In this study, we investigated the role of solid electrolyte interface (SEI) films in the cells fabricated with the ionic liquids ([N$_{2,2,1(2O)}$][TFSI]) and [Li(G4)][TFSI]). The SEI was introduced beforehand to the graphite electrode, which facilitated the intercalation of Li-ions into the graphite electrode in [Li(G4)][TFSI]. In addition, the discharge capacity in the case of the cell fabricated with [Li(G4)][TFSI] was almost similar to that observed in the case of the cell fabricated with organic electrolyte. The SEI performed the pulling apart combination of glyme and Li-ion. Identification analysis of the SEI component having action of extracting Li-ion from [Li(G4)] was carried out.

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Results and Discussion

Figure 2 shows the cyclic voltammograms of the three cell types with (a) fresh CGB-10 electrode, 1 M LiPF6/EC-DMC; (b) fresh CGB-10 electrode, 1 M LiPF6/[N2,2,1(2O1)][TFSI]; and (c) fresh CGB-10 electrode, [Li(G4)][TFSI] fabricated in this study. In the case of the cell fabricated with 1 M LiPF6/EC-DMC, the reduction peak appeared only in the first cycle at around 1.4–0.3 V vs. Li/Li+. This peak indicated the formation of the SEI film on the surface of graphite electrode. The oxidation/reduction peaks that originate because of the intercalation and de-intercalation of Li-ions into the graphite electrode were observed in the low potential region (0.3–0.005 V). Such peaks were not observed in the cell fabricated with the 1 M LiPF6/[N2,2,1(2O1)][TFSI] electrolyte. The reduction peak at around 2.0–1.0 V is considered to depend on the electrolyte decomposition or on the previously occurring intercalation of [N2,2,1(2O1)] cations, rather than Li-ions. In the case of the cell fabricated with [Li(G4)][TFSI], the peaks were observed at various potentials. The reduction peak observed only in the first cycle at around 1.6–1.0 V is thought to be due to decomposition reaction of free glyme which isn’t coordinated with Li-ions. Since the amount of free glyme not coordinated to Li-ions is negligible, this reaction is considered to be observed only in the first cycle. Furthermore, the reduction peak could be confirmed also in the low potential region (1.0–0.005 V). This peak seems to be derived from the reaction between solvated Li-ions (Li(G4)+) and graphite negative electrode. This reaction is generally confirmed only in the first cycle as SEI production reaction, but this system was also confirmed in the second and third cycles. Therefore, it was found that [Li(G4)][TFSI] can’t produce favorable SEI on the graphite negative electrode. In general, reversible oxidation/reduction reactions found around 0.3–0.005 V couldn’t be confirmed in this system.

To prevent the decomposition of the electrolyte, the SEI formed in the CGB-10 electrode were introduced in the ionic liquids. Figure 3 shows the cyclic voltammograms of the cells (b)’ CGB-10 electrode formed SEI film, 1 M LiPF6/[N2,2,1(2O1)][TFSI], and (c)’ CGB-10 electrode formed SEI film, [Li(G4)][TFSI] fabricated in this study. No noticeable change in the cyclic voltammograms was observed in the case of the cell fabricated with 1 M LiPF6/[N2,2,1(2O1)][TFSI]. The SEI couldn’t prevent the preferential intercalation of [N2,2,1(2O1)] cations into the graphite electrode. In the case of the cell fabricated with [Li(G4)][TFSI], the reduction peak was observed in the first cycle at around 1.6–1.0 V. The oxidation/reduction reactions at various potential were controlled. Furthermore, the curves similar to those of the redox reaction in organic electrolyte were obtained. The peak corresponding to the intercalation of Li-ions was confirmed in the low potential region. In the case of the cell fabricated with [Li(G4)][TFSI], the CGB-10 electrode formed SEI suppressed the decomposition of electrolyte and facilitated the intercalation of Li-ions into the graphite electrode. The cause of this difference was possible due to difference structure of electrolyte. A common organic electrolyte is consisted of solvated Li-ion and anion. 1 M LiPF6/[N2,2,1(2O1)][TFSI] is composed of two types of cation and two types of anion, and its solution structure is different. On the other hand, the solvation structure of Li-ion and formation of ion pairs in electrolyte solutions composed of G4 and a TFSI were similar to that of organic electrolyte.

Figure 4 shows the charge–discharge behaviors of each electrolyte solution (I) fresh CGB-10, 1 M LiPF6/EC-DMC; (II) fresh CGB-10, [Li(G4)][TFSI] and (III) CGB-10 formed SEI, [Li(G4)][TFSI]. In the case of the cell fabricated with 1 M LiPF6/EC-DMC, the potential flat domain originating as a result of the insertion of Li-ions appeared at about 250–5 mV. This indicates the charging of the Li-ions. On the other hand, in the case of [Li(G4)][TFSI] before the formation of SEI on the graphite electrode, the potential flat domain in the low potential region was not observed. Moreover, the charge–discharge action showed big irreversible capacity to the first cycle. Similarly, when the CGB-10 electrode formed SEI were used in [Li(G4)][TFSI], the potential flat domain in the low potential region was not observed. However, the Li-ions could be intercalated by charging with a constant potential of 5 mV. The SEI are considered to have prevented electrolyte decomposition and helped desolvation of Li-ion from glyme. The SEI were stable without decomposition since discharge capacity had not decrease at each cycle. In organic liquid, this result is indicated

![Chemical structures](image1)

Figure 1. Chemical structures of (a) Bis(trifluoromethane sulfonfonyl)imide, (b) N,N-Diethyl-N-methyl-N-(2-methoxyethyl)ammonium, and (c) Li-tetraglyme.

![Voltammograms](image2)

Figure 2. Voltammograms of CGB-10 electrodes in each electrolyte: (a) 1 M LiPF6/EC-DMC, (b) 1 M LiPF6/[N2,2,1(2O1)][TFSI], and (c) [Li(G4)][TFSI], 25°C, 1 mVs⁻¹.

![Voltammograms](image3)

Figure 3. Voltammograms of CGB-10 electrodes formed SEI films in each electrolyte: (b)’ 1 M LiPF6/[N2,2,1(2O1)][TFSI] and (c)’ [Li(G4)][TFSI], 25°C, 1 mVs⁻¹.
possibility of similar intercalation mechanism with organic electrolyte. In addition, the discharge capacity of fresh CGB-10 electrode in 1 M LiPF$_6$/EC-DMC and SEI formed CGB-10 electrode in [Li(G4)][TFSI] exceeded theoretical capacity.

We considered that there were different mechanisms of intercalation and deintercalation of Li-ion into the graphite layer from in LiPF$_6$/[N$_2$,2,1(2O1)][TFSI] and [Li(G4)][TFSI]. In 1 M LiPF$_6$/[N$_2$,2,1(2O1)][TFSI], SEI formation reaction on the surface of fresh graphite negative electrode (fresh CGB-10) could not occur. From this result, 1 M LiPF$_6$/[N$_2$,2,1(2O1)][TFSI] could have a low Li$^+$ conductivity. Therefore, even though the graphite negative electrode coated with SEI derived from the organic electrolyte, the intercalation and deintercalation of Li-ion into the graphite layer did not occur in 1 M LiPF$_6$/[N$_2$,2,1(2O1)][TFSI]. On the other hand, [Li(G4)][TFSI] reacted with the fresh graphite negative electrode. However, SEI formed on the surface of the graphite negative electrode had the low Li$^+$ conductivity. Hence, the intercalation and deintercalation of Li-ion into the graphite layer did not take place. Thus, SEI formed on graphite electrode derived from the organic electrolytic solution which had a high Li$^+$ conductivity was necessary for the intercalation and deintercalation of Li-ion into the graphite layer in [Li(G4)][TFSI].

The coulomb efficiency at the third cycle of the graphite electrode in 1 M LiPF$_6$/EC-DMC was 96.9%. Also, the coulomb efficiency at the third cycle of the graphite electrode in [Li(G4)][TFSI] before and after formation of SEI was 63.2% and 94.4%. The reason why the low coulomb efficiency in [Li(G4)][TFSI] was considered to be attributable to Li$_2$CO$_3$ formed by decomposition of [Li(G4)][TFSI], and Li$_2$CO$_3$ might increase the internal resistance.

Furthermore, the intercalation of Li-ions into the graphite electrode was confirmed using XRD. Figure 5 shows the XRD patterns of (i) fresh CGB-10, (ii) fresh CGB-10 after charge in [Li(G4)][TFSI], and (iii) SEI formed CGB-10 after charge in [Li(G4)][TFSI]. The XRD pattern of the fresh CGB-10 after charging indicated peaks corresponding to the different structures of the lithium–graphite intercalation compound. In the case of fresh CGB-10 after charging in [Li(G4)][TFSI], the XRD peak at 26.6° disappeared. However, gentle peaks were observed at around 24.4°–25.7°. These peaks might be attributed to the intercalation of Li-ions into the graphite electrode. However, it was impossible to confirm the formation of the stage structures. The XRD peak of the CGB-10 formed SEI after charge in [Li(G4)][TFSI] appeared around 24.0°–25.3°. The XRD patterns at 24.0° and 25.3° correspond to the first and second stage structures, respectively. These results indicate that the SEI separated Li-ion and glyme, in addition to enabling the intercalation of Li-ions into the graphite electrode.

Figure 6 shows SEM images of Fresh CGB-10 and SEI formed CGB-10 charged and discharged in 1 M LiPF$_6$/EC-DMC. The fresh CGB-10 electrode, fresh CGB-10 after charge/discharge in [Li(G4)][TFSI], and SEI formed CGB-10 after charge/discharge in [Li(G4)][TFSI].

Figure 5. XRD patterns of (i) fresh CGB-10, (ii) fresh CGB-10 after charge in [Li(G4)][TFSI], and (iii) SEI formed CGB-10 after charge in [Li(G4)][TFSI].
system of SEI formed CGB-10 and [Li(G4)][TFSI], precipitates were uniformly deposited on the entire electrode surface as in the case of the organic electrolyte. We inferred that SEI derived from organic electrolyte suppressed the reaction between the binder and [Li(G4)][TFSI] since no rod-like precipitates were observed. However, as shown in Table I, since the ratio of the carbon is decreased and the ratio of the oxygen is increased as compared with the system of the organic electrolyte, SEI derived from [Li(G4)][TFSI] seem to be deposited on SEI derived from organic electrolyte. The reason why charging and discharging can be performed despite the existence of SEI derived from [Li(G4)][TFSI] is considered to be due to SEI derived from organic electrolyte has a function of extracting Li⁺ from [Li(G4)].

Figure 7 shows the comparison of C 1s and O 1s XP spectra measures on Fresh CGB-10 and SEI formed CGB-10 charged and discharged in 1 M LiPF₆/EC-DMC and [Li(G4)][TFSI]. For the Fresh CGB-10 charged and discharged for three cycles in 1 M LiPF₆/EC-DMC, the C 1s spectrum shows peaks at 281.8 eV (Li₂C₂), 284.0 eV (C sp²) and 288.1 eV (ROCO₂Li) and the O 1s spectrum shows peaks at 529.0 eV (Li₂O), 530.4 eV (O = C/O-Li). In the case of the SEI formed CGB-10 charged and discharged in [Li(G4)][TFSI], the C 1s spectrum shows peaks of Li₂C₂, C sp², ROCO₂Li and Li₂CO₃ and the O 1s spectrum shows peaks of O = C/O-Li, Li₂O and ROCO₂Li. These results indicative that the decomposition products (Li₂CO₃) of [Li(G4)][TFSI] do not contribute to intercalation of Li⁺ into graphite layers. Moreover, these results indicative that when [Li(G4)][TFSI] is used as an electrolyte, ROCO₂Li have Li⁺ conductivity and have not electronic conductivity.

As a results of impedance measurement (Figure 8), SEI (ROCO₂Li) from derived 1 M LiPF₆/EC-DMC have an effect of reducing charge transfer resistance of electrode-electrolyte interface. However, SEI (Li₂CO₃) from derived [Li(G4)][TFSI] have an effect of increasing charge transfer resistance of electrode-electrolyte interface.

This result revealed that ROCO₂Li which was the decomposition products of the 1 M LiPF₆/EC-DMC was particularly necessary to adapt the [Li(G4)][TFSI] as an electrolyte.

**Conclusions**

The graphite electrode in [Li(G4)][TFSI] achieved theoretical capacity by introducing stable SEI derived from 1 M LiPF₆/EC-DMC. The capacity was identified as intercalation of Li-ions into the graphite electrode in ionic liquid electrolyte. From the results of XPS, it was found that ROCO₂Li was required as SEI in order to adapt [Li(G4)][TFSI] as an electrolyte for LIBs. However, the SEI could not prevent the preferential intercalation of [N₂₂₂₁, Li][C₄] cations into the graphite electrode. This result suggest that SEI derived 1 M LiPF₆/EC-DMC do not conform to full range ionic liquids. Consequently, in ionic liquids that do not undergo reversible charge and discharge reaction of Li-ions, the possibility of charge and discharge could be indicated by introducing the SEI beforehand. These results confirm the importance of SEI in ionic liquids.

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