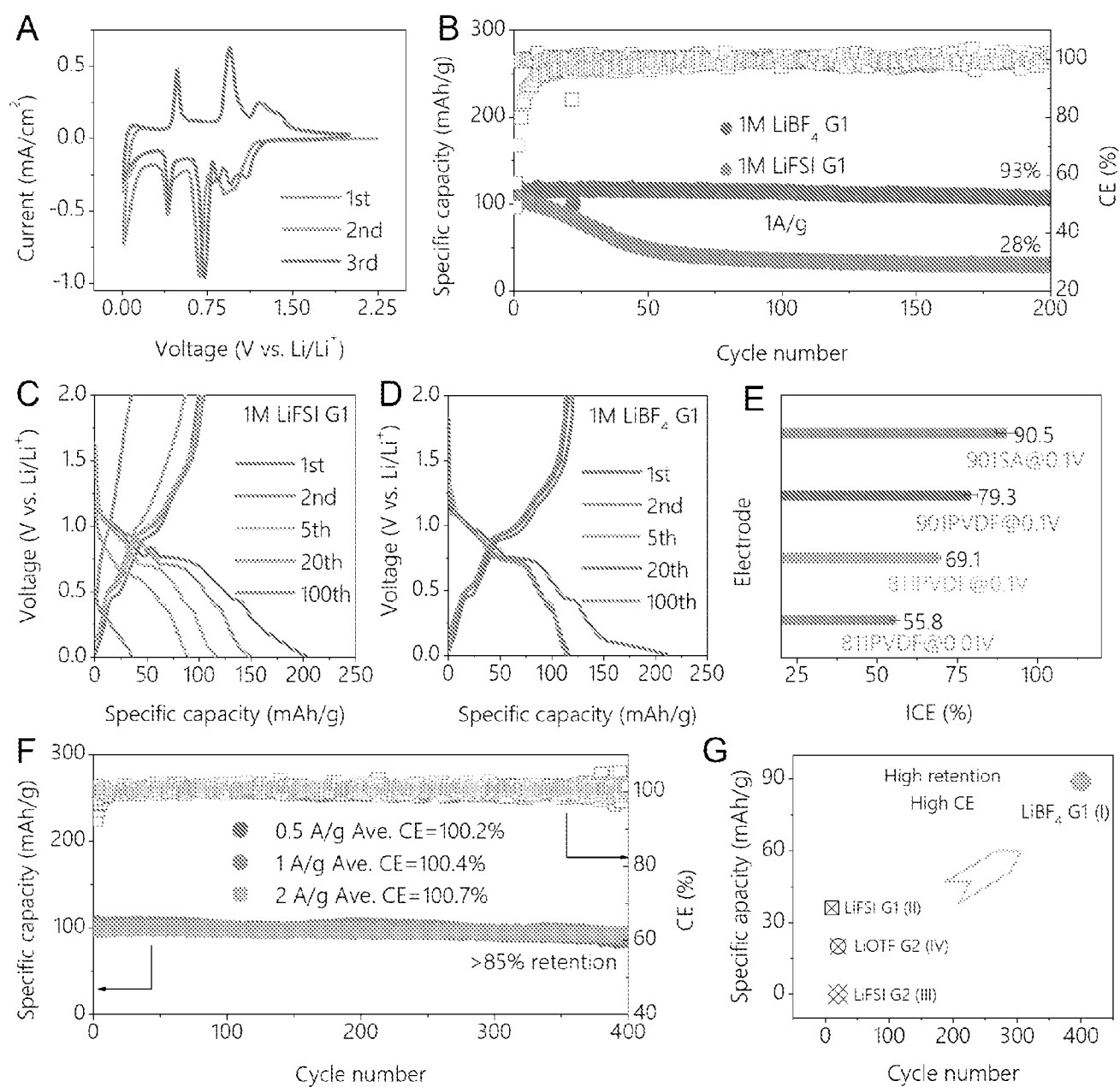


FIG. 7

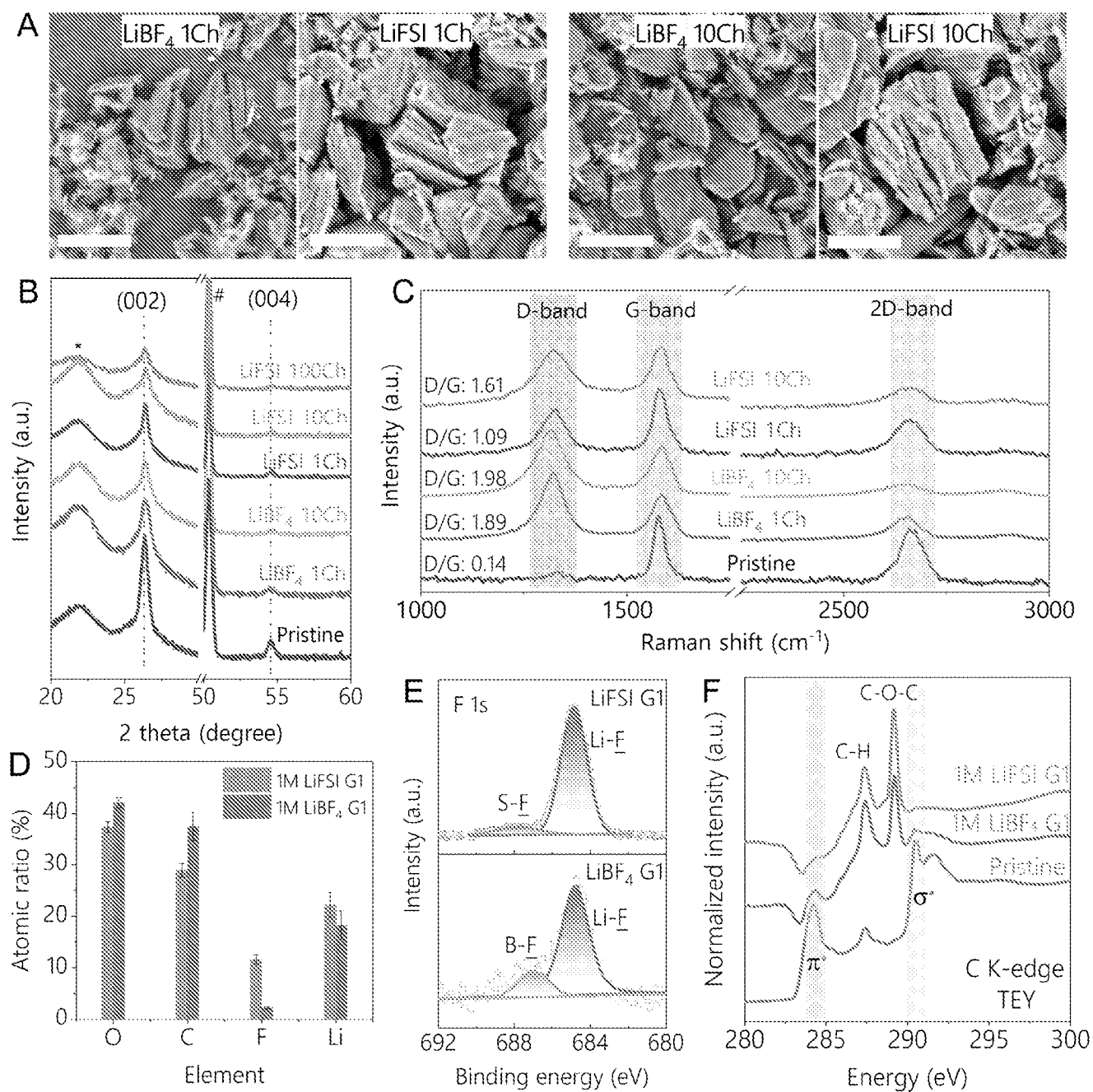


FIG. 8

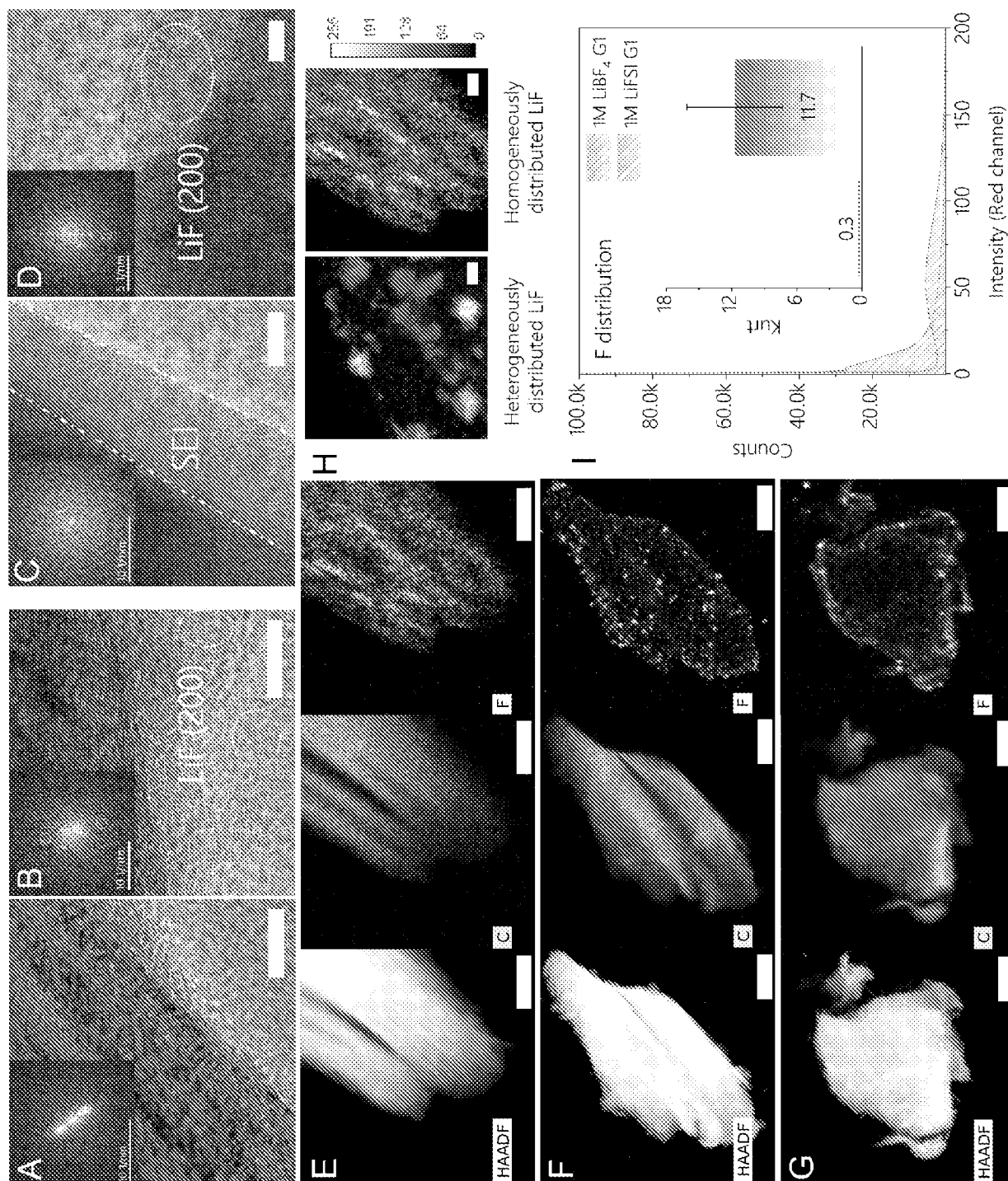


FIG. 9

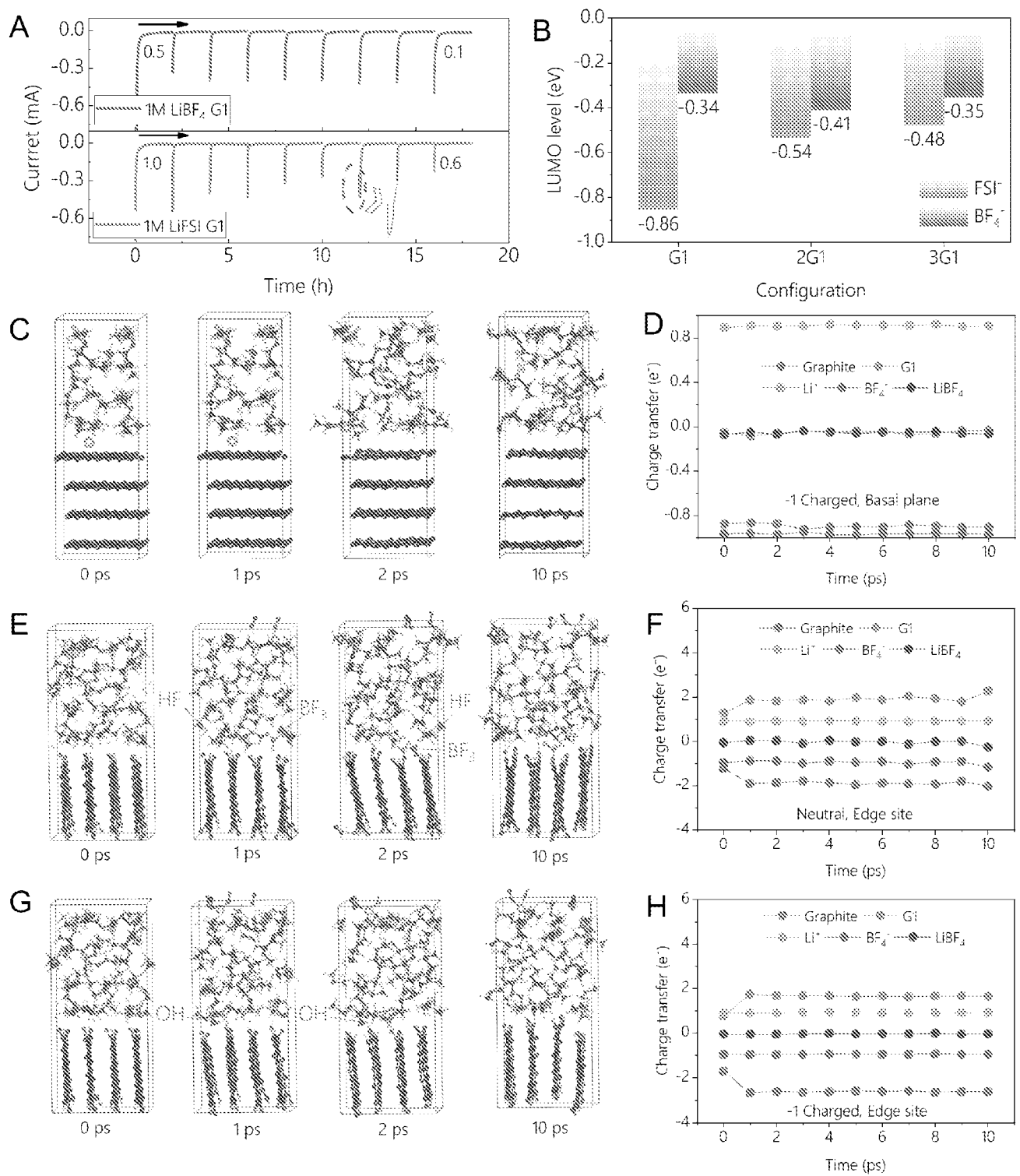
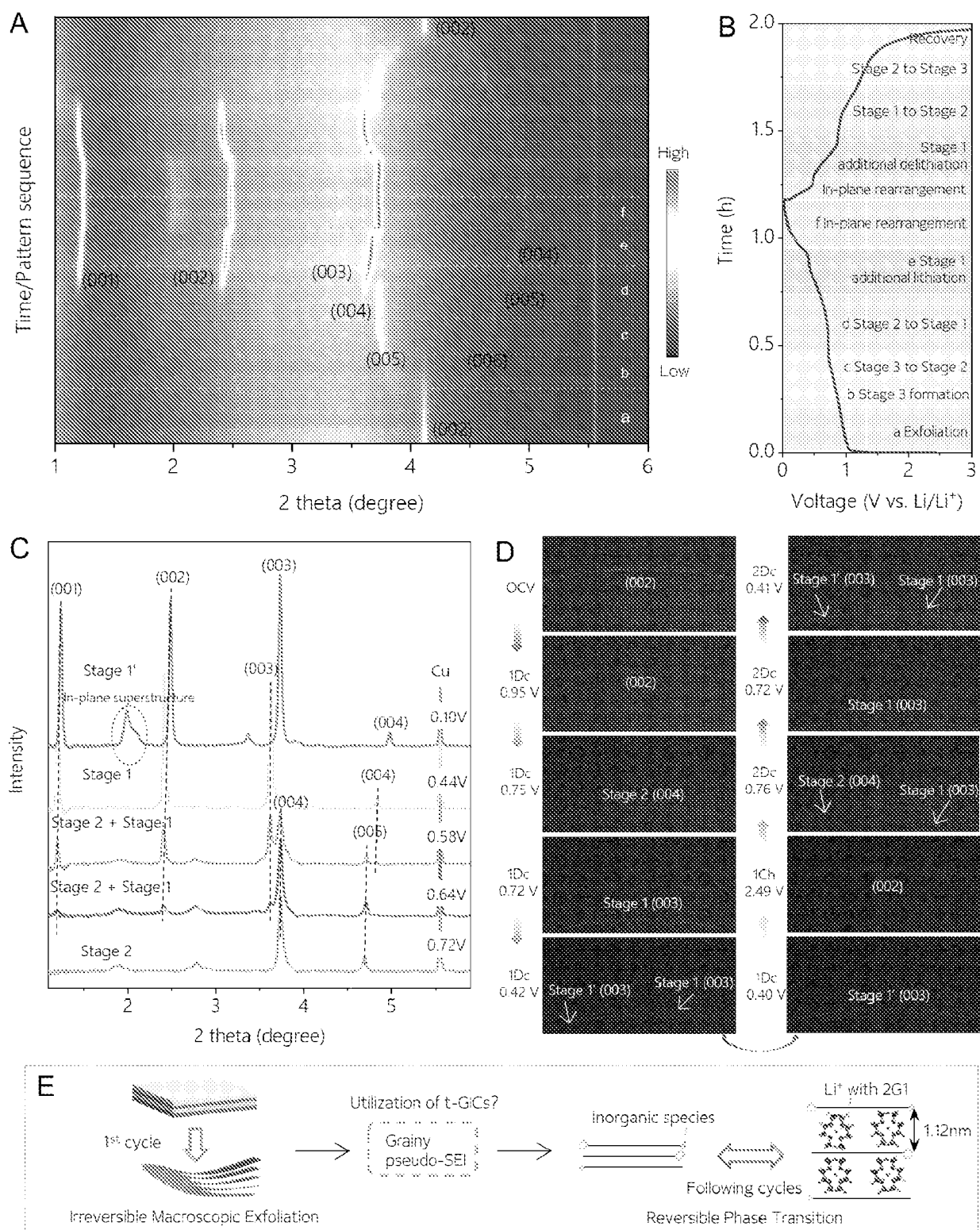


FIG. 10



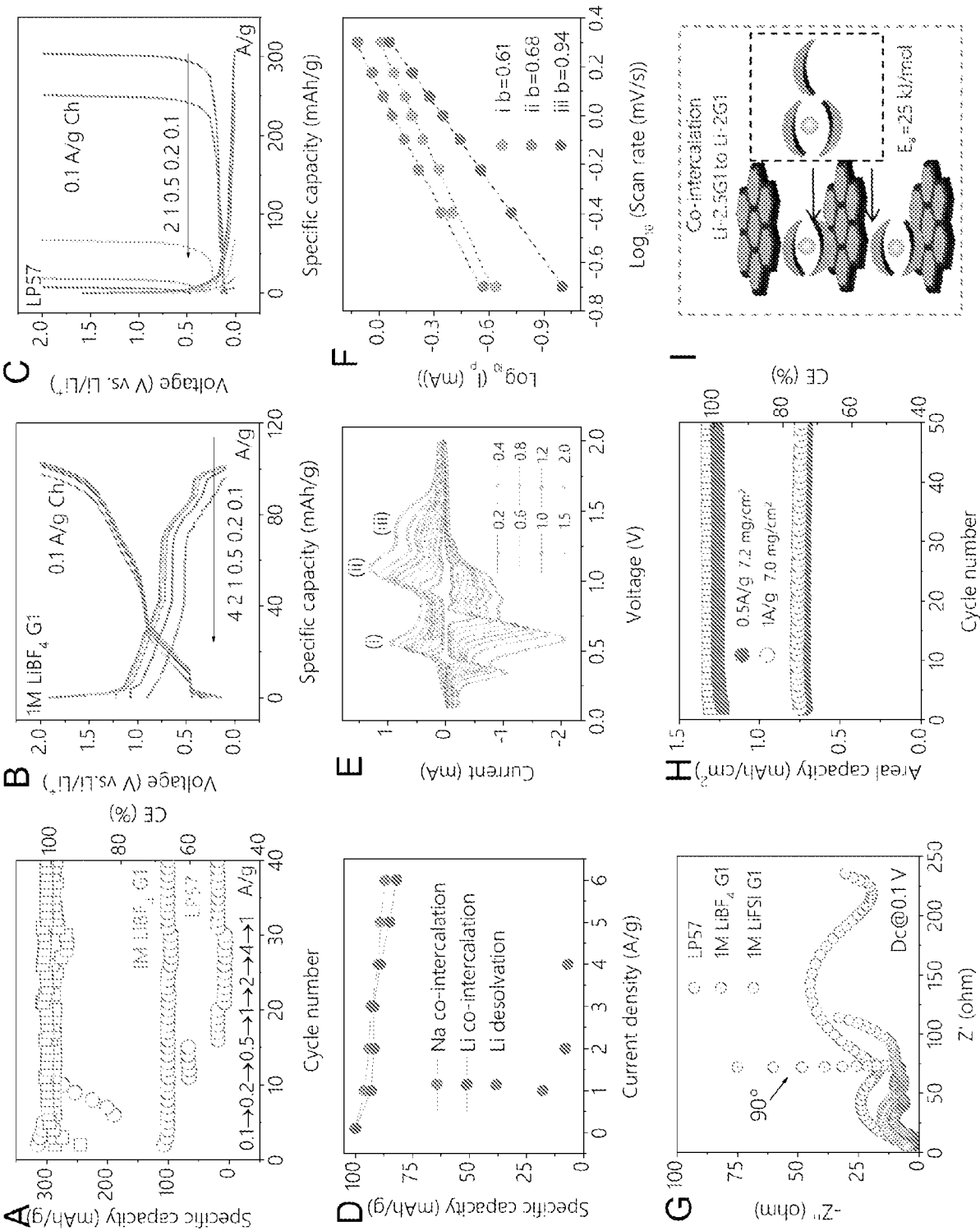
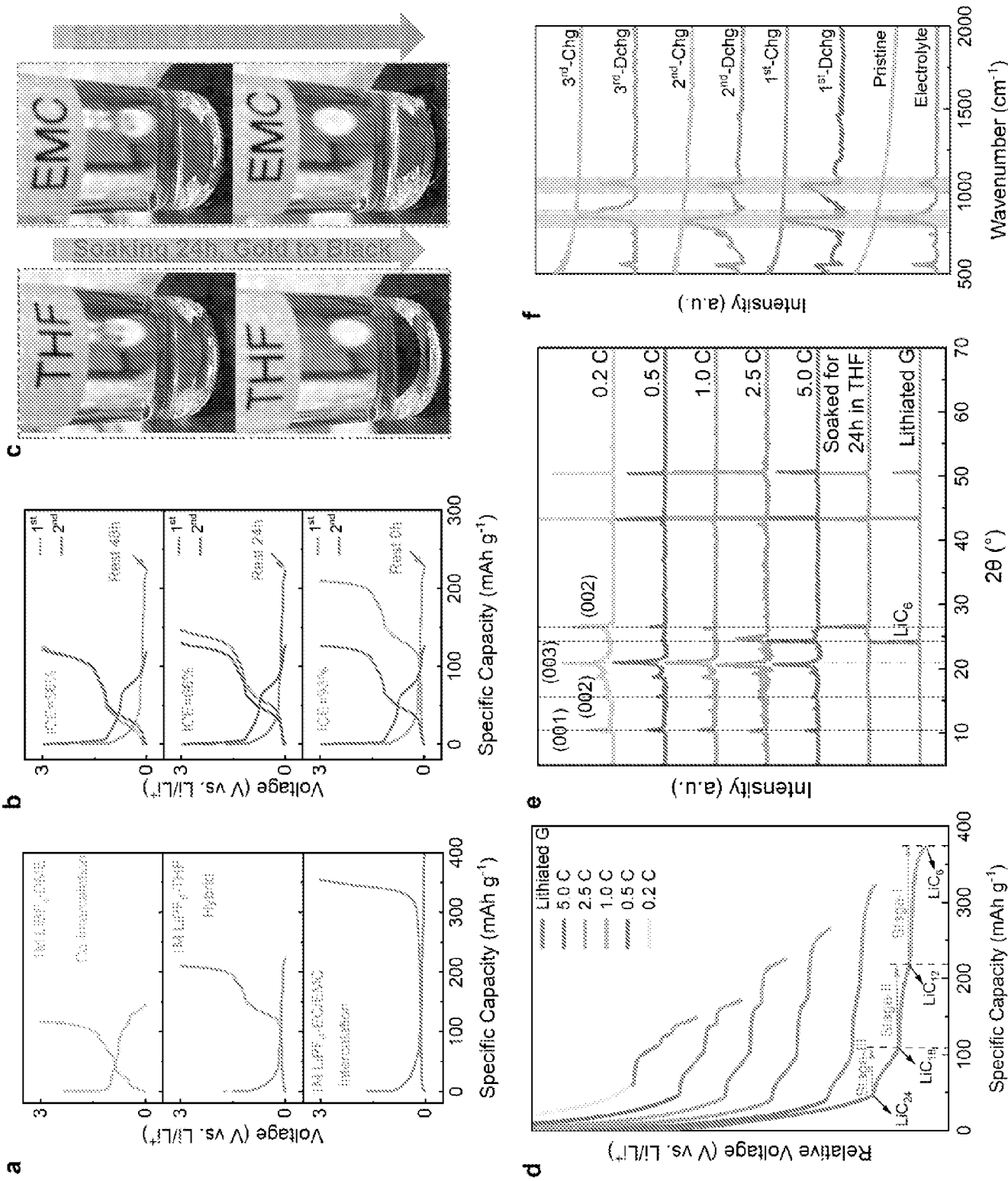


FIG. 12



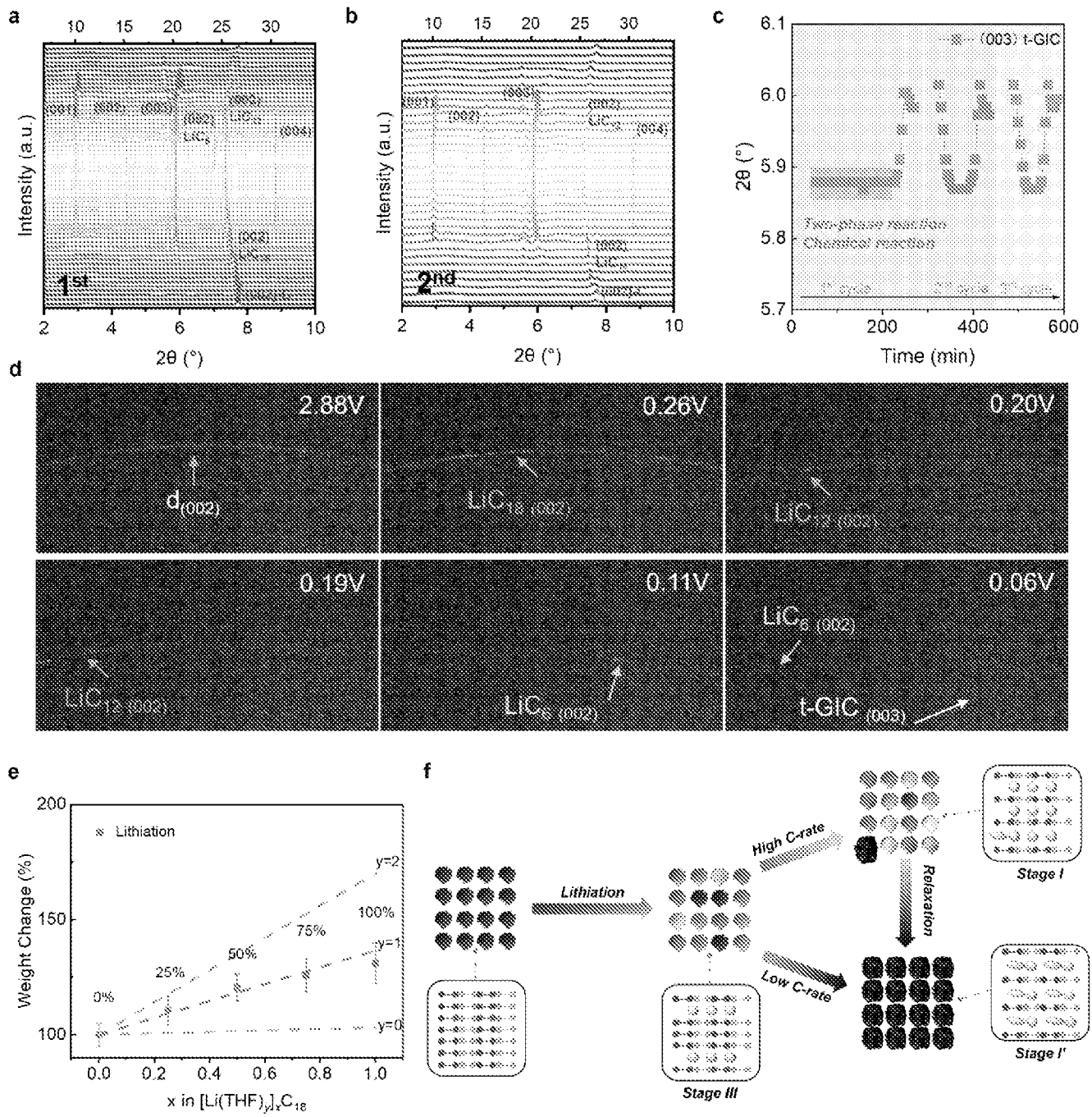


FIG. 14

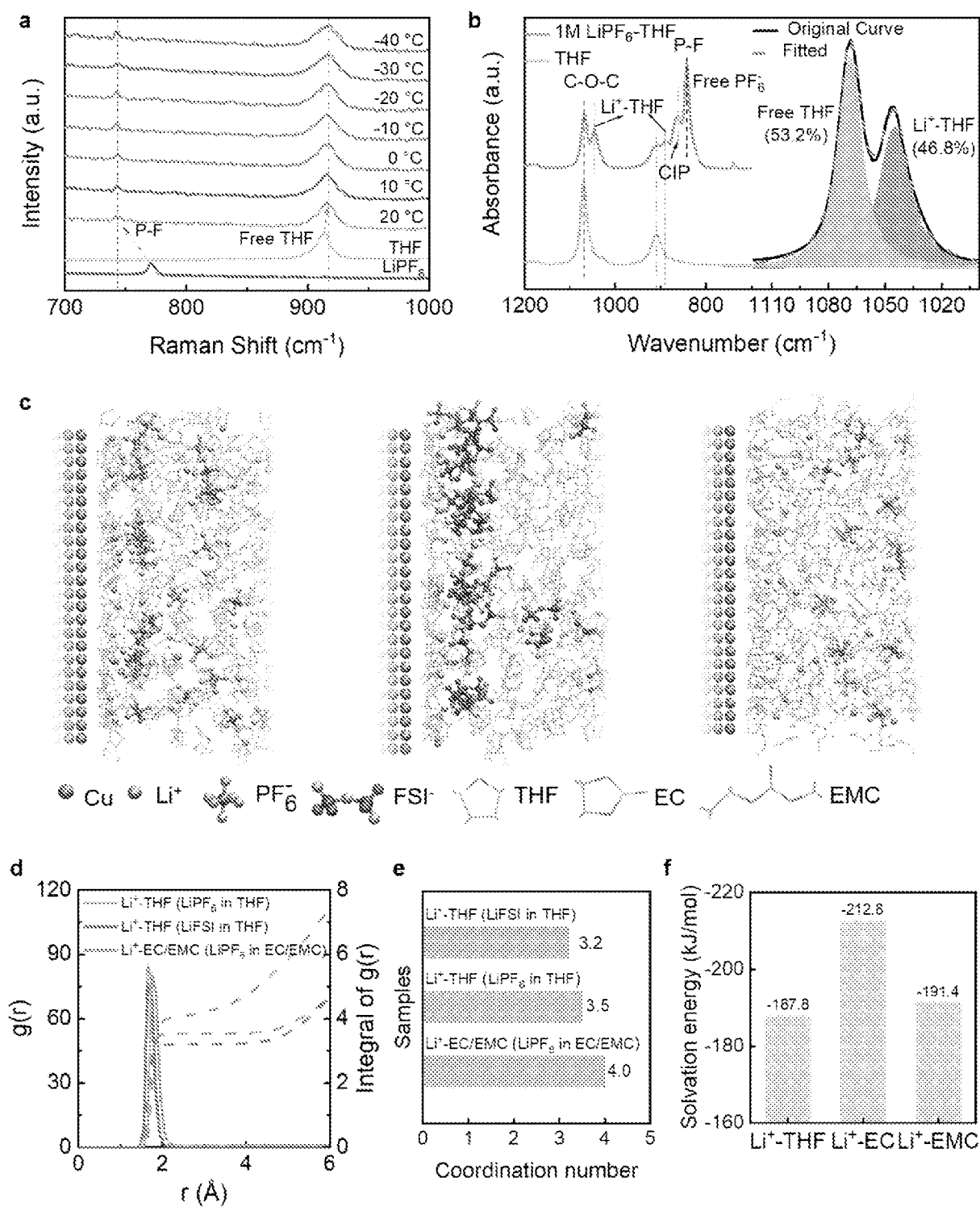


FIG. 15

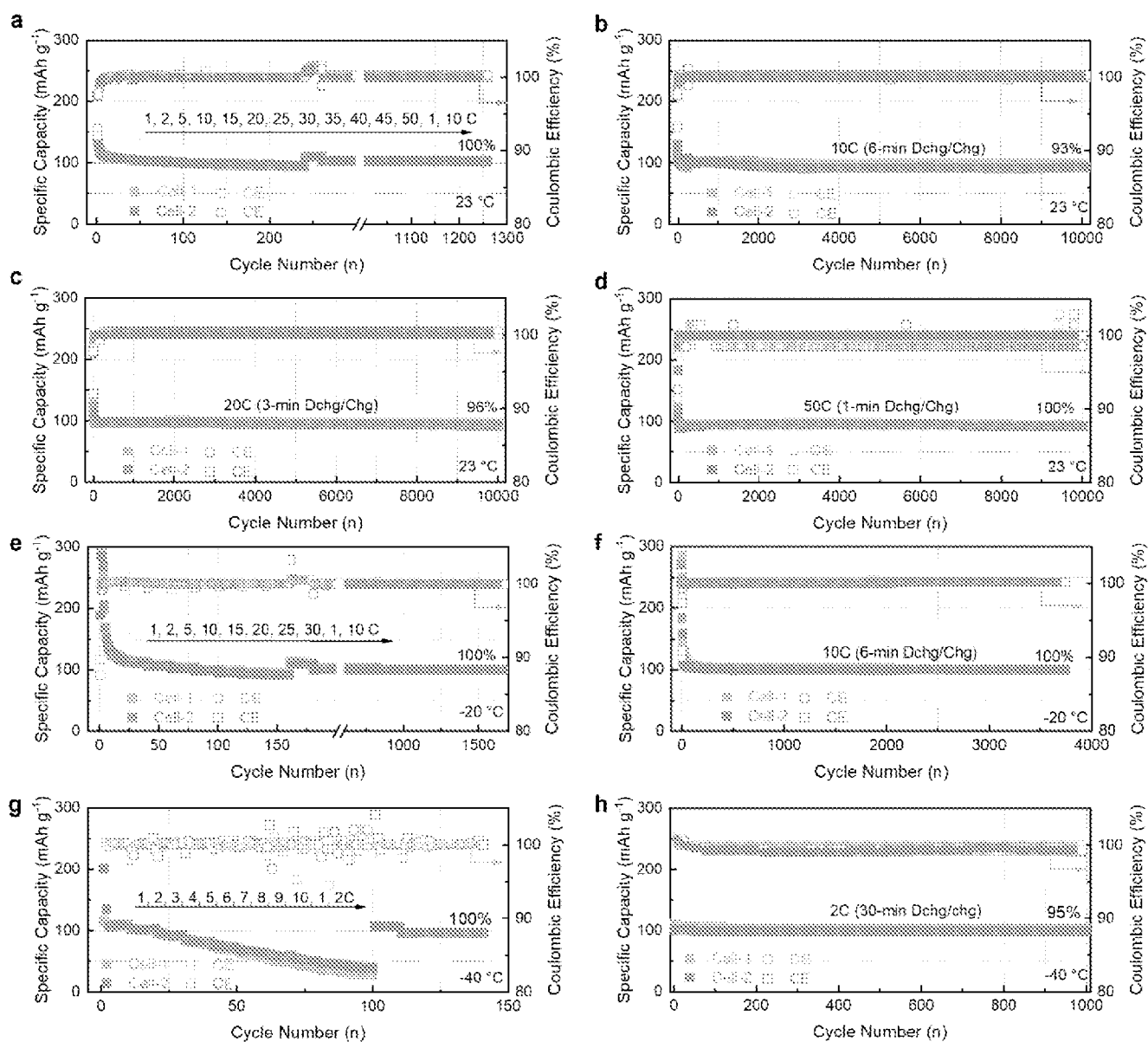


FIG. 16

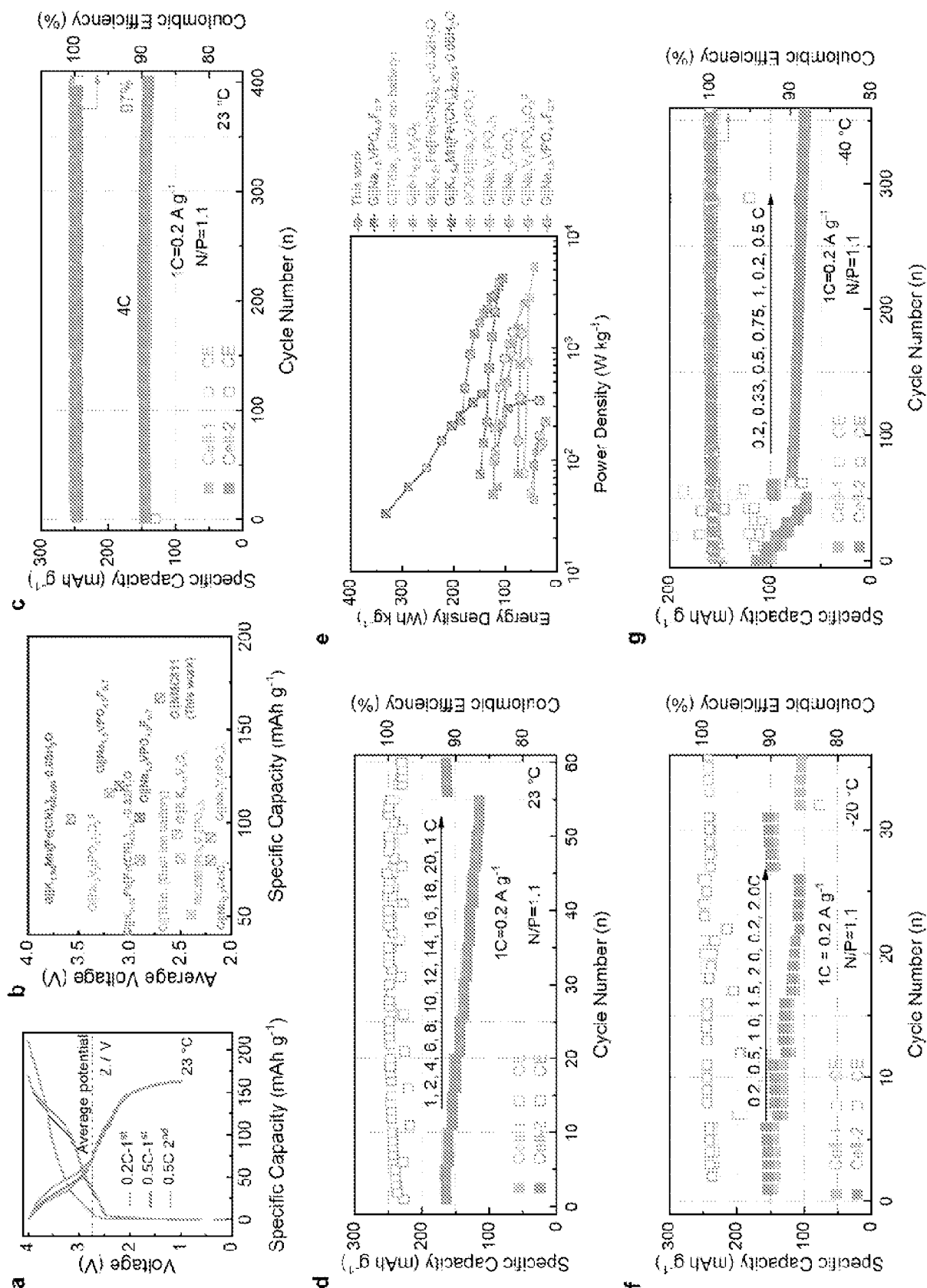


FIG. 17

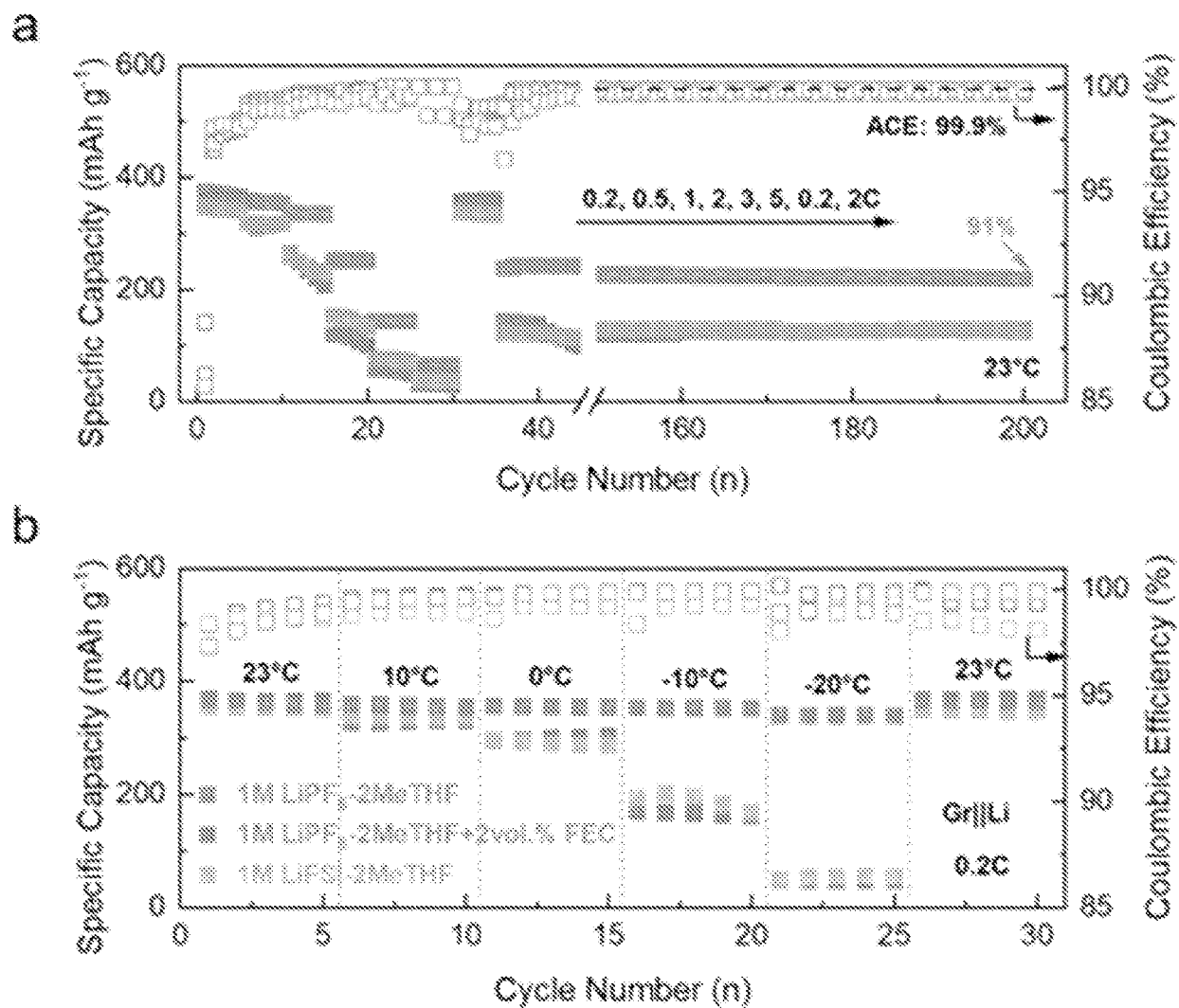


FIG. 18

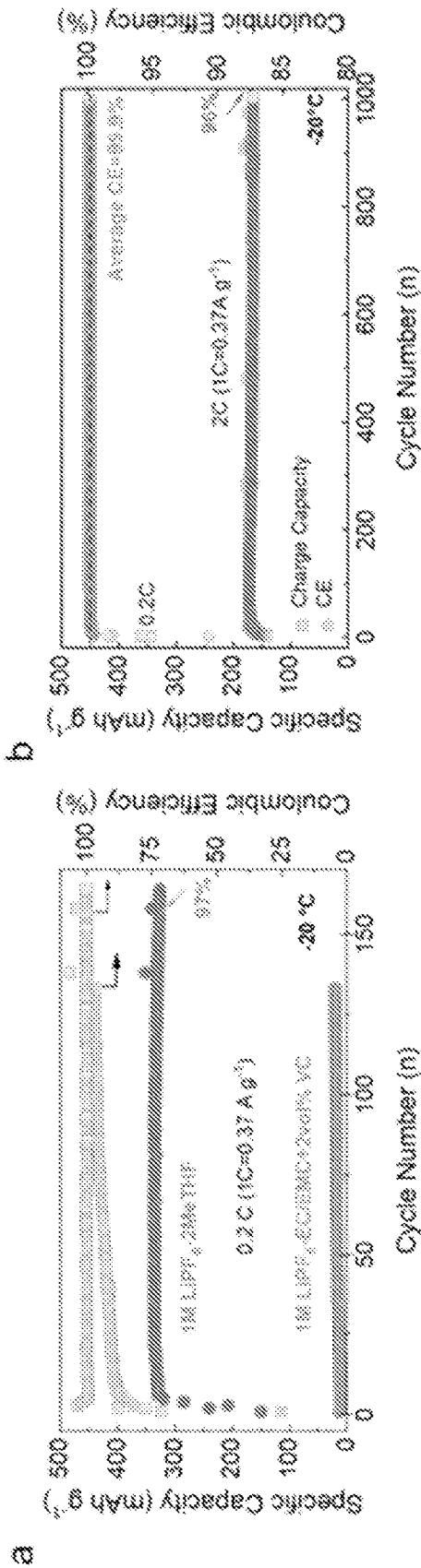


FIG. 19

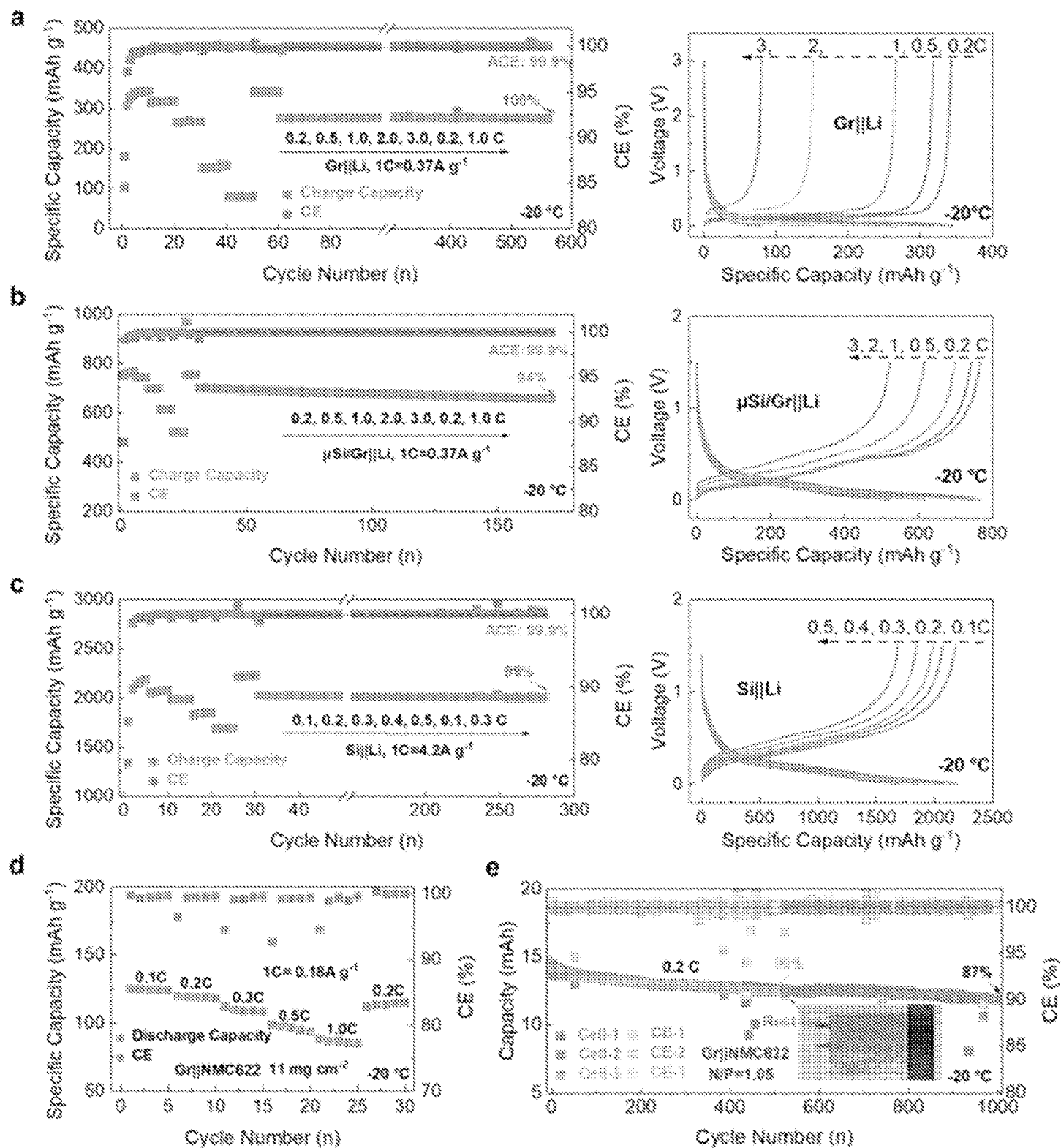


FIG. 20

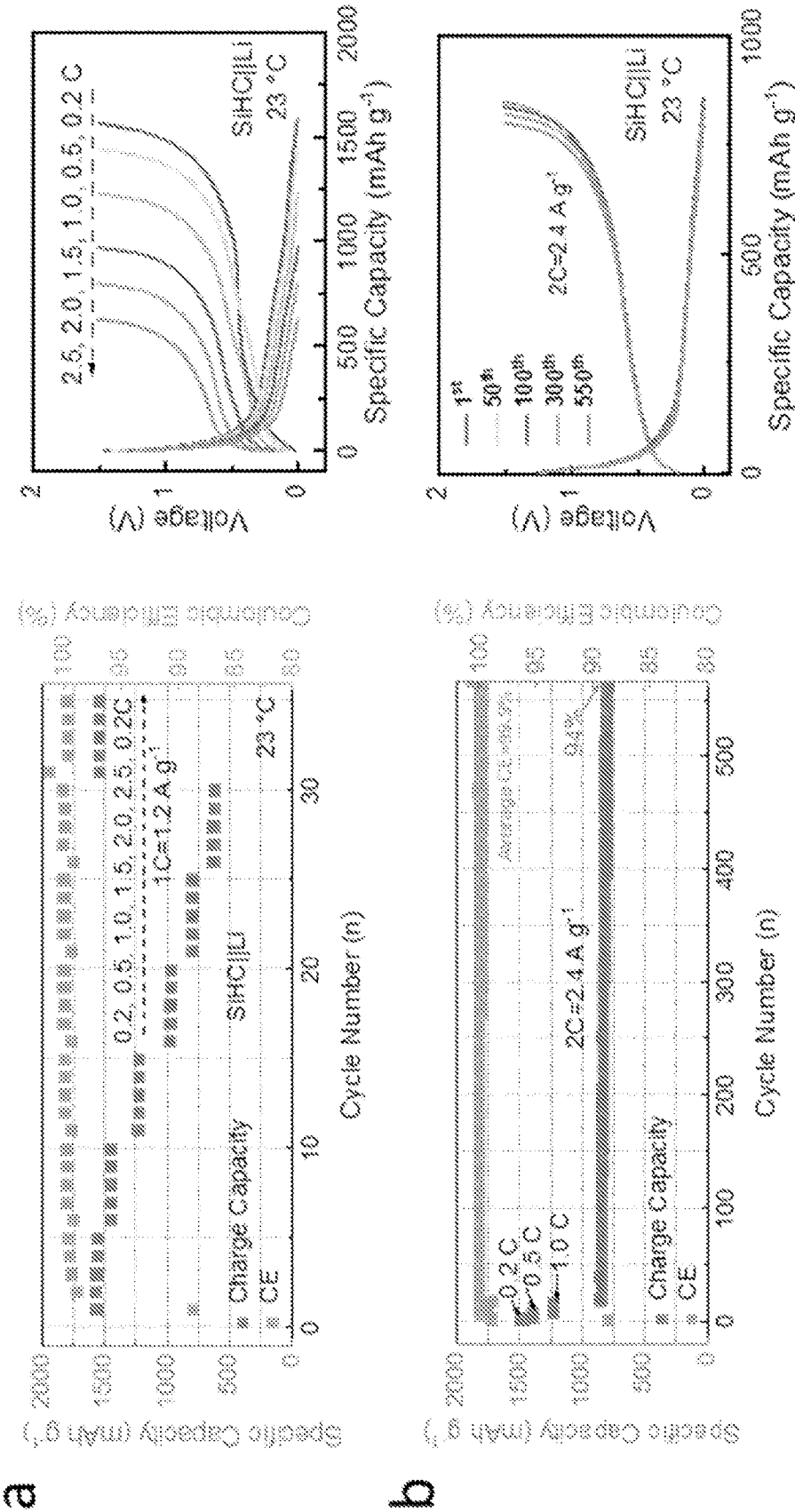


FIG. 21

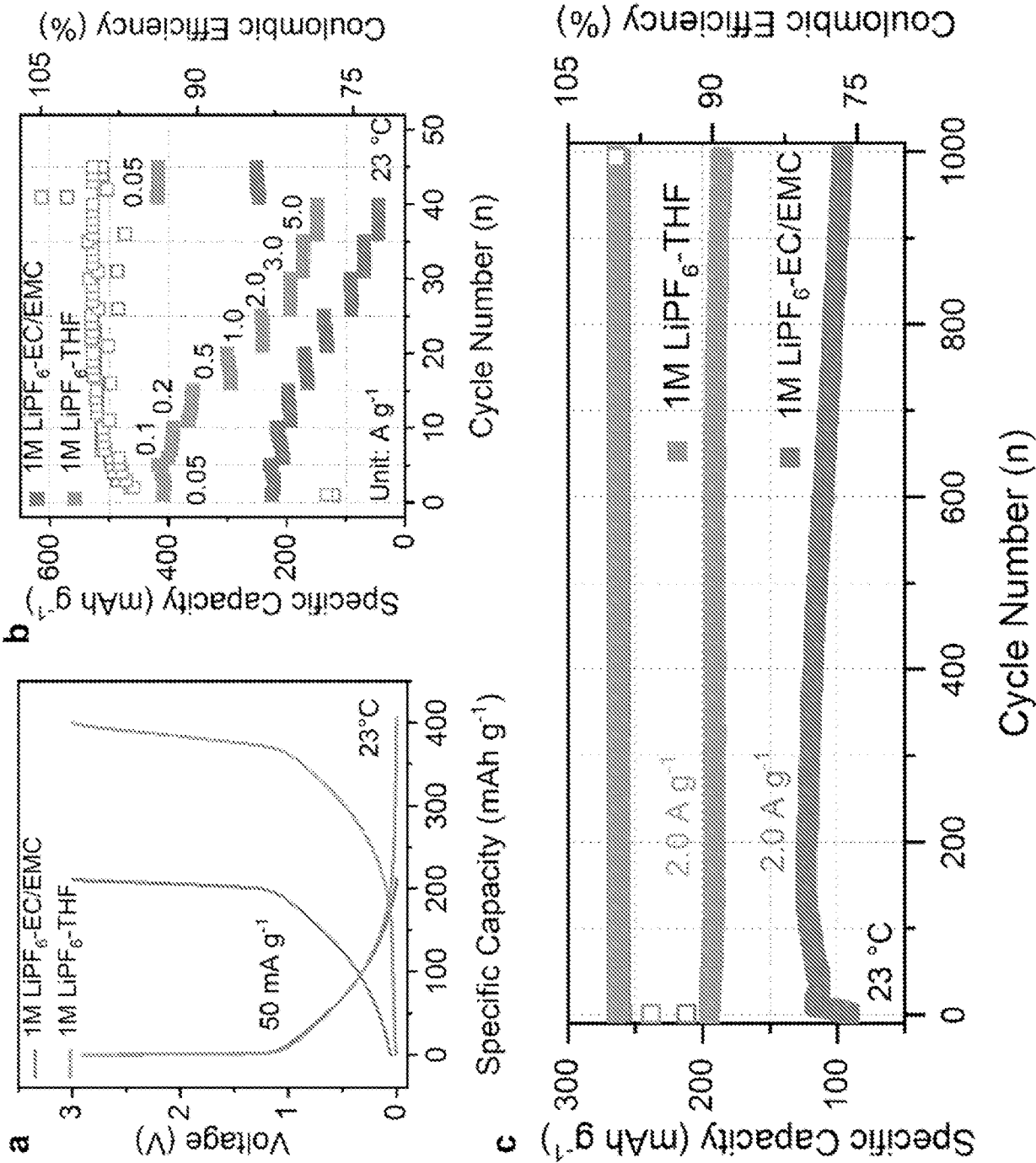


FIG. 22

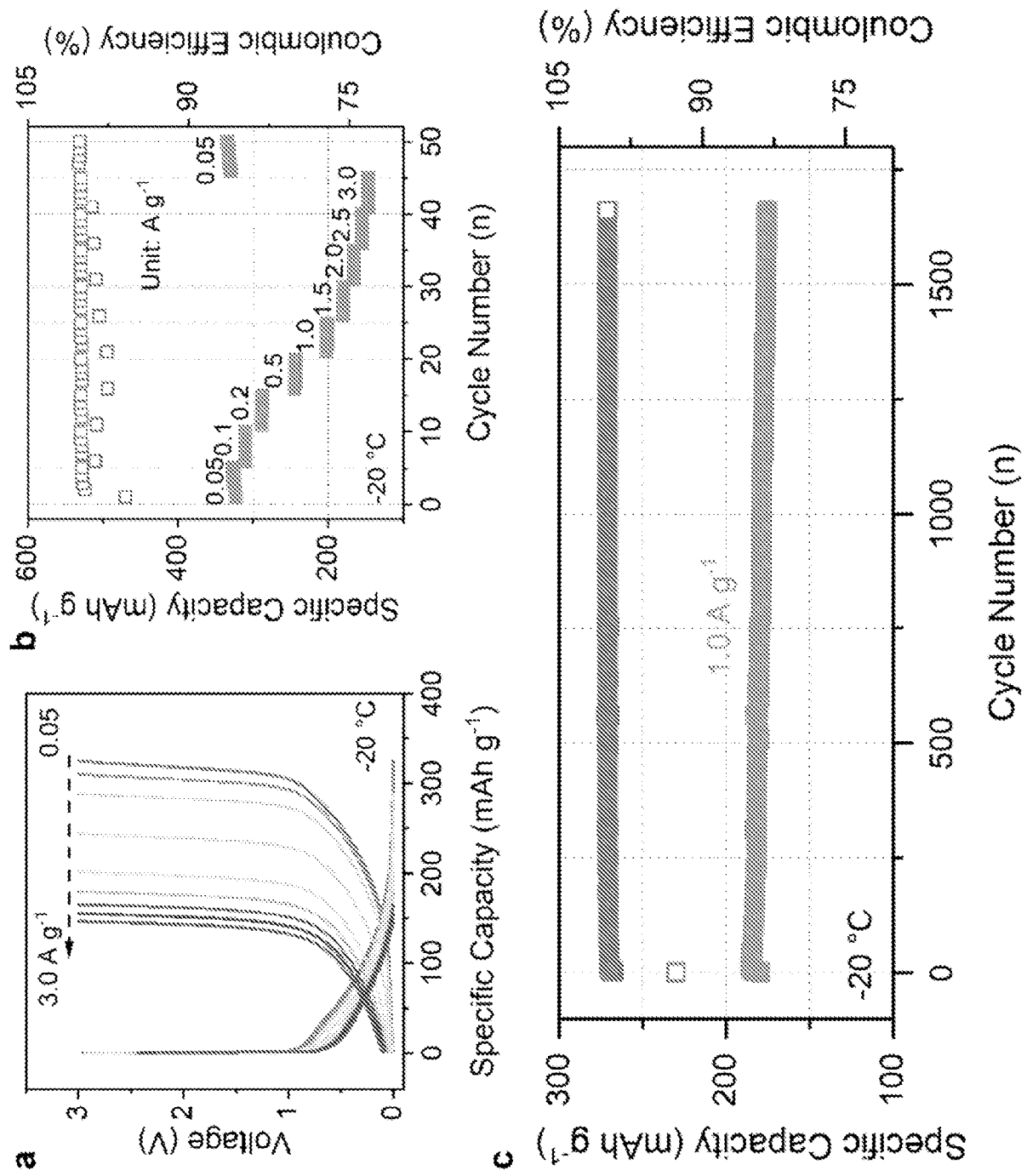


FIG. 23

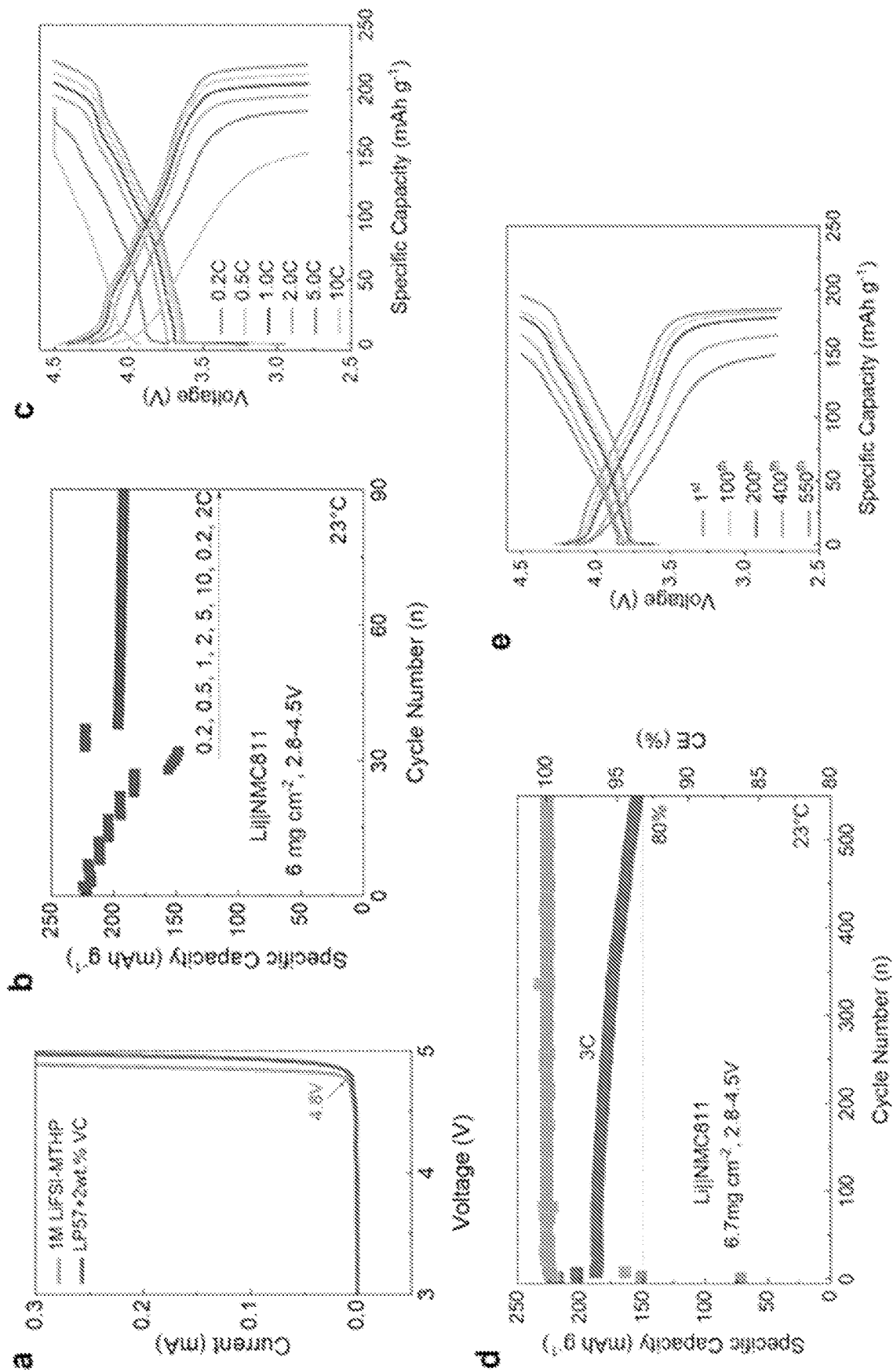


FIG. 24

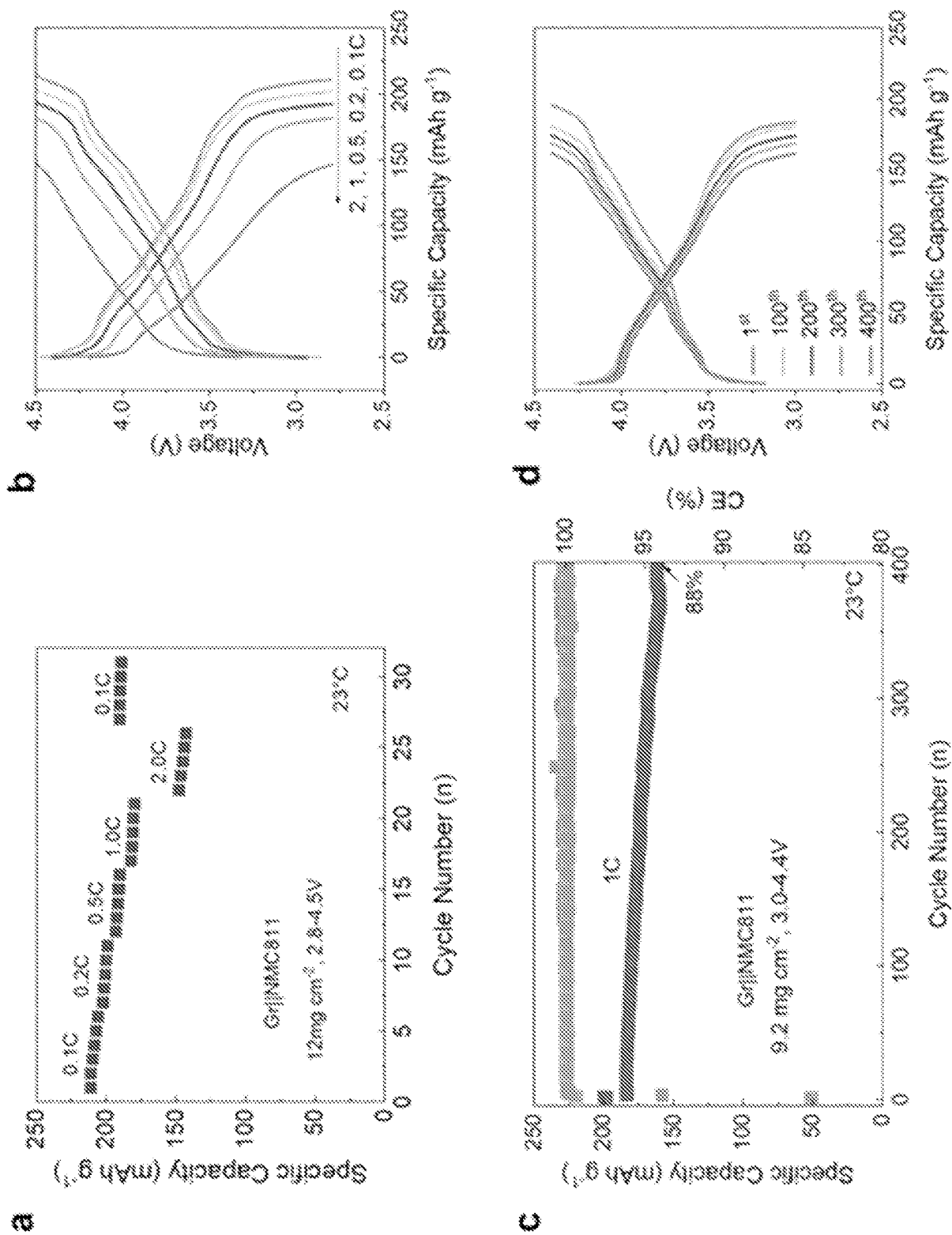


FIG. 25

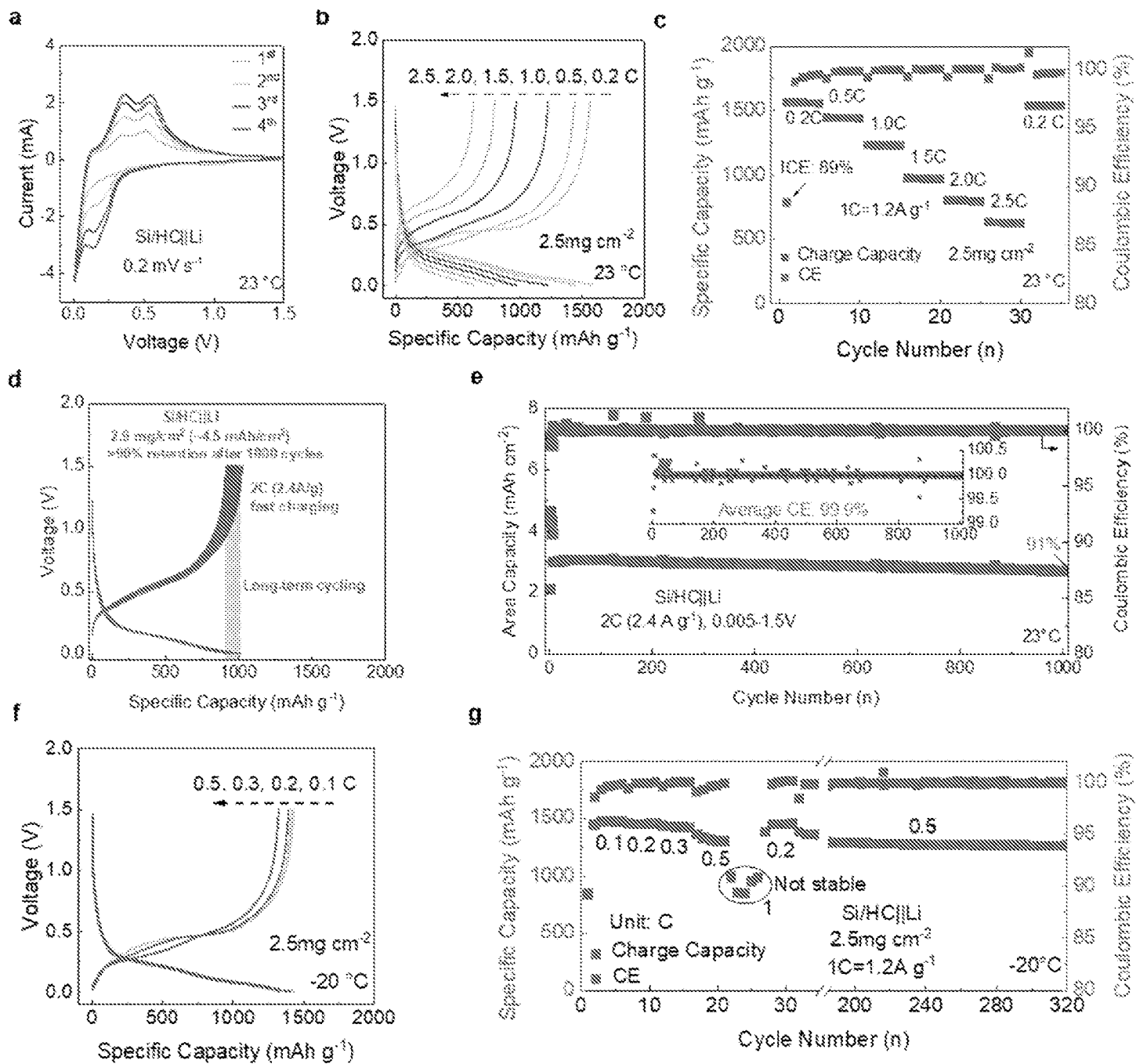


FIG. 26

FIG. 27

