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Charge–Discharge Behavior of Graphite Negative Electrodes in FSA-Based Ionic Liquid Electrolytes: Comparative Study of Li-, Na-, K-Ion Systems

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K-ion batteries utilizing ionic liquid (IL) electrolytes are promising candidates for next-generation batteries because of the abundance of potassium resources, low redox potential of potassium, and high safety of ILs. Our major interest is in the comprehensive understanding of electrochemical alkali metal intercalation/deintercalation into graphite negative electrodes, because graphite can easily form graphite intercalation compounds (GICs) with various ionic species, but not with sodium. In this study, we investigated the potassium storage mechanism of graphite negative electrodes in bis(fluorosulfonyl)amide (FSA)-based ILs, and compared the electrochemical GIC formation of Li-, Na-, and K-ion systems. Charge–discharge tests of graphite in K[FSA]–[C₃C₁pyrr][FSA] IL (C₃C₁pyrr = *N*-methyl-*N*-propylpyrolidinium) at 313 K yielded an initial discharge capacity as high as 268 mAh (g-C)⁻¹, leading to the formation of several K-GICs including stage-3 KC₃₆, stage-2 KC₂₄, and stage-1 KC₈. The electrochemical behavior of graphite among M[FSA]–[C₃C₁pyrr][FSA] (M = Li, Na, and K) ILs at 298 K indicated that the formation of binary M-GICs is localized in the potential range below -2.85 V vs. Fc⁺/Fc (Fc = ferrocene), which possibly hinders Na-GIC formation.

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In recent years, growing concern regarding global environmental issues has led to several innovations for the utilization of renewable energy resources such as solar and wind energy.^{1,2} With increasing global warming, realizing a sustainable society has become increasingly important. However, the energy generated from renewable resources, such as wind, rain, sunlight, and tides, depends on weather and climate conditions. Batteries can play a significant role in providing clean, reliable, and affordable energy by storing the electrical energy obtained from renewable resources.^{3,4} Li-ion batteries (LIBs), because of their high energy densities, have been pioneer as significant power storage devices in microgrids.^{5,6} They have been widely used in portable electronic devices such as computers and mobile phones for several years. However, the uneven distribution of lithium and cobalt resources and rising costs have raised concerns about the long-term sustainability.^{7,8} Thus, Na-ion batteries (NIBs)^{9–11} and K-ion batteries (KIBs)^{12–14}

are regarded as potential alternatives to current LIBs because of the abundance of sodium and potassium reserves¹⁵ and the similar chemical properties of lithium, sodium, and potassium, belonging to the same group in the periodic table. The redox potential for potassium, $E(K^+/K)$, in an aqueous solution (-2.936 V vs. standard hydrogen electrode (SHE)) is close to the redox potential of Li⁺/Li (-3.040 V vs. SHE) as compared with Na⁺/Na (-2.714 V vs. SHE).¹⁶ which is an important factor in determining plausible batteries that are competitive with LIBs with respect to high operating voltage and energy density. Moreover, sodium does not form intercalation compounds with graphite, which is one of the most widely used negative electrode materials in commercial LIBs because of its ability to store cations between graphene layers to form graphite intercalation compounds (GICs).¹⁷⁻¹⁹ Unlike sodium,^{20–23} potassium can easily form intercalation compounds with graphite (K-GICs),^{24–27} thereby making it a more viable option in batteries that are successors to LIBs.

The organic solvent electrolytes used in commercial LIBs are highly flammable and volatile in nature, which leads to the risk of ignition accidents.²⁸ Therefore, we have focused on ionic liquids (ILs) as safer electrolytes because of their non-flammability and negligible volatility, and have reported various amide-based IL electrolytes for NIBs^{29–33} and KIBs.^{34–38} Among them, bis(fluor-osulfonyl)amide (FSA)-based ILs exhibit high conductivity, wide electrochemical windows, and high thermal and electrochemical stability, thereby highlighting their suitability as battery electrolytes operating in a wide temperature range including room temperature.^{11,39}

For instance, we previously reported physicochemical and electrochemical studies on M[FSA]–[C₃C₁pyrr][FSA] ILs (M = Li, Na, K; C₃C₁pyrr = *N*-methyl-*N*-propylpyrrolidinium).³⁴ It was found that the K[FSA]–[C₃C₁pyrr][FSA] IL at the composition of *x* (K[FSA]) = 0.20 (*x*(K[FSA]): molar fraction of K[FSA]) exhibits a moderate ionic conductivity of 4.8 mS cm⁻¹ and a wide electrochemical window of 5.72 V at 298 K. Moreover, the trend of $E(M^+/M)$ values in these FSA-ILs differs significantly from those in aqueous solutions. The redox potential (V vs. Fc⁺/Fc; Fc = ferrocene) of K⁺/K (-3.31) is more negative than those of Li⁺/Li (-3.07) and Na⁺/Na (-2.96), which indicates that, in the IL electrolytes, KIBs are likely to show higher operating voltages than LIBs and NIBs.

In this study, charge–discharge mechanism of graphite negative electrodes was investigated in the K[FSA]– $[C_3C_1pyrr]$ [FSA] IL electrolyte at 313 K by X-ray diffraction (XRD) analysis. For a comprehensive understanding of the reactivity of graphite with alkali metal cations, we also systematically compared the charge–discharge behavior of graphite as a negative electrode in M[FSA]– $[C_3C_1pyrr]$ [FSA] (M = Li, Na, K) ILs.

Experimental

(a) Materials preparation.—The electrolytes were prepared by mixing the liquid [C₃C₁pyrr][FSA] (Kanto Chemicals Co., Inc.) and solid M[FSA] salts (M = Li, Na, K) at a composition of x(M[FSA]) = 0.20, commensurate with the M[FSA] molar concentration of ca. 1 mol dm⁻³. Before use, [C₃C₁pyrr][FSA] was dried at 333 K for 1



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Figure 1. (a) Initial charge–discharge curves of a K/graphite cell in K[FSA]– $[C_3C_1pyrr]$ [FSA] (x(K[FSA]) = 0.20) electrolyte at 313 K. Current rate: 0.1C. (b) XRD patterns of graphite electrodes at different charge–discharge states; numbering provided in the figure corresponds to points plotted in Fig. 1a.

d. Na[FSA] and K[FSA] (Nippon Shokubai Co., Ltd.) were dried at 353 K for 2 d. Li[FSA] (Kishida Chemical Co., Ltd.) was used as received. To prepare the graphite composite negative electrode, commercially available natural graphite powder (SNO-3, SEC Carbon, particle size: 3 μ m) and sodium carboxyl methylcellulose (CMC, #2200, Daicel Miraizu Ltd.) were mixed at a weight ratio of 90:10 with the requisite amount of deionized water to obtain a homogeneous dispersion. The CMC binder solution in an optimized 2 wt% ratio was used to prepare the slurry. The resultant slurry was then cast onto copper foil (thickness: 20 μ m) using the doctor blade method and vacuum-dried at 353 K overnight (12 h). The electrodes were then punched out along with the copper foil and vacuum-dried at 333 K for 24 h. Then, prior to cell assembly, the electrodes were vacuum-impregnated at 353 K overnight with the M[FSA]–[C₃C₁pyrr][FSA] electrolytes. The average mass loading of graphite in the prepared graphite electrodes was 1.3 mg cm⁻ ². A 2032 coin-type cell with a two-electrode configuration was assembled, where K metal (Kojundo Chemical Laboratory Co., Ltd., 99.5% purity) was pasted on an aluminum current collector and used as the counter electrode. The Li/graphite and Na/graphite coin cells were assembled with the almost same procedures, using Li (Honjo Chemical Co., Ltd., 99.98% purity) on a stainless steel disk and Na (Sigma-Aldrich, 99.95% purity) on an aluminum disk as the counter electrode. A two-ply glass fiber filter (Whatman, GF/A, thickness: 260 μ m) was used as the separator. Moisture- and air-sensitive materials were handled in a glovebox in dry deoxygenated argon gas.

(b) Characterization.—All electrochemical measurements were conducted under an argon atmosphere using a potentiostat (HZ-7000, Hokuto Denko Co., Ltd.; or VSP, Biologic Co.). In this study, the capacity (mAh g^{-1}) and current density (mA g^{-1} or C rate) were expressed based on the weight of graphite in the electrodes. Charge-discharge tests, cyclic voltammetry (CV), and galvanostatic titration technique (GITT) were performed using 2032-type twoelectrode coin cells. The electrochemical measurements of the K/ graphite coin cells were performed at 313 K after resting for 1 h. The rate capability was tested at constant rates in the sequence of 0.2C, 0.5C, 1C, 2C, and 0.2C (where 1C corresponds to a current density of 279 mA g^{-1} assuming the formation of KC₈) within the voltage range of 0.010-1.500 V. After completing the rate capability tests, cycling tests were performed using the same cell at constant rates of 0.5C and 1C in the same voltage range as that used in the rate capability test for 100 cycles each. GITT measurements were performed by applying a constant rate of 0.1C for 20 min, followed by voltage relaxation for 1 h. The relaxed potentials were taken as the final plots of the relaxation periods. The potential for the formation of M-GICs was investigated through charge-discharge measurements using a three-electrode cell (EC Frontier Co., Ltd.). In the three-electrode cell, the graphite composite on copper foil was used as the working electrode, and Li, Na, or K metal were used as both the counter and reference electrodes. A two-ply glass fiber filter (Whatman GF/A, diameter: 25 mm) was used as the separator. The XRD patterns were recorded in the Bragg-Brentano geometry using an X-ray diffractometer (Ultima IV, Rigaku, Co.) equipped with Cu- $K\alpha$ radiation ($\lambda = 1.5418$ Å) at 40 kV and 40 mA. The samples for the XRD measurements were set in an airtight cell under a dry argon atmosphere.

Results and Discussion

(a) Potassium storage mechanism and electrochemical performance.—The intercalation/deintercalation behavior into/from graphite was examined by fabricating K/graphite half-cells using 2032type coin cells. In this study, the intercalation (potassiation) and deintercalation (depotassiation) processes are referred to as charge and discharge, respectively. The coin-cell measurements of K-ion system were conducted at 313 K due to the following reasons: Firstly, the ionic conductivity of K[FSA]–[C₃C₁pyrr][FSA] IL for *x* (K[FSA]) = 0.20 increases from 4.8 mS cm⁻¹ at 298 K to 7.9 mS cm⁻¹ at 313 K,³⁴ enhancing the cell performance. Secondly, the potential polarization of potassium metal counter electrode could be smaller at higher temperatures, which is beneficial to the proper performance evaluation of graphite negative electrodes.

Figure 1a shows the initial charge-discharge curves of a graphite electrode in a K[FSA]– $[C_3C_1pyrr]$ [FSA] (x(K[FSA]) = 0.20) IL electrolyte measured at a constant current rate of 0.1C (27.9 mA g^{-1}) and 313 K. A charge capacity of 316 mAh g^{-1} is obtained during the first charge process. The charge curve consists of three regions: the steep sloping region in the voltage range of 0.4-1.5 V possibly caused by the formation of a solid electrolyte interphase (SEI), the gentle sloping region in the range of 0.2–0.4 V, and a long voltage plateau region at approximately 0.15 V. As the charge capacity exceeds the theoretical value (279 mAh g^{-1}), the gentle slope and plateau regions are also likely to include the SEI formation. In the first discharge process, a discharge capacity of 268 mAh g^{-1} (Fig. 1a) is obtained with an initial coulombic efficiency of 85%, which is commensurate with 96% of the theoretical capacity. As with the charging process, the discharge profile is composed of a long voltage plateau at approximately 0.3 V and a step-wise sloping region above 0.4 V. The initial performance is consistent with that reported in our previous study using the same IL electrolyte.³⁶ On the basis of the capacity calculation in the discharge curve, assuming the formation of the KC₈ phase at the fully charged state, the KC₂₄ and KC₃₆ phases may be formed at a cumulative capacity of approximately 130 (end point of the long discharge plateau) and 100 mAh g^{-1} , respectively.

To investigate the potassiation-depotassiation mechanism of graphite in this IL electrolyte, a charge-discharge test was conducted for three cycles at 0.05C rate and 313 K, as shown in Fig. S1a (available online at stacks.iop.org/JES/169/050507/mmedia), and the corresponding dQ/dV curves are shown in Fig. S1b. According to the dO/dV curves in the first charge process, several current peaks are observed at approximately 0.37, 0.28, 0.25, 0.20, and 0.18 V. During the first discharge process, the peaks are observed at 0.25, 0.36, 0.39, 0.44, and 0.50 V, which corresponds to the depotassiation steps of K-GICs. A pair of sharp redox peaks at 0.18 V in the first charge and 0.25 V in the first discharge reflects the long flat plateaus in the charge-discharge curves (Fig. S1a). In the second cycle, small changes are observed in the charge process. The redox peak at the highest voltage shifts from 0.37 to 0.42 V, indicating the formation of facile reaction pathways in the graphite electrode during the first cycle. Moreover, the highest negative charging peak at approximately 0.18 V is split into two peaks. This is likely due to the formation of an intermediate phase such as KC₁₆, which was proposed in a previous study.²⁶ Although no significant changes are observed after second discharging profile, the splitting of the dQ/dVpeak in the voltage range of 0.15-0.20 V almost disappears in the third charge cycle, indicating the instability of the intermediate KC_{16} phase. As shown in Fig. S1c, CV measurements yielded results similar to those of the charge-discharge test (i.e., dO/dV curves), in which four or five peaks appear during the charge and discharge processes. However, the voltage polarization in the CV curves appears to be higher than that in the dQ/dV curves; this can be explained by considering the reaction timescales of potassiation/ depotassiation for both measurements. The rate of 0.05C in the charge-discharge measurements corresponds to a 20 h reaction time for the charge and discharge processes. However, in the CV measurement at a scan rate of 0.02 mV s^{-1} , potassiation or depotassiation occurs in the voltage range of 0-0.6 V, which is commensurate with ca. 8 h. This indicates that the charge-discharge rates in the CV measurements are virtually faster than those in the galvanostatic charge-discharge test, consequently leading to a larger voltage polarization.

Further investigation was conducted to acquire the charge-discharge profiles approaching thermodynamic equilibrium, as shown in Fig. S2. The GITT measurements were also performed using a K/graphite coin cell at a temperature of 313 K. Prior to GITT measurements, the cell was cycled twice in the voltage range of 0.010-1.500 V at a constant current rate of 0.1C to ensure stable conditions. Then, a constant current density of 0.1C was applied for 20 min, followed by the relaxation period of 1 h. The titration and relaxation steps were repeated until the potential during the titration step reached 0.010 V for charging and 1.500 V for discharging. As shown in the GITT curves in Fig. S2a, a step-wise slope region and a long flat plateau region are observed, which are similar to the results of the charge-discharge test. However, a few differences are observed in the voltage polarization of each titration step from the relaxed potentials. The overall polarization during charging appears to be larger than those observed in the discharging step, particularly for the long potential plateau at approximately 0.2 V, which indicates that the deintercalation rate of K⁺ ions between the graphene layers is marginally higher than that in the intercalation process. According to the plots of the relaxed open-circuit potentials shown in Fig. S2b, a potential hysteresis is distinctly observed in the slope region at 0.2-0.4 V vs. K⁺/K, indicating that the phase transition of K-GICs differs in the charge and discharge processes, and the details are being investigated.

To ascertain the structural evolution of K-GICs during the charge and discharge processes, *ex-situ* XRD measurements were performed for graphite electrodes at the selective states of charge during the first cycle of galvanostatic charge–discharge at 0.1C rate in the K[FSA]–[C₃C₁pyrr][FSA] (x(K[FSA]) = 0.20) electrolyte, as illustrated in Fig. 1b. The intercalation of K⁺ ions into graphite produces several stage-*n* GICs, where *n* denotes the number of graphene layers present between adjacent intercalant layers. To calculate the stage number, n, we need to refer to Bragg's law to calculate the interlayer distance, d, between the K intercalated layers.

$$\lambda = 2dsin\theta$$
[1]

where λ is the wavelength of the X-rays (1.5418 Å for Cu- $K\alpha$), d is the d-spacing, which is the distance between the origin and corresponding planes of the diffraction indexes, and θ is the diffraction angle. In general, the stage number n of GICs is determined using the following equation:

$$I_c = (n - 1)d_0 + d_i$$
[2]

where I_c is the repeat distance of the GICs, d_0 is the original distance between two adjacent graphene layers, and d_i is the distance between the layers in which the alkali metal ions are intercalated.

In the pristine graphite electrode (point 1 (0 mAh g^{-1} , 2.96 V)), a sharp peak corresponding to an interlayer distance of 3.35 Å appears at 26.58° on the 002 diffraction line of graphite.¹⁷ At point 2 (55.8 mAh g^{-1} , 0.27 V), no diffraction peaks assignable to K-GICs are observed and the prominent graphite-like peak remains near 26.6°. Thus, most of the capacities obtained between points 1 and 2 appear to be consumed for the irreversible SEI formation on the graphite electrode surface. However, its intensity significantly decreases and the peak width slightly broadens compared with that of pristine graphite. This decrease in intensity and broadening of the peak may be attributable to the formation of a dilute stage of the K-GIC phase with low crystallinity. In this dilute phase, K^+ ions are randomly intercalated between graphene layers,²⁶ which indicates that a fraction of the capacities between points 1 and 2 may be reversible, and is being investigated. After charging to point 3 (90.6 mAh g^{-1} , 0.20 V), five broad peaks appear, indicating the formation of several K-GICs. Two characteristic broad peaks appear at around 22.5° and 29.3°, which are assignable to stage-3 $\hat{\text{KC}}_{36}$. The other three peaks at approximately 23.4°, 27.8°, and 28.7° correspond to the formation of higher stages (n > 3). However, they cannot be assigned to a certain stage, because their n values are not calculated to be a natural number. Such phenomena are explained by the "stage mixing" reported in a recent study of fluorosilicate GICs.⁴⁰ Thus, assuming that the d_i value for K-GICs is approximately 5.35 Å according to previous studies,¹⁷ the diffraction peaks at 23.4° and 28.7° are assigned to a mixture of stage-4 and stage-5 K-GICs. Similarly, the peak at 27.8° is considered to be the result of diffraction from the mixture of stage-8 and stage-9 K-GICs. However, the diffraction peak at 27.8° may also be assigned to the dilute phase, because the orderly stacking of potassium between the graphene layers may be challenging for K-poor compositions. The presence of three K-GICs at this state suggests the slow kinetics of K intercalation into graphite during charging at a rate of 0.1C, further investigation will be required to elucidate this behavior (see Fig. S3).

Upon further potassiation, at point 4, two dominant peaks assignable to stage-2 KC₂₄ appear at 20.26° (d = 4.38 Å) and 30.90° (d = 2.89 Å), while the diffraction peaks of stage-3 KC₃₆ vanishes. In addition, a pair of small peaks are observed at approximately 16.6° and 33.4°, indicating the formation of the stage-1 KC₈ phase. The intensities of the diffraction peaks from KC₈ increases as the charging state reaches point 5 (223 mAh g^{-1} , 0.12 V). Finally, at point 6 (261 mAh g^{-1} , 0.01 V), the fully charged state, the diffraction peaks of KC24 virtually disappeared, and only two characteristic peaks with significantly high intensity assignable to KC₈ at 16.61° (d = 5.34 Å) and 33.54° (d = 2.67 Å) are observed, indicating the complete potassiation of the graphite electrode. Because points 4-6 are present in the lowest long plateau during charging, this plateau corresponds to the coexisting state between KC₂₄ and KC₈. The interlayer distance (d_i) of stage-1 KC₈ is observed to be 5.34 Å, which is a factor of 1.6 higher than that between graphene layers ($d_0 = 3.35$ Å) before intercalation. This change in interlayer distance during charging is much larger than



Figure 2. (a) Charge–discharge curves and (b) cycling properties of K/ graphite cell obtained at different current rates of 0.2, 0.5, 1, and 2C at 313 K.

that during Li-GIC formation ($d_i = 3.70 \text{ Å}^{18}$; higher than d_0 by a factor of 1.1). The experimentally obtained values of I_c and the distance between the intercalated layers (d_i) for stage-*n* K-GICs are summarized in Table S1.

During the discharging process, at points 7 and 8 in the long plateau at approximately 0.3 V, the peak intensities from KC8 decrease and those from KC₂₄ appear, indicating a reversible reaction corresponding to the charging process. Then, after discharging to point 9, only a pair of diffraction peaks assignable to KC_{36} is observed at 22.24° (d = 4.00 Å) and 29.44° (d = 3.03 Å), which is different from the XRD pattern at the corresponding state (point 3) in the charging process, forming higher stages of K-GICs. This discrepancy can be explained by the hysteresis in the charge-discharge curves and GITT profiles. As shown in Fig. S2, the differences between the relaxed potentials in the capacity region of 40–100 mAh g^{-1} are particularly higher than those in other regions. As this region corresponds to the compositional range (y in KC_y) of 22-56, the phase transition mechanism for KC₃₆ and the higher stages of K-GICs may be different for the charging and discharging processes. A graphite-like peak and its shoulder appear at point 10, and then, the prominent peak assignable to the 002 diffraction peak of graphite is reformed after complete discharging (point 11). The peak intensity of graphite after one cycle is lower than that of pristine graphite, indicating a decrease in the crystallinity of graphite during the potassium intercalation/deintercalation, likely caused by the aforementioned variation in the interlayer distance of graphite. The overall phase transition behavior observed using XRD is consistent with the results of the charge-discharge tests and GITT measurements.

To further elucidate the phase evolution behavior of graphite in potassium-poor regions, *ex-situ* XRD measurements were performed for graphite electrodes during the initial charge and discharge processes at a slow current rate of 0.05C (13.96 mA g^{-1}) and 313 K to obtain the phase close to equilibrium. Figures S3a and 3b

illustrate the initial charge-discharge curves of a graphite electrode measured at a current rate of 0.05C and 313 K using K[FSA]–[C₃C₁pyrr][FSA] (x(K[FSA] = 0.20)) electrolyte, and the ex-situ XRD measurement data, respectively. The numbers mentioned in the ex-situ XRD data correspond to the points plotted in charge-discharge curves. The obtained I_c and d_i values are summarized in Table S2. During initial potassium intercalation, the 002 Bragg diffraction peak of pristine graphite located at $2\theta = 26.58^{\circ}$ decreases in intensity while retaining almost same peak position up to point 1 (41.8 mAh g^{-1} , 0.35 V). As potassiation proceeds, broadening of the peak is observed at point 2 (55.8 mAh g^{-1} , 0.33 V), which is explained by random intercalation of potassium ions between graphene layers and thereby stacking disorder in the higher stage regions (See also Fig. 1b). At point 2, two other peaks appear at around 24.8° (d = 3.59 Å) and 27.7° (d = 3.22 Å). Although the values of stage number n cannot be deduced as a natural number, the former peak can be formally assigned to stage-8 or higher (n > 8)and the latter one corresponds to n > 9. Considering the broad appearance of the peaks, these diffraction peaks likely correspond to the formation of dilute phases of K-GICs, as mentioned in the discussion of Fig. 1b. Upon potasssiation up to point 3 (62.7 mAh g^{-1} , 0.32 V), two peaks at 23.77° (d = 3.74 Å) and 28.46° (d =3.14 Å) corresponding to stage-5 K-GIC are observed. As described in Fig. 1b, the formation of stage-5 K-GIC is not observed during charging at 0.1C rate. However, with slow rate operation at 0.05C rate, even higher stage compounds appear in the intercalation process. Up to point 4 (69.7 mAh g^{-1} , 0.31 V), the position of the peaks remains almost same and only the intensity of the peaks increases, indicating more prominent formation of stage-5 K-GIC. At point 5 (76.8 mAh g^{-1} , 0.30 V), the pair of diffraction peaks of the K-GICs has abruptly shifted to 23.12° ($d = 3.85^{\circ}$ Å) and 28.95° (d = 3.08 Å), which may correspond to K-GIC phase transition from stage 5 to stage 4. Upon further potassiation, at point 6 (83.7 mAh g^{-1} , 0.27 V), two sharp peaks assignable to stage-3 KC₃₆ appear at 22.07° (d = 4.03 Å) and 29.65° (d = 3.01 Å) while the peaks corresponding to stage-4 K-GIC virtually disappear. In contrast, around this point during charging at 0.1C current rate, indistinct broad peaks combining a mixture of higher stages and KC36 are obtained, while explicitly sharper peaks of KC36 are obtained at a current rate of 0.05C. Upon charging up to point 7 (97.6 mAh g^{-1} , 0.24 V), the peak position for stage-3 KC₃₆ remains the same and its intensity slightly increases.

In the depotassiation process, at point 8, two peaks appear at approximately 23.3° and 28.8°, which cannot be assigned to a stage index of natural number. As mentioned in discussion of Fig. 1b, they might correspond to a mixture of stage-5 and stage-4 K-GICs. Further depotassiation to point 9 results in the formation of two peaks at 24.12° ($d = 3.69^{\circ}$ Å) and 28.22° ($d = 3.16^{\circ}$ Å) assignable to stage-6 K-GICs, which is not clearly observed during higher current rate operations. Finally, at point 10, a graphite-like peak with decreased intensity once again appears at 26.58° (d = 3.35 Å) and the graphite structure is reformed. The phase transition behavior during the depotassiation process is different from the potassiation process for the potassium-poor regions. This hysteresis is also observed in the capacity region of 40–110 mAh g^{-1} for GITT profiles provided in Fig. S2b and in the capacity region of 40-140 mAh g^{-1} for the charge–discharge curves shown in Fig. S3a, which manifest the differences in the phase evolution mechanism for both potassiation and depotassiation processes. Most previous studies of graphite negative electrodes in K-ion system using organic solvent have not mentioned such hysteresis behavior.^{24–27} However, a recent report investigated the hysteretic effect between potassiation and depotassiation by operando XRD using the K/graphite cell with an organic solvent-based electrolyte containing 1 mol dm⁻³ K[FSA].⁴ In terms of the existence of the hysteresis behavior, our study agrees with the recent report.

The rate performance of this system was evaluated using a K/ graphite two-electrode coin cell in the voltage range of 0.010-1.500 V at 313 K, as shown in Figs. 2a and 2b. High discharge capacities



Figure 3. (a) Charge–discharge curves and (b) cycling properties of K/ graphite cell at rates of 0.5 and 1C at 313 K after cycling for 25 cycles at different current densities (See Fig. 2).



Figure 4. XRD patterns of graphite electrodes prepared by charging Na/ graphite cells in Na[FSA]–[C₃C₁pyrr][FSA] (x(Na[FSA] = 0.20)) electrolyte at a current density of 1.5 mA g⁻¹ and +0.001 V holding potential in CC–CV mode at 313, 333, and 353 K for 7 d each.

of 255 and 232 mAh g^{-1} are obtained at current rates of 0.5 and 1C, respectively. The capacity abruptly decreases to 95.9 mAh g^{-1} at a moderately high charge–discharge rate of 2C corresponding to the disappearance of the most negative plateau. Although this decline in capacity is caused by an increase in polarization for the long plateau, the reversible capacities of the sloping region are virtually the same at all rates. Thus, the utilization ratios of the active material are

likely to remain unchanged, and the K metal counter electrode in the two-electrode coin cell possibly contributes to the increase in polarization. When the charge–discharge rate reverts to 0.2C after 20 cycles, the reversible capacity recovers to a value as high as 260 mAh g^{-1} with 99.5% coulombic efficiency. In addition, as shown in Fig. 2a, the charge–discharge curves at the 5th and 25th cycles overlap each other, indicating a negligible degradation of the graphite electrode during cycling at higher current rates.

To substantiate the long-term stability of the graphite negative electrodes in the FSA-based electrolyte, the cycling performance was investigated using the same cell after the rate capability test, as shown in Figs. 3a and 3b. At a current density of 0.5C (26-125th cycle), the K/graphite cell shows significant cycling stability and discharge capacity retention. The discharge capacity at the 125th cycle is 249 mAh g^{-1} , commensurate with a capacity retention as high as 98.4% corresponding to the capacity in the first cycle of 0.5C (26th cycle). The charge-discharge profiles also entirely overlap, indicating the extremely stable performance of the graphite negative electrode in this electrolyte. During cycling at a rate of 1C (126--225th cycle), a decline in capacity is observed at the beginning stage, which may be due to a transient increase in the graphite electrode resistance immediately after switching to the rapid cycling mode. Subsequently, the reversible capacity significantly recovers and maintains a virtually stable capacity of approximately 230 mAh g^{-1} . Although the reason for this recovery could not be elucidated, the reaction pathways in graphite electrodes may be reformed by the change in the nature of the SEI, adapting to the high charge-discharge rate environment. The details will be investigated in future studies. The discharge capacity in the final (225th) cycle is 233 mAh g^{-1} , commensurate with a capacity retention of 100% with respect to the capacity in the first cycle of 1C (126th cycle). An average coulombic efficiency as high as 99.8% is achieved even after 225 cycles, thereby demonstrating the excellent compatibility between the graphite negative electrode and K[FSA]-[C₃C₁pyrr][FSA] electrolyte.

(b) Comparison of graphite negative electrode performance in $M[FSA]-[C_3C_1pyrr][FSA]$ (M = Li, Na, K) IL electrolytes.— Graphite is a well-known negative electrode material predominantly used in LIBs, because it delivers a high capacity of 372 mAh g⁻ corresponding to the formation of the LiC₆ phase. In the previous section, we demonstrated that the graphite negative electrode forms several K-GICs such as KC8, KC24, and KC36, delivering a capacity as high as 268 mAh g^{-1} . In contrast to lithium and potassium, sodium negligibly intercalates into graphite to form GICs, which has been the topic of investigation for several tens of years. From the experimental and computational aspects, numerous studies have been conducted 20-22,42-46; however, their conclusions did not comprehensively analyze these phenomena. The possibility that the non-formation of Na-GICs is due to the ionic size of alkali metals is excluded, because K⁺ ions, which are larger than Na⁺ ions, can form GICs by intercalating between graphene layers. Previous studies have shown the electrochemical formation of Na-GICs with low sodium contents (NaC₆₄₋₇₀) in polymer-based electrolytes.^{20,21} In a recent study, Kondo et al. investigated the thermodynamic as well as kinetic properties for electrochemical Na⁺ ion intercalation into graphite in organic solvent-based electrolytes composed of ethylene carbonate and dimethyl carbonate (1:1 volume ratio) containing 0.9 mol kg^{-1} Na[FSA] with and without 5 wt% fluoroethylene carbonate, and observed that sodium can only be intercalated near the surface and not in the bulk of graphite.²² The reason for the inability of formation of Na-GICs may be more thermodynamic than kinetic. However, few studies have been conducted on IL-based electrolyte systems. According to the computational studies conducted by Lenchuk et al.,46 the total formation energies for GICs are expressed as the sum of the deformation energy (energy required to deform the graphite structure upon the intercalation of alkali metal) and the binding energy. For the Li-ion system, because of the small size of Li, a small structural



Figure 5. Initial charge–discharge curve for M/graphite cell (M = Li, Na, K) using M[FSA]–[C₃C₁pyrr][FSA] (x(M[FSA]) = 0.20, M = Li, Na, K) electrolyte at 298 K using three-electrode cell configuration. Current rates: 37.2, 1.5, and 27.9 mA g⁻¹ for Li-, Na-, and K-ion system, respectively.

deformation occurs in graphite, which is counteracted by the contributions of the high binding energy. Thus, the formation of Li-GICs is thermodynamically favorable. Furthermore, in the case of the K-ion system, although large structural deformation occurs owing to the larger size of K^+ ions, a significant binding energy leads to the formation of K-GICs. In contrast, in the case of Na-GICs, the binding energy is insufficient to counteract the structural deformation energy, and hence the formation of Na-GICs is thermodynamically unfavorable.

In this study, to investigate the formation of Na-GICs in FSAbased IL electrolyte, charge-discharge measurements were performed for Na/graphite cells using the Na[FSA]-[C₃C₁pyrr][FSA] electrolyte. The constant-current-constant-voltage (CC-CV) mode was adopted and the cells were operated at a wide range of temperatures. The cells were first charged to +0.001 V at a current density of 1.5 mA g^{-1} and then a constant voltage of +0.001 V was maintained for 7 d at 313, 333, and 353 K. Further, ex-situ XRD measurements were performed for the above-mentioned cells to examine the formation of Na-GICs electrochemically. Figure 4 illustrates the XRD patterns for the Na/graphite cells, which elucidates critical information regarding the formation of Na-GICs. The intensity of the 002 diffraction peak of graphite at 26.6° (d = 3.35 Å) decreases with temperature and potential holding time (Fig. S4). As shown in Table S3, the highest charging capacity of 173 mAh g^{-1} is obtained for the 353 K sample with the lowest graphite peak intensity, indicating some incorporation of Na⁺ ions into the graphite interlayers. Although no peak corresponding to low-stage Na-GICs is observed, the intercalation of Na⁺ ions into graphite may proceed only at the surface and not in the bulk of the graphite structure. Another possible explanation is the formation of amorphous-like compounds after Na⁺ ion incorporation into the graphene layers, consequently resulting in the loss of crystallinity owing to the deformation of the original structure.

To gain new insights into the intercalation behavior of alkali metal ions between graphene layers, the electrochemical performance of graphite negative electrodes was further compared among Li-, Na-, and K-ion systems in IL-based electrolytes. Figure 5 shows the initial charge–discharge curves for the M/graphite cells in the M[FSA]–[C₃C₁pyrr][FSA] (M = Li, Na, K) electrolyte, where *x*(M [FSA]) = 0.20 (corresponding to ca. 1 mol dm⁻³) at 298 K. The potentials of charge–discharge curves were calibrated to the Fc⁺/Fc redox couple (Fc = ferrocene). According to our previous study, the redox potentials of M⁺/M (M = Li, Na, and K) in M[FSA]–[C₃C₁pyrr][FSA] (*x*(M[FSA]) = 0.20) at 298 K are -3.07, -2.96, and -3.31 V vs. Fc⁺/Fc, respectively,³⁴ which are denoted by dotted lines in Fig. 5. The first discharging capacities of 348 and 253 mAh g⁻¹ were obtained for the Li- and K-ion cells, respectively, at a current rate of 0.1C. However, a significantly low discharging capacity of 8.37 mAh g⁻¹ is obtained for the first cycle at a current density of 1.5 mA g⁻¹ for Na-ion cells, because sodium negligibly intercalates into graphite. Figure S5 shows the XRD patterns of graphite electrodes obtained at the fully charged states of Li- and Na-ion coin cells when cycled at 313 K and at a current density of 0.1C (37.2 mA g⁻¹) and 10 mA g⁻¹, respectively. For the Li/graphite coin cell, two peaks assignable to stage-1 LiC₆ are detected at 24.16° (d = 3.68 Å) and 49.36° (d = 1.85 Å), leading to $d_i = 3.69$ Å, which is consistent with the results of a previous study.¹⁸ However, for the Na/graphite coin cell, only a sharp peak assignable to graphite is obtained at 26.6°, indicating that most of the capacity is likely to be consumed by SEI formation.

Throughout this comparative study of M-GIC formation, the charge-discharge profiles shown in Fig. 5 indicates that the formation of binary M-GICs occurs in a potential range lower than -2.85V vs. Fc⁺/Fc. Furthermore, with a closer inspection of the corresponding potential region, the onset potential of the M-GIC formation negatively shifts from Li (ca. 2.85 V) to K (ca. 3.00 V). Although the formation of any crystalline Na-GICs could not be confirmed by XRD in the case of the ionic liquid electrolyte, the decrease in peak intensities was clearly detected after charging process as shown in Figs. 4 and S4. Thus, the possibility of the formation of high stage Na-GICs cannot be excluded, leading to the conclusion that the "virtual" onset potential of Na-GIC formation is likely to lie above the Na⁺/Na potential (-2.96 V vs. Fc⁺/Fc). Moreover, according to our previous study,³⁴ the Na⁺/Na potential is more positive than the Li⁺/Li potential only by 0.11 V. Then, the formation of the low stage (stage 1) Li-GIC occurs in the narrow potential range of ca. 0.2 V between the onset potential (-2.85 V)vs. Fc⁺/Fc) and the Li⁺/Li potential (-3.07 V vs. Fc⁺/Fc). Thus, the potential difference between the "virtual" onset potential of Na-GIC formation and the Na⁺/Na potential should be considerably smaller than 0.2 V, which indicates that the "virtual" onset potential of Na-GIC formation does not lie beyond the onset potential of the Li-GIC formation. Under these careful considerations of the alkali metal-GIC formation, the onset potential i.e., the formation potential of high stage Na-GICs should lie somewhere between the Li-GIC $(-2.85 \text{ V vs. Fc}^+/\text{Fc})$ and K-GIC $(-3.00 \text{ V vs. Fc}^+/\text{Fc})$. Namely, since the "virtual" onset potential for high stage Na-GIC formation is very close to the Na⁺/Na potential, it is likely that the formation of low stage Na-GIC is thermodynamically prohibited. In previous studies on the chemical synthesis of Na-GICs using liquid Na metal,^{42,43} the elevated reaction temperatures higher than 423 K are required even for the formation of stage-6 or 7 Na-GICs, implying the difficulty of electrochemical reactions at lower temperatures.

Conclusions

We successfully investigated the charge-discharge behavior of negative electrodes graphite for KIBs using the K[FSA]–[C₃C₁pyrr][FSA] electrolyte at 313 K. In this electrolyte, high initial charge and discharge capacities of 316 and 268 mAh g were achieved for the K/graphite cell, entailing the formation of several K-GICs such as stage-3 KC₃₆, stage-2 KC₂₄, and stage-1 KC₈, which was confirmed by XRD. Furthermore, the ex-situ XRD measurement of K/graphite cells cycled at slow current rates revealed the formation of higher stages including stage-4, stage-5, stage-6, and dilute stage K-GICs during potassiation and depotassiation processes. The K/graphite cells exhibited an excellent cycling performance, delivering a capacity retention of 98% after 225 cycles at different current rates with an average coulombic efficiency of 99.9%. Furthermore, the electrochemical formation of M-GICs (M = Li, Na, K) was compared in the M[FSA]– $[C_3C_1pyrr]$ [FSA] electrolytes at 298 K. In contrast to the stage-1 GIC formation for Li- and K-ion systems, no Na-GIC formation was confirmed in the IL electrolyte, which is mostly consistent with the results of previous studies. Although no peaks corresponding to the low-stage Na-GICs were obtained from the ex-situ XRD data, the decreasing intensity of the graphite peak with increasing temperature and potential holding time indicated that the incorporation of Na⁺ ions must have occurred only at the surface of graphite. We concluded that this behavior can be explained by the Na⁺/Na potential, which is close to the "virtual" onset potentials for Na-GIC formation.

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