Interface stabilization via lithium bis(fluorosulfonyl)imide additive as a key for promoted performance of graphite||LiCoO₂ pouch cell under −20 °C

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ABSTRACT

The effects of lithium bis(fluorosulfonyl)imide, Li[N(SO₂F)₂] (LiFSI), as an additive on the low-temperature performance of graphite||LiCoO₂ pouch cells are investigated. The cell, which includes 0.2M LiFSI salt additive in the 1M lithium hexafluorophosphate (LiPF₆)-based conventional electrolyte, outperforms the one without additive under −20 °C and high charge cutoff voltage of 4.3 V, delivering higher discharge capacity and promoted rate performance and cycling stability with the reduced change in interfacial resistance. Surface analysis results on the cycled LiCoO₂ cathodes and cycled graphite anodes extracted from the cells provide evidence that a LiFSI-induced improvement of high-voltage cycling stability at low temperature originates from the formation of a less resistive solid electrolyte interphase layer, which contains plenty of LiFSI-derived organic compounds mixed with inorganics that passivate and protect the surface of the cathode and anode from further electrolyte decomposition and promotes Li⁺ ion-transport kinetics despite the low temperature, inhibiting Li metal-plating at the anode. The results demonstrate the beneficial effects of the LiFSI additive on the performance of a lithium-ion battery for use in battery-powered electric vehicles and energy storage systems in cold climates and regions.

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I. INTRODUCTION

Nowadays, lithium (Li)-ion batteries (LIBs) are ubiquitously utilized as power sources for various electronic devices, electric vehicles (EV), and stationary energy storage systems (ESS). State-of-the-art LIB technology, however, still shows a drastic decrease in energy and power at low temperatures below 0 °C^{1,2} and in special environments such as high latitude, cold weather, and aerospace. Much less attention has been paid to the phenomena and performance improvement of LIBs at low temperatures than high temperatures, despite the exposure of commercialized EV and ESS to changing temperatures outdoors. The low-temperature performance of LIB is hampered by multiple factors including the

reduced Li⁺-ion conductivity in the cathode/anode, the electrolyte, the solid electrolyte interphase (SEI) layer, and a phase change of high melting-point (mp) electrolyte component from liquid to solid.¹⁴ A commercial LIB includes a conventional carbonate-based organic liquid electrolyte that is typically composed of lithium hexafluorophosphate (LiPF₆) salt, ethylene carbonate (EC), and linear carbonate solvents such as dimethyl carbonate (DMC), diethyl carbonate (DEC), and/or ethyl methyl carbonate (EMC). EC is a high melting-point (mp) molecule (mp = 36 °C), and the mp of EMC is relatively low (mp = −14.5 °C). Despite the high ionic conductivity of LiPF₆ salt, its disadvantage is thermal instability and reactivity to moisture or protic species releasing a toxic, highly aggressive, and undesirable gases, including HF, which is a safety

issue.⁵ Importantly, a major issue in low-temperature LIB operation is the occurrence of severe Li metal-plating and its dendritic growth at the graphite anode due to the sluggish diffusion kinetics of Li^+ -intercalation, which is different from that at room temperature. Unless otherwise being charged at quite a low rate such as 0.02C taking 50 h, Li metal-plating occurs by the sluggish kinetics of Li^+ -diffusion in the electrolyte as well as at both surfaces and bulk of the graphite anode during a sub-freezing charge, which is permanent and cannot be removed with cycling, leading to a sudden performance failure and safety hazard.⁵ In the perspectives of electrolyte technology, various approaches have been suggested to improve LIB performance, including the blending of several solvents to ternary and quaternary electrolytes^{4,6–8} for lowering the mp and the use of functional electrolyte additives^{3,9} and mixed lithium salts or lithium salt as an additive, most of which, however, focus on the performance improvement under room and elevated temperatures.² A few literature studies on the development of new lithium salts such as lithium bis(oxalate)borate (LiBOB) or lithium difluoro(oxalato)borate (LiDFOB) for low-temperature operation of LIBs are available.¹⁰ For example, 0.9M LiDFOB:0.1M lithium tetrafluoroborate (LiBF_4) mixed salts in EC:dimethyl sulfoxide (DMS):EMC mixed solvents (1:1:3 by volume) showed an improved cycling stability at -20°C than the LiPF_6 -based electrolyte.¹¹ Recently, lithium bis(fluorosulfonyl)imide (LiFSI) attracts considerable attention as a new salt for both Li-ion and Li metal batteries, despite high cost. This salt shows an improved thermal and electrochemical stability, higher ionic conductivity, and a higher Li transference number compared to conventional LiPF_6 .^{5,12,13} LiFSI does not hydrolyze in the presence of water to release HF, showing the improved chemical durability and electrochemical performance of various half-cells of LiCoO_2 ,¹³ graphite,^{14–16} and Si,¹⁷ and full-cells of graphite|| LiCoO_2 ¹³ and graphite|| $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ ¹² when being used as main salt or mixed salt under room and elevated temperatures. Wang *et al.* reported that the function of LiFSI as a mixed salt is limited when being charged to high voltages up to 4.45 V.^{12,18} Studies of the use and effects of LiFSI as an additive on the low-temperature performance of high-voltage LiCoO_2 -based LIB have yet to be reported and clarified.

Herein, we present a LiFSI additive-assisted graphite|| LiCoO_2 high-voltage pouch full-cell that achieves a Li metal-plating-free LIB under -20°C , in contrast to the occurrence of Li metal-plating in the cell with a commercial LiPF_6 -based electrolyte under the same test condition. Furthermore, systematic studies of the effects of the LiFSI additive on the interfacial phenomena of the graphite anode and the LiCoO_2 cathode were conducted utilizing *ex situ* surface-sensitive attenuated total reflectance (ATR) FTIR spectroscopy and x-ray photoelectron spectroscopy (XPS). A basic understanding on the interfacial reaction behavior among cathode, anode, and LiFSI additive-containing electrolyte and its correlation with the enhanced low-temperature cycling performance are discussed, which would pave the way for a wider use of LIB-powered EV and ESS.

II. EXPERIMENTAL SECTION

A. Electrochemistry

The anodes were prepared by coating the slurry with the composition of 85 wt. % natural graphite active material (BTR), 5 wt. %

carbon black (super-P, Timcal), and 10 wt. % polyvinylidene fluoride (PVdF; Aldrich) onto a copper foil. The cathodes, whose slurry was composed of 80 wt. % LiCoO_2 active material (supplied from an industry), 10 wt. % carbon black (super-P, Timcal), and 10 wt. % PVdF (Aldrich), were coated on an Al foil. Active mass loading of the LiCoO_2 cathode was $\approx 4 \text{ mg cm}^{-2}$, and the N/P ratio was 1.1. The coated anodes and cathodes were dried at 110°C for 12 h under vacuum prior to battery assembly.

The ionic conductivity of electrolytes, which are 1M LiPF_6 /EC:EMC (3:7 volume ratio, Panax E-Tec) as the base electrolyte (henceforth, Base EL) with various concentrations of LiFSI (battery grade, >99.99% purity, Lichem, Ltd.) from 0M to 0.5M resulting in the total concentration of Li^+ ion in the electrolyte from 1.0M to 1.5M, was measured using a conductivity meter (Mettler Toledo S230) at room temperature under Ar atmosphere. The conductivity meter was calibrated with the standard solution of $1413 \mu\text{S cm}^{-1}$ conductivity before the measurement. We determined 0.2M (according to $\approx 3.07 \text{ wt. \%}$) as the optimized concentration of LiFSI salt type-additive in maintaining a high enough ionic conductivity of the electrolyte [Fig. 1(a)].

Linear sweep voltammetry (LSV) of electrolytes was conducted to evaluate the anodic stability of electrolytes at a scan rate of 1 mV s^{-1} from an open-circuit potential of ≈ 3.4 to 6.0 V vs Li/Li^+ for charging of full-cells to 4.3 V (corresponding to 4.35 V vs Li/Li^+) using a three-electrode cell that included LiCoO_2 working electrode, lithium metal counter electrode, lithium metal reference electrode, and base electrolyte without and with 0.2M LiFSI additive.

FIG. 1. (a) Changes in the room temperature ionic conductivity of the electrolyte as a function of the concentration of LiFSI added to the base electrolyte (Base EL) of 1M LiPF_6 /EC:EMC (3:7 volume ratio) and (b) linear sweep voltammograms of three-electrode cells including the LiCoO_2 working electrode and Base EL without and with 0.2M LiFSI additive.

The dimension of the LiCoO_2 cathode for pouch cells was 20 mm $\times$ 20 mm, and that of the graphite anode was 22 mm $\times$ 22 mm. The pouch cells were 60 mm long, 60 mm wide, and 3.5 mm thick. An Al tab was welded to the cathode, and a Ni tab was welded to the anode for connecting to external circuits. Pouch cells included the separator (Celgard C210) and were filled with 1 ml of base electrolyte without and with 0.2M LiFSI additive in a dry room with a controlled dew point of less than -45°C . After electrolyte filling, the pouch cells were vacuum sealed with a compact vacuum sealer. The resultant graphite $\parallel$ LiCoO₂ pouch full-cells were cycled under -20°C for 50 cycles at a rate of 0.2C (28 mA g⁻¹) in the constant temperature chamber (TH-KE-065, JEIO Tech) after a formation cycle between 3.0 V and 4.3 V at 0.1C (14 mA g⁻¹) at room temperature, using a multichannel battery cycler (WBCS3000, Won-A Tech). 1C in this work is defined as 140 mA g⁻¹, which is the current required to charge the LiCoO₂-based battery in one hour at room temperature. AC impedance measurement was conducted at -20°C after the 1st and 50th cycles using an impedance spectroscopic analyzer (VSP SP-150, Bio-Logic) in the frequency range from 100 kHz to 10 mHz with an amplitude of 10 mV. The rate capability of the pouch cells was tested under -20°C by first charging to 4.3 V at 0.1C and then discharge to 3.0 V at variable rates ranged from 0.1C to 5C.

B. Characterization

To monitor a possible Li metal-plating, particle morphology changes of graphite anodes with cycling were analyzed using field emission scanning electron microscopy (FE SEM; FEI Sirion) at 10 kV. Crystal structural changes of graphite anodes and LiCoO₂ cathodes were examined using *ex situ* x-ray diffraction (XRD) analysis. Those were mounted in a tightly sealed sample holder to avoid atmospheric contamination and measured from 10° to 80° at a scan rate of 1° min^{-1} at 40 kV and 40 mA using a powder x-ray diffractometer (Rigaku D/MAX-2200) equipped with Ni-filtered Cu-K α radiation. The composition of the SEI layer of graphite anodes and LiCoO₂ cathodes was analyzed by *ex situ* ATR FTIR spectroscopy using a Nicolet 6700 FTIR spectrometer equipped with a MCT detector. The cycled anodes and cathodes in the pouch cells were washed with DMC for the removal of the residual electrolyte followed by drying in the glove box at room temperature. They were directly mounted on the tightly closed ATR unit in the glove box to avoid atmospheric contamination during transportation to a dry nitrogen-purged sample compartment of the IR instrument as well as during IR measurement. The spectra were collected with 512 scans and a spectral resolution of 4 cm^{-1} . XPS surface analysis was conducted using XPS (Thermo, MultiLab 2000) with an Al K α X-ray source at 15 kV. High resolution spectra were obtained at a power of 150 W under a base pressure of 5×10^{-10} mbar with a pass energy of 100 eV. The cycled anodes and cathodes after washing with DMC were transferred from the glove box to the XPS chamber using a vacuum-sealed container without exposure to the air. The spot size was about 500 μm , and the pass energy was 30 eV. Binding energy was corrected based on the C 1s level at 284.5 eV.

III. RESULTS AND DISCUSSION

A. Ionic conductivity and linear sweep voltammetry

Figure 1(a) shows the change in the room temperature ionic conductivity of the electrolyte as a function of the concentration of

LiFSI that was added to 1M LiPF₆/EC:EMC. As increasing the concentration of LiFSI from 0M to 0.5M, corresponding to the total concentration of Li⁺-ion in the electrolyte from 1.0M to 1.5M, the ionic conductivity of the electrolyte slightly decreases from 9.12 mS cm⁻¹ of base electrolyte of 1M LiPF₆/EC:EMC. The addition of LiFSI beyond 0.3M (total concentration of Li⁺ ion >1.3M) causes a drastic reduction in the ionic conductivity below 8.5 mS cm⁻¹. This is the similar tendency to the electrolyte of LiPF₆ only that was reported in the literature;^{19,20} the maximum ionic conductivity is reached on 1M, from which ionic conductivity decreases as increasing the concentration of LiPF₆ (>1.2M). Despite higher ionic conductivity of LiFSI than LiPF₆ at the fixed same concentration, the reduction in the ionic conductivity with the concentration of LiFSI is due to an increase in the viscosity and the salt association as described by Ding *et al.*²⁰ To keep the ionic conductivity high enough and to emphasize the effectiveness LiFSI, we determined 0.2M [Fig. 1(a)] as the optimized concentration of LiFSI additive.

The anodic stability of the base electrolyte without and with 0.2M LiFSI additive was comparatively tested utilizing LSV with three-electrode cells including the LiCoO₂ working electrode. Both electrolytes [Fig. 1(b)] exhibit two anodic peak currents at ≈ 4.1 V and ≈ 4.5 – 4.6 V, which are associated with Co oxidation from Co³⁺ to Co⁴⁺ along with electrochemical electrolyte oxidation. A large anodic current rise from 5.2 V is due to the oxidative decomposition of a whole electrolyte. A detailed look at the voltage region of 4.0–4.2 V in the inset presents the anodic peak current of the LiFSI additive-containing electrolyte at 4.086 V, which is slightly lower than 4.115 V of the base electrolyte. The LiFSI additive is electrochemically oxidized prior to LiPF₆ probably contributing to the formation of the SEI layer at the cathode and anode. As a reference, LSV was conducted on Al foil (not shown) with LiFSI additive; the anodic peak current rise of the LiFSI additive-containing electrolyte is observed from 3.97 V, which is slightly earlier than ≈ 4.2 V of the base electrolyte only. No corrosion of Al is observed.

B. Electrochemical cycling performance of graphite $\parallel$ LiCoO₂ pouch cells under -20°C

Figure 2 compares the electrochemical cycling performance of graphite $\parallel$ LiCoO₂ pouch cells under -20°C in the base electrolyte of 1M LiPF₆/EC:EMC without and with 0.2M LiFSI additive between 3.0 V and 4.3 V at 0.2C. In the first charge curves of voltage profiles [Figs. 2(a) and 2(b)], both cells exhibit two voltage plateaus {anodic peaks in dQ/dV plots [Figs. 2(a') and 2(b')]} at ≈ 3.9 and ≈ 4.0 V that are attributed to the oxidation of Co³⁺ to Co⁴⁺ by Li⁺-deintercalation. In the subsequent discharge curves, two vague plateaus {cathodic peaks in dQ/dV plots [Figs. 2(a') and 2(b')]} at ≈ 3.67 and ≈ 3.95 V are due to the reduction of Co⁴⁺ to Co³⁺ by Li⁺-intercalation.^{21,22} In the base electrolyte, initial charge and discharge capacities of 66 mA h g⁻¹ and 64 mA h g⁻¹ correspond to the initial coulombic efficiency (ICE) of 97% from which capacities decrease gradually with cycling [Figs. 2(a), 2(c), and 2(d)] resulting in the capacity retention of 72% after 50 cycles [Figs. 2(a) and 2(c)]. The loss of structural resolution in dQ/dV plots [Fig. 2(a')] and a new cathodic peak at ≈ 3.476 V that appears at the 50th cycle in the base electrolyte indicate the degradation of the LiCoO₂ crystal structure by a phase transition from the hexagonal to a monoclinic phase.²³ Strain might form and accumulate by repetitive structural

FIG. 2. Voltage profiles of graphite||LiCoO₂ pouch cells between 3.0 V and 4.3 V at 0.2C under -20°C in (a) Base EL of 1M LiPF₆/EC:EMC without and (b) with 0.2M LiFSI additive and (a') and (b') their differential capacity plots, (c) cycling performance, and (d) coulombic efficiency.

stress during Li⁺-deintercalation and -intercalation processes^{24,25} under higher charge cutoff voltage 4.3 V than conventional 4.2 V, as reported in the earlier literature.²³ On the other hand, with the use of the LiFSI additive [Figs. 2(b), 2(c), and 2(d)], cycling performance is dramatically improved; initial charge and discharge capacities increase to 91 mA h g⁻¹ and 90 mA h g⁻¹, respectively, with an increase in the ICE to $\approx 99\%$. In addition, a higher capacity retention of 92% after 50 cycles and Coulombic efficiencies than those with the base electrolyte are achieved [Figs. 2(c) and 2(d)].

The impedance spectral evolution during cycling is a relative measure of an electrolyte-dependent increase in internal interfacial resistance of the cells. The semicircle in the high-frequency region after the first cycle, attributed to the summed resistance of the SEI formation at the cathode and anode,^{26,27} is smaller upon the use of the LiFSI additive [Fig. 3(b)] than that of the base electrolyte [Fig. 3(a)]. After the 50th cycle with LiFSI additive [Fig. 3(b)], the

semicircles tend to maintain, in contrast to a large increase in the cell with the base electrolyte [Fig. 3(a)] with cycling. The LiFSI additive might form a less resistive SEI layer at the surface of the cathode and anode and reduces the impedance rise, effectively stabilizing the cathode/anode-electrolyte interfaces. This is correlated with the higher capacity and improved cycling stability, as observed in Figs. 2(c) and 2(d).

Figure 4 displays the rate capability of pouch cells in the base electrolyte without and with 0.2M LiFSI additive between 3.0 V and 4.3 V under -20°C at different rates from 0.1C to 5C. Overall, with LiFSI additive, much higher capacities are delivered at all rates [Figs. 4(b) and 4(c)]; discharge capacities at 0.1C, 0.2C, 0.5C, 1C, 2C, and 5C are 106 mA h g⁻¹, 103 mA h g⁻¹, 97 mA h g⁻¹, 89 mA h g⁻¹, 69 mA h g⁻¹, and 17 mA h g⁻¹, respectively. However, the base electrolyte [Figs. 4(a) and 4(c)] produces somewhat lower discharge capacities of 79 mA h g⁻¹, 74 mA h g⁻¹, 68 mA h g⁻¹, 61 mA h g⁻¹,

FIG. 3. AC impedance spectral evolution of graphite||LiCoO₂ pouch cells after the 1st and 50th cycles between 3.0 V and 4.3 V at 0.2C under -20°C in (a) Base EL of 1M LiPF₆/EC:EMC without and (b) with 0.2M LiFSI additive.

48 mA h g⁻¹, and 15 mA h g⁻¹ at the same rates, respectively. A discharge capacity of 69 mA h g⁻¹ delivered at 2C with LiFSI additive is 67% of the capacity delivered at 0.2C, which is higher than just 48 mA h g⁻¹ in the base electrolyte that is 65% of the capacity

FIG. 4. Discharge curves of graphite||LiCoO₂ pouch cells between 3.0 V and 4.3 V at different rates of 0.1–5C under -20°C in (a) Base EL without and (b) with 0.2M LiFSI additive and (c) their rate capability depending on the electrolyte.

at 0.2C. When the discharge rate is back to 0.1C [Fig. 4(c)], the cell with LiFSI additive still achieves 96 mA h g⁻¹ that is 91% retention of 106 mA h g⁻¹ delivered at the initial 0.1C. In the case of base electrolyte [Fig. 4(c)], the discharge capacity upon the return to 0.1C is just 65 mA h g⁻¹, corresponding to the 82% retention of 79 mA h g⁻¹ delivered at the initial 0.1C. The rate capability is influenced by multiple factors such as Li⁺-ion conductivity of the electrolyte, Li⁺-ion diffusion kinetics to both the surface and bulk of the graphite anode and LiCoO₂ cathode, and interfacial resistance that depends on the properties of the surface protective SEI layer at the graphite anode. In particular, as Li⁺-ion transport kinetics is predicted to be sluggish at low temperatures, rate-capability would be inferior as lowering the battery operation temperature. Despite the relatively lower ionic conductivity of the LiFSI additive-containing 1.2M electrolyte [Fig. 1(a)] than the 1M base electrolyte, the improved rate of capability and stability of the LiFSI additive-assisted pouch cell under -20°C imparts the benefits of lower interfacial resistance by the formation of the less resistive SEI layer at the cathode/anode,^{13,14} as observed in impedance spectra [Fig. 3(b)].

C. LiFSI additive-derived inhibition of Li metal-plating at graphite anode

The photographs of graphite anodes obtained after cycling in the base electrolyte without and with 0.2M LiFSI additive under -20°C are displayed in Fig. 5. The cycled anode with the base electrolyte [Fig. 5(b)] clearly shows the formation of light-colored Li metal deposits, compared to a clean and smooth surface of the pristine anode [Fig. 5(a)]. Continuation of low-temperature cycling

FIG. 5. Photographs and SEM images, respectively, of [(a) and (a')] pristine and cycled graphite anodes obtained from graphite||LiCoO₂ pouch cells between 3.0 V and 4.3 V at 0.2C under -20°C in Base EL [(b) and (b')] without and [(c) and (c')] with 0.2M LiFSI additive.

without a death of the pouch cell, despite the occurrence of Li metal-plating, might be due to neither Li-dendrites growth nor penetration through the separator. Safety hazard through shorting is yet to be occurred but lower capacities and inferior performance as well as impedance rise should originate from this Li metal-plating phenomenon at the graphite anode and blocked Li^+ -ion intercalation into interlayers. The corresponding SEM image [Fig. 5(b')] clearly shows the presence of aggregated Li metal particles, but no long-shaped Li-dendrites. On the other hand, the anode cycled with LiFSI additive displays a well-maintained smooth and Li metal-plating-free surface morphology [Fig. 5(c')], and overall remained particle morphology of pristine [Fig. 5(a')]. It ensures the role of the LiFSI additive in inhibiting the occurrence of Li metal-plating and thus improving low-temperature battery performance (Figs. 2 and 4).

D. Bulk structural changes of graphite anode and LiCoO_2 cathode

XRD analyses were conducted to examine the bulk structural changes in graphite anodes and LiCoO_2 cathodes with cycling without and with LiFSI additive under -20°C . First, Fig. 6(A) shows the comparison of powder XRD patterns of pristine and cycled graphite anodes. After cycling, in common, the peak of interlayer spacing, d_{002} , of pristine ($3.3511\text{ \AA}$) shifts to a lower 2θ region along with the reduction of peak intensity as well as peak broadening, particularly, at a higher degree in base electrolyte only ($3.3534\text{ \AA}$) [Fig. 6(A'-b)]

than the one with LiFSI additive ($3.3512\text{ \AA}$) [Fig. 6(A'-c)]. The resultant crystallite size along the c -axis (L_c) [Fig. 6(A)], calculated from the patterns, decreases from 128.13 nm of pristine to 107.89 nm with LiFSI additive to 103.49 nm with the base electrolyte without additive. This indicates that the c -dimension of the graphite crystallite and the number of graphene layers decrease by the loss of both crystallinity and structural order, particularly more in the base electrolyte. It, in turn, reveals that the use of the LiFSI additive provides a better maintenance of the bulk structure of the graphite anode with cycling.

Noticeable structural changes are observed on the cathodes, as shown in Fig. 6(B). The XRD pattern of the pristine LiCoO_2 cathode [Fig. 6(B-a)] indicates a well-defined $\alpha\text{-NaFeO}_2$ -type hexagonal ($R\bar{3}m$) layered structure with the a and c lattice parameters of $2.8742\text{ \AA}$ and $13.9410\text{ \AA}$, respectively, and the c/a ratio of 4.8504 and unit cell volume of $99.73\text{ \AA}^3$. After cycling, in common, the coexistence of two hexagonal phases (H1 and H2) is found and their corresponding split peaks are indexed in Figs. 6(B') and 6(B''). The H2 phase is known to form by the phase transition from H1 to H2 during the charge process and to have the same hexagonal crystal structure (CdCl_2 type) to H1 but a larger c lattice parameter.²³ The presence of H2 phase, despite after 50 cycles under -20°C that was ended as discharged, indicates that the bulk structure of the LiCoO_2 did not reversibly transform back to H1.^{28,29} Simultaneously observed after cycling in common is the shift of the (003) peak of the H1 phase to a lower 2θ region [Fig. 6(B'-b) and Fig. 6(B'-c)], representing the lattice expansion along the c -axis, particularly, at a higher degree in base electrolyte [Fig. 6(B'-b)]. As a result, cell volume [Fig. 6(B-b)] increases at a higher degree in base electrolyte. In addition, peaks of the H1 phase [Figs. 6(B'), 6(B''-b), and 6(B''-c)] are broadened and weakened, particularly, at a higher degree on the cathode cycled in the base electrolyte [Figs. 6(B'-b) and 6(B''-a)] and the one cycled with LiFSI additive [Figs. 6(B'-c) and 6(B''-c)]. In turn, this is the clear evidence that the bulk crystal structure of the LiCoO_2 cathode is better maintained during cycling with LiFSI additive, representing a higher reaction reversibility, which is consistent with the greater maintenance of structural resolution in dQ/dV plots [Fig. 2(b')] and improved cycling performance [Figs. 2(c) and 2(d)]. It is curious how the LiFSI electrolyte additive induces to maintain better the bulk structure of LiCoO_2 as well as the graphite anode so dramatically under -20°C . Because, in general, the electrolyte and additive should be first in contact with the anode and cathode at their interfaces and the electrochemical reaction begins at the interface (i.e., the surface of the anode and cathode), surface chemistry perspective can give an insight into the roles of the LiFSI additive in this -20°C LIB. We, thus, conducted the surface characterization of anodes and cathodes using surface sensitive analytical tools.

E. Surface chemistry

1. SEI characterization of graphite anodes

Figure 7 compares the ATR FTIR spectra of pristine and cycled graphite anodes under -20°C . All cycled anodes [Figs. 7(b) and 7(c)] show peaks at $2970\text{--}2910\text{ cm}^{-1}$ and $1460\text{--}1413\text{ cm}^{-1}$ attributed to methyl ($\text{CH}_3\text{--}$) and methylene ($\text{--CH}_2\text{--}$) groups of alkyl functionalities that come from newly formed sur-

FIG. 6. Power XRD patterns of (A) the graphite anode and the reflection of the (A') (002) plane and (B) the LiCoO_2 cathode and the reflections of (B') (003) and (B'') (104) planes obtained from graphite $\parallel\text{LiCoO}_2$ pouch cells between 3.0 V and 4.3 V at 0.2C under -20°C , (a) pristine and cycled anodes and cathodes in Base EL (b) without and (c) with 0.2M LiFSI additive.

FIG. 7. ATR FTIR spectral comparison of (a) pristine and cycled graphite anodes of graphite||LiCoO₂ pouch cells between 3.0 V and 4.3 V at 0.2C under -20 °C in Base EL (b) without and (c) with 0.2M LiFSI additive.

face compounds in addition to the PVdF binder of pristine [Fig. 7(a)].^{30–32} Also shown [Figs. 7(b) and 7(c)] are peaks at 1740–1720 cm⁻¹ attributed to $\nu_{\text{sym}}(\text{C}=\text{O})$ of ester ($\text{RCO}_2\text{R}'$; $\text{R}, \text{R}' = \text{alkyl group}$), which are confirmed with the peaks at 1270 cm⁻¹ and 1160–1150 cm⁻¹ due to $\nu(\text{C}-\text{O}-\text{C})_{\text{asym}}$ and $\nu(\text{C}-\text{O}-\text{C})_{\text{sym}}$.^{30–34} New peaks at 1660–1580 cm⁻¹ are attributed to $\nu_{\text{sym}}(\text{C}=\text{O})$ of

alkyl carbonate salt (ROCO_2Li) and carboxylate salt (RCO_2Li).^{30,33} A prominent peak near 1470 cm⁻¹ is due to the $\nu(\text{CO}_3)_{\text{sym}}$ of Li_2CO_3 , along with $\delta(\text{CO}_3)$ at 850 cm⁻¹. Peaks at 1320 cm⁻¹, 1040 cm⁻¹, and 964 cm⁻¹ are due to $\nu(\text{P}=\text{O})$, $\nu(\text{P}-\text{O}-\text{C})_{\text{asym}}$, and $\nu(\text{P}-\text{O}-\text{C})$, respectively, of organic phosphorus fluorides ($\text{O}=\text{PF}_{3-y}(\text{OR})_y$).^{30,32,33} Also observed are PF-containing species at 930 and 839–828 cm⁻¹, formed by LiPF_6 decomposition. What is distinguished with the use of the LiFSI additive [Fig. 7(c)] from the base electrolyte [Fig. 7(b)] is relatively stronger absorbance of organic compounds of ester and alkyl carbonate salt implying their higher concentration, whereas reduced intensity of Li_2CO_3 due to lower concentration. In addition, new features at 1210–1180 cm⁻¹ attributed to $\nu(\text{S}=\text{O})$ of $(\text{RO})_2\text{SO}$ and $-\text{SO}_2\text{N}-$ functionalities might be derived from LiFSI decomposition products.

IR analysis results on cycled graphite anodes reveal that the LiFSI additive alters the SEI composition and concentration (i.e., SEI thickness and/or surface coverage). With the use of the LiFSI additive, the SEI layer is composed of a plenty of organic compounds including ester, alkyl carbonate salt, and carboxylate salt and organic phosphorus-fluoride compound along with LiFSI decomposition products passivating better the surface of the graphite anode; the SEI formed in the base electrolyte includes Li_2CO_3 and LiPF_6 decomposition products as well-known major species^{5,35} and organic compounds at a relatively lower concentration.

Figure 8 shows XPS spectral changes on the surface elements of the graphite anode with cycling. In the C 1s spectra, after cycling

FIG. 8. XPS spectral comparison of surface elements of (a) pristine and cycled graphite anodes in graphite||LiCoO₂ pouch cells between 3.0 V and 4.3 V at 0.2C under -20 °C in Base EL of 1M $\text{LiPF}_6/\text{EC}:\text{EMC}$ (b) without and (c) with 0.2M LiFSI additive.

[Figs. 8(b) and 8(c)], new peaks of C—O (286.2 eV), C=O (288.3 eV), and CO₃ (290 eV) containing species are commonly observed,^{30,32,36} in addition to C—C/C—H from carbon black, and those at 291 eV and 285.6 eV of C—F and C—H from the PVdF binder³² of pristine [Fig. 8(a)]. Those might be of organic compounds such as ester, alkyl carbonate salt, and carboxylate salt that we observed in IR spectra (Fig. 7). Their relatively stronger intensity upon the use of LiFSI additive [Fig. 8(c)] is associated with higher concentration of organic compounds, consistent IR observation (Fig. 7). In addition, still strongly remained features of carbon black and the PVdF binder of pristine on the cycled anode in the base electrolyte [Fig. 8(b)] contrary to their vague features with LiFSI additive indicate a lower surface coverage by the SEI species in the base electrolyte.

In O 1s spectra, no peak is observed on pristine. A broad peak on cycled anodes [Figs. 8(b) and 8(c)] is, thus, due to oxygen-containing species of the SEI layer. A stronger peak intensity upon the use of the LiFSI additive implies the presence of higher concentration of oxygen-containing species such as ester, alkyl carbonate salt, carboxylate salt, consistent with C 1s spectra. In the Li 1s spectra, the concentration of Li₂CO₃ is relatively lower with LiFSI additive [Fig. 8(c)] consistent with the IR spectrum [Fig. 7(c)], as well as LiF at 685 eV that is consistent with F 1s spectra. Electrically resistive LiF might contribute to the increase in the interfacial resistance [Fig. 3(a)]. The surface feature of plated Li metal is vaguely detected probably due to its formation in the limited area [Fig. 5(b)]. In P 2p spectra, while OPF_{3-y}(OR)_y/Li_xPF_yO_z type compounds mainly form upon the use of the LiFSI additive [Fig. 8(c)], phosphates/phosphites are also equal major species in the base electrolyte [Fig. 8(b)]. The use of the LiFSI additive [Fig. 8(c)] induces to form its trace in S 2p and N 1s spectra; a peak of the —SO_y— bond^{17,36–38} at 169 eV in the S 2p spectrum and a peak of the —N— bond at 400.8 eV^{39,40} in the N 1s spectrum are attributable to FSI reductive decomposition products, consistent with IR observation. The data reveal that while the Li metal-plating-free [Figs. 5(c) and 5(c')] surface of the cycled graphite anode with LiFSI additive is covered with a plenty of organic compounds (i.e., soft matters) along with LiFSI decomposition products, inorganic species including Li₂CO₃ and LiF are at a relatively higher concentration despite lower surface coverage in the base electrolyte, along with the occurrence of Li metal-plating [Figs. 5(b) and 5(b')], as illustrated in Scheme 1(a). A possible metal-dissolution from the cathode followed by metal-deposition at the anode surface as a result of high-voltage charge and cathode degradation was checked with the Co 2p spectra, but no signature for

the deposited Co species is observed. Given that improved low-temperature cycling performance (Fig. 2) is achieved by the use of the LiFSI additive, the effective surface passivation of the graphite anode with the LiFSI-derived stable and less resistive and softer SEI layer is believed to be the key in inhibiting the Li metal-plating.

2. SEI characterization of LiCoO₂ cathodes

ATR FTIR spectra of pristine and cycled LiCoO₂ cathodes of the pouch cell operated under -20 °C are compared in Fig. 9. Pristine [Fig. 9(a)] exhibits major peaks at 1400 cm⁻¹, 1170 cm⁻¹, and 1072 cm⁻¹, characteristic of the PVdF binder.^{30–32,34} The spectra of cycled cathodes [Figs. 9(b) and 9(c)] show in common the peaks at 2970–2910 cm⁻¹ and 1470–1410 cm⁻¹ due to methyl (CH₃—) and methylene (—CH₂—) groups of alkyl functionality from new surface compounds,^{30,33} in addition to the PVdF binder. Both cycled cathodes present a new peak near 1730–1710 cm⁻¹, characteristic of ν_{sym}(C=O) from ester (RCO₂R'), which is confirmed with the presence of ν(C—O—C)_{asym} and ν(C—O—C)_{sym} at 1280 cm⁻¹ and 1170 cm⁻¹.^{30–34,41} Also, in common, observed at 1650–1640 cm⁻¹ and 1580 cm⁻¹ are attributed to alkyl carbonate salt ROCO₂M (M = Li/Co) and carboxylate salt RCO₂M,^{30,32,33} which are at a relatively higher concentration upon the use of the LiFSI additive [Fig. 9(c)]. A tiny peak of Li₂CO₃ near 1472 cm⁻¹^{33,34} is observed on the cycled cathode with the base electrolyte [Fig. 9(b)], whereas it is absent upon the use of the LiFSI additive. Peaks at 1324 cm⁻¹ and 1050 cm⁻¹, attributed to ν(P=O) and ν(P—O—C)_{asym}, respectively, of organic phosphorus fluorides POF_{3-y}(OR)_y,^{30,33,35} A strong peak at 931 cm⁻¹ together with those at 823 and 798–744 cm⁻¹ is by the presence of ν(P—F) from different PF-containing species such as Li_xPF_y, Li_xPOF_y, and organic phosphorus fluorides, which are at a relatively higher concentration in the base electrolyte [Fig. 9(b)], similar to the case of the graphite anode. The trace of ν(S=O) of (RO)₂SO and —SO₂N— functionalities of LiFSI decomposition products [Fig. 9(c)] at 1210 cm⁻¹ and 1170 cm⁻¹³⁴ is observed for the cycled cathode with LiFSI additive.

The IR analysis results of cycled LiCoO₂ cathodes reveal that while the LiFSI additive-containing electrolyte induces to form organic compounds at a relatively higher concentration along with LiFSI decomposition products as the SEI species, lower concentration of organic compounds and higher concentration of LiPF₆-derived inorganic compounds are present at the surface of the cathode cycled in the base electrolyte.

Figures 10(a)–10(c) compare the XPS spectra of pristine and cycled LiCoO₂ cathodes without and with LiFSI additive. The Li

SCHEME 1. Schematic representation of interfacial phenomena occurring in the graphite||LiCoO₂ pouch cells between 3.0 V and 4.3 V at 0.2C under -20 °C in Base EL of 1M LiPF₆/EC:EMC (a) without and (b) with 0.2M LiFSI additive.

FIG. 9. ATR FTIR spectral comparison of (a) pristine and cycled LiCoO_2 cathodes in graphite $\parallel\text{LiCoO}_2$ pouch cells between 3.0 V and 4.3 V at 0.2C under -20°C in Base EL of 1M $\text{LiPF}_6/\text{EC}:\text{EMC}$ (b) without and (c) with 0.2M LiFSI additive.

1s spectrum of the pristine cathode [Fig. 10(a)] shows the peak of lattice Li—O but after cycling; the cathode surface is fully covered with newly produced Li-containing surface compounds despite weak peak intensity. The Co 2p spectrum of pristine [Fig. 10(a)] presents two peaks at ≈ 780 eV and ≈ 795 eV due to the $2p_{3/2}$ and $2p_{1/2}$ of Co—O bonds, respectively.^{24,42} With cycling, peaks become unclear to analyze, probably due to the full surface coverage with

electrolyte decomposition products. The O 1s spectrum of pristine [Fig. 10(a)] has two peaks, characteristic of lattice oxygen (Co—O) at 530 eV and surface oxygen at 531.7 eV.^{24,39,40,42} Although both peaks significantly weakened with cycling in both electrolytes at the growth of new strong and broad peaks of C—O/P—O (533.1–533.7 eV) and C=O (532.3–532.6 eV) [Figs. 10(b) and 10(c)]^{36,39,43} of new surface species, the peak of lattice oxygen is better maintained upon the use of the LiFSI additive, implying improved structural maintenance of the LiCoO_2 cathode. In the C 1s spectra, new peaks of C—O (286.2 eV), C=O (288.3 eV), and CO_3 (290 eV)^{30,32,36} are observed on both cycled LiCoO_2 cathodes [Figs. 10(b) and 10(c)], besides the peaks of C—H/C—C and C—F (PVdF) of pristine [Fig. 10(a)]. Little difference is seen, regardless of the use of the LiFSI additive. A clear difference without and with LiFSI additive is shown in the P 2p spectra; LiPF_6 -derived organic phosphorus fluoride/ $\text{Li}_x\text{PO}_y\text{F}_z$ compounds and LiF are present at both cycled cathodes, but those form at a relatively higher concentration in the base electrolyte [Fig. 10(b)], consistent with the F 1s spectrum and IR data. In the F 1s spectra, both cycled cathodes show new peaks near 686.7 eV and 684.9 eV, attributable to $\text{OPF}_{3-y}(\text{OR})_y/\text{Li}_x\text{PF}_y\text{O}_z$ and LiF, respectively, in addition to the peak of the PVdF binder at 688.2 eV of pristine.^{30,32,39,40} The S 2p and N 1s spectra exhibit features of LiFSI decomposition products on the cathode cycled with LiFSI additive [Figs. 10(c)],^{17,37–40} similar to the case of the graphite anode.

XPS analysis results on cycled cathodes indicate that while the SEI layer formed in the base electrolyte includes a relatively higher

FIG. 10. XPS spectral comparison of surface elements of (a) pristine and cycled cathodes in graphite $\parallel\text{LiCoO}_2$ pouch cells between 3.0 V and 4.3 V at 0.2C under -20°C in Base EL of 1M $\text{LiPF}_6/\text{EC}:\text{EMC}$ (b) without and (c) with 0.2M LiFSI additive.

concentration of $\text{OPF}_{3-y}(\text{OR})_y/\text{Li}_x\text{PF}_y\text{O}_z$ and LiF, LiFSI decomposition products are additionally present as the SEI species at the surface of the LiCoO_2 cathode cycled with LiFSI additive. Recollecting the earlier oxidative decomposition of LiFSI than LiPF_6 that was observed in LSV [Fig. 1(b)], the LiFSI additive might undergo earlier sacrificial decomposition in the early cycles forming the relatively softer SEI layer that effectively passivates the surface of both LiCoO_2 cathode and graphite anode [Scheme 1(b)]. Thus, reduced chance of LiPF_6 decomposition and release of HF and gases⁵ are given to the pouch cell cycled with LiFSI additive under -20°C .

IV. CONCLUSIONS

The effects and roles of the LiFSI additive in promoting the cycling performance of graphite|| LiCoO_2 Li-ion pouch cells between 3.0 V and 4.3 V at 0.2C under -20°C are investigated. Systematic surface chemistry studies reveal how the LiFSI additive influences the composition, surface coverage, and stability of the SEI layer formed at the graphite anode and LiCoO_2 cathode. As the LiFSI additive undergoes earlier sacrificial decomposition during early cycles forming the surface-passivating SEI layer at both LiCoO_2 cathode and graphite anode, a reduced chance of LiPF_6 decomposition is given to the pouch cell cycled under -20°C . A robust, less resistive, and softer SEI layer, which is enriched with organic compounds formed by carbonates, solvent decomposition along LiFSI-derived inorganic compounds, and reduced concentration of LiPF_6 decomposition products, contributes to an effective passivation of the surface of both cathode and anode, leading to the inhibition of Li metal-plating at the graphite anode. The resultant data indicate that enhanced interfacial stability via the LiFSI additive plays a key role in dramatically increasing the capacity and promoting the cycling performance and rate capability at the reduced interfacial resistance despite under low temperature of -20°C and high-voltage charge cutoff voltage of 4.3 V. We believe that the design and control of interfacial chemistry of the anode-electrolyte and cathode-electrolyte in LIBs operated at low temperatures based on a basic understanding of interfacial phenomena are essential in enabling high battery performance and safety.

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