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Energy Accumulation Enabling Fast Synthesis of Intercalated Graphite and Operando Decoupling for Lithium Storage

Zhao Wang, Chang Yu,* Huawei Huang, Wei Guo, Changtai Zhao, Weicheng Ren, Yuanyang Xie, and Jieshan Qiu*

Metal chloride-intercalated graphite with multiple/versatile functions is one of the promising categories for charge storage, especially in achieving high volumetric and gravimetric performance simultaneously. Herein, a novel field-induced energy accumulation strategy is proposed and demonstrated to achieve minute-level fast preparation of stage-1 dominated FeCl₃-graphite intercalation compounds (GICs). The microwave-induced Joule heat and electron excitation from the graphite conjugated system produce the arc plasmas with high energy density in the limited microenvironment, accompanied by the enhanced internal energy of gaseous reactant molecules and the strengthened intercalation reaction kinetics. When evaluating the anode for lithium storage, the FeCl₃-graphite intercalation compounds feature the promoted self-activation characteristics and deliver a high volumetric capacity up to 1650 mAh cm⁻³. In particular, with the assistance of the operando Raman technique, it is interesting to find that the electronic decoupling effect among graphite and FeCl₃ layers is responsible for the self-activation process. Thus, it is reasonable to believe that this work can further offer an insightful and referable idea into the in-depth investigation of metal chloride intercalated graphite, especially for applications in lithium storage.


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1. Introduction

Graphite intercalation compounds (GICs) are formed by inserting guest ions, atoms, and molecules into sp²-bonded carbon host interlayers, further, the difference of guest species in GICs finally leads to the adjustable/multiple features in van der Waals gap and Fermi level. These super characteristics endow GICs with diverse physicochemical properties in terms of superior superconductivity, lubricity, magnetism, energy storage, and catalytic activity. Typically, the intercalation process can be easily driven by acid-base reactions or the redox reactions between guest and graphite host. The former generally results from the dipole interaction between the non-oxidizing Brønsted acids (such as H₃PO₄ and C₂H₂Cl₂O₂) and the polarizable graphite layers. The latter for redox-driven intercalation, the charge transfer process among guest and host can facilitate the opening of the galleries, which usually lead to oxidation, reduction, or even covalent modification of carbon atoms on graphite layers. The redox-driven intercalation is the widely-used approach due to the high intercalating efficiency and ease of operation, which have been achieved by versatile methodologies including electrochemical method, molten salt, molten metal, and liquid intercalation. On account of this, most oxidizing acids, molecular oxidants, and metallic reductants have been successfully intercalated into graphite interlayer, ultimately leading to the positively modulated physical/chemical properties. In addition, as for some guests featuring an inferior lattice match with graphite, sequential intercalation (BrCl)C₆, K₂H₄/3C₆, etc.) and co-intercalation (KBio₁₆C₆, K₁₃Au₁₅C₄, etc.) strategies can also be adopted to facilitate the synthesis of corresponding GICs by decreasing the formation energy.

The systematic studies of metal chlorides-intercalated graphite began to take shape as early as the last century, followed by its raised applications for superconductivity and energy storage/conversion. However, the harsh synthesis conditions and sluggish intercalating kinetics still hinder its further practical application. Generally, the intercalation of metal chlorides toward graphite is generally enabled by the molten salt method and result in compounds that contain both neutral and ionized intercalators. It was reported and widely accepted that the ionized species were usually formed by the reaction of metal chlorides and Cl₂ in gas phase. And the
Activation energy of its nucleation at the graphite edge plane is 105 kJ mol⁻¹, which is much higher than the value for the diffusion along graphite galleries (about 8–13 kJ mol⁻¹).[10,13] Thus, the nucleation process of ionized species at the graphite edge plane governs and determines the whole intercalating rate, while the metal chloride/Cl₂ threshold pressure must be attained to ensure the timely and appropriate generation of nucleus. Typically, the additional Cl₂ was also required to initiate/promote the redox reaction, which increased the risk of the experiment.[14] For certain metal chlorides, such as FeCl₃, MoCl₅, and WCl₆, the generated Cl₂ by self-decomposition under high temperature can initiate the intercalation process to some extent. However, the intercalating kinetics are still limited by the low Cl₂ content and productivity of these precursors, resulting in the time-consuming intercalating processes where several hours or even days are required.[15] Accumulating or increasing the internal energy of reactant molecules might be an efficient & promising strategy to accelerate the intercalating reaction.

Microwave, as the typically external driven field involved in the electric field and magnetic field components, can provide rapid and affordable approaches to triggering the thermocatalysis and conversion reactions by constructing the uniformly thermal room or localized heating microenvironment.[16] Remarkably, the good interaction between microwave and carbon materials usually leads to fantastic fast/volumetric heating effects as well as super-heating effects in the forms of hotspots and arc plasmas.[17] Excitingly, the arc plasmas driven by microwave are results of π-electron excitation from the conjugated regions on the basal plane of carbon, leading to the ionization of the surrounding molecules in tiny space and limited time. Further, it delivers a high-energy-density characteristic, thus enabling the accumulation of energy in confined discharge regions and producing multiple and versatile functions (such as controllable doping, exfoliation, and reduction).[18] With this in mind, microwave-driven arc plasmas would be favorable for intensifying the metal chlorides intercalation process by enhancing the internal energy of gaseous reactant molecules around the graphite surface.

Herein, driven by the electric field component of microwave, the intensive arc plasmas containing the ionized Cl₂ and Fe₂Cl₆ are generated to construct a pulse-energized microenvironment, facilitating/accelerating the synthesis of a stage-1-dominated graphite intercalation compounds (AP-GICs) in a minute timescale. In detail, the generated Joule heat boosts the vaporization and decomposition of adjacent FeCl₃ on graphite surface. Meanwhile, the π-electrons driven by the high-frequency microwave can jump out of the conjugate network and convert the kinetic energy into the internal energy of surrounding molecules, producing the ionized gaseous with the visualized and intensive electric-arc sparking/plasmas. As a consequence, the internal energy has been accumulated in the limited space. The enrichment of FeCl₅ on graphite surface can be achieved due to the fast reaction of Cl₂ and Fe₂Cl₆ polymer in plasmas, which accelerates its nucleation on graphite edge plane and promotes the subsequent intercalation processes. The verified experiments for the validity of arc plasmas-accelerated approach further reveal that a SiC reaction tube with highly responsive interactivity towards microwave cannot fast activate the intercalation process due to the shielded interaction among π-electrons and electric field component. The synthesized AP-GICs-1 anode is able to achieve a reversibly ultra-high volumetric capacity of 1650 mAh cm⁻³ for Li-ions storage as well as the promoted self-activation process during cycles. Furthermore, the operando Raman spectra reveal that the electronic decoupling among graphite and FeCl₃ layers is responsible for the self-activation process and enable the sufficient exposure of inner active sites of FeCl₃ molecule and interlayered graphene. The microwave plasmas-accelerated approach to preparing the metal chloride-intercalated graphite as well as the decoupling on the involved energy storage mechanism could enrich the research toolbox for intercalation chemistry and bring new opportunities for the fundamental research as well as practical applications in a broad scope of GICs-based materials with well-tailored lithium-storage performance.

2. Results and Discussion

The intercalation processes of FeCl₃ towards graphite were performed in the home-built setups with the quartz reaction. In comparison, the SiC tube was used as reaction vessels to verify the field-induced energy accumulation strategy. Before the reaction, filling the reactor with flowing N₂ was indispensable to avoid the deliquescence/oxidation of reactant and hazard of exhaust gas. Subsequently, microwave irradiation was conducted on the vessels to promote the intercalation reactions. In fact, as shown in Figure 1a, the quartz tube exhibits high penetration depth as well as microwave-transparent characteristics, and thus the inner graphite can serve a dual function role on account of the interaction between electric field component with π-electrons: one is as the heating medium to convert the microwave energy into thermal energy due to the high-frequency collision with carbon atoms, the other is to ionize surrounding molecules as the arc plasmas generator by the π-electrons excitation from conjugated regions. In consequence, the selective/fast heating towards FeCl₃/graphite mixture is performed, accompanying the uniform distribution of thermal field inside the tube. Different from quartz, the SiC, as the representative dielectric loss material, can absorb the incident microwave.[19] It functions to screen the direct interaction of graphite with the electric field component, and thus the arc plasmas, as well as the derived super-heating effects, are suppressed. As a result, only the SiC tube can be heated effectively and possesses a uniform temperature distribution, while the filled FeCl₃-graphite can be heated by thermal conduction from the SiC tube.

Figure 1b shows the corresponding visualized evolutionary processes of the mixture in quartz tube with the reaction time. Concretely, the intensive light emission can be detected at the beginning of the fourth second and maintained in the subsequent experiment. After irradiating, part of un-reacted FeCl₃ recrystallizes on the inner wall, while the final products denoted as AP-GICs remain at the bottom of the tube. During the intercalation process, as illustrated in Figure 1c, the guest FeCl₃ around the graphite surface suffers from the fast heating effects, then, vaporizes and decomposes into the complex gaseous mixture including Fe₂Cl₆, Cl₂, and Fe₃Cl₈, as...
demonstrated in Equation S1–S3, Supporting Information. Meanwhile, part of \( \pi \)-electrons on the carbon surface, which receive enough energy from the alternating electric field, get rid of the bondage of conjugated systems and collide with gaseous molecules, leading to the fast energy exchange and ionization of the surrounding atmosphere with obvious light emission. The resulting plasmas deliver a characteristic of high-energy-density and arouse the localized super-heating effects in a tiny space. And this can accelerate the formation of the ionized FeCl\(_4^-\) around the graphite surface. Therefore, the nucleation as well as intercalation processes of FeCl\(_4^-\) towards graphite will be accelerated, as demonstrated in Equation S4, Supporting Information. As a result, the enlarged interlayer-space enables Fe\(_2\)Cl\(_6\) and Fe\(_3\)Cl\(_8\) distribution throughout the graphite interlayers with considerable velocity, thus achieving the ferric chloride-intercalated graphite (Equation S5, Supporting Information).

The structure evolution of AP-GICs with microwave irradiation time was further revealed by X-ray diffraction (XRD) patterns. In Figure S1a, Supporting Information, after irradiating mixture for 10 s under 650 W, the diffraction peaks at 7.1°, 14.1°, 21.0°, and 28.1° can be assigned to the (001), (002), (003), and (004) planes of stage-2 GICs, where the peaks at 16.9° and 26.8° can be indexed to the (002) facet of graphite and the (003) face for stage-3 AP-GICs, respectively. However, as microwave time goes on, the peaks referring to the stage-2 phase exhibit the downtrend obviously. The disappearance of the intercalation phase might be imputed to the excessive heating on target products, as summarized and discussed in Figure S2a, Supporting Information, where the quick heating rates of the mixture inside the quartz tube are presented. Thus, a pulse-type heating mode using the 30% power with a duty ratio of 9/30 is subsequently applied to prolong the intercalating time for relieving excessive-heating effects. Remarkably, after irradiating for 3 min, the intensity of peaks at 9.4° and 18.8° distinctly raises, which are corresponding to the (001) and (002) faces of stage-1 AP-GICs. However, the intensities of these peaks also demonstrate a decreasing trend with the prolonged microwave time to 5 min (Figure S1b, Supporting Information). In addition, as shown in Figure S3, Supporting Information, the excessive FeCl\(_3\) recrystallizes on the inner wall of the tube.
accompanied by a tendency to move away from the bottom as the increase of irradiation time due to the excessive heating process. Particularly, the three different samples with graphite, stage-1 and stage-2-dominated compounds (AP-GICs-0, AP-GICs-1, and AP-GICs-2) obtained in 0, 3, and 5 min pulsed irradiation, respectively) are chosen as demonstrations to reveal the micro/nano-scale structures and energy storage characteristics. Moreover, the reaction conditions and structural characteristics of the AP-GICs-1 compounds were compared with the hybrids in literature and the results were shown in Table S1, Supporting Information. It is noted that the AP-GICs-1 with the stage-1 dominated intercalation structure indeed delivers a short preparation time, indicative of the practicability of the proposed energy accumulation strategy.

As for the adopted SiC reaction tube as comparison, the slow heating rates for mixture depending on the thermal conduction are presented (Figure S2b, Supporting Information). Given this, a preheating of tube with microwave for 10 min is essential to guarantee the sufficient fusion/vaporization of inner FeCl$_3$. After that, additional heating for 3 min under 30% of irradiating power is performed on the vessel for comparison. As shown in Section S1c, Supporting Information, compared with that of AP-GICs-1, an intensive diffraction peak corresponding to the (002) face of graphite can be detected in the intercalation compounds obtained by microwave-heated SiC tube (SiC-GICs), accompanied by the weak peaks assigned to the (001), (002) and (003) reflections of the stage-1 phase. Obviously, the SiC-GICs are dominated by pristine graphite with the weak characteristic peaks of the stage-1 phase. In a word, without the localized super-heating effects caused by arc plasmas, the intercalation process of SiC-GICs is restricted by the sluggish nucleation rate of ionized species, which is similar to the traditional molten salt method, thus delivering a low intercalation efficiency.

As a verification of the concept that the FeCl$_3$ is essential for the arc plasmas generation, the microwave reactions for FeCl$_3$-graphite mixtures were executed without an N$_2$ atmosphere (Figure S4, Supporting Information). The same phenomenon of light emission can be detected, which further demonstrates that the species derived from FeCl$_3$ are capable of irritating the arc plasmas generation. In addition, the pure graphite was also irradiated by microwave under a vacuum environment. Obviously, there is also some light emission performed at the beginning of the fourth second, but this only maintains a fraction of a second. It can be found that the ephemeral light emission is distinct from the arc plasmas and might be assigned to the ball lighting plasmas as reported in previous work.[20] After this process, most of the absorbed energy is supplied to the carbon matrix and eventually transferred into heat, causing a distinctly red heat phenomenon. The microwave irradiation on pure graphite under an N$_2$ atmosphere was also performed. Obviously, the introduced N$_2$ can only be ionized at the interface of graphite and N$_2$ with localized light emission. These results further indicate that the light emission is the result of ionization of gas molecules generated from FeCl$_3$, while the introduced protective gas during the reaction process will have no effects on the generation of arc plasmas.

In order to further decouple the microstructure evolution process of AP-GICs when explored to the high-temperature field, ex situ Raman spectroscopy measurements were performed on the basal plane of AP-GICs-1 by tuning the irradiating power and time with 532 nm laser (Figure 2a). The laser, as the typical electromagnetic wave, can also induce the high-frequency motion of free electrons on carbon surface as the microwave does, resulting in strong heat dissipation in well-defined irradiating regions.[21] Figure 2b illustrates the Raman spectra of AP-GICs-1 with a set of distinct peaks after different laser irradiation time. At the initial stage, the peak at 287 cm$^{-1}$ corresponds to the A$_{1g}$ (H) Raman-active mode of intercalated FeCl$_3$ due to the rotation of Fe--Cl bonds, which is different from the result in bulk FeCl$_3$ as reported previously.[3] The characteristic peak of the G band located at 1581 cm$^{-1}$ is associated with pristine graphite phase, meanwhile, the upshifted G peaks at 1614 and 1626 cm$^{-1}$ can also be detected. The position of the G peak that is related to the Fermi level of carbon atoms in sp$^2$-hybridized states, can be tuned by the p-type doping level of molecular oxidant in graphite and has been widely used to identify the staging of GICs.[5,9] Herein, the distinct G peaks at 1614 and 1626 cm$^{-1}$, as the results of the FeCl$_3$ doping in graphite, can be assigned to stage-2 and stage-1 intercalation phases of composites. In addition, the 2D band is the second order of the D peak, and the symmetry of the corresponding peak can be used to identify the number and stacking structure of graphene layers. As can be observed, the quasi-symmetrical 2D peak at 2714 cm$^{-1}$ means that most of the graphite layers behave as few- or mono-layer due to the significant decrease of interlayer interaction derived from the well doping of FeCl$_3$ as well as the enlarged interlayer spacing.

After irradiating the basal plane of AP-GICs-1 for 120 s under the full power, an obvious etching can be detected due to the partial oxidation of surface carbon atoms, accompanied by the distinct characteristic peaks of Fe$_2$O$_3$ originated from the oxidation of inner FeCl$_3$, as can be seen in Figure S5, Supporting Information. Herein, a moderate irradiating power (5%) was applied to heat the basal plane and avoid the oxidation of composite as far as possible and the related results are shown in Figure 2b. As a consequence, the peak intensity at 287 cm$^{-1}$ reduces with the irradiating time goes on, accompanied by the fade-away phenomenon of G band blueshift. Remarkably, an abnormal intensification of the peaks at about 1614 cm$^{-1}$ can be detected after irradiating for 20 s. It might be attributed to the subtle rearrangement of interlayered FeCl$_3$ molecules, which triggers the structural evolution from stage-1 to stage-2 based on the Daumas–Hérold structure model as shown in Figure S6, Supporting Information.[22] Moreover, the 2D band gradually splits into multiple peaks at 2686 and 2720 cm$^{-1}$ that can be generally detected in pristine graphite. That is to say, with laser irradiation time goes on, the thermal energy in the irradiated region can be accumulated, resulting in the stepwise escape of intercalated species from interlayers. This can be analogous to the microwave heating process and serve as the proof of the concept that the excessive heating process can arouse the structural transformation from stage-1 to graphite-dominated compounds.

The inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis reveals that the mass ratio of graphite in AP-GICs-0, AP-GICs-1, and AP-GICs-2 are about 70, 40, and 54%, as shown in Figure 2c. Furthermore, the thermogravimetric
(TG) and derivative thermogravimetry (DTG) analysis of AP-GICs samples in air are carried out in Figure 2d. The multi-step weight loss in the temperature range of 230 to 560 °C for AP-GICs-0, AP-GICs-1, and AP-GICs-2 are 16, 14, and 17%, respectively, which is attributed to the stepwise escape of intercalating species from graphite galleries as is clearly seen from the DTG curves. The next weight loss process in the temperature range of 600 to 1000 °C might be attributed to the oxidation of graphite and residual FeCl₃. After heating to 1000 °C, about 4, 21, and 12% mass ratio for different samples can be maintained after the thermal decomposition process. According to the previous study, the residues can be indexed to Fe₂O₃ that originated from the oxidation of residual FeCl₃ component in an oxygen-containing environment. Consequently, the calculated contents of FeCl₃ in AP-GICs-0, AP-GICs-1, and AP-GICs-2 composites are about 24, 57, and 41% (corresponding to the graphite contents of 76, 43, and 59%), approximately consistent with the results derived from ICP-OES analysis.

Furthermore, the large-area mapping of the G band for different samples are collected and summarized in Figure 2e. Herein, the G band is divided into three part: the G₁ in the range of 1560 to 1598 cm⁻¹ can be used to identify the graphite phase, while the G₂ (from 1598 to 1619 cm⁻¹) and G₃ (from 1519 to 1650 cm⁻¹) are generally associated with the intercalating phases. More specifically, the AP-GICs-0 exhibits the uniform/obvious distribution of the G₁ band, while the AP-GICs-1 exhibits a G₃ band-dominated distribution. As for AP-GICs-2, the G₂ band with the highest intensity than others can be detected. These results further confirm the distinguishable intercalation phase for different samples, and the microwave time is the significant process parameter to dynamically tune the intercalation structure of AP-GICs.

The morphology and microstructure of the as-made AP-GICs-1 were characterized in detail to have a deep understanding of the intercalation process. As can be seen in scanning electron microscopy (SEM) images, the pristine graphite presents an ordered structure composed of parallel graphene sheets. (Figure S7a–c, Supporting Information) After irradiation, the lamellar structure of AP-GICs-1 is well maintained with the slightly loose arrangement along with the direction of the interlayer of adjacent graphene layers (Figure S7d–f, Supporting Information), which would be favorable for infiltration and diffusion of reactants in the following application. The transmission electron microscopy (TEM) further examines the nanostructure of composites. As shown in Figure 3a–c, the high-resolution TEM (HR-TEM) images clearly present the (001) fringes of stage-1 and stage-2 phases with the lattice spacings of about 0.93 nm and 1.25 nm, which are consistent with the theoretical value as mentioned in Figure S8, Supporting Information. The lattice fringe with a spacing of 0.17 nm might be corresponding to the (012) planes of FeClO nanodots on the surface, where the oxygen might originate from the trace.
amount of water in FeCl$_3$ precursor. This concept has been confirmed by the characterization analysis (Figure S9, Supporting Information) of FeClO-dominated graphite intercalation compounds (FeClO-GICs) that are obtained by adding the additional deionized water before reaction. The distribution of C, Fe, Cl, and O elements have been detected by energy-dispersive X-ray (EDX) mapping shown in Figure 3d, which have confirmed that the ferric chloride nanocrystals, as well as FeClO nanodots, uniformly disperse in/on the graphite sheets.

The chemical states of the concerned composites have been further examined by in-depth X-ray photoelectron spectroscopy (in-depth XPS), as shown in Figure 3e–g. The C, O, Cl, Fe, and Ar elements coexist in the full survey spectra of the sample, where the peaks of Ar atoms originate from the residual signal after different Ar-etching times (Figure S10, Supporting Information). Moreover, there are no peaks assigned to the N element, indicating that the nitrogen functionalization towards graphite driven by the ionized N$_2$ is negligible during the reactions. The O 1s spectra can be fitted into four peaks: the peaks at 533.4, 523.1, 531.0, and 530.4 eV can be assigned to C—O, (CO$^*$)OH, C=O, and O$^{2-}$ bonds, respectively (Figure 3e). The former three peaks coexist in the surface and inner of composites and result from residual oxygen species binding with carbon atoms. The latter one can only be detected on the surface and can be indexed to the Fe—O bond. For the Cl 2p spectra (Figure 3f), the two main peaks are located at about 200.1 and 198.5 eV, corresponding to the Cl 2p$_{3/2}$ and Cl 2p$_{1/2}$ with a spin-orbit splitting of 1.6 eV, which might be derived from the Fe—Cl bonds on the surface. After Ar-etching, the peaks of inner Cl atoms located at 200.8 and 199.2 eV emerge, assigned to the Cl 2p$_{3/2}$ and Cl 2p$_{1/2}$ of intercalated FeCl$_2$.[12b,23] It is noteworthy that the Fe—O, as well as Fe—Cl bonds on the surface, can be indexed to the less FeClO on the AP-GICs-1. As for the Fe 2p spectra (Figure 3g), the two main peaks at 725.0 and 711.6 eV correspond to the Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$ of Fe$^{3+}$, respectively. The satellite peaks at binding energies of 730.4 and 716.2 eV can be assigned to the splitting of main peaks. After Ar ion etching, the new peaks at 723.3, 709.7, 720.6, and 707.4 eV emerge, corresponding to the Fe$^{2+}$ 2p$_{3/2}$, Fe$^{2+}$ 2p$_{1/2}$, Fe$^0$ 2p$_{3/2}$, and Fe$^0$ 2p$_{1/2}$, respectively. The presence of Fe$^{2+}$ and Fe$^0$ might origin from the reduction induced by Ar plasmas.

Typically, the characteristics of internal densification for metal chloride-intercalated graphite, together with optimized ion diffusion channels, will hold considerable potential for lithium-ion storage.[24] As the demonstration, the electrochemical performances of AP-GICs-0, AP-GICs-1, and AP-GICs-2 as anode materials for lithium storage were first detected and evaluated using galvanostatic charge/discharge (GCD) cycling, where the gravimetric capacity calculation is based on the total mass of composites. The cycling performance of corresponding composites at a current density of 1 A g$^{-1}$ is shown in Figure 4a. In detail, the initial charge/discharge capacities of 648/1183, 445/1056, and 371/909 mAh g$^{-1}$ for AP-GICs-0, AP-GICs-1, and AP-GICs-2 are obtained. After 400 cycles, the high charge/discharge capacities of 600/603 mAh g$^{-1}$ can be delivered for AP-GICs-1 electrode, while the corresponding value for AP-GICs-0 and AP-GICs-2 are 379/385 and 498/500 mAh g$^{-1}$, respectively. It can be seen that the AP-GICs-1 with the maximum FeCl$_3$ content exhibits the well-optimized self-activation process with the highest terminal reversible capacities after cycles. In fact, in
the present system, the folded active sites in terms of the unreacted FeCl$_3$ molecules in graphite interlayers and/or unexposed interlayer space might hinder the sufficient release of intrinsic capacity in the first few cycles.$^{[25]}$ As cycles go on, the reversible capacities correspondingly arise, thanks to the dynamically facilitated and modulated exposure of active sites. This self-activation process also promotes the charge transfer kinetics of the electrode, contributing to improve the rate performance and achieve the high volumetric-specific capacity of 1650 mAh cm$^{-3}$, as shown in Figure S11, Supporting Information.

Moreover, the actual value (603 mAh g$^{-1}$) delivered by AP-GICs-1, as obtained by GCD measurement, is far higher than the theoretical capacity of AP-GICs-1 up to 402–447 mAh g$^{-1}$, which is calculated by Equation S6, Supporting Information, based on the content of different components. In order to reveal this exceptional performance, the voltage of 0.2 V is chosen as the boundary condition to roughly separate the discharge capacity contribution of different components based on the cyclic voltammetry (CV) and GCD results of AP-GICs-1, where the graphite and FeClO-GICs are also measured for comparison (Figure S12, Supporting Information). The capacity in the range of 0.2 to 0.01 V originates from the intercalation process of Li$^+$ towards pristine graphite phase (C$_G$), and the capacity at 0.2–3.0 V can be attributed to the conversion reactions involved in intercalated FeCl$_3$ and surface FeClO nanodots (C$_{Fe}$). The statistical data is summarized in Figure 4b. As for C$_G$, the practical value is consistent with the theoretical ones as estimated above for AP-GICs-1 in the first 100 cycles, and then demonstrates an upward trend from 100th to 400th cycle with a capacity increase of 14%. In comparison, the obvious decay process in the first 50 cycles can be observed with the capacity retentions of 82% for C$_G$, and a more distinct increment of 66% in capacity can also be detected in subsequent cycles. The initial capacity decay might origin from the inevitable dissolution of intermediate LiCl generated on the electrode surface, which have been proved by the relatively low intensity of surface Cl 2p signal and emerged Fe$^0$ signal after 50 cycles as shown in Figure S13, Supporting Information. The fully exposed active sites of inner FeCl$_3$ after cycles might be one of the reasons for the increased capacity. Moreover, the weakened Vander Waals force among the adjacent graphene sheets due to the steric effects of intercalated FeCl$_3$ layers will result in the change of lithium storage mechanism, for example, in addition to the typical intercalation process (onset potential: ~0.2 V vs Li/Li$^+$) the reversible deposition of Li layers on single-layer graphene (onset potential: ~1.0 V vs Li/Li$^+$) can also provide the considerable capacity as previously reported.$^{[12a,26]}$

The Li$^+$ charge storage behavior in the AP-GICs-1 electrode was further investigated using the traditional CV and a multiple potential step chronoamperometry (MUSCA) technique (Figure S14a, Supporting Information).$^{[27]}$ In comparison, as illustrated in Figure 4c, the calculated CV curve via MUSCA measurement shows a slight mismatch with the traditional one at 0.1 mV s$^{-1}$, especially for the shift of 0.14 and 0.05 V at peaks 1 and 2. Moreover, the drift of redox peaks in traditional CV plots increases with scan rates (Figure S14b, Supporting Information), which might originate from the ohmic limitation and intrinsic electrochemical kinetics of the electrode. As for the calculated CV curves, the ohmic drop contribution was eliminated to a large extent, which can be proved by the vanished
drift of current peaks. Thus, the calculated CV curves will be helpful in revealing the intrinsic reaction kinetics of the electrode. In theory, the equation $i = av^b$ can be used to describe the functional relationship between the peak current $i$ and the scan rate $v$, where $a$ and $b$ are adjustable parameters. Here, the $b$ value is an indicator of the charge storage behavior. If $b = 0.5$, the redox reaction is limited by a diffusion-controlled charge storage process, while $b = 1$, it is enslaved to a surface-controlled process. As demonstrated in Figure S14c,d, Supporting Information, the reconstructed CV curves from 0.028 to 0.5 mV s$^{-1}$ are used to analyze the charge storage behavior, from which the as-obtained $b$ values at different redox peaks can be obtained. It can be seen that the lithium insertion process in graphite (peak 3 and 4) have high $b$ values approaching 1, indicative of a fast surface-controlled process; while the conversion reaction involved in FeCl$_3$ and surface FeOCl has $b$-values close to 0.5, implying the diffusion-controlled reactions (Figure 4d). To further reveal the practical application of AP-GICs-1 for lithium storage, a full cell was assembled with a LiFePO$_4$ cathode, where the electrochemical performances are shown in Figure S15, Supporting Information. Notably, the LiFePO$_4$/AP-GICs-1 full cell exhibits a steady cycle performance at 200 mA g$^{-1}$ with a reversible capacity of 122 mAh g$^{-1}$ and capacity retention of 99% after 100 cycles.

The operando Raman spectroscopy was conducted to have a deeper insight into the structural change and related self-activation mechanism during the electrochemical cycling process. Figure S16, Supporting Information, shows the schematic diagram of the operando Raman testing equipment. The charge and discharge curves of AP-GICs-1 for operando measurement are similar to those observed in coin cells, and the detailed operando spectra of the G band for the first cycle is clearly summarized in Figure 5a. At the initial stage of discharge, the typically shifted G band at an approximate 1626 cm$^{-1}$ is detected and assigned to the stage-1 phase as proved above. Upon cathodic process, the G band-related peak shifts towards low wavenumbers begin at about 1.5 V and have been completed at 1.0 V, while a shifted G peak at 1593 cm$^{-1}$ is observed. The downshift of the G peak means that the electron transfer from the graphite layer to FeCl$_3$ is weakened. At the voltage range of 1.5–1.0 V, the conversion reaction of Li$^+$ and inner FeCl$_3$ is performed, accompanied by the formation of LiCl molecules and Fe$^0$ atoms in graphite interlayer space. Meanwhile, the ordered structure of the FeCl$_3$ molecular layer is destroyed, causing the

![Figure 5. a) First-cycle CV curve and corresponding operando Raman mapping/spectra of the AP-GICs-1 electrode at selected potentials. b) The simulated diagrams of lithium storage and microstructure evolution process for AP-GICs-1 electrode.](image-url)
electronic decoupling among host and guest. In subsequence, the slight G-band blueshift to 1598 cm\(^{-1}\) is further observed at 0.55 V, while its position remains virtually constant upon the following lithiation. In detail, the upshift of G peak upon cathodic process should be attributed to a change of the equilibrium lattice parameter with a consequent stiffening of the G-band due to the negative doping\(^{[26b]}\). Subsequently, a shoulder peak at 1582 cm\(^{-1}\) arises from 0.55 to 0.01 V, which might be attributed to the partial downshift of G peak due to the ultra-high Li doping on graphene layers.\(^{[3]}\) This result matches well with previously reported work especially for the lithium storage process, as demonstrated on single-layer graphene.\(^{[26b]}\) Generally, the single-layer graphene exhibits a higher reversible capacity than graphite due to the reversible deposition/doping of Li layers on both sides of graphene. Based on this, the interlayered graphene that suffers from the electronic decoupling process with the FeCl\(_3\) layer can store excessive lithium in the form of a single layer, which might be one important reason for the ultrahigh practical capacity.

In subsequent charge process or even further cycles, the G band cannot recover to the initial wavenumbers (Figure S17, Supporting Information), which means that the electronic decoupling effect among graphite and FeCl\(_3\) layer is irreversible and the structure of AP-GICs-1 (particularly for the ordered FeCl\(_3\) molecular layer) cannot be restored to the original state after charge/discharge processes. It might be converted into a composite in which the intercalated FeCl\(_3\) in the forms of nanosized clusters is sandwiched between graphite layers.\(^{[8]}\) After 400 cycles, the TEM image of AP-GICs-1 shows the sheet structure with a slightly-wrinkled surface (Figure S18a, Supporting Information). However, in the elemental mapping (Figure S18b, Supporting Information), the signals of O, Cl, and Fe elements approximately match with that of the C element except for the slight gathering in forms of nanoclusters. In addition, as shown in Figure S18c, Supporting Information, the characteristic peak of stage-1 phase at 28.1° disappears and no sharp peaks corresponding to large FeCl\(_3\) crystal can be detected after 400 cycles, which can also confirm the disappearance of ordered intercalation structure as well as the low crystallinity of FeCl\(_3\) clusters. Moreover, due to the slight gathering effect, the Vander Waals force can be further weakened. As such, this process can facilitate the electrolyte ion diffusion toward the inner active sites and promote the transformation of diffusion-controlled reaction to surface-controlled ones, which is further confirmed by a district GCD curve change from flat to linear response in the range of 1.25 to 2.0 V, as observed in Figure S18d, Supporting Information.

As summarized in Figure S5b, the simulated diagrams are devoted to illustrating the lithium storage process inside the AP-CICs-1 electrode. In the first discharge process, the conversion reaction of Li\(^{+}\) and intercalated FeCl\(_3\) occur, resulting in the disordering of FeCl\(_3\) layers as well as the electron decoupling effect with graphite layers. Afterwards, excessive lithium ions adsorb or even deposit on the interlayered graphene, leading to the capacity beyond the theoretical value of graphite. Moreover, after the charging process, the disordered state of FeCl\(_3\) molecules can be maintained in the confined space. In the subsequent cycles, these disordered molecules are dynamically transformed into nanoclusters, which further broaden the interlayer spacing and promote the sufficient exposure of inner active sites, thus boosting the release of capacity.

3. Conclusions
An accelerated intercalation reaction of ferric chloride towards graphite was achieved by a field-induced energy accumulation strategy, and more importantly, this process is capable of shortening the preparation time of intercalation compounds from days to minutes. During the microwave irradiation, the arc plasmas with localized high-energy-density characteristics are generated due to the ionization of gaseous reactant molecules, which facilitates the accumulation of internal energy and finally promotes the intercalation of ionized FeCl\(_3^{−}\) nucleus at the edge plane of graphite. As the consequence, the enlarged interspace enables the uniform distribution of Fe\(_2\)Cl\(_4\) and FeCl\(_3\) throughout the graphite interlayers with considerable velocity, thus achieving the FeCl\(_3\)-intercalated graphite in minute timescale. Furthermore, the laser irradiation test confirmed the structure regulation process of AP-GICs upon microwave time. The as-obtained AP-GICs-1 delivers a high volumetric capacity of 1650 mAh cm\(^{-3}\) based on the volume of the electrode after cycles. Moreover, the operando Raman study reveals that the boosted capacity is mainly originated from the electronic decoupling with graphite and the irreversible disordering of FeCl\(_3\) layers as well as the lithium storage on interlayered graphite layer as the graphene did. In summary, the simple acceleration strategy via arc plasmas driven by microwave field was proposed here, where the involved methodologies and detailed decoupling regarding the self-activation mechanism would provide many opportunities and inspirations for advancing graphite intercalation compounds in energy storage and related fields.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

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