Understanding High-Rate K\textsuperscript{+}-Solvent Co-Intercalation in Natural Graphite for Potassium-Ion Batteries

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Abstract
© 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim Graphite shows great potential as an anode material for rechargeable metal-ion batteries because of its high abundance and low cost. However, the electrochemical performance of graphite anode materials for rechargeable potassium-ion batteries needs to be further improved. Reported herein is a natural graphite with superior rate performance and cycling stability obtained through a unique K⁺-solvent co-intercalation mechanism in a 1 m KCF₃SO₃ diethylene glycol dimethyl ether electrolyte. The co-intercalation mechanism was demonstrated by ex situ Fourier transform infrared spectroscopy and in situ X-ray diffraction. Moreover, the structure of the [K-solvent]+ complexes intercalated with the graphite and the conditions for reversible K⁺-solvent co-intercalation into graphite are proposed based on the experimental results and first-principles calculations. This work provides important insights into the design of natural graphite for high-performance rechargeable potassium-ion batteries.

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Understanding High-Rate K⁺-Solvent Co-Intercalation in Natural Graphite for Potassium-Ion Batteries

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Abstract: Graphite shows great potential as anode material for rechargeable metal-ion batteries because of its high abundance and low cost. However, the electrochemical performance of graphite anode materials for rechargeable potassium-ion batteries needs to be further improved. Reported herein is a natural graphite with superior rate performance and cycling stability obtained through a unique K⁺-solvent co-intercalation mechanism in a 1 M KCF₃SO₃ diethylene glycol dimethyl ether electrolyte. The co-intercalation mechanism was demonstrated by ex situ Fourier transform infrared spectroscopy and in situ X-ray diffraction. Moreover, the structure of the [K-solvent]⁺ complexes intercalated in graphite and the conditions for reversible K⁺-solvent co-intercalation into graphite are proposed based on the experimental results and first-principles calculations. This work provides important insights into the design of natural
graphite for high-performance rechargeable potassium-ion batteries.

Introduction

The rapid consumption of fossil fuels and the destruction of the environment make the case for clean and sustainable energy sources as well as efficient energy storage and conversion devices.\cite{1-3} Lithium-ion batteries (LIBs) have achieved tremendous success during the past two decades as one of the most promising energy storage systems.\cite{4-6}

The huge consumption and limited resources of lithium, however, hinder its application in large-scale energy-storage systems.\cite{7,8} Thus, developing new battery systems based on more abundant elements (such as sodium, potassium, magnesium, calcium, zinc, and aluminum) is very important.\cite{9-13} Among these new battery systems, potassium-ion batteries (PIBs) have been attracting increasing attention because of the abundance of potassium resources and the low redox potential of $\text{K}^+/\text{K}$ in organic electrolyte ($-2.93$ V versus standard hydrogen electrode).\cite{14,15} In addition, PIBs show the “rocking-chair” mechanism, which is similar to that of LIBs. Thus, PIBs could be promising potential candidates for large-scale energy storage systems.

The main challenge for the development of PIBs is to find suitable electrode materials. This challenge arises because the ionic size of $\text{K}^+$ (1.38 Å) is much larger than that of $\text{Li}^+$ (0.76 Å).\cite{16-19} Graphite is the allotrope of carbon which has been extensively applied as anode for commercial LIBs, and it also shows activity toward electrochemical intercalation of $\text{K}^+$ at room temperature.\cite{20-23} For example, Ji et al. reported electrochemical potassium insertion in graphite in 0.8 M KPF$_6$ ethylene-carbonate (EC)/diethyl-carbonate (DEC) electrolyte, showing a reversible capacity of 273 mA h g$^{-1}$ with the formation of stage-one K-graphite intercalation compounds.
The graphite anode showed poor rate performance (80 mA h g$^{-1}$ at 1 C) and cycling stability (capacity retention of 50.8% after 50 cycles), which blocked its practical application. Recently, some reports that K/graphite cells can exhibit good cycling stability and high rate capability through K$^+$-solvent co-intercalation into graphite.$^{[24-26]}$ The demonstration of potassium ion co-intercalation into graphitic carbon electrodes by the group of Pint show superior electrochemical performance.$^{[24]}$

Soon after, the group of Kang investigated that the intercalation behavior of various solvated alkali ions (Li, Na, K) intercalated into graphite.$^{[25]}$ Most recently, Wang et al. studied the electrochemical performance of graphite as a PIB anode in carbonate-based and ether-based electrolytes.$^{[26]}$ Although the K$^+$-solvent co-intercalation phenomena has been proposed, however, these works are mainly focused on the electrochemical behavior of graphite in ether-based electrolyte. Moreover, the K$^+$-solvent co-intercalation mechanism and the condition for reversible K$^+$-solvent co-intercalation in natural graphite have not been systematically investigated. A deeper understanding of the K$^+$-solvent co-intercalation in graphite can provide insights into the design of natural graphite anode materials for high-performance rechargeable PIBs.

Herein, we investigated the electrochemical performance of natural graphite in 1 M KCF$_3$SO$_3$ diethylene glycol dimethyl ether (DEGDME) electrolyte. The natural graphite electrode showed superior rate performance, good cycling stability, and high initial Coulombic efficiency. Ex situ Fourier transform infrared spectroscopy (FTIR) and in situ X-ray diffraction (XRD) were applied to reveal the unique K$^+$-solvent co-intercalation mechanism. The stage number of final ternary GICs was determined by measuring the height expansion of highly ordered pyrolytic graphite (HOPG). The structure of the [K-solvent]$^+$ complexes intercalated in graphite and the solvent
dependency of the K intercalation were investigated by experiments and first-principle calculations. In addition, the reason for the fast kinetics of the natural graphite is also discussed.

**Results and Discussion**

The XRD pattern of natural graphite in Figure 1a shows an obvious diffraction peak at 26.6°, corresponding to the (002) planes of graphite. The Raman spectrum exhibits a weak D band and a strong G band (Figure S1a). Both the XRD and Raman spectrum indicated the well-defined crystalline of natural graphite. The scanning electron microscope (SEM) image reveals that the natural graphite exists in bulk form with particle size of several micrometers (Figure 1b). The surface area of the natural graphite is around 4 m² g⁻¹ (Figure S1b). The potassium storage behavior of natural graphite electrode in ether-based electrolyte was investigated by cyclic voltammetry (CV). As shown in Figure 1c, the CV curve of natural graphite electrode in 1 M KCF₃SO₃ DEGDME electrolyte shows several obvious reversible redox peaks, indicating a series of thermodynamically defined structures that subsequently evolve during electrochemical cycling.[27,28] The typical galvanostatic charge/discharge profiles of a natural graphite electrode in 1 M KCF₃SO₃ DEGDME electrolyte are shown in Figure 1d. The natural graphite electrode shows a reversible capacity of 105 mAh g⁻¹ with a high average discharge voltage. The initial Coulombic efficiency of natural graphite electrode is 62.9%, which is higher than that of most of carbon materials in PIBs.[29-31] However, this value of K⁺-solvent co-intercalation in PIBs is still lower than that of Na⁺-solvent co-intercalation in sodium-ion batteries.[32,33] The relatively low initial
Coulombic efficiency in case of potassium is likely attributable to side reactions between K metal anode and electrolytes, which is another challenge in PIBs.[34]

Figure 1. (a) XRD pattern and (b) SEM image of natural graphite. (c) CV curve of natural graphite electrode in 1 M KCF$_3$SO$_3$ DEGDME electrolyte at a scan rate of 0.1 mV s$^{-1}$. (d) Typical charge/discharge curves of natural graphite electrode in 1 M KCF$_3$SO$_3$ DEGDME electrolyte at a current density of 500 mA g$^{-1}$. (e) Rate performance and (f) Cycling stability of natural graphite electrode.

Then, we further studied the electrochemical performance of the natural graphite electrode. Figure 1e shows the rate performance of natural graphite electrode at different current densities. The reversible discharge capacities are 110.4, 99.1, and 90.4 mA h g$^{-1}$ at 1, 2, and 5 A g$^{-1}$, respectively. Even at an ultrahigh current density of 10 A g$^{-1}$, the capacity of 77.8 mA h g$^{-1}$ could be retained, which indicates a fast kinetics of the natural graphite electrode.[35] In general, the rate performance of electrode materials is influenced by the loading. To avoid the influence of the loading, the rate performance
of the natural graphite electrode with similar loading in 1 M KCF$_3$SO$_3$ EC/DEC electrolyte was tested. As shown in Figure S2, the natural graphite electrode in 1 M KCF$_3$SO$_3$ EC/DEC electrolyte shows poor rate performance, indicating that the K$^+$-solvent co-intercalation is beneficial for improving the rate performance of the natural graphite. In addition, when the current density was decreased to 1 A g$^{-1}$, the reversible capacity could recover to the original values, indicating the superior cycling stability of natural graphite electrode. As shown in Figure 1f, the natural graphite electrode shows good capacity retention of 88.5% (based on the second discharge capacity) after 100 cycles and a high Coulombic efficiency (close to 100%) at a current density of 2 A g$^{-1}$.

As shown in Figure S3, we observed an obvious dilation (~82%) of the sample during intercalation. In general, the large volume expansion of the electrode materials is not beneficial for long cycle life, which would destroy the mechanical integrity and structure of the electrode materials. To understand the reason of the good cycling stability of natural graphite electrode, SEM and XRD of the natural graphite electrode after 50 cycles were measured. As shown in Figure S4, the natural graphite electrode shows no obvious change of the flake shape and the particle size (several micrometers), even after 50 cycles, indicated the superior mechanical integrity of the natural graphite electrode. In addition, the natural graphite electrode after 50 cycles shows sharp (002) peak (characteristic peak of natural graphite, Figure S5). Thus, the good cycling stability of the natural graphite electrode would be ascribed to the superior mechanical integrity and structural stability of the natural graphite.

Although the K$^+$-solvent co-intercalation phenomenon has been proposed for years, the mechanism is still unclear. The K storage mechanism was first investigated by ex situ transmission electron microscopy (TEM), FTIR and Raman. Figure S6 shows the TEM-HAADF image and corresponding EDS elemental maps of natural graphite.
electrode at the first discharge state. The TEM EDS mapping images clearly show the existence of K element after discharged, which demonstrated successful K insertion into natural graphite. In addition, we notice the O element shows similar distribution of K element, which indicated for K\textsuperscript{+}-solvent co-intercalate mechanism. To further prove the K\textsuperscript{+}-solvent co-intercalation mechanism, we characterized the natural graphite electrodes in the pristine and discharged states by ex situ FTIR (Figure S7). Compared with pristine natural graphite electrode, the characteristic peaks of 1 M KCF\textsubscript{3}SO\textsubscript{3} DEGDME electrolyte (in blue shaded rectangles) emerged in the FTIR spectrum of co-intercalated natural graphite electrode after discharge. Interestingly, the FTIR spectra of the natural graphite electrode after discharged in 1 M KCF\textsubscript{3}SO\textsubscript{3} EC/DEC electrolyte shows no characteristic peaks of 1 M KCF\textsubscript{3}SO\textsubscript{3} EC/DEC electrolyte. The experiment results indicate that the K\textsuperscript{+}-solvent co-intercalated mechanism of natural graphite in 1 M KCF\textsubscript{3}SO\textsubscript{3} DEGDME electrolyte\textsuperscript{[36]} Ex-situ Raman was used to investigate the potassium storage process (Figure S8). The Raman spectrum of pristine natural graphite electrode exhibits a weak D band and a strong G band. After discharging to 0.01 V, the intensity of D band increased, indicating that the well-ordered interlayers became disordered. When charging to 2.0 V, the intensity was reversibly recovered to the original state. These results indicate that the K\textsuperscript{+}-solvent co-intercalation/deintercalation in natural graphite electrode is highly reversible.

To further clarify the K\textsuperscript{+}-solvent co-intercalated mechanism of a natural graphite electrode in 1 M KCF\textsubscript{3}SO\textsubscript{3} DEGDME electrolyte, we investigated the structural evolution of natural graphite electrode by in situ XRD. We designed a homemade in
situ XRD battery to monitor the structural evolution of natural graphite electrode in real
time during electrochemical cycling. Figure 2a shows the in situ XRD patterns of
natural graphite electrode in the second cycle. Before discharge, only one diffraction
peak at 26.6° can be observed, corresponding to the (002) planes of natural graphite
cathode. During the process of discharging, the intensity of the (002) peak declined,
and then split into two peaks, which indicated the formation of regularly ordered high-
stage GICs. [27] Subsequently, the main peak of natural graphite disappeared, while the
two new peaks shifted to lower and higher angles, respectively. Finally, the two peaks
shifted to 22.06° and 29.50°, and a new peak at 14.70° appeared. The XRD pattern is
similar to the previous reported stage 1 K-DEGDME ternary GICs, indicating the
formation of a stage 1 GICs after full discharge. [24] In the subsequent charging process,
the peaks change is reversible, and the (002) peak of natural graphite appeared at the
end of charge (2.0 V). As shown in Figure 2b, c, the color intensity change is highly
reversible, indicating the superior cycling stability of natural graphite electrode. In
addition, the new peaks that appeared during charge/discharge process can be indexed
as (00l) and (00l + 1) according to Bragg’s law and following equations. [37–39]

\[
\lambda = 2d \sin \theta = 2 \frac{I_c}{l} \sin \theta_{(00l)} \quad (1)
\]

\[
l = \frac{1}{\left[ \frac{\sin \theta_{(00l+1)}}{\sin \theta_{(00l)}} - 1 \right]} \quad (2)
\]

\[
n = \frac{l_c - l_1}{d_g} + 1 \quad (3)
\]

where \( \lambda \) is the wavelength of the X-ray. \( d \) is the \( d \)-spacing value. \( I_c \) is the c-axis
lattice parameter for each stage of graphite intercalation compounds, which
corresponds to the repeated distance. \( l \) is the Miller indices. \( n \) is the stage index of
GICs. $l_1$ is the $c$ lattice parameter for stage 1 GICs corresponding to the repeated distance, and $d_g$ is the $d$-spacing value of the pristine natural graphite.

The XRD pattern of the typical K-GICs in the charge/discharge process are shown in Figure 2d. In general, the evolution of K-GICs can be grouped into five parts (Figure 2e). To analyze the evolution of the stage number of K-GICs, we first determined the stage number of the final K-GICs. As shown in Figure 2d, the final K-GICs shows three peaks at 14.70°, 22.06°, and 29.50°, which can be indexed as (002), (003), and (004), respectively. The $c$ lattice parameter after discharge is about 12.09 Å, which is close to the results of a previous report.\[24\] The enlarged interlayer spacing suggests that the solvent co-intercalated into the layers of natural graphite. Figure 2f-h shows the schematic diagram of the hypothetical stage 1 GIC, stage 2 GIC and stage 3 GIC with a $l_c = 12.09$ Å. The theoretical height expansion value of formed stage 1 GIC, stage 2 GIC and stage 3 GIC are 261%, 80% and 20%, respectively. To determine the stage number of the final K-GICs, we employed a HOPG chip as a demonstration and observed the height expansion of the HOPG after fully potassiated. The optical photograph of the original and fully potassiated HOPG chip with two K-blocks are shown in Figure 2i, j. Compared with pristine HOPG, the height of the fully potassiated HOPG was significantly increased as measured by the micrometer caliper. The height of the pristine and fully potassiated HOPG were 1.503 and 4.834 mm, respectively (Figure 2k, l). The experimentally observed height expansion value is about 222%, which is close to the theoretical height expansion value of stage 1 GIC (261 %). Thus, a stage 1 GIC with a $c$ lattice parameter of 12.09 Å was formed after discharge.
Figure 2. (a) *In situ* XRD patterns of natural graphite electrode in the second cycle. (b, c) Color-mapped curves for *in situ* XRD patterns for different angular ranges. (d) The partially XRD pattern of characteristic stage GICs and (e) corresponding charging/discharging curves (Note: G, graphite; S4, stage 4; S3, stage 3; S2, stage 2; S1, stage 1). Schematic of the hypothetical (f) stage 1 GIC, (g) stage 2 GIC and (h)
stage 3 GIC with a $I_c = 12.09 \, \text{Å}$. Photograph of the (i) original and (j) fully potassiated HOPG chip with two K-blocks. Photograph showing the thickness of (k) the original and (l) fully potassiated HOPG chip.

Based on the experiments above, the value of $I_1$ in equation (3) was determined. Thus, we can further analyze the evolution of the stage number of GICs. In the part I, the natural graphite undergoes a consecutive phase transition until the formation of stage 4 K-GICs ($l = 6$ and $I_c = 22.10 \, \text{Å}$) accompanied by the emergence of XRD peaks at $24.16^\circ$ (006) and $28.32^\circ$ (007) from 2 to 1.14 V (corresponding to the peak C5 in the CV curve, Figure S8). The stage 4 K-GICs rapidly transforms to stage 3 K-GICs in part II (the voltage range of 1.14–1.06 V, C4). The stage 3 K-GICs ($l = 5$ and $I_c = 18.77 \, \text{Å}$) shows two characteristic XRD peaks at $23.70^\circ$ (005) and $28.64^\circ$ (006). Subsequently, the stage 2 K-GICs ($l = 4$ and $I_c = 15.44 \, \text{Å}$), with characteristic XRD peaks at $23.04^\circ$ (004) and $28.96^\circ$ (005), was formed in the voltage range of 1.06–0.92 V (C3, part III). Afterwards, the stage 2 K-GICs will be further transformed into stage 1 K-GICs ($l = 3$ and $I_c = 11.99 \, \text{Å}$) with characteristic XRD peaks at $22.16^\circ$ (003) and $29.62^\circ$ (004) in the part IV (0.92–0.76 V, C2). In the part V, the $I_c$ of stage 1 K-GICs will be slightly increased to $12.09 \, \text{Å}$ (from 0.76 to 0.01 V, C1). The increased $I_c$ of stage 1 K-GICs and the enhanced capacity could be attributed to the additional potassiation to stage 1 K-GICs. Figure S9 and Table S1 show the detailed stage evolution of natural graphite during discharge process. During the subsequent charge process, the natural graphite undergoes five similar but reversed parts (part V′, IV′, III′, II′ and I′).
Based on the *in-situ* XRD and *ex-situ* FTIR above, the K⁺-solvent co-intercalation into graphite was demonstrated, where the solvated K⁺ intercalate into graphite according to Equation (4),

\[
C_n + e^- + K^+ + y\text{DEGDME} \rightleftharpoons K^+(\text{DEGDME})_y C_n^-
\]  

(4)

where \(y\) and \(n\) are the number of DEGDME molecules and carbon atoms. The experimental reversible capacity of the natural graphite anode was about 105 mAh g⁻¹, indicating one \(K^+(\text{DEGDME})_y\) complex per 21 carbon atoms. To further determine the value of \(y\), we measured the weight change of the natural graphite electrode. The weight change of the natural graphite electrode at different discharge state is very close to \(y = 1\), which indicates that one DEGDME molecules intercalated with one K⁺ (Figure S10).

We further optimized the structures of [K-DEGDME]⁺ complexes intercalated in graphite. As shown in Figure S11, the optimized structure of [K-DEGDME]⁺ complex shows that the solvated K⁺ is coordinated with three oxygen atoms of DEGDME. The size of the K⁺-solvent complex ion is \(9.00 \times 4.82 \times 2.94\) Å³. The optimized structures of one, two, and three [K-DEGDME]⁺ complexes intercalated in graphite are shown in Figure 3a-c. The structure model is determined by the principle of minimum energy. The interlayer distances of the three optimized structures are 7.54 Å, 11.48 Å, and 15.12 Å, respectively. Considering that the experimental value of the interlayer distance is 12.09 Å, the structure composed of two [K-DEGDME]⁺ complexes intercalated in graphite with only 5.0% difference, is more reasonable.
The experiments above reveal the unique \( \text{K}^+ \)-solvent co-intercalation mechanism of natural graphite electrode in 1 M \( \text{KCF}_3\text{SO}_3 \) DEGDME electrolyte, although the conditions for reversible \( \text{K}^+ \)-solvent co-intercalation are still not clear. As shown in Figure 4a, the natural graphite electrodes show different electrochemical responses in various electrolytes (DEGDME, tetraethylene glycol dimethyl ether (TEGDME), EC/DEC, and propylene carbonate (PC)-based electrolytes). In DEGDME and TEGDME-based electrolytes, the natural graphite electrodes exhibit reversible \( \text{K}^+ \)-solvent co-intercalation behavior. Reversible \( \text{K}^+ \) intercalation/deintercalation into/from natural graphite electrode is clearly observed in common EC/DEC-based electrolyte. The natural graphite electrode has only one obvious reduction peak in PC-based electrolyte, however, which is similar to what occurs in the Li-PC and Na-PC systems.\[^{40,41}\] The experimental results above indicate that the potassium storage behavior of the natural graphite electrode is affected by the solvent species. In addition,
the K storage behavior of natural graphite in DEGDME with different salts (KPF$_6$ and KCF$_3$SO$_3$) was also investigated (Figure S12). Note that there is no obvious difference between the charge/discharge profiles of natural graphite electrode in different salts, indicating that the anions in the electrolytes have no effect on the possibility of K$^+$- solvent co-intercalation within the selected voltage range.$^{[42]}$

To investigate the conditions for reversible K$^+$-solvent co-intercalation, density functional theory was used to calculate the solvation energy ($E_s$) values of the K$^+$- solvent complexes. According to previous reports, the high $E_s$ of the K$^+$-solvent complexes would tend to hinder the desolvation process and promote the co-intercalation.$^{[40,41]}$ The $E_s$ is calculated by the following equation:

$$E_s = E_{[K-solvent,x]^+} - x \times E_{solvent} - E_{K^+}$$

(5)

where $E_{[K-solvent,x]^+}, E_{solvent}$, and $E_{K^+}$ are the Gibbs free energies of the K$^+$-solvent complex, the solvent molecule, and the K ion, respectively. The [K-solvent$_x$]$^+$ represent a K ion solvated by $x$ solvent molecule. Figure S11 shows the optimized structures of the solvents and the [K-solvent$_x$]$^+$ complexes, where $x$ refers to the number of solvent molecules in the structure and is omitted where $x = 1$. The calculated solvation energy $E_s$ values of [K-DEGDME]$^+$, [K-DEGDME$_2$]$^+$, [K-TEGDME]$^+$, [K-TEGDME$_2$]$^+$, [K-EC]$^+$, [K-EC$_2$]$^+$, [K-DEC]$^+$, [K-DEC$_2$]$^+$, [K-PC]$^+$, and [K-PC$_2$]$^+$ are -1.56, -2.49, -2.46, -2.70, -1.02, -1.79, -0.81, -1.50, -1.06, and -1.88 eV, respectively (Figure 4b).

Compared with [K-solvent]$^+$, [K-solvent$_2$]$^+$ shows higher stability due to the increased K-O coordination. Among these solvent molecules, DEGDME and TEGDME show the ability to strongly solvated K ions, which is beneficial for K$^+$-solvent co-intercalation.
This phenomenon coincides very well with the experimental results of K⁺-solvent co-intercalation in natural graphite electrodes.

It is well-known that the desolvation process at the interface between the electrode and electrolyte would affect the electrochemical reaction process. To investigate the conditions for K⁺-solvent co-intercalation in graphite, the desolvation energy ($E_{des,x}$) of one solvent molecule pull away from [K-solvent,x]⁺ complexes was calculated by:

$$E_{des} = E_{[K-solvent_{x-1}]^+} + E_{solvent} - E_{[K-solvent_{x}]^+}$$ (6)

As shown in Figure 4c, the [K-EC]⁺ complex shows the highest $E_{des}$ (1.02 eV) in EC and DEC solvent. Considering that the K⁺ intercalation is observed for EC/DEC-based electrolytes, this phenomenon indicates that $E_{des,x} > 1.02$ eV is necessary for reversible K⁺-solvent co-intercalation. Therefore, only [K-DEGDME]⁺, [K-TEGDME]⁺, and [K-PC]⁺ complex ions are suitable for reversible co-intercalation. As the K⁺-solvent co-intercalation in PC-based electrolyte is irreversible, we investigated the morphological evolution of the natural graphite electrodes by SEM. It is obvious that the natural graphite electrode is exfoliated after discharge in PC-based electrolyte (Figure S13). In DEGDME-based electrolyte, however, the natural graphite electrode shows no obvious morphological change, even after 50 cycles (Figure S4). According to the previous reports, this phenomenon is related to the stability of the K⁺-solvent complexes in the natural graphite host. The relative stability of the alkali metal (AM)-solvent (AM = Li, Na) complex ions in graphite can be observed by comparison of the lowest unoccupied molecular orbital (LUMO) level of an [AM-solvent]⁺ and the Fermi energy of graphite.[41] Similarly, to investigate the relative stability of the [K-solvent]⁺ complex
ions in graphite, we calculated the LUMO levels of the [K-solvent]$^+$ complexes. As shown in Figure 4d, the LUMO levels of [K-DEGDME]$^+$ and [K-TEGDME]$^+$ are higher than the Fermi energy of the graphite, indicating their stability in graphite. Remarkably, the LUMO level of [K-PC]$^+$ is lower than the Fermi energy of the graphite, which implies that the decomposition reaction of [K-PC]$^+$ and graphite is more likely to occur. This finding is consistent with the experimental results, indicating that higher LUMO levels of [K-solvent]$^+$ than the Fermi energy of the graphite are necessary for reversible K$^+$-solvent co-intercalation. Based on the experimental and calculated results, the K storage behavior in graphite can be divided into three categories: (i) reversible co-intercalation (high $E_s$ of K$^+$ and LUMO level of the [K-solvent]$^+$ complexes, Figure 4e), (ii) irreversible co-intercalation (high $E_s$ of K$^+$ and low LUMO level of the [K-solvent]$^+$ complexes), (iii) reversible K$^+$ intercalation (low $E_s$ of K$^+$).
Figure 4. (a) CV curves in different electrolytes. (b) Solvation energy of K⁺-solvent complexes. (c) Desolvation energy of K⁺-solvent complexes. (d) Comparison on LUMO levels of [K-solvent]⁺ complexes and the Fermi level of graphite. (e) Schematic of the conditions for reversible K⁺-solvent co-intercalation.
Considering the large size of the K⁺-DEGDME complex ion, the superior rate performance of complex ions intercalated into natural graphite electrode is unusual. To reveal the reason for the superior rate performance, we first investigated the charge storage mechanism of natural graphite electrode in DEGDME-based electrolyte by CVs at various scan rates (Figure 5a). The area of the CV curve represents the total stored charge contributed by both capacitive and intercalation reactions. The capacitive contribution of natural graphite electrode can be calculated by:[43-45]

\[ i = av^b \]  

(7)

where \( i \) and \( v \) are the peak current (A) and the scan rate of the CV (mV s\(^{-1}\)), respectively. Both \( a \) and \( b \) are adjustable values. In addition, \( b \) also represent the slope of the plot of \( \log(|i|) \) vs. \( \log(v) \). \( b \) takes on a value between 0.5 and 1. When \( b = 0.5 \), the electrochemical reaction is diffusion-controlled intercalation. When \( b = 1 \), the surface-limited capacitive contribution dominates the electrochemical process. As shown in Figure 5b, the \( b \) values of C1, C2, C3, C4, and C5 are 0.63, 0.54, 0.85, 0.87, and 0.73, respectively, indicating that the K⁺-solvent co-intercalation into natural graphite electrode in DEGDME-based electrolyte is determined by both capacitive and intercalation reactions. The pseudocapacitive behavior of natural graphite electrode could be attributed to the enlarged space of the natural graphite during the charge/discharge process. The high \( b \) values (0.85, 0.87) suggest fast kinetics for the natural graphite electrode.
Figure 5. (a) CV curves of natural graphite electrode in 1 M KCF$_3$SO$_3$ DEGDME electrolyte. (b) the calculated $b$ values. (c) GITT profile and calculated diffusion coefficient of natural graphite electrode.

Subsequently, the galvanostatic intermittent titration technique (GITT) was used to confirm the diffusion coefficient of natural graphite electrodes.$^{[46-48]}$ The ion diffusion coefficient can be calculate by:$^{[49]}
\begin{equation}
D = \frac{4}{\pi \tau} \left( \frac{m_b V_M}{M_B S} \right)^2 \left( \frac{\Delta E_s}{\tau (dE_t/d\tau)} \right)^2, \quad \tau \ll \frac{L^2}{D} \end{equation}
\tag{8}

where $D$, $m_b$, $V_M$, $M_B$, and $S$ are the diffusion coefficient, active material mass, molar volume of natural graphite, molar mass of natural graphite, and area of the electrode, respectively. $\tau$ is the current pulse duration and $L$ is the average thickness of the natural graphite electrode. $\Delta E_s$ and $\Delta E_t$ are shown in Figure S14. In this work, the voltage $E$ is linearly related to $\sqrt{\tau}$ (Figure S15). Thus, the Equation 8 can be
The diffusion coefficient of $\text{K}^+$-DEGDME complex in natural graphite electrode (measured by GITT) is about $10^{-9}$ cm$^2$ s$^{-1}$ (Figure 5c) during charge/discharge processes, implying fast $\text{K}^+$-solvent complex diffusion kinetics. The diffusion coefficient of $\text{K}^+$-DEGDME complex in natural graphite electrode is higher than that of the $\text{K}^+$ (\(\sim 10^{-11}\) cm$^2$ s$^{-1}$).[39] The high $\text{K}^+$-DEGDME complex diffusion coefficient could be attributed to the DEGDME molecules that surround the K ions are nearly flat, which completely solvate the K ions in the interlayer space of graphite, resulting in weak interaction between $\text{K}^+$ and graphite layers, similar to that in Na$^+$-solvent co-intercalation process.[50] The high $\text{K}^+$-solvent complex diffusion coefficient is responsible for the superior rate performance of natural graphite electrode in DEGDME-based electrolyte.

The reason of the fast kinetics of the natural graphite electrode was first investigated by theoretical calculation. Compared with the pure $\text{K}^+$ intercalation, the $\text{K}^+$-DEGDME co-intercalation avoid the sluggish desolvation process, which improves the kinetics (Figure 4c).[40] Subsequently, we investigate the electrolyte wettability and electrochemical impedance spectra (EIS) of natural graphite electrode. Wettability between the electrode and the liquid electrolyte has a significant influence on the electrochemical performance. A good electrolyte wettability could ensure the fast ionic transfer during the cycling process. As shown in Figure S16, the 1 M KCF$_3$SO$_3$ in DEGDME electrolyte shows a low contact angle (9.6°) on the surface of natural graphite electrode, which indicates a good wettability between the electrolyte and graphite electrode. Besides, the EIS of the K/graphite battery shows a straight line in the low-frequency and a depressed semicircle at high-frequency region (Figure S17). The K/graphite battery shows an extremely low interfacial resistance at high-frequency
region. This phenomenon illustrates that more favourable K⁺-solvent co-intercalation/deintercalation kinetics can be achieved. Both of good electrolyte wettability of graphite electrode and low charge-transfer resistance of K/graphite battery are beneficial for improving the rate performance.

**Conclusion**

We have systematically investigated the electrochemical performance and potassium-ion storage mechanism of natural graphite electrode in 1 M KCF₃SO₃ DEGDME electrolyte. The natural graphite electrode in DEGDME-based electrolytes shows good cycling stability (capacity retention of 88.5% after 100 cycles), superior rate performance (77.8 mAh g⁻¹ at 10 A g⁻¹), and high initial Coulombic efficiency (62.9 %) in PIBs. The ex situ FTIR and in situ XRD results demonstrate the unique K⁺-solvent co-intercalation mechanism of the natural graphite electrode in 1 M KCF₃SO₃ DEGDME electrolyte. After discharged to 0.01 V, the stage 1 GICs was formationed through multiple staging reactions. We proposed the structure of two [K-DEGDME]⁺ complexes intercalated in graphite. Moreover, we discovered that the reversible K⁺-solvent co-intercalation requires the superior thermodynamic and chemical stability of the K⁺-solvent complexes. The fast kinetics of natural graphite could be ascribed to the fact that the [K-DEGDME]⁺ complexes avoids a sluggish desolvation process. This work suggests that natural graphite could be a promising anode for high-performance PIBs.

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Keywords
batteries • density-functional calculations • graphite • potassium • reaction mechanisms

References


