Communication—Intercalation/De-Intercalation Behavior of Li-Ion Encapsulated by 12-Crown-4-Ether into Graphite Electrode

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Electrochemical intercalation/de-intercalation behavior of Li ion encapsulated by 12-crown-4-ether into/from graphite electrode was studied and compared with a commercially available Li-ion battery electrolyte. In electrolyte solution in which Li ion is coordinated by 12-crown-4-ether, the interlayer of graphite expanded from 0.335 nm to 1.137 nm at charged state of 0.1 V, which is three times larger than that (0.371 nm) in the commercial electrolyte. Charge transfer reaction without desolvation process using Li ion encapsulated by 12-crown-4-ether was successfully progressed even at the high rate of 2C. The insight obtained in this study extend the diversity of carrier ion.

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According to the characteristic of devices, the development of different type rechargeable batteries has required and the diversity of carrier ion is increasing from the perspective of resource strategy. In view of abundance of Mg and advantage originated from divalent ion, Mg-ion batteries have attractive attention as a next-generation energy device.1,2 In the case of using Mg metal as a negative electrode, the development of electrolytes which enable reversible Mg-deposition/dissolution reactions is still a challenge. Since Mg ion is a stronger Lewis acid than monovalent ion such as Li ion and Na ion when using carbonate-based solvent employed in commercially available Li-ion batteries (LIBs), Mg ion is more stabilized by solvation molecules.3–4 Consequently, in regard to graphite as a host material, carbonate-based electrolyte with highdielectric constant blocks intercalation (charge transfer) reaction involved in desolvation.5,6 Meanwhile, one of cyclic ether, crown ether with repeating unit being ethyleneoxy (−CH2CH2O−) has high affinity and selectivity to alkali metal ion and alkaline-earth metal ion and encapsulates in itself to form complex.7–9 As a strategy for storage of Mg ion in graphite interlayer, we considered a reversible battery reaction based on the intercalation of the solvated ions without desolvation. The electrochemical co-intercalation of solvated Li ion is mainly limited to the use of oligoether (glyme) regardless of carrier ion to the best of authors knowledge.5,6 As a preliminary stage to a study of an electrochemical behavior of graphite electrode in the presence of encapsulated Mg ion by crown ether, we investigated intercalation/de-intercalation properties of Li ion coordinated by 12-crown-4-ether having a suitable cyclic size for encapsulation.10 In the present study, solvation structure of Li ion and the influence of encapsulation on formation for electrochemical graphite intercalation is discussed.

Experimental

Lithium trifluoromethanesulfonate (LiOTf), diglyme (G2), and 12-crown-4-ether (12C4) were used without further purification. In electrolyte solution in which Li ion is coordinated by 12-crown-4-ether, the interlayer of graphite expanded from 0.335 nm to 1.137 nm at charged state of 0.1 V, which is three times larger than that (0.371 nm) in the commercial electrolyte. Charge transfer reaction without desolvation process using Li ion encapsulated by 12-crown-4-ether was successfully progressed even at the high rate of 2C. The insight obtained in this study extend the diversity of carrier ion.

Results and Discussion

Figure 1 compares Raman spectra of Li salt (LiOTf), solvent, and electrolyte solutions in the frequency range of 750 to 900 cm⁻¹ which shows the interaction between Li ion and solvent (Figure S1, Supporting Information).

![Figure 1](image-url)

**Figure 1.** (a) Raman spectra of LiOTf, G2 (diglyme), LiOTf/G2, 12C4, and LiOTf-12C4/G2 in the range of 750 to 900 cm⁻¹. (b) Proposed solvation structures of Li ion in LiOTf/G2 and LiOTf-12C4/G2 solutions. (c) Identification of experimental vibration frequency.
Supplemental material). In G2 and 1.0 mol kg\(^{-1}\) LiOTf/G2 systems, the Raman band located at 805, 827, and 850 cm\(^{-1}\) can be attributed to CH\(_2\) rocking and C–O stretching vibration modes.\(^{10}\) The new band (coupled Li–O) involved in interaction between Li ion and G2 solvent appeared at 878 cm\(^{-1}\), meaning that Li ion is solvated by G2 to form [Li(G2)]\(^{+}\) complex.\(^{11,12}\) The solvation number (x) is referred to be about two.\(^{13,14}\) As for 12-crown-4-ether, bands derived from C–O–C stretching mode were observed at 783, 800, 816, 844, and 898 cm\(^{-1}\). In the case of mixing LiOTf and 12C4 by an equimolar ratio, colorless crystalline solid was formed. Before starting the experiment, we planned to realize co-intercalation reaction using an electrolyte composed only of LiOTf and 12C4. However, it resulted in solid and we therefore used the [Li(12C4)]\(^{+}\) complex as a carrier ion. After the addition of equimolar mixture of LiOTf/12C4 to G2 as a solvent with 0.5 mol kg\(^{-1}\), Raman bands related to 12C4 disappeared and then bands of free G2 (having no interaction) and G2 interacting Li ion appeared with slight intensity. In term of the size of Li ion (Shannon’s ionic radii: 76 pm), 12C4 is suitable cyclic size and Li ion should be encapsulated. Since 12C4 molecule has planarity and relatively low steric hindrance, a positive charge (Li\(^{+}\)) is not completely shielded and thereby presumably results in additional solvation of G2 to [Li(12C4)]\(^{+}\) complex. This is due to the appearance of band at 878 cm\(^{-1}\). The structure phase of graphite storing the carrier ion with the rate-determining step of charge transfer reaction in graphite.\(^{17–19}\)

Figure 2. XRD patterns of graphite electrodes during second charge–discharge cycle in (a) 1 mol kg\(^{-1}\) LiOTf/EC:DEC (50:50 vol.%) and (b) 0.5 mol kg\(^{-1}\) LiOTf-12C4/G2. The current density was set to 37.2 mA g\(^{-1}\). Inset: photographs of graphite electrodes charged at 0.005 V and 0.1 V (vs. Li/Li\(^{+}\)).

Figure 3. Charge–discharge (Li-intercalation/de-intercalation) properties of graphite electrodes under various current densities from 0.1C (37.2 mA g\(^{-1}\)) to 5C (1860 mA g\(^{-1}\)) in (a) 1 mol kg\(^{-1}\) LiOTf/EC:DEC (50.50 vol.%) and (b) 0.5 mol kg\(^{-1}\) LiOTf-12C4/G2. Inset: solvation structure of Li ion in the respective electrolytes.

with EC:DEC, voltage plateaus implying the formation of graphite intercalation compound (GIC) at each stage were observed at 0.2, 0.1, and 0.06 V (vs. Li/Li\(^{+}\)) (Figure S2, Supplemental material). On the other hand, a shoulder was recognized between 1.0–0.5 V in 0.5 mol kg\(^{-1}\) LiOTf-12C4/G2. XRD patterns of graphite in 1 mol kg\(^{-1}\) LiOTf/EC:DEC at a cutoff voltage of 0.005 V demonstrated that stage-1 and stage-2 GIC (LiC\(_6\) and LiC\(_{12}\)) were formed, which was also indicated by the color (gold) of the graphite. The d-spacing of (002) plane of graphite changed from 0.335 nm to 0.371 nm at charged state, and then reversibly returned to an original state (0.335 nm). In contrast, the lattice constant increased to 1.137 nm in the 0.5 mol kg\(^{-1}\) LiOTf-12C4/G2 at 0.1 V, which indicates the bilayer intercalate arrangement.\(^{15}\) The distance of 1.137 nm is close to that of graphite operated at 1 mol dm\(^{-3}\) LiOTf/tetraglyme (G4) system. Based on the previous reported literatures, a distance between two adjacent graphite layer becomes increasing as the chain length of glyme grows longer.\(^{16}\) We thought that the interlayer distance at charged state in the LiOTf-12C4/G2 system decreased than those in other glyme-based electrolytes because 12-crown-4-ether is molecule with high planarity. Contrary to our expectation, the intercalation of encapsulated Li ion resulted in an increase of the distance. On the other hand, the interlayer in 0.5 mol kg\(^{-1}\) LiOTf/G2 without 12-crown-4-ether was 1.124 nm (Figure S3, Supplemental material). These results suggested that the GIC in the LiOTf-12C4/G2 system was formed with additional G2 solvation present.

Rapid charge–discharge property was evaluated in the current density range from 0.1 to 5C (Figure 3). In the EC:DEC-based electrolyte, only about 20% capacity retention to that (334 mA h g\(^{-1}\)) obtained at 0.1C was maintained at 2C. On the other hand, for 0.5 mol kg\(^{-1}\) LiOTf-12C4/G2 in which Li ion is encapsulated by 12C4, a high retention of 66% was achieved. This is probably due to the absence of desolvation process in EC:DEC system which is the rate-determining step of charge transfer reaction in graphite.\(^{17–19}\)
Although graphite electrode can operate at the high rate capability in the electrolyte solution of LiOTf-12C4/G2, a surface layer induced by the electrolyte decomposition would be involved in charge transfer reaction at the interface between electrolyte and electrode. We therefore plan to compare and analyze composition of surface layer in the respective system as a future study.

**Summary**

For the purpose of diversifying carrier ions, intercalation behavior of Li-ion encapsulated by 12-crown-4-ether was studied using graphite electrode. Co-intercalation of the ion without desolvation expanded layer distance of graphite from 0.335 to 1.137 nm, and the reaction allowed a rapid charge–discharge performance with a capacity retention of 66% even at high rate of 2C compared with that obtained at 0.1C. Encapsulation of charged ion such as Li\(^+\), Na\(^+\), Mg\(^2+\), Ca\(^2+\), and Al\(^3+\) should broaden the development of new-type rechargeable batteries.

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