Kinetic Behavior of the Anion Intercalation/De-intercalation into the Graphite Electrode in Organic Solution

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This is the final version of an authors’ manuscript, submitted by the author(s) and accepted for publication after peer review and technical editing by the Editorial Board of The Electrochemical Society of Japan. This manuscript may contain minor errors or incomplete designs that do not affect the judgment for publication. It is the responsibility of the authors to correct any errors in the Just Accepted manuscript during galley proof review.
Title

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Abstract

Electrochemical anion intercalation/de-intercalation into the graphite electrode generally takes place at high electrode potential of over 4.5 V (Li⁺/Li), so it is attractive as the positive electrode reaction for the post lithium-ion batteries. In this study, the kinetic behavior of the anion intercalation reaction in the organic solution is studied. The interfacial activation energy of anion species is as low as about 25 kJ mol⁻¹, which is much lower than that of Li⁺-ion. The result means the anion intercalation reaction is essentially fast and therefore, it is suitable for the high power batteries. In addition, the activation energy is not influenced by the solvation ability in the solution and from the result, we conclude that the interfacial activation barrier will exist on the graphite electrode side, contrary to the Li⁺-ion case.

Keywords

anion intercalation

graphite

interface
Introduction

Since lithium-ion batteries (LIBs) were commercialized, they have been used as the power sources in small electric devices such as cellphones, laptop PCs, due to their high energy densities and long cycle life. In addition, with the rapid increase of the demand for the electric vehicles, the research and development of LIBs with higher energy densities, higher power and longer cycle life has been accelerated. On the other hand, LIBs are also faced with some serious problems such as the energy densities’ limit, high cost, and safety issues. Graphite negative electrode used in the typical LIBs shows the enough low electrode potential of about 0.2 V (vs.Li+/Li) and relatively large theoretical capacity of 372 mA h g\(^{-1}\) compared to the transition metal oxide positive electrode materials (ca.140 mA h g\(^{-1}\)), so the improvement of the positive electrode material will be preferable to realize the higher energy density. So far, the research and development of the positive electrode materials with higher electrode potential and/or larger capacity has been conducted and some attractive materials, such as LiCoPO\(_4\), LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\), or Li-excess oxide materials (Li\(_2\)MnO\(_3\) and so on) have been reported.\(^1-5\)

Contrary to the transition metal oxide above, the graphite positive electrode with anion intercalation/de-intercalation also shows the relatively high electrode potential more
than 4.5 V (vs. Li+/Li). In addition, carbonaceous materials are attractive due to their lower cost and environmental load, compared to the transition metal oxide materials. Therefore, the batteries using the anion intercalation reaction, i.e., the hybrid capacitors or dual carbon cells are also paid much attention as the post LIBs. On the other hand, large volumetric change by anion intercalation can be a serious issue for the long life charge/discharge cycles. For example, Yan et al. reported the galley height for TFSA− case to be 8.0–8.1 Å at stage 1-3.6 This means the volumetric change of the graphite electrode is as large as 40-140 %, depending on the depth of charge. Even for the smaller PF6− anion case, the galley height has been reported to be 7.7–7.8 Å, leading up to 130 % of volumetric change,7 while that of the traditional oxide materials is generally less than10 %.

So far, some groups have studied on the anion intercalation behavior in organic solution or ionic liquid electrolytes, especially focusing on the structure of the graphite intercalation compound or the search for the electrolyte solutions with high anti-oxidation capability or excellent cycle performance. For example, Seel et al. realized the 5 V class charge-discharge profile by combining the PF6− intercalation/de-intercalation and Li metal in 2 mol dm−3 LiPF6/ethyl methyl sulfone.9 Miyoshi et al. reported PF6− intercalation/de-intercalation showed the relatively high
capacity of 100 mA h g⁻¹ over 30 cycles. The result implies the stable charge/discharge will be achieved in spite of the large volumetric change mentioned above. Schmuelling et al. studied the electrochemical behavior of N(CF₃SO₂)₂⁻ (TFSA⁻) anion intercalation/de-intercalation in ionic liquid electrolytes by in-situ X-ray diffraction (XRD) and confirmed the stage 1 formation and the discharge capacity of 85 mA h g⁻¹, which corresponded to (TFSA)C₂₆ composition at 20 °C. Miyoshi et al. focused on the diffusivity of PF₆⁻ in the graphite and estimated the diffusion coefficient to be the order of 10⁻¹² cm² sec⁻¹, which was comparable or higher than that of Li⁺-ion in the positive electrode materials. Our group has adapted the TFSA⁻ intercalation to Mg based battery systems and realized the TFSA⁻ intercalation/de-intercalation over 3 V (vs. Mg²⁺/Mg) and Mg metal deposition in the Mg(TFSA)₂ : glyme =1:1(mol) solution. On the other hand, the kinetic behavior at the electrode/electrolyte interface has not been studied enough. Fukutsuka et al. studied the interfacial anion transfer and reported TFSA⁻ or fluorosulfonyl amide anion showed the low interfacial activation energy as low as 12–15 kJ mol⁻¹ in ethylene carbonate/diethyl carbonate (EC/DEC). The result motivated us to elucidate the mechanism of anion intercalation reaction and obtain the basic strategy for high power graphite positive electrode.

In the present study, we studied the kinetic behavior of the anion
intercalation/de-intercalation into the graphite electrode in the organic solution, aiming at the elucidating the origin of the interfacial activation barrier. We found the interfacial activation energies of anion species were much smaller than that of Li\(^+\)-ion case. Besides, the activation energies were kept to be low even in the aqueous solution, although H\(_2\)O would interact with anion much stronger than organic solvents did. From the results, we propose that the activation barrier for the anion intercalation reaction will exist on the graphite electrode side, rather than the solution side.

**Experimental**

The kinetic behavior of the anion intercalation reaction was investigated by a traditional beaker-type three electrode cell. In order to exclude the effect of the conductive additives, binders, or current collectors, we used the highly oriented pyrolytic graphite (HOPG, ZYH grade) as the model electrode. HOPG was cut into the size of ca. 5 mm x 5 mm x 0.25 mm and sandwiched with Pt wire, which was used as the working electrode. The counter and reference electrode were Li metal and unless otherwise mentioned, all electrode potentials were referred to Li\(^+\)/Li. The correlation between anion species and their kinetics was investigated by using the solutions consisting of 1 mol dm\(^{-3}\) LiTFSA, LiBF\(_4\), LiCF\(_3\)SO\(_3\) or LiClO\(_4\)/propylene carbonate
(PC). The effect of solvent species on the anion intercalation reaction was studied by 1 mol dm$^{-3}$ HClO$_4$(aq) solution. For aqueous solution, Ag/AgCl (+0.196 V vs.SHE) and Pt were used as the reference and counter electrode, respectively. HClO$_4$(aq) was purchased from Fujifilm Wako Chemicals and the other reagents were battery grade of Kishida Chemical Co.,Ltd, which were used without further purifications.

Electrochemical measurements were conducted with Solartron 1470E and 1260. Anion intercalation/de-intercalation into the graphite electrode was studied by cyclic voltammetry. The charge transfer resistance was estimated by A.C. impedance method with the frequency range of 100 kHz – 0.1 Hz. The formation of graphite intercalation compound (GIC) was investigated by X-ray diffraction pattern (XRD, Rigaku Ultima IV). For the organic solution systems, all cell fabrication was conducted in Ar filled glove box and the electrochemical measurements and XRD measurements were conducted under Ar atmosphere.

**Results and discussion**

Figure 1 shows the cyclic voltammogram (CV) in 1 mol dm$^{-3}$ LiTFSA/PC. The oxidation current appears from ca. 4.6 V and the corresponding reduction current is also confirmed, which indicates the TFSA$^-$ intercalation/de-intercalation takes place
reversibly. Placke et al. reported that the onset potential of the oxidation current shifted lower from the 2nd cycle, due to the increase of the interlayer gap distance at the 1st cycle.\textsuperscript{15} However, the lower shift is not clearly confirmed in our result. This is probably because of the size of the active materials. HOPG block used (mm order) in the study is much larger than the general graphite powder (nm or \( \mu \text{m} \) order), so the intercalated anion species will not be able to diffuse into the bulk of HOPG during CV measurement and as the result, the increase of the interlayer gap distance will not vary compared with the general graphite powder.

The anion intercalation is also confirmed by XRD. Figure 2 shows the XRD pattern of HOPG after potential holding at 4.65 V. Original pattern of pristine HOPG disappears and several new diffraction peaks are observed. The repeat distance \((I_c)\) is represented by the following equation (1).

\[
I_c = d_i + 3.35 \text{ Å (n-1)} = l d
\]  

(\(d_i\): the intercalant gallery height, \(n\): the stage number, \(l\): index of (00\(l\)) plane and \(d\): the interplanar distance obtained from the Bragg’s law)

According to the indices denoted in the figure, we estimate the \(d_i\) of 8.1 ~ 8.4 Å and confirm the stage 4 formation. The \(d_i\) value shows good accordance with the reported in the literature,\textsuperscript{6} so our attribution will be valid.
Figure 3 shows the complex impedance plot of HOPG in 1 mol dm$^{-3}$ LiTFSA/PC at 4.65 V. The typical Randles-type behavior, i.e., one semi-circle with the characteristic frequency of 1 kHz and the following slope are obtained. The semi-circle is not observed at OCP potential, so we ascribed the semi-circle as the charge transfer resistance ($R_{ct}$). From the temperature dependency of $R_{ct}$, we can estimate the interfacial activation energy ($E_a$) to be 28 kJ mol$^{-1}$. The result seems a little larger than that of the previously reported case (15 kJ mol$^{-1}$). The difference will be caused by the several factors. Firstly, when $R_{ct}$ is relatively small, the error of its temperature dependency tends to become large. In this study, $R_{ct}$ is estimated to be at most $10^2$ Ω order in all cases, which is much smaller than those of solid/liquid interface cases we previously reported ($10^3$–$10^5$ Ω). In fact, we’ve also confirmed $E_a$ less than 20 kJ mol$^{-1}$, but mostly obtained 25-28 kJ mol$^{-1}$ during a series of measurement. Secondary, $E_a$ can be influenced by the condition of the graphite electrode, and the detail is discussed later.

Abe et al. have studied the Li$^+$-ion transfer at the graphite/electrolyte solution interfaces and reported 50–60 kJ mol$^{-1}$ and from the result, they concluded the high activation barrier would be caused by the de-solvation process.$^{16}$ Compared to the Li$^+$-ion, $E_a$ for TFSA$^-$ in this study is much smaller. The result will be caused by the much weaker interaction between TFSA$^-$ and PC solvents. The smaller $E_a$ also leads the
conclusion that TFSA$^-$ intercalation reaction is essentially much faster than Li$^+$-ion and favorable for the higher power batteries. In fact, the rate constant is 100,000 times larger at room temperature if $E_a$ decreases from 55 kJ mol$^{-1}$ to 28 kJ mol$^{-1}$, assuming that the rate constant is presented by the Arrhenius equation and the frequency factor is identical. Of course, the diffusion process in the electrode will also have the large influence for the reaction rate. As mentioned above, Miyoshi et al. estimated the diffusion coefficient ($D$) of PF$_6^-$ in the graphite electrode to be $10^{-12}$ cm$^2$ sec$^{-1}$ by the galvanostatic intermittent titration technique.$^{12}$ Also, Heckmann et al. reported that $D$ of TFSA$^-$ to be $10^{-15}$ cm$^2$ sec$^{-1}$. On the other hand, the diffusivity of Li$^+$-ion in the transition metal oxide materials are generally reported in the range of $10^{-10}$–$10^{-14}$ cm$^2$ sec$^{-1}$,$^{18-20}$ so we can conclude that the diffusivity of anion species in the graphite electrode will be comparable with that of Li$^+$-ion in the positive electrodes and therefore, the anion intercalation/de-intercalation into the graphite electrode will be attractive for new battery systems with high power.

In order to study the mechanism of the anion intercalation reaction in detail, the kinetic behavior of the several anion species was also investigated. As shown in Fig.4, all anion species in this study can intercalate/de-intercalate into graphite electrode reversibly. The intercalation onset potential is the order of TFSA$^-$ < CF$_3$SO$_3^-$ < BF$_4^-$, ClO$_4^-$, which is
the reverse order of anion size (Table 1). Considering any clear overvoltage does not appear in all anion cases, the onset potential will be determined by the thermodynamic stability, however, the detail is under investigation. Although the current density also seems to show some connection with the anion size, we can not discuss in detail because the size of HOPG electrode, i.e., the net surface area is not arranged strictly.

$R_{ct}$ and its temperature dependency for each anion was estimated in the same way as TFSA$^-$ case. Figure 5 shows the temperature dependencies of $R_{ct}$ for the anion species and the interfacial activation energies are summarized in Table 1. All anion species also show the low $E_a$ less than 30 kJ mol$^{-1}$ and essentially fast electrode reactions are expected, like TFSA$^-$. The results will also be reflected by the weak interaction between anion and PC solvent.

As mentioned above, for the interfacial Li$^{+}$-ion transfer case, the de-solvation process is reported to be the rate determining step, i.e., the interaction between Li$^{+}$-ion and solvent species has the large influence on the phase transfer.$^{16}$ The solvation ability toward cation species is represented as the donor number (DN) and we’ve confirmed that the larger DN led the larger $E_a$.$^{21}$ On the contrary to DN, the acceptor number (AN) is also used as the index of the solvation ability to anion species. In order to elucidate the correlation between AN and $E_a$ for anion species, we studied the ClO$_4^-$ intercalation
reaction in aqueous solution. Note that we also tried the TFSA$^-$ intercalation in the HTFSA(aq), however, the stable $R_{ct}$ was not obtained. Water has much larger AN (54.8) than PC (18.3), so we expect the larger $E_a$ will be obtained in the aqueous solution. Figure 6(a) shows CV in 1 mol dm$^{-3}$ HClO$_4$(aq). Although the reversible redox couple corresponding to the intercalation/de-intercalation of ClO$_4^-$ is observed again, the current is much larger than that in PC solution. This is because of the lower viscosity and high dissociation of the solute in the aqueous solution. We can also confirm the high reactivity in the aqueous solution from the lower $R_{ct}$, as shown in Fig.6 (b). On the other hand, contrary to our expectation, $E_a$ in the aqueous solution is as low as 19 kJ mol$^{-1}$, which is comparable or lower compared with the PC solution case. The result will indicate the interaction between anion species and solvent has less influence for the interfacial anion transfer, in other words, the de-solvation process will not be the major activation barrier.

So far, we’ve studied the Na$^+$-ion transfer at the solid electrolyte/solution interface and found that $E_a$ was not influenced by the solvation ability, and from the result, we concluded the activation barrier would exist on the solid electrolyte side. This is caused by the much weaker interaction between Na$^+$-ion and organic solvent than that of Li$^+$-ion, due to the weaker Lewis acidity of Na$^+$-ion. Generally, the interaction between
anion species and organic solvents is negligible, so we can conclude that the activation barrier for the anion transfer would exist on the graphite electrode side, as well as the Na$^+$-ion case. The idea will be supported by the correlation between the anion size and $E_a$, summarized in Table 1. In general, the larger sized anion is more de-localized, so the interaction with solvent will be weaker. Therefore, if the de-solvation process influenced the interfacial anion transfer, $E_a$ would be the order of TFSA$^-$ < CF$_3$SO$_3$ < ClO$_4$ < BF$_4$. However, the actual $E_a$ shows the reverse order, i.e., the larger sized anion shows the larger $E_a$. Therefore, we speculate the activation energy will reflect the spreading/shrinking of the graphene layers or the re-orientation of graphene sheets by the anion intercalation. If that is the case, the difference of $E_a$ for TFSA$^-$ in PC between our result (28 kJmol$^{-1}$) and the reported one (15 kJ mol$^{-1}$) discussed above can also be explained. In our study, HOPG was bound by Pt wire, so the strength to tie will influence $E_a$. Now we study the effect of the applied pressure on the reactivity of anion intercalation and the results will be reported elsewhere.

Recently, some groups have proposed that anion intercalated into the graphite electrode with some solvent species, i.e., the co-intercalation took place.$^{25-28}$ If so, de-solvation will no longer occur and our conclusion will also be supported. In the case, the intercalant size will be varied depending on the solvent species, so $E_a$ will not be the
identical for our case (PC) and reported above (EC/DEC). Abe et al. reported that $E_a$ for
the co-intercalation of Li$^+$-ion into the graphite electrode was as small as 25 kJ mol$^{-1}$,\textsuperscript{16} which is comparable with our results about the anion intercalation. The result will imply
the reaction mechanism of the co-intercalation of Li$^+$-ion and anion intercalation is
similar, so our result will support the possibility of the co-intercalation reaction for
anion species. However, we can not discuss in detail whether the co-intercalation takes
place or not from $E_a$, so now we are studying the effect of the coordination of anion in
the solution on the kinetic behavior of the intercalation reaction, and the results will be
reported elsewhere.

**Conclusions**

In this work, the kinetic behavior of the anion intercalation/de-intercalation into the
graphite electrode in the organic solutions was studied. The interfacial activation energy
showed much lower value than that of Li$^+$-ion. The difference will be caused by the
interaction with the solvents; Li$^+$-ion needs large activation energy for de-solvation,
while the interaction between anion species and solvents is much weaker. The
interfacial activation energy for the aqueous solution case was also weaker than that of
organic solution cases, although H$_2$O has the much larger acceptor number. Besides, the
larger sized anion species showed the larger $E_a$. From the results, we conclude the interfacial activation barrier for the anion intercalation reaction will exist on the graphite electrode side.

Acknowledgement

This work was financially supported by JFE 21st Century Foundation

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Table 1 The summary of the interfacial activation energy for anion species and their ionic radius

Fig.1 Cyclic voltammogram of HOPG in 1 mol dm$^{-3}$ LiTFSA-PC.

Fig.2 XRD pattern of HOPG after potential holding at 4.65 V in 1 mol dm$^{-3}$ LiTFSA-PC

Fig.3 Nyquist plot of HOPG at (square) OCP and (circle) 4.65 V in 1mol dm$^{-3}$ LiTFSA-PC

Fig.4 The comparison of cyclic voltammograms for anion species in PC solution.

Fig.5 Temperature dependencies of the interfacial resistance for anion species.

Fig.6 (a) Cyclic voltammogram, (b) Nyquist plot at 1.6 V (vs.Ag/AgCl) and (c) temperature dependency of $R_\alpha$ for 1 mol dm$^{-3}$ HClO$_4$(aq).
Table 1 The summary of the interfacial activation energy for anion species and their ionic radius

| Anion   | $E_a$ (kJmol$^{-1}$) | Ionic radius (nm) |
|---------|----------------------|-------------------|
| TFSA$^-$| 28                   | 0.325             |
| CF$_3$SO$_3^-$ | 25       | 0.270             |
| ClO$_4^-$ | 24                   | 0.237             |
| BF$_4^-$ | 20                   | 0.229             |
Fig. 1
Fig. 2
Fig. 3
Fig. 4
Fig. 5
\( E / V \) (vs. Ag/AgCl) vs. \( I / mA \)

\( E / V \) (vs. Li\(^+\)/Li)

\( Z''(\Omega) \)
\( Z'(\Omega) \)

\( t / ^\circ C \)

\( E_a = 19 \) kJ mol\(^{-1}\)

Fig. 6