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**A Depth-profiling Study on Solid Electrolyte Interface: Bis(fluorosulfonyl)imide
Anion toward Improved K⁺ Storage**

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Abstract

Solid electrolyte interface (SEI) significantly affects alkaline metal ion battery performance in terms of reversible capacity, coulombic efficiency and cycling stability. However, intrinsic properties of SEI layer in potassium ion batteries (KIBs), including structures, components, formation mechanism and corresponding K^+ storage behavior, are poorly understood. Here, we focus on the effect of electrolyte on SEI formation and K^+ storage behavior in self-supported nitrogen-doped graphite foams (NGFs). Two types of organic electrolytes, KPF_6 and $KN(SO_2F)_2$ (KFSI) salt in EC/DEC solution, were carefully selected and compared in detail to reveal the effect of SEI on K^+ ion storage mechanism. The experimental results, including *in-situ* electrochemical evaluations and depth-profiling XPS analysis, demonstrate that the salts of KFSI result in a more uniform, stable and thinner SEI layer compared with the SEI induced by KPF_6 . Particularly, the KFSI-induced SEI is rich in stable and uniformly distributed inorganic species and polycarbonates, whereas the KPF_6 -induced SEI is mainly composed of instable alkyl carbonates. This could be attributed to the larger FSI^- size over PF_6^- and lower LUMO levels than solvents according to theoretical calculations, which effectively prevent SEI from co-intercalation damage and thus leading to high stability of the as-obtained SEI layer. In general, the above-mentioned features could ensure high reversibility and good cycling stability of the self-supported NGFs electrode in KFSI-based electrolyte.

Keywords

solid electrolyte interphase; bis(fluorosulfonyl)imide; depth-profiling characterizations; reversibility and stability; potassium ion batteries

Introduction

Potassium ion batteries (KIBs) are emerging as one of the promising alternatives beyond lithium ion batteries (LIBs) due to the merits including comparable working window, efficient K^+ storage in carbonaceous anode¹, and low cost. For instance, in contrast to Na^+/Na and Li^+/Li redox couples, K^+/K redox couples exhibited the lowest standard reduction potential (vs. SHE) in propylene carbonate (PC), which is favorable for achieving higher energy densities of KIBs.²⁻⁴ Besides, the smaller solvated radius of K^+ ion compared with other alkaline metal ions, which is originated from its weaker Lewis acidity, results in higher mobility and faster transport of K^+ ion and are critical for obtaining good rate capability.⁵ Moreover, as a commercialized anode material for LIBs, graphite had a high theoretical specific capacity of 279 mAh g⁻¹ for KIBs by forming the graphite intercalation compounds (GICs) KC_8 .^{1, 6, 7} All these features, together, demonstrate the practical feasibility of KIBs.

Besides the graphite, other anode materials including hard carbon and metal sulfides have been explored for possible K^+ storage, which demonstrate significant progresses in recent years.⁸⁻¹⁰ Heteroatom doping including nitrogen exhibits good K^+ storage capability owing to the defective feature, enlarged crystal layer spacing and improved conductivity.¹¹ Nevertheless, the cycling capability and coulombic efficiency in these reported works cannot fulfil the standards for practical applications. Inspired from the experiences from LIBs and sodium ion batteries (NIBs), the achievement of high coulombic efficiency and good long-term performance for the KIBs still rely on an intact and stable solid electrolyte interface (SEI). Generally speaking, the morphology, chemical composition, thickness and stability of the as-performed SEI layers are strongly

dependent on the electrode morphology/structure, electrolyte constituents, as well as electrochemical conditions, *etc.*¹²⁻¹⁵ Although a lot of recent works have been reported, including i) micro/nanostructures optimization of the carbon-based anodes or composites, and ii) investigation of the effect of electrolyte on potassium ion batteries, the focus was mainly on the as-obtained SEI layer and related electrochemical performance whereas the SEI formation mechanisms are still poorly understood.^{16, 17}

Herein, the effect of different types of electrolyte (KPF₆ and KFSI in organic solvent) on the formation and growth of the SEI layers over freestanding carbonaceous anode materials for KIB applications has been comprehensively investigated through the microscopic, spectroscopic characterizations and theoretical simulations. The structure of KPF₆ salts is similar to that of LiPF₆, commonly used salts in LIBs, while the KFSI salts have been demonstrated to be one of the most appropriate conductive salts due to its high solubility in EC and PC solvent (compared to KPF₆ and KClO₄, *etc.*).¹⁸ The chemical constituents, morphologies and thickness of as-formed SEI layers are well characterized layer by layer and correlated with the electrolyte types and K⁺ storage behavior. The SEI layers induced by the KFSI salts were superior to those deriving from the KPF₆, including i) more intact and smooth surface, ii) more homogenous distribution of species throughout the SEI layers, iii) more stable species (inorganic salts and polycarbonates) forming the SEI layers, and iv) fewer unstable/soluble species (alky carbonates), revealed by the measurements, such as *ex-situ* SEM, TEM, FTIR and depth-profiling AES/XPS. As a consequence, the above-mentioned features leading to observed high coulombic efficiency and good cycling stability of the self-supported NGFs electrode.

Experimental Section

Material synthesis:

The nitrogen doped graphite foams (NGFs) were obtained by a one-step chemical vapor deposition (CVD) method. The nickel foams (NFs) were employed as the template and catalyst for NGF fabrications (area $\sim 20\text{ cm}^2$ and thickness $\sim 1\text{ mm}$). The NFs were pre-soaked in 5 wt. % HCl solution to remove surface defects and oxides. The precursor, melamine ($\sim 1.5\text{ g}$), containing both C and N, were put in a quartz container. The precursor and NFs were placed at low temperature zone ($\sim 400\text{ }^\circ\text{C}$) and the high temperature zone ($\sim 900\text{ }^\circ\text{C}$), respectively in a tube furnace. The temperature increased from room temperature to $900\text{ }^\circ\text{C}$ and kept at $900\text{ }^\circ\text{C}$ for 10 mins (ramping rate: $20\text{ }^\circ\text{C/min}$). The atmospheric pressure growth was conducted in a N_2 atmosphere ($20\text{ cm}^3/\text{min}$). Finally, the NGFs were obtained *via* release of NF skeletons in FeCl_3 solution (0.5 M).

Material characterization:

The Transmission Electron Microscope (TEM), (JEOL-2100F, acceleration voltage: 200 kW) and the Field Emission Scanning Electron Microscope (FE-SEM), (Model JEOL JSM 6700F) were employed to study material and electrode morphologies. The X-Ray Diffraction (XRD), (Bruker D8 Advance), Raman spectroscopy (Renishaw), (laser wavelength: 532 nm) and X-ray photoelectron spectroscopy (XPS), (VG ESCALAB 220i-XL, $h\nu = 1486.7\text{ eV}$) were used to examine the material and electrode structure and components.

In order to explore the passivation process of NGF based KIBs in different electrolytes, Fourier Transform Infrared Spectroscopy (FTIR, PerkinElmer Frontier GX), FE-SEM,

TEM, Auger Electron Spectroscopy (AES) and XPS were used to investigate the surface information of SEI. The discharged electrodes were first rinsed with diethyl carbonate in the glovebox, and then put into the holders for above mentioned test with N₂ protection. Specifically, the VG ESCALAB 220i-XL XPS system is equipped with an argon ion gun (beam energy 1.5 eV, pressure 2×10⁻⁵ Torr) to conduct the depth-profiling XPS measurements. The SEI layer were carefully studied layer by layer with ion gun etching (etching time t = 0 min, 2 mins, 7 mins, 17 mins, 40 mins and 100 mins). The binding energy was calibrated using the single-bonded (C-C/C-H) C1s at 284.6 eV as a reference. The electrode surfaces were further examined on Scanning Auger Microscopy (JEOL JAMP-7830F), with accelerating voltage of 10 keV and probe current of 10 nA and tilt angle of 30°. Depth profiling was done by exposing the surfaces to a 500 eV, 1.1×10⁻⁷ A Ar⁺ ion beam for various duration and the estimated etch rate is about 1.7 nm/min (based on SiO₂ on Si). The AES depth profiles were obtained at different depth surfaces, which exposed after etching time t of 0, 1, 2,..., 15 mins.

Computational details:

The density functional theory implanted in Gaussian 09 software were used to perform the first principle calculations.¹⁹ The equilibrium state structures with geometry optimization were carried out by employing the method of three parameter empirical formulation B3LYP^{20, 21} in conjunction with the basis set of 6-311++G(d, p). Then the energies of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for LiPF₆, KFSI, EC, and DEC were analyzed.

Electrochemical test:

The electrochemical performances of NGFs as the KIB anode were studied in a coin cell: positive electrode, NGF; negative electrode, K metal; electrolyte: 0.6 M $\text{KN}(\text{SO}_2\text{F})_2$ (KFSI) dissolved in EC/DEC (1:1 in volume) or KPF_6 dissolved in EC/DEC (1:1 in volume); separator, the Whatman grade GF/D glass microfiber filter. The coin cells were sealed accordingly in a glovebox with the protection of Ar atmosphere. The areal weight of the as-obtained NGF is around 1.9 mg cm^{-2} . The NGF electrode is a small disk with a total weight of around 1.5 mg (the disk diameter is 1 cm). Cyclic voltammetry curves were obtained in the potential range from 0.01 V to 1.5 V (vs K^+/K) and Nyquist plots were acquired in the frequency range from 0.01 Hz to 100 kHz, both performed on CHI760D (SHANGHAI) Electrochemical workstation. The Nyquist plots were obtained at an AC amplitude of 10 mV and a cell charge voltage of 1.5 V in the frequency range of 100 kHz to 0.01 Hz. The galvanostatic tests were performed on Neware Technology testing system in the potential range from 0.01 V to 1.0 V (vs K^+/K).

Results and Discussions

Self-supported nitrogen doped graphite foams (NGFs) were directly employed as the positive electrode in the half cell. The binder- and additive-free electrode design simplified the SEI components/structures studies without introducing any fluorine. The morphological and structural information of NGF were provided by HRTEM, XRD, Raman and XPS characterizations in Supplemental Information. As shown in Fig. S1 a, NGFs are composed dozens of layers of graphene stacked along (002) lattice plane. The lattice planes shown in TEM image are curved, which indicates the nitrogen doping induced defective structure. The well-defined graphitic structure with lattice plane of (002) has also been identified by XRD (Fig. S1b). The peak $\sim 1350 \text{ cm}^{-1}$ (D band) in

Raman spectrum (Fig. S1c) reveals defective structures of the as-synthesized NGF, which is beneficial for K^+ storage.^{22, 23} The nitrogen doping content ~ 5.12 at. % is determined by XPS spectra as shown in Fig. S1d.

The cyclic voltammetry (CV), galvanostatic discharge/charge (GDC) profiles and electrochemical impedance spectroscopy (EIS) were performed to study the electrochemical performances of NGF-based a potassium ion battery. The CV curves of the NGF-based potassium ion batteries with both electrolytes (Figs. 1a and 1b) show broad peaks at around 0.7 - 0.9 V during first potassiation, which disappear in the following cycles and corresponds to the consumption/reduction of the electrolyte and the formation of SEI layer. ~~Note that this SEI band is more evident in Fig. 1a than Fig. 1b, corresponding to the thicker SEI layers observed in KPF₆ cell than in KFSI cell.~~ The subsequent cathodic peaks present from 0.4 V to 0.02 V are ascribed to the formation of K graphite intercalation compounds (K-GICs) at different stages.⁶ The broad anodic peaks from 0.3 V to 0.6 V are due to the corresponding K^+ de-intercalation process. In contrast to the significant variations of CV curves for KPF₆-based cell, unnoticeable changes of the CV curves for KFSI-based cell has been identified (Fig. 1b) between 2-10 cycles, demonstrating superior reversibility of the KFSI-based cell over KPF₆-based cell. Particularly, the anodic peak at around 0.5 V can be clearly distinguished for KFSI cell (Fig. 1b), which is almost undetectable for KPF₆-based cell (Fig. 1a).

Fig. 1 Electrochemical behaviors of (a and c) KPF₆-based and (b and d) KFSI-based potassium ion batteries. (a), (b) CV curves obtained at 0.1 mV s⁻¹, the first, second, third, fifth and tenth cycle, respectively in both battery configuration (KPF₆- and KFSI -based). (c), (d) Nyquist plots were acquired after first, second, third, fifth and tenth CV cycle. Inset of d presents the equivalent circuit diagram used for all Nyquist plots fitting. (e), (f) Corresponding charge transfer and SEI induced resistances of KPF₆-based and KFSI -based cells.

The EIS data of KPF₆ and KFSI based cells were also collected and compared, with the Nyquist plots obtained after different cycling numbers shown in Figs. 1c and 1d. Typically, all Nyquist plots exhibit a depressed semicircle in the high-frequency range and a straight line in the low-frequency (*Z_w*) range. The former one is related to charge transfer resistance (*R_{ct}*) and interphase contact resistances in the KIBs, especially for SEI layer (*R_{SEI}*). The latter one corresponds to K⁺ ions diffusion in the electrode materials.²⁴ The solid-state diffusion coefficient (*D*) of K ions were calculated according to $D = R^2 T^2 / (2 F^4 S^2 n^4 C^2 \sigma^2)$ and $Z'(Z_{rel}) = R_s + R_{ct} + \sigma \omega^{-1/2}$,²⁵⁻²⁶ the ion diffusion coefficient calculated is 1.6×10^{-13} and 4.9×10^{-13} cm²s⁻¹ for KPF₆ and KFSI based cells, respectively. This is indicative of better kinetics in KFSI based potassium ion batteries. The fitted curves and results are exhibited in Fig. S3 and Table S1. According to the equivalent circuit proposed in Fig. 1c,²⁷ the Nyquist plots are fitted with the impedance parameters plotted in Fig. 1e and Fig. 1f. KFSI-based cell delivers smaller interface resistance *R_{SEI}* (26.6 ~ 55.9 Ω), smaller charge-transfer resistance *R_{ct}* (760.4 ~ 1070.0 Ω), and superior K⁺ diffusion (4.9×10^{-13} cm²s⁻¹) compared to KPF₆-based cell. Particularly, the interface resistance *R_{SEI}* increases slightly upon cycling for KFSI-based cell while that for KPF₆-based cell increases rapidly. This implies that i) continuous degradation of the electrolyte and formation of the SEI layer are involved for both cases and ii) the degradation is much more serious for KPF₆-based cell compared with the KFSI-based cell. This is also consistent with the CV curves.

Fig. 2 Electrochemical performances of KPF₆ and KFSI -based cells. Coulombic efficiency during the first 30 cycles' test of (a) KPF₆ and (b) KFSI-based cells. (c) Rate capability test and (d) cycling stability test of KPF₆ and KFSI-based cells.

The advantages of KFSI cell in comparison with the KPF₆ cell are further confirmed according to the GDC profiles (Fig. S2). The initial discharge specific

capacities is 446.7 mAh g⁻¹ for KFSI-based cells and 430.5 mAh g⁻¹ for KPF₆-based cells, with the 1st columbic efficiency of 49% and 41%, respectively.^{1, 6, 28} The KFSI-based cells maintain almost 100% columbic efficiency after first cycle (Fig. 2b), while for KPF₆-based cells the columbic efficiency reaches 100% after ~30 cycles (Fig. 2a). These observations reveal the formation of a stable and intact SEI layer during the initial several cycles for KFSI-based electrolyte, whereas it takes more than salt for KPF₆-based cells. These further verify the EIS results as discussed above. The gradual SEI layer thickening upon cycling leads to further consumption of K⁺ ions and salts, which increases the cell resistance (Fig. 1c), degrades the coulombic efficiency (Fig. 2a), and therefore harmful to the cell performance.

The differences in K⁺ storage behavior of KFSI and KPF₆-based cells are also manifested by rate capability and cycling performance. As exhibited in Fig. 2c, the specific capacity of KFSI-based cell is 254 mAh g⁻¹ at current density of 10 mA g⁻¹ and 115 mAh g⁻¹ at current density of 160 mA g⁻¹, with a capacity retention of 45.3% which is much higher than that of KPF₆-based cell (28% capacity retention). Moreover, the capacity recovered to 238 mAh g⁻¹ when the current density decreases to 10 mA g⁻¹ for KFSI-based cells, and furthermore retained 74% capacity after another consecutive 100 cycles. In contrast, the recovered capacity is only 177 mAh g⁻¹ (~50% capacity retention) for KPF₆-based cell. The better rate capability of KFSI-based cell could be partially attributed to a well generated SEI layer, which exhibiting better ion diffusion as indicated in Fig. 1c. The specific capacity retention for KFSI-based cell after 100 cycles is ~84%, which is much better than that in KPF₆-based electrolyte, with a capacity retention of only ~69%. Furthermore, 81% capacity retention has been observed for NGF electrode in

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3 KFSI-based electrolyte after 200 cycles. The significant differences in K^+ ion storage
4 behavior in two electrolytes-based cells could be explained by the formation of different
5 SEI layers during the first discharge process, which could greatly affect the
6 electrochemical performance.²⁹
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13 As shown in Fig. 3a, the KPF_6 -induced SEI exhibits rough and ruptured features,
14 while the KFSI-induced SEI shows smooth and intact surface (Fig. 3b). The comparison
15 of SEM images obtained after first discharge (Fig. S4) also reveals that an integrated and
16 smooth SEI layer can be identified at NGF anode's surface in KFSI-based electrolyte
17 during the first cycle, while the formation of intact SEI takes dozens of cycles in KPF_6 -
18 based electrolyte, agreeing with the electrochemical characterizations. From Figs. 3c and
19 3d it can be clearly seen that a uniform SEI layer with 20 nm thickness was formed in
20 KFSI-based electrolyte, whereas an interlaced SEI layer with thickness ranging from 10
21 to 60 nm was generated in KPF_6 -based electrolyte. Moreover, well-defined NGF lattice
22 fringe and clear NGF/SEI interface have been identified in KFSI-based cell.
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37 To get a better understanding of the disrupted structure and interlaced SEI layer
38 generated in KPF_6 -based electrolyte, we have conducted theoretical calculations.
39 Thermodynamically, the electrolytes' decomposition with the SEI layer formation at
40 anode surface is related to reduction potential.^{30, 31} The molecular structures of potassium
41 salts KPF_6 and KFSI are exhibited in Fig. 3e. The electrolyte salts are dissolved in mixed
42 EC and DEC solvent as electrolyte. The weak coupling between the salt molecules does
43 not modulate obviously the lowest unoccupied molecular orbital (LUMO) energy level of
44 each molecule. Therefore, the reduction voltage of the electrolyte is correlated to the
45 electrochemical reduction potentials (thus LUMOs) of potassium salt as well as the
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solvent molecules. The LUMO energy levels of these molecules were calculated by first principle method (Fig. 3f). It could be found that the LUMO level increases in the order of $\text{KFSI} < \text{KPF}_6 < \text{EC} < \text{DEC}$, which means that the salts KPF_6 and KFSI with lower LUMO levels are easier reduced than the solvents EC/DEC . Thus, the salts KPF_6 and KFSI take a major role in the initial discharging process, while the reduction of EC/DEC requires or takes place at higher potentials.¹⁵

Fig. 3g schematically illustrates the SEI layer formation in KPF_6 and KFSI -based electrolytes. Similar to LIBs,¹⁵ the cathodic reduction reactions of the organic electrolyte and the graphitic electrode happen in the potential range of 0.8 V to 0.2 V during first discharge cycle, resulting in the SEI layer with multicomponents (Step 1). With K^+ ions intercalation into the graphite layers from the edges contacted with electrolyte, the salt anion PF_6^- (or $\text{N}(\text{SO}_2\text{F})_2^-$) is possibly co-intercalate into the graphite layers due to the strong interaction (about 2.5 eV) between K^+ and PF_6^- (or $\text{N}(\text{SO}_2\text{F})_2^-$). The intercalation of K^+ ions into graphite is facilitated below 0.2 V (Step 2), and the K ion intercalated graphite intercalation compounds (K-GICs) formed above 0 V (Figs. 1a, 1b, S2a, S2b).¹ Since the size of PF_6^- is smaller than $\text{N}(\text{SO}_2\text{F})_2^-$ (Fig. 3e), it is easier for PF_6^- to diffuse into graphite layers, resulting in large volume expansion^{15 32} and damage to KPF_6 -induced SEI layer, therefore the electrolyte will continue been reduced for repair/regeneration of SEI in following cycles (Step 3). In contrast, the $\text{N}(\text{SO}_2\text{F})_2^-$ in KFSI is relatively difficult to diffuse into graphite layers due to its large size and strong interaction between dangling bond at the edge of graphite and oxygen of $\text{N}(\text{SO}_2\text{F})_2^-$ ³³ (Step 3), thus leading to a more uniform and stable SEI layer.

Fig. 3 The high-resolution SEM and TEM images of NGF electrodes in (a, c) KPF₆-based and (b, d) KFSI-based electrolytes at the discharge potential of 0.01 V (20th discharge). Insets in (a), (b) are the low magnification SEM/TEM images. (e) Molecular structure for KPF₆ and KFSI. (f) The calculated HOMO and LUMO energy levels for KPF₆, KFSI and the solvents EC, DEC. (g) Schematic illustration of SEI layer formation in KPF₆ and KFSI-based electrolytes: ① Electrolyte reduction/decomposition in the potential range of 0.8 - 0.2 V during the first discharge cycle; ② K⁺ intercalation below 0.2 V during first cycle discharge; ③ Electrolyte reduction/decomposition in the potential range of 0.8 - 0.2 V during following discharge cycles.

We further conducted *ex-situ* FTIR and depth-profiling XPS/AES to gain more insights into the chemical and constituent information of KPF₆ and KFSI-induced SEI layer. As observed in the FTIR spectra (Fig. 4a), the peaks located at 835, 1078, 1300, 1387, 1659 and 2949 cm⁻¹, are ascribed to the bending of -OCO₂ (δ -OCO₂), the stretching of C-O (ν C-O), the symmetric stretching of C=O (ν_s C=O), the bending of -CH₂ (δ -CH₂), the asymmetric stretching of C=O (ν_{as} C=O), and the stretching of C-H (ν C-H), respectively.³⁴ These characteristic peaks are originated from the alkyl carbonates, C₂H₅OCOOK and (CH₂OCO₂K)₂, the reduction products of EC and DEC in the SEI layer.^{31, 35-37} It could be clearly observed that the peak located at 835 cm⁻¹, ascribed to the bending mode of -OCO₂, and the peaks located at 1300 and 1659 cm⁻¹, assigned to the symmetric/asymmetric stretching modes of C=O, are much weaker in KFSI-induced SEI layer than that in KPF₆-induced SEI. These observations indicate more ROCO₂K in KPF₆-induced SEI layer because of severe reduction of EC and DEC solvents. Generally, alkyl carbonates are easily decomposed to RCH₂OK or K₂CO₃ upon long cycling. Therefore, the electrode is easily to be attacked by the electrolyte, resulting in inferior stability of the KPF₆ containing cells.³⁵⁻³⁷ In addition, for KFSI-induced SEI, the peaks positioned at ~1190 and ~1388 cm⁻¹ for KFSI-induced SEI (Fig. 4a) likely originate from the reduction products, like KFSO₂ and KNSO₂.^{38, 39} In KPF₆-induced SEI, the peak at 1175 cm⁻¹ is originated from the stretching mode of P=O due to the KPF₆ degradation.⁴⁰ The presence of peaks (~1780 and 1805 cm⁻¹) in both SEI layers could be originated from the EC, DEC solvents.^{40, 41}

The depth profile has been used to study the spatial distribution of elements and compositions across SEI layer. Here the depth profiling XPS and AES are chosen to

characterize the SEI layers generated in KPF₆-based and KFSI-based electrolytes in both qualitative and quasi-quantitative manner. Auger surveys of SEI layers obtained in KPF₆ and KFSI-based electrolytes were acquired after Ar⁺ gun sputtering for different time (i.e., 0, 1, 2, ..., 15 mins) (Fig. S5). The Auger surveys reveal that the KFSI-induced SEI layer contains C, K, S, O and F, while KPF₆-induced SEI layer is composed of C, K, O, F and P, which are in good agreement with Energy-Dispersive X-ray Spectrometry (EDS) mappings (Fig. S6). Interestingly, the KFSI-induced SEI layer is mainly composed of F, S, whereas the SEI layer formed in KPF₆-based electrolyte is rich in F and P elements. The uniform distribution of all elements, also indicating homogenous feature of the as-formed SEI layers.⁴²

Furthermore, Auger surveys obtained at the outermost surfaces (t = 0 min) are compared in detail (Fig. 4b). Auger peaks of C KLL (~268.9 eV), K KLL (~247.8 eV), O KLL (~488.9, 509.6 eV), F KLL (~654.6 eV), P KLL (~118.9 eV) and S KLL (~153.2 eV) are identified.⁴³ The continuous increase in carbon contents (Fig. 4c) and continuous decreases in oxygen contents (Figs. 4d, 4e) reveal that both SEI layers are etched away layer by layer from the carbon-based electrode surfaces. The oxygen content in KPF₆-induced SEI is much higher compared to KFSI-induced SEI layer, with atomic ratios of 13.5 at. % (KPF₆-based) and 5.8 at. % (KFSI-based) at the outermost surfaces, 7.6 at. % (KPF₆-based) and 3.4 at. % (KFSI-based) after 15 mins' Ar⁺ sputtering. This could be attributed to the much more severe decomposition of KPF₆-based electrolyte as aforementioned, since the oxygen-containing organic/inorganic carbonates/semi-carbonates are the main components of SEI layer.⁴⁴ Moreover, the large amounts of oxygen (7.6 at. % after 15 mins' Ar⁺ bombardment) also indicates the KPF₆-induced SEI

layer is thicker than KFSI-induced SEI layer. From Figs. 4d and 4e we can see that the sulfur content in KFSI-induced SEI is more than the phosphorus content in KPF_6 -induced SEI. The sulfur or phosphorus containing inorganic species are more stable compared to the oxygen containing ones, further emphasizing the importance of using bis(fluorosulfonyl)imide salt for generating stable SEI layers. Together with SEM, TEM and FTIR results, the Auger profiles further confirm that KPF_6 -based cells suffering more serious irreversible reactions related to continuous SEI layer formation upon cycling (Fig. 2a), thus leading to low coulombic efficiency.

Fig. 4 (a) FTIR spectra of the NGF electrodes after 20th discharge to 0.01 V in above two electrolytes. (b) Auger lines in the differentiated mode at the outermost surfaces, $t = 0$ min. Auger sputter depth profiles for (c) C in KPF_6 and KFSI induced SEI layers, (d) K, O, F, and S in KPF_6 -induced SEI layer and (e) K, O, F, and P in KFSI-induced SEI layer.

To further examine the chemical states and elemental environments in SEI layers, XPS depth profiles are acquired and plotted in Fig. 5. For KPF₆-based NGF (Fig. 5a), the C1s spectra displays a broad peak positioned at ~285 eV, which can be deconvoluted to several carbon contributions including C-C (284.6 eV), C-O (~285.8 eV), C=O (~287.5 eV) and poly(CO₃) (~291 eV).³¹ The C-C bonding is originated from the graphitic anode materials and the C-O, C=O bonding is originated from organic species in SEI.^{31, 36, 45, 46} From Table S2, we could observe that the KPF₆-based SEI layer exhibits a low C-C ratio of ~9.6 % at SEI surface (t = 0 min). Upon Ar ion etching (from t = 2 min to t = 100 mins), the C-C peak intensity increases gradually, demonstrating continuous stripping of the thick SEI layer.^{47, 48} In contrast, the C-C (~284.6 eV) is hard to detect (4.2%) of the KFSI-induced SEI surface (t = 0 min) (Fig. 5d), indicating the formation of a compact SEI layer. 2 mins' Ar⁺ bombardment results in the appearance of C-C peak, however, it does not change obviously in intensity upon further sputtering, which confirms the generation of a thin SEI layer.⁴⁹ From Fig. S7a, we could clearly observe the difference between KFSI and KPF₆-induced SEI. Furthermore, the amounts of oxygen contained organic and inorganic products (285–291 eV) in KFSI-induced SEI are apparently less than that in KPF₆-induced SEI, suggesting less degradation of KFSI-based electrolyte. In general, the above results clearly indicate that the KFSI-based cell can achieve higher initial Coulombic efficiency and better cycling performance compared to the KPF₆ containing batteries.

Fig. 5 Depth-profiling XPS spectra. (a) C1s, (b) O1s, (c) F1s for KPF₆-based and (d)C1s, (e)O1s and (f) F1s for KFSI-based at different time of Ar⁺ bombardment of discharged electrode. The outmost surface of SEI is t = 0 min.

The O1s XPS spectra are also fitted and deconvoluted into three peaks including C-O/C=O in polycarbonates poly(CO₃) (Figs. 5b and 5e), which are originated from the reduction products of EC and DEC, in order to figure out the relative amount of different

oxygen containing species. The carbonyl C=O at ~531.5 eV might be traced to the alkyl carbonates and the C-O located at ~533.5 eV could be attributed to the ether oxygen.^{31, 50-52} The peak located at ~534 eV is ascribed to poly(CO₃), which are polymerized from the solvents, as well as the alkyl carbonates.⁴⁵ It can be found that the atomic ratio of polymerized poly(CO₃) in KFSI-induced SEI is more than that in KPF₆-induced SEI across the whole layers (Fig. S7b & Table S3). The poly(CO₃) is believed for favorable SEI electrochemical stability owing to i) it could act as a binder which holding together all components in the SEI layer; ii) it protects the electrode from electrolyte attack when fast ion diffusion still could be maintained.^{31, 49} Therefore, the large amounts of poly(CO₃) in KFSI-induced could be beneficial for high battery stability.

Finally, the XPS spectra of F 1s, P 2p, and S 2p are examined to gain more insight into the SEI composition. From Fig. 5c we can see for KPF₆-induced SEI, the F 1s spectrum at the outmost SEI surface (t = 0 min) exhibits a well-defined peak positioned at 688.1 eV, which is related to the salt anion -PF₆. This is further confirmed by the presence of the peak located at ~138 eV in P 2p spectrum (Fig. S8a). 2 min Ar⁺ ion sputtering leads to appearance of two strong peaks located at 684.5 eV, 688.5 eV, indicating the generation of a SEI layer rich in KF and P-F. The peak intensity decreases with the Ar⁺ ion sputtering time, suggesting the exfoliation of the SEI layer from the electrode surface.^{44, 47} For KFSI-induced SEI layer, two distinct peaks located at 684.5 eV, 688.3 eV are observed in F 1s spectra as shown in Fig. 5f, which is ascribed to the KF and S-F in decomposed products, like KNSO₂ and KFSO₂.⁵³ As shown in S 2p spectra (Fig. S8b), K₂SO₃, KSO₂F and KNSO₂ are observed in KFSI-induced SEI.^{47, 54, 55} The sulfites could easily accept electrons compared to oxygen containing species. KFSI-

induced SEI with sulfites could accept electrons from the solvents and the interaction between them could prevent solvents and K^+ ion co-intercalation into electrode material, which could improve the battery stability.⁵⁶

As shown in Fig. S9 below, the electrode surface (SEI layer) were examined by wide scan XPS before (discharge to 0.8 V) and after (discharge to 0.01 V) intercalation reaction of potassium in both electrolytes. From Fig. S9a, we could observe that the P2p, K2p, N1s, O1s and F1s signal are greatly increase after K^+ intercalation (battery discharged to 0.01 V) compared to that before the intercalation reaction. The increase of N1s signal could be due to the 'break' of SEI layer after K^+ intercalation. Meanwhile, the increase of O1s and F1s signal is due to the degradation of more electrolyte to 'repair' the SEI layer. Interestingly, there is no obvious increase in the peak intensity in Fig. S9b, indicating that the SEI layer generated in KFSI-based electrolyte is stable and no 'breakdown' happens during K^+ intercalation.

Conclusions

Summarizing the findings on the SEI layers, it is found that both KPF_6^- and KFSI-induced SEI layers are mainly consist of organic salts and carbon/oxygen containing organic species (including alky carbonates and polycarbonates). Moreover, according to both theoretical calculations and depth-profiling tests, the KFSI contributes to a stable SEI layer for potassium ion batteries which featuring i) The generation of a thin, smooth and intact SEI; ii) The SEI consists of uniformly distributed elements and species; iii) The SEI is rich in insoluble inorganic species with the absence of unstable alkyl carbonates, thus ensuring high stability; and iv) Presence of large amount

polycarbonates is beneficial for forming a stable SEI layer by holding different species together without sacrificing K^+ ion intercalation.

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Conflict of interest

The authors declare no competing financial interest.

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI:

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