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Electrochemical intercalation of bis(fluorosulfonyl)amide anions into graphite from aqueous solutions

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1. Introduction

Ions and molecules are intercalated into graphite by both chemical and electrochemical methods, and graphite intercalation compounds (GICs) are formed. GICs have been studied as potential materials for many applications [1]. For example, electrochemical Li⁺ intercalation is seen as a reaction at the negative electrode in lithium-ion batteries [2], and GICs are also used to produce graphene oxides (GOs) as a mother material for exfoliated graphite and graphite sheets [3]. Since GOs can be potentially used in electronics, conductive films, electrode materials, and composites, numerous studies have been performed to explore an efficient route for the mass production of GICs [4].

Conventionally, a solution of sulfonic acid is used to form a precursor GIC (C₆H₅SO₃⁻·2H₂SO₄) for GO production [5]. The solution of sulfonic acid should be concentrated to at least 50 wt% H₂SO₄; otherwise, water decomposition (i.e., oxygen evolution) will hinder the formation of GICs. Such strong acid solutions, however, require post-treatment for neutralization, which is a high-maintenance process and could damage the surface of graphite. On the other hand, while non-aqueous electrolyte solutions are also used for the formation of GICs [6–9], they are very expensive and environmental problems should be considered. Therefore, there is a great need for a process for the formation of GICs using environmentally friendly aqueous solutions.

There are serious concerns regarding the stability of aqueous solutions at high electrode potentials. Generally, during the formation of GICs, the electrode potential must be above the upper limit of the potential window of water. Recently, highly concentrated aqueous electrolyte solutions with alkali metal cation-organic anion salts with a wide potential window have been reported for aqueous lithium-ion batteries and aqueous sodium-ion batteries [10–12]. For example, large amounts of lithium bis(trifluoromethanesulfonyl)amide (LiTFSA) and sodium bis(fluorosulfonyl)amide (NaFSA) can be dissolved in water at room temperature. These concentrated aqueous electrolytes are neutral, and the electrochemical potential window of neutral aqueous electrolyte solutions is expanded [13]. In addition, a high concentration of anion is favorable for anion intercalation, since the standard potential of anion intercalation/de-intercalation should be shifted negatively with an increase in the concentration, according to the Nernst equation. Therefore, highly concentrated aqueous solutions are promising candidates as electrolytes, in which GICs can be formed.

In this study, the intercalation of bis(fluorosulfonyl)amide (FSA) anion into graphite is investigated using highly concentrated aqueous solutions of NaFSA. This is because FSA salts are known to be much more highly soluble than other anion salts owing to the weaker inter- and intra-molecular interactions [9,14]. Previously, we reported the intercalation of FSA anion in non-aqueous solutions [9]. FSA-GIC was formed at a high potential (5 V vs. Li⁺/Li), which is far above the potential window of water. Therefore, the potential window of aqueous solutions should be expanded to suppress the oxygen evolution reaction. Concentrated NaFSA aqueous solutions are neutral, relatively safer and low toxic, compared with acid solutions, organic electrolytes, and ionic liquids. To the best of our knowledge, there is no previous report about the intercalation of organic anions into graphite using aqueous solutions.

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2. Experimental

A three-electrode cell was used for electrochemical measurements. The working electrode consisted of a highly oriented pyrolytic graphite (HOPG, Momentive) wrapped in a platinum mesh, and the counter electrode and reference electrode were a platinum mesh and Ag/AgCl electrode. HOPGs were cut into a slab measuring ca. 5 mm × 5 mm × 0.5 mm with a weight of ca. 15 mg. Electrolyte solutions consisted of aqueous solutions of 1 and 19 mol kg\(^{-1}\) NaFSA. The aqueous solution in this study was almost saturated at 19 mol kg\(^{-1}\) NaFSA at ambient temperature. Cyclic voltammetry was conducted between the open circuit potential (OCP) and 1.7 V (vs. Ag/AgCl), and the scan rate was set at 1 mV s\(^{-1}\). Chronopotentiometry was also conducted with various constant currents in a potential range of 0.2 to 1.7 V. Notably, positive currents (i.e., oxidation) correspond to the intercalation of anions and negative currents (i.e., reduction) correspond to the de-intercalation of anions. Applied currents are normalized by the weight of HOPG electrodes. X-ray diffraction (XRD) measurement and Raman spectroscopy were used to investigate the structural changes of graphite by applying currents. XRD patterns were taken using CuKα radiation over a 2θ range of 5–60°. Raman spectroscopy was carried out using a 515 nm laser (100 mW). All electrochemical measurements were carried out using an HSV-100 (Hokuto-Denko) and HJ1001SD8 (Hokuto-Denko).

3. Results and discussion

Fig. 1 shows the CVs of HOPG electrodes in aqueous solutions of 1 and 19 mol kg\(^{-1}\) NaFSA. While large oxidative currents were observed at around 1.5 V in 1 mol kg\(^{-1}\) NaFSA aq., oxidative currents were strongly suppressed in 19 mol kg\(^{-1}\) NaFSA. Possible oxidation reactions at high potentials include FSA\(^{-}\) intercalation and water decomposition. With various kinds of salts, water decomposition is suppressed in aqueous solutions with low water concentrations [13]. The water concentration of 19 mol kg\(^{-1}\) NaFSA aq. was 21 mol dm\(^{-3}\), and this relatively lower value caused the suppression of water decomposition [13]. The molar ratio of NaFSA/water for 1 mol kg\(^{-1}\) NaFSA aq. and 19 mol kg\(^{-1}\) NaFSA aq. were ca. 1/56 and 1/3, respectively. In addition, Raman spectrum of 19 mol kg\(^{-1}\) NaFSA aq. was measured to clarify the solution structure. As shown in Fig. S1 (Supporting information), the OH stretching band of water in 19 mol kg\(^{-1}\) NaFSA aq. was relatively narrow like the Raman spectrum of “water-in-salt” solution (21 mol kg\(^{-1}\) LiTFSA aq.) [11], indicating that free water molecules decreased owing to the high concentration. As a result, the suppression of water decomposition resulted in low oxidative currents. In addition, reductive currents were clearly observed at around 1.5 V. Such oxidative and reductive currents imply that the intercalation/de-intercalation of FSA\(^{-}\) proceeded on graphite in 19 mol kg\(^{-1}\) NaFSA aq. In a non-aqueous solution, the intercalation/de-intercalation of FSA\(^{-}\) occurred when the concentration of FSA\(^{-}\) was 1 mol dm\(^{-3}\) (LiFSA) [9]. Therefore, we consider that the formation of FSA-GIC occurred, even in 1 mol kg\(^{-1}\) NaFSA aq., but it immediately vanished by reacting with water. In contrast, formed FSA-GIC was successfully retained in 19 mol kg\(^{-1}\) NaFSA aq., where water molecules were inactive so that the de-intercalation of FSA\(^{-}\) was also observed.

Under the application of constant currents, the potential curves of HOPG electrodes as a function of electric charge (Q) in aqueous solutions of 1 and 19 mol kg\(^{-1}\) NaFSA are shown in Fig. 2. When we applied +10 mA g\(^{-1}\) in 1 mol kg\(^{-1}\) NaFSA aq., the potential did not reach the cut-off potential of 1.7 V and stayed at about 1.4 V. As in Fig. 1(a), water decomposition mainly occurred on the HOPG electrode and showed a constant potential. In contrast, the potential rose to 1.7 V in 19 mol kg\(^{-1}\) NaFSA aq. under the application of +10 mA g\(^{-1}\). To form FSA-GIC, a high electrode potential is necessary to intercalate FSA– into graphite. In the non-aqueous solution, FSA-GIC was formed at about 5 V (vs. Li\(^+/\)Li), which corresponds to 1.7 V (vs. Ag/AgCl), but
such potential is far beyond the potential window of water [9]. Therefore, the concentrated aqueous solution (19 mol kg⁻¹ NaFSA) has an advantage to achieve a high electrode potential even using aqueous solutions. Furthermore, a reversible electric charge was observed in 19 mol kg⁻¹ NaFSAaq. under the application of −10 mA g⁻¹, implying that the de-intercalation of FSA⁻ from GICs occurred during reduction. The reason for this reversible charge in 19 mol kg⁻¹ NaFSAaq. was not the difference between the conductivities of electrolyte solutions, but rather the difference between potential windows because the conductivity of 19 mol kg⁻¹ NaFSAaq. is higher than that of 1 mol kg⁻¹ NaFSAaq. [11].

To clarify the structural changes of HOPG after electrochemical polarization, XRD measurements and Raman spectroscopy were performed after a 2nd oxidation (+10 mA g⁻¹). Fig. 3 shows the XRD patterns of HOPG electrodes after oxidation, compared with pristine HOPG. No new peak was observed after oxidation in the normal aqueous solution (1 mol kg⁻¹ NaFSA), and therefore there was no change in the structure of graphite. In contrast, in 19 mol kg⁻¹ NaFSAaq., new peaks clearly appeared at 2θ = 26.5°, 43.58°, 50.00°, and 56.92° for oxidized HOPG, and the original peaks (2θ = 26.5° and 55°) of pristine HOPG disappeared. These new peaks were indexed with the same sandwich distance (0.78 nm) as FSA-GIC produced in the non-aqueous solutions [9], and are denoted by 00l in Fig. 3. A calculated repeating distance of 1.45 nm on the c axis is in agreement with the formation of stage 3 GIC: 0.78 nm × 2 = 1.45 nm. Hence, the formation of stage 3 FSA-GIC was confirmed in the aqueous solution with a high concentration of NaFSA. De-intercalation capacity of ca. 20 mAh g⁻¹ corresponding to C112FSA in aqueous solutions was almost the same as LiTFSA-organic solution system [15]. One possible explanation for such low capacity is the decline of the intercalation capacity by the co-intercalation with water molecules. Recently, the co-intercalation of organic solvents during anion intercalation in non-aqueous solutions was reported [16,17]. Co-intercalation with solvents can make the intercalation capacity smaller. Actually, the de-intercalation capacity of amide anion in organic electrolyte solutions (55 mAh g⁻¹) [17] were smaller than that in ionic liquid electrolytes (80 mAh g⁻¹) [15]. The de-intercalation capacity of 20 mAh g⁻¹ for stage 3 FSA-GIC, in this study, was consistent with the discharge capacity of 60 mAh g⁻¹ for stage 1 FSA-GIC synthesized in 1 mol dm⁻³ LiFSA organic solution [9]. To clarify whether co-intercalation occurred or not, further study is needed in the future.

Fig. 4 shows the Raman spectra of HOPG electrodes after oxidation, compared with pristine HOPG. The spectrum of pristine HOPG shows the G-band at ca. 1580 cm⁻¹ and the band at ca. 1555 cm⁻¹ derived from O₂, and the spectrum did not change after oxidation in 1 mol kg⁻¹ NaFSAaq. In contrast, the G-band became very weak and was slightly shifted, and the new band derived from GICs appeared at 1612 cm⁻¹ after oxidation in 19 mol kg⁻¹ NaFSAaq. Based on the intensity ratio of the G-band and new band, stage 2 and 3 FSA-GICs coexisted near the surface of HOPG. In this study, stage 3 FSA-GIC was obtained inside the bulk of HOPG as the lowest-stage GIC. As already mentioned, we produced stage 1–2 FSA-GICs in non-aqueous solution by electrochemical oxidation [9]. Generally, much more energy (i.e., higher potential) is required to produce lower-stage acceptor-type GICs, which contain anions as a guest. If the potential had been raised beyond 1.7 V, the formation of lower-stage FSA-GICs would be achieved. Water decomposition, however, is also accelerated at a potential higher than 1.7 V, dominates the oxidation current according to the Butler-Volmer equation. As a result, further lowering of the stage of FSA-GICs is inhibited by water decomposition. To produce stage 1–2 FSA-GICs in aqueous solutions, it will be necessary to explore other approaches for suppressing water decomposition, in addition to using concentrated solutions.

4. Conclusion

Electrochemical synthesis of FSA-GICs was performed in a highly concentrated aqueous electrolyte solution using NaFSA as an electrolyte salt. In cyclic voltammograms, only oxidative currents were observed in a dilute aqueous electrolyte, but large redox peaks at high potential appeared in a highly concentrated aqueous electrolyte, indicating the intercalation/de-intercalation of FSA anions. XRD patterns show the formation of stage 3 FSA-GICs in highly concentrated aqueous solutions, which is also confirmed by Raman spectroscopy. For the first time, acceptor-type GICs of organic anions were synthesized in aqueous solutions.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.elecom.2019.01.015.
Conflicts of interest

There is no conflict of interest.

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