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Electrochemical Rubidium Storage Behavior of Graphite in Ionic Liquid Electrolyte[†] Alisha YADAV,[§] B Hironobu KOBAYASHI,[§] Takayuki YAMAMOTO,^{*,§§} B and Toshiyuki NOHIRA^{§§§}

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ABSTRACT

Electrochemical intercalation behaviors of alkali metals into graphite have been vigorously studied in academic and industrial fields, whereas their mechanisms are still unclarified. In this study, we report a novel rubidium-ion battery utilizing an ionic liquid electrolyte and natural graphite as the negative electrode material operating at room temperature. The electrochemical phase evolution behavior of rubidium–graphite intercalation compounds was elucidated using X-ray diffraction. The graphite negative electrode exhibited an initial discharge capacity of 216 mAh g^{-1} at 0.05 C rate, and retained its capacities of around 180 mAh g^{-1} even at 0.5 C rate for 50 cycles.



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Keywords : Rubidium-ion Battery, Ionic Liquid, Negative Electrode, Graphite

1. Introduction

Graphite is known to intercalate various guest species between its layers to form graphite intercalation compounds (GICs). GICs impart a wide variety of phases with diverse compositions and crystal structures.^{1,2} The intercalation and deintercalation mechanisms have garnered substantial attention from researchers worldwide. Specifically, GICs are of particular interest owing to their potential applications in energy conversion and storage devices.³ Alkali-metal GICs (AM-GICs) with Li, K, Rb, and Cs have been extensively studied over the past few decades. Among them, rubidium GICs (Rb-GICs) are one of the first to be synthesized using physical and chemical methods.⁴⁻⁷ In 1926, Fradenhagen et al. were the first to prepare AM-GICs by reacting graphite with an alkali metal in a molten or vapor state in a vacuum-sealed tube at various temperatures and vapor pressures. The products obtained were in an approximate composition of MC₈ (M = K, Rb, Cs).⁴ In 1932, Schleede et al. conducted X-ray diffraction (XRD) studies to determine the formula and crystal structure of these compounds.⁵ Subsequently, lamellar compounds of the composition MC_{12n} $(n \ge 2; n = \text{stage index}; M = K, Rb, Cs)$ were chemically prepared using Heróld's two-bulb technique. The staging-structural evolution of Rb-GICs upon Rb intercalation into graphite was studied by Rüdorff et al.⁶ Several other studies have been conducted by employing XRD and neutron diffraction techniques to determine the distance between the graphene layers of GICs and the evolution of the sequential staging phenomenon upon the intercalation of rubidium.8-14 However, studies on the electrochemical formation of Rb-GICs and the phase evolution of these compounds using non-aqueous electrolytes have not been conducted yet.

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Ionic liquid (IL) electrolytes are being extensively investigated due to their negligible volatility and nonflammability, ensuring fire safety. Moreover, they possess wide electrochemical windows, excellent thermal and electrochemical stabilities, and moderate ionic conductivities.¹⁵ As next-generation batteries, our research group has focused on sodium and potassium secondary batteries based on IL electrolytes.¹⁶⁻²¹ In particular, the charge-discharge performance of graphite negative electrodes in IL electrolytes was systematically investigated, and the formation of Li-, Na-, and K-GICs was found to likely occur at similar potentials.²⁰ However, no comparative studies have been conducted on the electrochemical formation of AM-GICs. Thus, the physicochemical and electrochemical properties of M[FTA]– $[C_4C_1pyrr]$ [FTA] ILs (M = Li, Na, K, Rb, and Cs; $FTA = (fluorosulfonyl)(trifuorosulfonyl)amide, C_4C_1pyrr = N-bu$ tyl-N-methylpyrrolidinium) were investigated previously to perform comparative studies on graphite negative electrodes for alkali metalion batteries.²¹ Consequently, it was found that the Rb[FTA]- $[C_4C_1pyrr][FTA]$ (molar fraction of Rb[FTA]: x(Rb[FTA]) = 0.20)electrolyte shows the second most negative redox potential (-3.71)vs. Ag^+/Ag) among alkali metals, a moderate ionic conductivity of 2.3 mS cm⁻¹, and a wide electrochemical window of 5.64 V at 298 K. Therefore, Rb-FTA-based electrolytes are envisioned to be suitable for electrochemical measurements.

In this study, Rb[FTA]–[C₄C₁pyrr][FTA] was utilized as an electrolyte for Rb-ion batteries (RbIBs), and the electrochemical performance of graphite negative electrodes was investigated. The ex-situ XRD technique was employed to accurately investigate the phase evolution of the Rb-GICs upon charge and discharge. To the best of our knowledge, this is the first report on the room-temperature synthesis of Rb-GICs. Most previous studies have reported the synthesis of Rb-GICs at higher temperatures.

2. Experimental

Rb[FTA] salt and [C₄C₁pyrr][FTA] IL were purchased from Provisco CS Ltd. and vacuum-dried at 333 K for 1 d before use. $Rb[FTA]-[C_4C_1pyrr][FTA]$ IL electrolyte with a composition of x(Rb[FTA]) = 0.20, commensurate with a molar concentration of Rb[FTA]: $C(Rb^+) \approx 0.8 \text{ mol dm}^{-3}$, was prepared by mixing two salts in an Ar-filled glove box. The working electrodes were prepared by mixing commercially available natural graphite powder (SNO-3; SEC Carbon, average particle size: 3 µm) with a sodium carboxymethylcellulose (CMC; #2200 Daicel Miraizu Ltd.) binder in a weight ratio of 90: 10 and the required amount of deionized water to form a homogeneous slurry. To fabricate the counter electrodes, natural graphite powder (SNO-10; SEC Carbon, average particle size: 10 µm) was mixed with polyvinylidene fluoride (PVdF; Kishida Chemicals Co., Ltd.) binder in a weight ratio of 93:7 and the required amount of N-methylpyrrolidone (NMP; Wako Pure Chemical Industries). It is known that FTA- anions are reversibly intercalated into graphite in the FTA-based IL electrolytes.²² Thus, graphite was adopted as the counter electrode in this study to suppress the decomposition of IL. Using the doctor blade method, the resultant slurry was pasted onto a copper or aluminum foil current collector for working or counter electrode, and dried overnight at 353 K in a vacuum oven. Electrodes with a diameter of 16 mm were then punched out and vacuum-dried overnight at 353 K. The average loading mass densities of the active material were approximately 1 mg cm^{-2} and 8 mg cm^{-2} for the working and counter electrodes, respectively. The reference electrode consisted of a Ag wire immersed in $[C_3C_1pyrr]$ [FSA] IL $(C_3C_1pyrr = N$ -methyl-N-propylpyrrolidinium, FSA = bis(fluorosulfonyl)amide)containing 0.05 mol dm^{-3} of silver trifluoromethanesulfonate (Ag[TfO]), which was separated in a glass tube equipped with porous frit as a liquid junction with the main FTA-based electrolyte. [C₃C₁pyrr][FSA] and Ag[TfO] were vacuum-dried at 333 K for 1 d before use.

All electrochemical measurements were conducted using cells in a three-electrode configuration (SB3A-S; EC Frontier Co., Ltd.) and a charge-discharge unit (HZ-7000 or HZ-Pro, Hokuto Denko Co. Ltd.). Before cell assembly, the electrodes were vacuum-impregnated overnight at 333 K with Rb[FTA]-[C₄C₁pyrr][FTA] (x(Rb[FTA]) = 0.20) electrolyte. A two-ply glass fiber filter (Whatman, GF/A, 25 mm in diameter and 260 mm in thickness) was used as the separator. The cell assembly process was conducted in a glove box under dry and deoxygenated Ar gas. Before electrochemical measurements, the cells were sealed in an airtight flask to avoid contact with the air because of the highly reactive nature of the Rb-GICs. In this study, the capacity $(mAhg^{-1})$ and current density $(mAg^{-1} \text{ or } C \text{ rate})$ were expressed based on the weight of the active material (graphite) in the working electrode. Charge-discharge measurements were conducted for initial 3 cycles at a current rate of 0.2 C (where 1 C corresponds to a current density of 279 mA g⁻¹, assuming the formation of RbC8 at the full-charged state) within the potential range of -3.62 V to -2.1 V vs. Ag⁺/Ag. Subsequently, the charge-discharge rate was changed to 0.05 C, and the cell was cycled in the potential range of -3.69 V to -2.1 V vs. Ag⁺/Ag. Furthermore, cycling tests were performed at a constant current rate of 0.5 C for 50 cycles in the potential range of -3.69 V to -2.1 V vs. Ag⁺/Ag. The potential values are designated with respect to the Ag^+/Ag redox couple.

Ex-situ X-ray diffraction (XRD) patterns were obtained in Bragg-Brentano geometry on a Rigaku Ultima IV diffractometer with Cu- $K\alpha$ radiation ($\lambda = 1.5418$ Å; $1 \text{ Å} = 10^{-10}$ m) at 40 kV and 40 mA. The samples for the XRD measurements were set in an airtight cell under a dry Ar atmosphere.

3. Results and Discussions

Figure 1 illustrates the charge–discharge curves of the graphite negative electrode for the initial three cycles measured at a constant current rate of 0.2 C (55.8 mA g⁻¹) and 298 K. The intercalation and



Figure 1. (a) Charge–discharge curves of a graphite negative electrode in Rb[FTA]– $[C_4C_1pyrr]$ [FTA] (x(Rb[FTA]) = 0.20) ionic liquid electrolyte at 0.2 C current rate and 298 K. (b) An enlarged view of Fig. 1a.

deintercalation process of Rb⁺ ion into and from graphite corresponds to charge and discharge, respectively.

Three distinct potential regions corresponding to Rb⁺ intercalation were identified for the first charge process: a steep sloping region I from -2.0 to -3.2 V (vs. Ag⁺/Ag), a gradual sloping region II from -3.2 to -3.4 V, and a long plateau region III from -3.4 to -3.6 V. The first region originates from the irreversible decomposition of the electrolyte, i.e., solid electrolyte interphase (SEI) formation, and it is largely suppressed in subsequent cycles. The latter two regions are characteristic of the staging process of GICs, which has also been observed in electrochemical K-GIC formation.²⁰ The first cycle at 0.2 C current rate showed a charge capacity of 293 mAh g⁻¹. The capacity contribution after eliminating the irreversible loss due to the formation of the SEI film (region I) was estimated to be approximately 275 mAh g^{-1} . This is commensurate with 98.5% of the theoretical capacity of 279 mAh g⁻¹, assuming the following redox reaction: $Rb^+ + e^- + e^ 8C \Rightarrow RbC_8$, which suggests that the formation of the stage-1 RbC₈ compound occurs at the end of the first charge. However, during the first discharge process, the graphite electrode showed two voltage plateaus at around -3.3 and -3.1 V, and a discharge capacity of $185 \,\mathrm{mAh}\,\mathrm{g}^{-1}$, which was accompanied by an initial coulombic efficiency of 63 %. Although this initial capacity loss is partly contributed by the SEI formation in the potential region I in the first charge process, the large irreversible capacity indicates that the gentle sloping and plateau regions, which correspond to regions II and III, are also likely to include SEI formation. The initial Rb⁺ intercalation occurred below -3.2 V and the potential for deintercalation was above -3.3 V vs. Ag⁺/Ag. This potential gap over 0.1 V was also observed in the K⁺ intercalation/deintercalation behavior of graphite negative electrodes,²⁰ in which slightly larger polarization was confirmed in the intercalation process. Thus, a similar phenomenon is presumed to be occurring in this system. For the subsequent cycles, intercalation and deintercalation occur in the potential region between -3.1 and -3.5 V. The larger potential margin between the charging plateau and metal deposition potential $(-3.71 \text{ V vs. Ag}^+/\text{Ag})$ is critical as it mitigates the risk of alkali metal formation on the graphite surface during operation. In the 3rd cycle, the irreversible capacity was significantly reduced as the coulombic efficiency increased to 82 %, and the discharge capacity was maintained at 181 mAh g^{-1} .

To elucidate the phase evolution behavior of graphite, ex-situ XRD measurement was performed on the graphite negative electrodes at different states of charge (SOCs), which were prepared by operating at 0.05 C in a voltage range of -3.69 to -2.1 V vs. Ag⁺/Ag. Before charge–discharge measurement at 0.05 C, the cells were cycled at a current rate of 0.2 C for three cycles in the voltage range of -3.62 to -2.1 V to ensure SEI formation (see Fig. 1). Figure 2a depicts the charge–discharge curves of the graphite negative electrode at 0.05 C rate. The cell showed a charge capacity of 382 mAh g⁻¹, entailing a steep sloping region from -2.1 to -3.24 V, a gentle sloping region from -3.24 to -3.44 V, and a plateau region from -3.44 to -3.69 V. A discharge capacity of 216 mAh g⁻¹ was obtained with a coulombic efficiency of 57 %.

Figure 2b shows the ex-situ XRD patterns of the graphite negative electrodes in Rb[FTA]–[C₄C₁pyrr][FTA] IL electrolyte. For the measured samples, 00*l* Bragg diffraction peaks are observed owing to the preferred orientation of the graphite particles. The intercalation and deintercalation of Rb⁺ ion into and from graphite produce several-stage GICs with the formula RbC_x, denoted as stage-*n* GICs. The stage index *n* represents the number of graphene layers present between the adjacent intercalated layers. The stage index *n* is calculated using the following equation:

$$I_{\rm c} = (n-1)d_0 + d_{\rm i} \tag{1}$$



Figure 2. (a) Charge–discharge curves of a graphite negative electrode in Rb[FTA]–[C₄C₁pyrr][FTA] (x(Rb[FTA]) = 0.20) ionic liquid electrolyte at 298 K. Current rate: 0.05 C (13.95 mA g⁻¹) after cycled at 0.2 C for 3 cycles. (b) Ex-situ XRD patterns of graphite electrodes at different charge–discharge states; numbering provided in the figure corresponds to points plotted in Fig. 2a. (c) Photos of pristine and fully charged graphite electrode.

where I_c represents the repeat distance, d_0 is the interlayer distance between two adjacent graphene layers in the pristine graphite sample, and d_i is the distance between the graphene layers after alkali metal-ion intercalation. The value of *d* for 00*l* reflections can be calculated using Bragg's law as follows:

$$\lambda = 2d\sin\theta \tag{2}$$

where λ is the wavelength of the Cu-K α X-ray (1.5418 Å), *d* is the interplanar spacing, and θ is the incident angle.

Initially, a 002 Bragg diffraction peak of the graphite electrode was observed at 26.58°, corresponding to an interlayer distance of 3.35 Å. Two broad peaks were observed at point 1 (90 mAh g⁻¹, -3.42 V). A graphite-like peak near 26.5° was observed with a significantly lower intensity and broadened peak width. The other broad peak at 29.0° (d = 3.07 Å) corresponds to the stage-3 compound with $I_c = 12.32$ Å, which results in the d_i value of 5.62 Å. These values are close to those calculated by Rüdorff et al.⁶

and Leung et al.^{9,10} Three peaks were observed at point 2 (120 mAh g⁻¹, -3.44 V). Two peaks at 19.59° (d = 4.53 Å) and 29.60° (d = 3.02 Å) correspond to the stage-2 compound, whose d_i value is calculated to be 5.70 Å. The peaks corresponding to stage 3 almost completely vanished at this point, however, a broad graphite-like peak at a higher 2θ value was observed, which is attributed to the formation of a dilute stage, where Rb⁺ ions are randomly and heterogeneously intercalated between graphene layers. The formation of compounds with different Rb⁺ ion concentrations suggests that the orderly stacking of rubidium between graphene layers is challenging.

Upon charging up to 294 mAh g⁻¹ and -3.55 V (point 3), two sharp peaks corresponding to stage 2 were observed at 19.58° and 29.65°. At this point, the peaks corresponding to stage 1 also started to appear. Finally, for the full-charged state at 382 mAh g⁻¹ and -3.69 V (point 4), two characteristic peaks with significantly high intensity, assignable to RbC₈, were observed at 15.70° (d = 5.65 Å) and 31.67° (d = 5.65 Å), with a calculated d_i value of 5.65 Å indicating complete intercalation of rubidium into the graphite structure, which is consistent with previous studies.^{6,9,10,13} Furthermore, the color change into dark brown was observed on the graphite electrode surface, as shown in Fig. 2c, which is characteristic of RbC₈ formation.

As the deintercalation process begins at point 5 (263 mAh g^{-1} and -3.24 V), various peaks were observed corresponding to stage 2 and stage 1. The peaks of stage 1 start to decrease in intensity and those of stage 2 become stronger. Upon further discharge at a cumulative capacity of 238 mAh g^{-1} and -3.18 V(point 6), the intensity of stage 2 was higher than that of stage 1, and very small peaks assignable to stage 3-like compound were also observed. The presence of three stages of Rb-GICs at this point, as a consequence of the inhomogeneity of the graphite electrode, suggests the slow kinetics of Rb⁺ deintercalation from graphite even at a low current rate of 0.05 C. A small graphite-like peak also appeared at this point. Upon complete discharging up to 216 mAh g^{-1} and -2.1 V, the graphite peak was restored at 26.58°. No other peaks were observed, indicating complete deintercalation. However, the intensity of the peak is lower compared to the pristine sample, which indicates the decrease in crystallinity upon rubidium intercalation or deintercalation. One may wonder the mismatch between the RbC8 formation confirmed by XRD and the obtained reversible capacity of $216 \,\mathrm{mAh}\,\mathrm{g}^{-1}$, which is lower than the theoretical capacity of RbC_8 formation (279 mAh g⁻¹). There are two possible reasons. The first is the uneven reaction distribution of graphite in the electrode. As stated above, the slow kinetics is involved in the Rb⁺ intercalation and deintercalation processes, evidenced by the multiphase formation during operation, suggesting that the state of charge is dependent on the position or depth in the electrode. Thus, even at the full-charged state, there may be residual Rb-GICs of higher stages in the electrode, which cannot be clearly detected by XRD. The second possible reason is the formation of the stage-1 Rb-GICs with different interlayer concentrations of rubidium between graphene layers, because the obtained reversible capacity of 216 mAh g^{-1} corresponds to a composition around RbC_{10.3}. For instance, assuming that metastable RbC12 is also formed as a stage-1 GIC with a lower interlayer concentration of rubidium, this composition can be explained as the coexisting state of RbC8 and RbC_{12} phases. The I_c and d_i values calculated for the Rb-GICs are listed in Table 1. The obtained d_i values lie within the range of 5.62– 5.70 Å, which is almost consistent with the previous studies on the chemical synthesis of Rb-GICs.^{5,6,8–14} The I_c and d_i values from the present and previous studies are summarized in Table 2.

To ascertain the long-term cycling stability of graphite negative electrodes for RbIBs, charge–discharge tests were conducted at a relatively high current rate of 0.5 C and 298 K, as shown in Fig. 3. According to Fig. 3a, the initial charge curve mainly consists of a

Table 1. Obtained values of repeated distance (I_c) and the distance between the intercalated layers (d_i) for stage-*n* Rb-GIC samples prepared at the current rate of 0.05 C and 298 K.

Compound	Stage index (<i>n</i>)	1	۸ ر ا	
		Intercalation	Deintercalation	$u_{\rm i}/A$
RbC ₈	1	5.65	5.65	5.65
RbC ₂₄	2	9.05	9.05	5.70
RbC ₃₆	3	12.32	(12.48)	5.62

Table 2. Summary of the present and representative previous studies on Rb-GICs.

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Year	Authors	Stage index (<i>n</i>) or Compound	I _c /Å	$d_{\rm i}/{ m \AA}$	Remarks	Ref.
2022	Yadav et al.	Stage 1 (RbC ₈)	5.65	5.65	X-ray diffraction	This work
		Stage 2 (RbC ₂₄)	9.05	5.70		
		Stage 3 (RbC ₃₆)	12.32	5.62		
1932	A. Schleede et al.	Stage 1	5.70	5.70	X-ray diffraction	5
1954	W. Rüdorff et al.	Stage 1 (RbC ₈)	5.65	5.65	X-ray diffraction	
		Stage 2 (RbC ₂₄)	9.02	5.67		6
		Stage 3 (RbC ₃₆)	12.34	5.64		
1977	Ellenson et al.	Stage 1 (RbC ₈)	5.64	5.64	Neutron Scattering	8
1979	Leung et al.	Stage 1 (RbC ₈)	~5.65	~5.65	X-ray diffraction (MoKα)	9
		Stage 2 (RbC ₂₄)	~9.05	~5.70		
1980	Leung et al.	Stage 1	5.65	5.65	X-ray diffraction	
		Stage 3	12.34	5.64		10
		Stage 6	22.43	5.68		
1980	Suematsu et al.	Stage 2 (RbC ₂₄)	~9.03	~5.68	Neutron diffraction	11
1981	N. Wada	Stage 1 (RbC ₈)	~5.657	~5.657	X-ray diffraction	12
1981	Leung et al.	Stage 1	5.65	5.65	X-ray diffraction	
		Stage 2*	9.01	5.66		13
			9.07	5.72		
		Stage 4	15.77	5.72		
1985	Ohshima et al.	Stage 2 (RbC ₂₄)	9.03	5.70**	X-ray scattering	14

*Results obtained for two different stage-2 graphite samples, ** $d_0 = 3.33$ Å.

potential slope above -3.2 V and a distinct plateau at around -3.4 V, giving the capacity of 316 mAh g⁻¹. In the initial discharge process, the potential plateaus appear above -3.3 V and the capacity is as



Figure 3. (a) Charge–discharge curves and (b) cycling properties of a graphite negative electrode in Rb[FTA]–[C₄C₁pyrr][FTA] (x(Rb[FTA]) = 0.20) ionic liquid electrolyte at 0.5 C rate and 298 K.

high as 199 mAh g⁻¹, corresponding to the initial coulombic efficiency of 63 %. As illustrated in Fig. 3b, the capacities decrease after the 2nd cycle and then recover approximately at the 10th cycle, which was also observed for the graphite negative electrodes of potassium secondary batteries at higher current rates.²⁰ After the 10th cycle, the reversible capacities of 180–200 mAh g⁻¹ were obtained up to the 50th cycle. Charge–discharge profiles of the 10th, 25th, and 50th cycles are almost overlapped with each other with a negligible increase of polarization, indicating the stable cycling performance of graphite negative electrodes for RbIBs using the IL electrolyte.

4. Conclusions

In this study, the charge–discharge behavior of graphite negative electrodes for RbIBs was successfully investigated using the Rb[FTA]–[C₄C₁pyrr][FTA] electrolyte at 298 K. In this electrolyte, high initial charge and discharge capacities of 383 mAh g⁻¹ and 216 mAh g⁻¹, respectively, were achieved at a rate of 0.05 C. Ex-situ XRD measurements revealed the formation of stage-1 Rb-GIC (RbC₈) with $d_i = 5.65$ Å. Furthermore, the formation of higher stages, including stage-2 and stage-3 Rb-GICs, during the intercalation and deintercalation processes was also confirmed. Finally, stable cycling characteristics were observed for 50 cycles, indicative of the good compatibility between graphite negative electrodes and the IL electrolyte in the RbIB system.

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CRediT Authorship Contribution Statement

- Alisha Yadav: Data curation (Equal), Investigation (Equal), Methodology (Equal), Validation (Equal), Writing original draft (Lead)
- Hironobu Kobayashi: Data curation (Equal), Investigation (Lead), Methodology (Equal), Validation (Equal), Writing review & editing (Supporting)
- Takayuki Yamamoto: Conceptualization (Lead), Data curation (Lead), Funding acquisition (Lead), Methodology (Equal), Supervision (Equal), Validation (Equal), Writing – review & editing (Equal)
- Toshiyuki Nohira: Conceptualization (Equal), Methodology (Equal), Supervision (Equal), Validation (Equal), Writing review & editing (Equal)

Conflict of Interest

The authors declare that they have no known competing financial interests.

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