New insights on ultrafast Na[solv]⁺ coinserted graphite driven by an electric field

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ABSTRACT Sodium ions (Na⁺) and ether electrolyte co-inserted graphite possesses a considerable volume expansion effect. However, the mechanism fails to clearly explain its stability. In response to this deficiency, the co-inserted reaction is proposed, which is affected by the Lorentz force of the applied electric field under the high-current condition. The Na⁺ ions are separated out, while the ethylene glycol dimethyl ether molecules remain between the graphite layers. This insight provides a reasonable explanation for the extraordinary stability of this material. *In situ* X-ray diffraction and density functional theory calculations confirm the separation and release of Na⁺. On the basis of this result, unmodified commercial graphite was stably cycled 6400 times at a current density of up to 10 A g⁻¹, and the capacity retention rate was as high as 97.2%. The full battery assembled in the laboratory has a maximum output power of 14,846 W kg⁻¹ and an output energy density of 103 W h kg⁻¹ (relative to the weight of anodic and cathodic active materials). The new mechanism provides innovative ideas for the design of large-scale energy storage devices.

Keywords: co-insertion, graphite, sodium-ion battery, power density

INTRODUCTION

Owing to abundant sodium resources, sodium-ion batteries (SIBs) are expected to satisfy large energy storage systems for renewable energy and smart grids [1,2]. Compared with lithium ions, sodium ions (Na⁺) have a larger radius and atomic weight, thus displaying slower ion transfer kinetics and lower energy density. The development of matching anode materials is slower than that of cathode materials with high-rate behaviors [3,4]. New carbon materials [5–7], alloys with complex structural designs and conversion anode materials have been

successively developed, such as Bi@graphite [8] and a three-dimensional (3D) MoS₂@CNFIG nanohybrid with unique interpenetration networks [9].

However, the abovementioned materials often have the disadvantages of limited synthesis, low volume energy density, and large resistance during industrialization. For lithium-ion batteries (LIBs), graphite is an excellent anode material. Unfortunately, graphite cannot be the anode material for SIBs [10,11]. It is generally believed that this is because the Na⁺ radius is larger than the layer spacing of natural graphite, which results in the inability of Na⁺ to be inserted between graphite layers. However, K⁺ with a larger radius than Na⁺ can be stably inserted between graphite layers to provide a stable capacity of ~244 mA h g⁻¹ [12]. Therefore, Na⁺ radius is not the main factor that hinders the insertion of Na⁺ into graphite. Nobuhara *et al.* [11] used density functional theory (DFT) calculations to show that thermodynamic instability begins to occur in NaC₁₆ and NaC₁₂ species even at low sodium concentrations, while NaC₈ and NaC₆ are also thermodynamically unstable. Thus, graphite cannot store sodium because the sodium graphite intercalation compound is thermodynamically unstable. This condition fundamentally negates the possibility of using graphite as the anode for SIB. Interestingly, Jache *et al.* [13] and Kim *et al.* [14] recently determined that an electrolyte based on diglyme as a solvent can undergo Na⁺ and solvent co-intercalation reactions and reversible cycling hundreds of times. The phenomenon of co-intercalation of solvents was reported in previous studies on LIBs.

Scholars have failed to explain the reasons for the excellent performance of graphite. According to the first-principles calculations, the diffusion rate of Na⁺-diglyme complexes is five orders of magnitude faster than that of Li⁺-diglyme complexes [15]. The insertion process seems

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to take only a few seconds [16]; at the same time, the material will undergo volume expansion of nearly 300%, and in subsequent cycles, the material will undergo a process similar to “breathing” [17]. Such drastic volume changes will inevitably lead to problems such as the structural collapse of the material and material falling off the current collector. Good stability is not expected, which is why the stability of the system still needs further research.

In this study, for the NaPF_6 /1,2-dimethoxyethane (DME) electrolyte system, a faster diffusion rate of the transmission medium was observed under high currents. Further *in situ* synchrotron X-ray diffraction (XRD) characterization confirmed that the content of Na^+ decreased in the sample after charging, whereas the DME molecule still maintained a high content. On the basis of this phenomenon, we propose a new insight for the co-intercalation reaction under high-current conditions; Na^+ ions separate out alone, and DME molecules are left between graphite layers. This situation seems to reasonably explain the excellent cycle stability of 6400 cycles and a capacity retention rate of 97.2% under the condition of 10 A g^{-1} . DFT theoretical calculations show that Na^+ has a lower diffusion energy barrier than $\text{Na}[\text{solv}]^+$ units under the application of an electric field, which further confirms this mechanism. The full battery assembled in the laboratory has a maximum output power of $14,846 \text{ W kg}^{-1}$ and an output energy density of 103 W h kg^{-1} (relative to the total weight of anodic and cathodic active materials).

EXPERIMENTAL SECTION

Electrode preparation

Natural graphite was purchased from BTR. Graphite anode was prepared by dispersing graphite powder with carbon black (Super P) and polyvinylidene fluoride (PVDF) at a mass ratio of 8:1:1 in a solvent *N*-methyl-2-pyrrolidone (NMP). The obtained slurry was stirred for 6 h and then coated on copper foil by scraping and dried in a vacuum oven at 120°C overnight. The preparation of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ cathode material referred to literature [18]. A mixture with a stoichiometric ratio of NH_4VO_3 , Na_2CO_3 , and $\text{NH}_4\text{H}_2\text{PO}_4$ was used as the reactant. First, citric acid was dissolved in deionized water at 60°C . Then, NH_4VO_3 , Na_2CO_3 , and $\text{NH}_4\text{H}_2\text{PO}_4$ were added to the citric acid solution under constant stirring to achieve complete dissolution (molar ratio of NH_4VO_3 to citric acid is 6:7), and the mixture was stirred at 80°C for 3 h, then transferred to a vacuum oven at 80°C for drying for 15 h. Then the product was calcined at 350°C for 4 h and

sintered at 800°C for 8 h in an argon atmosphere. The obtained powder was made into a slurry with acetylene black and PVDF at a mass ratio of 7.5:1:1.5 and was applied on aluminum foil by blade coating.

The reference electrode and the counter electrode were metallic sodium, the graphite anode/ $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ cathode was the working electrode, and glass fiber (GF/F, USA) was used as the separator. A concentration of 1 mol L^{-1} NaPF_6 or NaCF_3SO_3 dissolved in DME was used as the electrolyte. The 2032 battery was assembled in an argon-filled glove box. With regard to the assembly of a full battery, $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ cathode and graphite anode were used to assemble a 2032-type coin cell with an active material mass ratio of 1:1.5. The energy density and power density of a full battery were calculated based on the total mass of the active material which did not include the mass of other components (such as separators, electrolytes, and coin cell components) [19–23]. Subsequently, a constant current charge/discharge process was performed using a LAND-2001A instrument at a potential range of 0–3 V (vs. Na^+/Na) and a full battery of 0.4–3.4 V at 25°C . Cyclic voltammetry (CV) tests were performed on an electrochemical workstation (Autolab PGSTAT302N) at various scan rates.

Characterization

All electrodes were charged/discharged on a LAND-2001A instrument at a current density of 10 A g^{-1} relative to the mass of the active material, and the batteries were disassembled in an argon-filled glove box. The disassembled electrode sheet was rinsed in NMP, the PVDF binder on the surface was washed away, and the sheet was baked at 150°C for 4 h. The electrode sheet obtained after the treatment was divided into four parts and then packaged in an aluminum-plastic film to be tested. The surface chemical states of all samples were observed by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI). The structure of the sample was tested by a Raman spectrometer (LabRAM HV Evolution, HORIBA, Japan) with a 532-nm laser in a scanning range of $200\text{--}4000 \text{ cm}^{-1}$. Fourier transformed infrared (FTIR) spectroscopy (FTIR-6700, Nicolet, USA) with attenuated total reflectance was used to characterize the chemical structure of the sample and electrolyte.

Electrochemical measurements

Electrochemical measurements were performed using coin-type 2025 cells, which were assembled in an argon-filled glove box. The working electrode was prepared by mixing active materials, carbon epoxy chloropropane,

and PVDF (5%) with a weight ratio of 8:1:1 and then pasted on pure copper foil. The loading mass of the active material was around 1.0 mg cm^{-2} . Pure Na foil was used as a counter electrode, and the separator was Whatman GF/D. The electrolyte was composed of 1.0 mol L^{-1} NaPF₆ in DME. The CV tests were performed on an Autolab PGSTAT302N at different sweep speeds from 0.2 to 10 mV s^{-1} . Galvanostatic charge/discharge experiments were implemented by a LANDCT2001A battery tester in the thermostatic tank (25°C) within 0–3 V. Galvanostatic intermittent titration technique measurements were executed on the above battery tester with charging and discharging test pulse at 50 mA g^{-1} for 15 min and rest for 1 h.

In situ XRD measurement

For *in-operando* XRD analysis, the holed coin cells, which were sealed by Kapton film with epoxy, were used. *In-operando* XRD patterns for graphite were collected on the 5A XRD beamline at PLS-II. The wavelength of the X-ray beam was $0.7653 \text{ \AA}$, and XRD patterns were recorded as a set of circles on a Mar 345-image plate detector in the transmission mode for approximately 1 min of exposure time. The storage ring was operated with an electron energy of 3.0 GeV and a current of 40 and 10 mA g^{-1} . The total recording time was approximately 2.6 min because of the scanning time of the image plate and transferring time of the spectral information.

RESULTS AND DISCUSSION

Fig. 1a and Fig. S1 show that the NaPF₆ DME system exhibits capacities of $128\text{--}111.1 \text{ mA h g}^{-1}$ at current densities of 50 mA g^{-1} – 5 A g^{-1} , respectively. Nevertheless, at 10 A g^{-1} , the capacity increases to $127.8 \text{ mA h g}^{-1}$, which is equivalent to the capacity at 50 mA g^{-1} . Owing to the range of the test instrument, different batteries were selected for testing in the current density range of $10\text{--}50 \text{ A g}^{-1}$. Fig. S2 shows the first cycle of electrochemical behavior that was consistent with that reported results [14]. The voltage plateau is approximately 0.6 V. In addition, the system was cycled 6400 times at a current density of 10 A g^{-1} ; the capacity retention rate was as high as 97.2% (Fig. S3). However, NaCF₃SO₃ has poor cycle stability owing to the characteristic of easy solute decomposition, as shown in Fig. 1b.

Fig. 1c and Fig. S4 show the CV curves at the sweep speeds of $1\text{--}300 \text{ mV s}^{-1}$, which is similar to the results of Jache *et al.*'s report [24]. Four reduction peaks (i', a, b, and c) and three oxidation peaks (i, ii, and iii) are found, which is uncommon in other literature. The sharp peak shape evolves into a gentle shape when the scan rate exceeds 70 mV s^{-1} . The charge-discharge time at this sweep speed is the same as that at 10 A g^{-1} , which may account for the improved capacity at a high current density. To further analyze the electrochemical reaction states, we calculated the ion diffusion rate at the oxidation peak (i) and the reduction peak (i'). For semi-infinite and

Figure 1 (a) Capacity retention at $0.05\text{--}10 \text{ A g}^{-1}$ for NaPF₆-DME and NaCF₃SO₃-DME; (b) NaPF₆-DME sodium storage stability for 6400 cycles at 10 A g^{-1} ; (c) CV curves of NaPF₆-DME at $1\text{--}50$ and $70\text{--}300 \text{ mV s}^{-1}$; (d) calculation of normal ion diffusion coefficient; (e) *b* value analysis based on the relationship between the peak current and scan rate.

finite diffusion, the peak current (i_p) is proportional to the square root of the scan rate (v) [25–27]. Therefore, for any individual redox reaction, the plotted CV curve can be expressed as the following equation:

$$i_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} v^{1/2} \Delta C_0, \quad (1)$$

where n represents the number of electrons of each reactive substance (for Na^+ , the value is 1), A is the immersion area of the pole piece into the electrolyte solution, D is the diffusion coefficient of Na^+ in the film, and ΔC_0 is the Na^+ concentration change in chemical reactions. With the similarity between the system and chemical reaction environment before and after the reaction, the values of n , A , and ΔC_0 should be the same. As shown in Fig. 1d, the slope of linear fit (cathodic: 0.00734; anodic: 0.00918) at $>70 \text{ mV s}^{-1}$ is greater than the linear fit slope at $<70 \text{ mV s}^{-1}$ (cathodic: 0.0052; anodic: 0.00675), indicating a faster ion diffusion coefficient. If the same medium shuttles in the electrochemical process, then it will inevitably lead to a situation where ion diffusion becomes slower when the power density increases. We used the method proposed by Wang *et al.* [28] to determine the enhanced electrochemical kinetics. The relationship between the peak current and sweep rate follows the formula: $i = av^b$, where $b = 0.5$ or 1.0 represents the diffusion- or capacitance-controlled behavior. From the linear fitting results of $\log i_p$ and $\log v$ (Fig. 1e), the slope of the anodic process did not considerably change (from 0.63 to 0.65), but the slope of the

cathodic process decreased (from 0.86 to 0.66). In general, this change occurs because slow diffusion kinetics cannot satisfy high-speed electrochemical processes at high power densities [29]. An interesting detail is that according to the previous calculation results, the ion diffusion coefficient of the system increases instead of decreases, which means that a subsequent decrease in the b value is caused by different mechanisms.

To illustrate the aforementioned phenomenon, we performed XPS, FTIR, and Raman tests on the electrodes before and after fully discharging and charging at 10 A g^{-1} . Fig. 2a–c and Figs S5–S7 show the XPS spectra of charging and discharging (Table S1). The C 1s signal can be divided into the C–C (phenyl) bond at 285.0 eV, C–O–C bond at 286.1 eV, O–C=O bond at 289.1 eV, C–H/C–C bond at 284.6 eV [30], and C–F bond at 290.2 eV [31]. The O 1s signal can be divided into the C–O–C bond at 532.34 eV [30], C=O bond at 533.93 eV [32], and Auger electron peak of sodium at 537 eV [33]. Interestingly, the signal of the C–O–C bond remains after charging, whereas it weakens after discharging, which is accompanied by a significant enhancement of the Na 1s signal peak. Two different electrodes were tested, and therefore the degree of PVDF cleaning on the surface was inconsistent, and the charged sample failed to show C–F bonds.

Fig. 2d shows that the stretching vibration of the C–O–C bond is near 1077 cm^{-1} (Fig. S8) [34]. The charged sample has a stronger signal. Fig. 2e, f show the Raman

Figure 2 (a) C 1s, (b) O 1s, and (c) Na 1s XPS spectra of NaPF₆-DME after charging and discharging at 10 A g^{-1} ; (d) FTIR spectra; (e) Raman spectra with the original graphite; (f) fractional spectra of Raman 2D peak.

test results of the two samples. The G peak of the charged sample is blue-shifted by 30 cm^{-1} , relative to the original graphite sample, and the G' peak red-shifted by 19.7 cm^{-1} (Fig. S9), both with the enhancement of the signal. This result is consistent with the Raman analysis of graphene proposed by Ferrari *et al.* [35], which shows that graphene characteristics appear with both the charged and discharged samples. To further verify the existence of the relevant properties of graphene, we used the theory proposed in the Refs [35–37] to process the Lorentzian G' peak. The results are shown in Fig. 2f. The G' peak was successfully divided into four Lorentzian peaks ($2D_{1B}$, $2D_{1A}$, $2D_{2A}$ and $2D_{2B}$), indicating that the samples of charging and discharging exhibited the characteristics of two layers of graphene, in which the $2D_{2A}$ and $2D_{2B}$ peaks

of the discharged samples drastically decreased, possibly due to the effects of Na^+ insertion. In summary, the XPS and FTIR results show that DME molecules are present at charging and discharging, and the signal of DME molecules is weakened after discharging, while Raman analysis confirms the existence of a two-layer graphene property. By combining the two conclusions, we can reasonably infer that DME molecules exist between graphite samples after charging and discharging.

To better construct the relationship of structure and performance, we also combined DFT theoretical calculations. We analyzed the structure of Na ions adsorbed on DME by designing two models of Na ion adsorption and calculating their adsorption energy, as shown in Fig. 3a, b. Lower adsorption energy means stronger adsorption. In

Figure 3 (a, b) Two different structures and adsorption energy changes of Na ion adsorption on DME (purple: Na atom, white: hydrogen atom, red: oxygen atom, gray: carbon atom). (c–e) Structures and adsorption energy changes of Na ion adsorption on DME between the graphite layers. (f) DME embedded between the graphite layers and Na-DME migration path. (g) Na ion and Na-DME migration energy changes. (h, i) Na-DME migration path between the graphite layers and the migration energy changes of Na ion and Na-DME under an applied electric field.

this study, we determined that Na ions are most easily adsorbed to O and C atoms in DME. Further construction of the structural model of DME inserted between the graphite layers shows that the pitch of the graphite layer is changed to 11.64 Å when a DME molecule is inserted between two graphite layers (Fig. S10). This calculation structure is in good agreement with the literature [16]. Therefore, we built a model of Na ion migration in DME between graphite layers that was based on the above model. After Na ion insertion, the three sites are near the oxygen atom in DME, the folds, and the center of the benzene ring between graphite layers, as shown in Fig. 3c–e. The Na⁺ can be adsorbed at all three sites, but the adsorption near oxygen atoms in DME is the easiest. The Na⁺ has a dependence on the selection of oxygen atoms in DME. Finally, the energy barriers of Na⁺ and DME migration from the graphite layer were calculated by the climbing image nudged elastic band method, and a certain electric field is applied to compare and analyze them. The migration paths of Na ions and DME are designed to migrate from one benzene ring position to the adjacent benzene ring center position (i.e., S1 and S2), as shown in Fig. 3f, h. In addition, the migration barriers are calculated in Fig. 3g, i. The conversion of electric field strength is shown in the Supplementary information. A large difference in migration barrier exists between Na ion alone and Na-DME coupling. These results imply that Na-DME coupling between the graphite layers can migrate more easily without applying an electric field. When a certain electric field is applied, the migration barrier of

Na ions is lower than that of Na-DME coupling, which means that Na ions will preferentially migrate when an electric field is applied.

Fig. 4 shows our proposed electrochemical mechanism at a high current density. When working at a low current density, DME molecules and Na⁺ chelate units are intercalated between the graphite layers, and during the charging process, Na[DME]⁺ units will come out together. This phenomenon was also observed in Goktas' report [17]. The *in situ* XRD results under a low current show the same peak change trend, and *ex situ* scanning electron microscopy images show repeated changes in the material volume, as shown in Fig. 4b and Figs S11–S13. When the current density increases, the working mechanism changes. After the insertion of Na[DME]⁺ units, DME molecules will stay between the graphite layers, while Na⁺ ions are released, which provides the charging capacity. This situation is reflected in the high-current XRD experiment shown in Fig. 4c; the material's peak does not return to the original peak after full charging, and the distance between layers remains. In subsequent cycles, Na⁺ was used as a transport medium to perform the corresponding electrochemical insertion and desorption processes. This mechanism seems to indicate that graphite is not affected by volume expansion during high-current cycles; thus, it has a stable chemical mechanism.

In addition to confirming the new mechanism under a high current, the full battery was assembled by matching graphite with the Na₃V₂(PO₄)₃ cathode material (Fig. S14). Fig. 5a shows a schematic of the working

Figure 4 (a) Schematic of high-current working mechanism; *In situ* synchrotron XRD patterns and the corresponding diffraction peak intensities maps of (b) 40 mA g⁻¹, and (c) 10 A g⁻¹.

Figure 5 (a) Capacity and voltage curves of the full cell under different current densities (0.1, 0.2, 0.5, 1, 2 A g⁻¹); (b) rate performance of the full battery; (c) cycle performance chart of the full battery at 1 A g⁻¹ current; (d) power density and energy density comparison chart of the full battery system and those in the literature [18,34–37].

principle of the full battery. The full battery has excellent rate performance and cycling stability (Fig. 5a, b). The capacity of 122.8–95.4 mA h g⁻¹ was delivered at current densities of 0.1–10 A g⁻¹ (relative to the negative electrode), with a capacity retention rate of 77.7%. Compared with previous studies on SIB systems, the full battery has an outstanding high power output performance (Fig. 5d, Table S2); the highest power density is up to 14,846 W kg⁻¹, and the energy density is up to 103 W h kg⁻¹ (relative to positive and negative active materials). In addition, the full battery system has good cycle performance at a current density of 1 A g⁻¹.

CONCLUSIONS

Through experiments, we observed a special phenomenon, namely, the increase in the Na ion diffusion rate under a high current. We used *in situ* synchrotron XRD analysis and other characterization approaches to determine that Na⁺ ions separate out under a high current. Therefore, for the first time, we proposed the reaction mechanism of the co-intercalation reaction under a current; specifically, Na⁺ ions separate out alone, while DME molecules remain between the graphite layers. This me-

chanism can explain the high stability of commercial graphite. The completely assembled battery has an excellent high power output performance. This mechanism provides guidance for the design of large-scale energy storage devices.

Received 1 March 2021; accepted 21 April 2021;
published online 2 July 2021

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Acknowledgements This work was supported by the National Natural Science Foundation of China (21978088, 91534202 and 51673063), sponsored by the Program of Shanghai Academic/Technology Research Leader (20XD1433600), the Program for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutes of High Learning, the Basic Research Program of Shanghai (17JC1402300), the Social Development Program of Shanghai (17DZ1200900), the Shanghai City Board of education research and innovation project, and the Fundamental Research Funds for the Central Universities (222201718002).

Author contributions Jiang N conceived and performed the research; Bi W participated in part of the experiments; Jiang N and Jiang H analyzed the data and charted the figures and table. All authors discussed the results and edited the manuscript.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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电场驱动下的超快 $\text{Na}[\text{solv}]^+$ 共嵌入石墨的新见解

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摘要 钠离子和醚电解质共嵌入的石墨呈现明显的体积膨胀效果, 无法对其稳定性做出合理的解释. 本文中, 我们发现共插入反应在大电流条件下受到施加电场的洛伦兹力影响, 钠离子被分离出来, 乙二醇二甲醚(DME)分子保留在石墨层之间. 此见解为这种材料的非凡稳定性提供了合理解释. 原位XRD和DFT计算证实了 Na^+ 的脱出. 根据该结果, 未改性的商品石墨以高达 10 A g^{-1} 的电流密度稳定地循环了6400次, 容量保持率高达97.2%. 在实验室组装的全电池最大输出功率为 $14,846 \text{ W kg}^{-1}$, 输出能量密度为 103 W h kg^{-1} (相对于阳极和阴极活性材料的重量). 该新机理为大规模储能提供了新的设计思路.