ABSTRACT: A rechargeable aluminum-ion battery based on chloroaluminate electrolytes has received intense attention due to the high abundance and chemical stability of aluminum. However, the fundamental intercalation processes and dynamics in these battery systems remain unresolved. Here, the energetics and dynamics of chloroaluminate ion intercalation in atomically thin single crystal graphite are investigated by fabricating mesoscopic devices for charge transport and operando optical microscopy. These mesoscopic measurements are compared to the high-performance rechargeable Al-based battery consisting of a few-layer graphene−multiwall carbon nanotube composite cathode. These composites exhibit a 60% capacity enhancement over pyrolytic graphite, while an ~3-fold improvement in overall ion diffusivity is also obtained exhibiting ~1% of those in atomically thin single crystals. Our results thus establish the distinction between intrinsic and ensemble electrochemical behavior in Al-based batteries and show that engineering ion transport in these devices can yet lead to vast improvements in battery performance.

KEYWORDS: aluminum-ion battery, chloroaluminate anion, intercalation behavior, diffusion coefficient, 2D graphitic composite cathode

INTRODUCTION

The rapid development of portable electronic devices, the promise of electric vehicles, and advances in the production of electricity from renewable sources have increased the demand for safe and low-cost electrochemical energy storage devices.1,2 Although lithium-ion batteries (LIBs)3 are widely used in portable consumer electronics and are rapidly entering into transportation and grid-scale storage sectors, the future of all types of Li-based batteries is the subject of much debate.4–7 These issues have prompted the pursuit of so-called “beyond Li-ion” batteries that use less lithium and/or use metals other than lithium.2,6

Recently, rechargeable Al-ion-based batteries (AIBs) utilizing $\text{AlCl}_4^-$ ions have intrigued researchers as promising alternatives to LIBs. Recent advances that include the use of ionic liquid electrolytes have resulted in the extraordinary cycling performance of AIBs.1,5–13 One of the hallmarks of these chloroaluminate batteries is their impressively high charging rates, which have been attributed to very fast anion diffusion within the graphite cathode. However, unlike LIBs, the fundamental interfacial intercalation chemistry and ion transport dynamics within the cathode remain to be investigated in AIBs.

Here, we perform systematic investigations into the electrochemistry and diffusion dynamics of $\text{AlCl}_4^-$ intercalation into graphite. We fabricate mesoscopic on-chip electrochemical cells with graphitic single crystals of controlled dimensionality from few-layer graphene to bulk graphite flakes and perform operando variable temperature charge transport measurements and optical microscopy. These measurements allow us to probe the intercalation reaction at the thinnest limit of the bulk intercalation compound (four-layer graphene) and to determine an upper bound for the diffusion coefficient of $\text{AlCl}_4^-$ in graphite. Built on this fundamental understanding, we also develop a more practical procedure to enhance the efficiency of Al-based batteries. We develop a method to synthesize a graphene−multiwalled carbon nanotube (CNT) hybrid composite cathode and assemble this cathode into a high-performance rechargeable AIB that exhibits high specific...
We fabricated Hall bar devices containing few-layer graphene (~10–30 nm thick hexagonal boron nitride (hBN) crystals (Figure S1 in Supporting Information). In addition to the electrochemical current response, $I$, as a function of potential, $E$ versus Al pseudoreference electrode. (d) Carrier densities extracted from Hall effect measurements as a function of $E$, showing transition from electron-doping to hole-doping.

### RESULTS AND DISCUSSION

**Electrointercalation in the 2D Limit of the AlCl$_4^-$/Graphite System.** We began by exploring the electrochemical properties of the graphite–AlCl$_4^-$ intercalation compound in the 2D limit with *operando* electronic transport measurements. We fabricated Hall bar devices containing few-layer graphene (2–6 layers) stacked between two 10–30 nm thick hexagonal boron nitride (hBN) crystals (Figure S1 in Supporting Information). We then constructed an on-chip electrochemical cell (Figures 1a,b) consisting of this hBN/4LG/hBN Hall bar as the working electrode (WE), and two separate Al electrodes to serve as the counter electrode (CE), and pseudoreference electrode (RE). The WE, RE, and CE were then covered by an ~10 μL droplet of AlCl$_4$–EMI, which was prepared from an ~3:2 molar ratio of AlCl$_4$ and EMI (see Methods in Supporting Information). In addition to the electrochemical current response ($I$), standard AC transport measurements were used to measure the longitudinal resistance ($R_{xx}$) of the Hall bar WE at 300 K as the potential ($E$) at the WE was swept from 0 V to +2.0 V versus the Al RE with a sweep rate of 2 mV s$^{-1}$.

Beginning with a four-layer graphene (4LG) device, examining plots of both $R_{xx}$ and $I$ as a function of potential (Figure 1c) throughout the sweep provides insight into the fundamental steps in the intercalation reaction. The plot of $R_{xx}$ shows two distinct regions. First, between 0 to 1.8 V, $R_{xx}$ decreases only slightly, that is, by less than 8% compared to $R_{xx}$ at 0 V. At 1.8 V, $R_{xx}$ decreases precipitously after a small initial upturn and then remains unchanged from 1.85 to 2.0 V. In the plot of $I$ as a function of $E$, minimal change in $I$ occurs until a significant increase at ~1.6 V, followed by the onset of a sharp increase in current at 1.8 V. To investigate the origin of these changes, we cooled these mesoscopic devices to 4 K under three applied biases (0, 1.55, and 2.0 V) and performed Hall effect measurements that allow us to precisely measure the carrier density in the graphene layers (Figure S2 in the Supporting Information). At 0 V, the positive slope of the Hall resistance curve reveals electron doping of the pristine 4LG, and we calculate a 2D carrier density, $n_{2D}$, of 3 × 10$^{13}$ cm$^{-2}$. At 1.55 and 2.0 V, the slopes of the Hall resistance curves are positive, which is the manifestation of holes as charge carriers, and $n_{2D}$ at 2.0 V is 4.4 × 10$^{13}$ cm$^{-2}$. These changes in $n$ are summarized in Figure 1d.

Our magneto-transport measurement described above provides key insight into the crucial steps in the intercalation of graphite by chloroaluminate ions and the ultimate capacity limits of the system. The initial decrease in $R_{xx}$, which is accompanied by a small change in $I$, yet switches the graphene from n-type to p-type conductor, is attributed to the purely electrostatic gating effect of the electrochemical double layer. As we have shown previously for Li$^+$ intercalation, the initial upturn in $R_{xx}$ at 1.8 V that coincides with an onset of a large increase in $I$ arises because intercalation leads to decreased electronic mobility owing to increased scattering between electrons in the graphene layers and chloroaluminate anions in the van der Waals (vdW) gap. This decreased mobility causes the resistance to increase initially but is then overwhelmed by the greatly increased hole carrier density that also accompanies AlCl$_4^-$ intercalation, resulting in a subsequent sharp drop in resistance. These charge transport measurements thus allow us to interrogate the intercalation mechanism directly in a manner that is not conflated with side reactions as in the sole measurement of $I$. Our measurements also allow us to estimate an approximate limit for the capacity of carbon-based chloroaluminate intercalation compounds; the Hall carrier density of fully intercalated 4LG devices (Figure 1d) translates into a capacity of ~85 mAh g$^{-1}$. In this estimate, we consider only the three graphene–graphene vdW interfaces...
of the hBN/4LG/hBN heterostructure as active for intercalation (thus neglecting the two peripheral hBN/G vdW interfaces). This assumption is based on previous studies that showed >10-fold decreased proclivity for hBN/G interfaces to intercalate Li$^+$ ions compared to that of G/G interfaces.16,17 Analogous experiments at 2LG achieved a carrier density of 1.0 × 10$^{12}$ holes cm$^{-2}$ at 2.5 V (Figure S3 in Supporting Information), which is more than 2 orders of magnitude lower than that observed for the aforementioned 4LG system. These results are consistent with only electrostatic gating but no substantial intercalation in the 2L limit up to 2.5 V. The dissolution of contact electrodes prohibited potential excursions in excess of 2.5 V. It is noteworthy that the staging limits for chloroaluminate–graphite intercalation compounds are typically stage 4, as we discuss in more detail below.

**Chloroaluminate Ion Diffusion Measurements via Optical Microscopy.** To estimate the diffusion coefficient of AlCl$_4^-$ ions in graphite-based electrodes, we assembled a two-electrode on-chip electrochemical cell under an optical microscope (Figure 2a). We observed reversible intercalation in an ~80 nm thick graphite crystal, manifested by changes in the optical contrast across the flake, which occurs due to a combination of interlayer expansion and changes in dielectric constant due to intercalation-induced doping.18–20 As anticipated by the transport measurements shown in Figure 1, no contrast change occurs when the applied potential between the graphite and counter electrode is less than 1.85 V. As the bias is increased beyond 1.9 V, we see evidence of AlCl$_4^-$ ions intercalating into, and diffusing through, the graphite lattice with a well-defined staging behavior. These optical changes are reversed when the potential returns to 1.5 V, however, the flake is left with some additional wrinkles from this intercalation–deintercalation cycle. Figure 2b shows a series of optical microscope images taken over a period of 2 s as under a bias of 1.9 V. These images clearly display the movement of the diffusion front with time, and the intercalated area was extracted from the image at each time point (see Methods in Supporting Information), allowing estimation of the diffusion coefficient, D, for AlCl$_4^-$ in graphite by linear regression analysis of the temporal evolution of intercalated area (Figure 2c) using a simplified continuum model (see Methods and Figure S4 in the Supporting Information). In this model, the D is related to the change in area ∆A and time by $^{21}$

$$D = \frac{\Delta A}{4\Delta t}$$

The resultant D we extract from the room-temperature measurements of Figure 2b,c is ~1.1 × 10$^{-6}$ cm$^2$ s$^{-1}$.

These ion dynamics were then probed over a wide temperature range of 320–220 K by fabricating disk-shaped graphite electrodes with thicknesses of 40–50 nm. This design allows for more quantitative determination of coverage area as a function of time at each temperature (see Methods and Figures S5–S7 in Supporting Information). We note that with decreasing temperature, higher potentials were required to initiate intercalation as monitored by optical contrast, which may be attributed to changes in equilibrium potential and/or changes to ohmic losses through the electrolyte in this two-electrode configuration. Regardless, D can be determined for each condition as summarized in Figure 2d. At 320 K, we extract $D = 9.6 \times 10^{-6}$ cm$^2$ s$^{-1}$, a value approaching the diffusion coefficient of chloride ions in water at room temperature (about $2 \times 10^{-5}$ cm$^2$ s$^{-1}$).22 Since practical cathodes consist of polycrystalline materials and also contain additives and binders, the values for D obtained serve as upper bounds for chloroaluminate ion diffusion in graphic cathodes. Employing this diffusion constant, we can also evaluate the performance of AIBs constructed with cathodes of varying composition and microstructure.
Preparation of Composite Graphite-Based Cathodes.

The excellent intrinsic properties of atomically thin graphite cathodes discussed above provide insight into approaches that can improve AIBs by nanostructuring the carbon cathode. Specifically, these results suggest that increasing the effective surface area while maintaining the minimum intercalation staging layers (approaching 4LG) is critical. In addition, establishing scalable composite cathodes are critical for battery applications. For this purpose, we prepare three types of cathodes with different microstructures: pyrolytic graphite (PG), few-layer graphene (FLG) coated on PG (FLG@PG), and FLG−CNT composite coated on the PG (FLG/CNT@PG) electrodes (Figure 3a−c). Scanning electron microscopy (Figure 3d−f) and transmission electron microscopy (Figure 3j,k) images of these samples show that PG comprises highly oriented graphene layers (Figure 3g), whereas more loosely stacked graphene layers are observed in the cross section of FLG@PG (Figure 3h). In FLG/CNT@PG, CNTs are observed to be interspersed among loosely stacked FLG sheets (Figure 3i−k), creating a mesoporous structure.

Electrochemical and Structural Analysis of Modified Graphite Composite Cathodes. The electrochemical intercalation characteristics of PG, FLG@PG, and FLG/CNT@PG electrodes were investigated via cyclic voltammetry and the results are presented in Figure 4a. All electrodes exhibit similar behavior showing three anodic peaks at 1.9, 2.2, and 2.4 V and two cathodic peaks at 1.7 and 2.1 V consistent with the multistep AlCl₄⁻ intercalation reported in the literature. Galvanostatic charge−discharge curves of PG, FLG@PG, and FLG/CNT@PG electrodes at a current density of 66 mA g⁻¹ (1 C rate) are presented in Figure 4b. These three electrode types display specific charge (discharge) capacities of 60 (58), 64 (62), and 74 (68) mAh g⁻¹, and...
Coulombic efficiencies of 97%, 97%, and 92%, respectively, showing that the addition of FLG to PG increases both the charge and discharge capacities by about 7%.

To understand the origin of this change in battery performance, we acquire X-ray diffraction (XRD) data for the PG, FLG@PG, and FLG/CNT@PG electrodes before and after 50 charge−discharge cycles and galvanostatic tests. Prior to the cycling tests, these electrodes exhibit similar XRD patterns characterized by narrow and sharp (002) peaks with a d-spacing of ∼3.3 Å. After the cycling tests, as shown in Figure 4c, the (002) peaks of the electrodes split into two or three peaks after electrochemical cycling, consistent with a well-defined staging process (Figure 4d) upon intercalation of AlCl$_4^-$ anions along the c-axis direction of graphite (in agreement with Figure 2b). The periodicity (h) along the c-axis for graphite intercalation compounds (GICs) with stage index, n, can be calculated as follows:

$$h = d_i + (n - 1)d_g$$

where $d_i$ is the interlayer distance between the nonintercalated graphene sheets (3.35 Å), and $d_g$ is the gallery height after intercalating AlCl$_4^-$ ions. The d-spacing of the (00l) peaks of the GIC is then related to $n$ by

$$d_{(00l)} = \frac{1}{l}(d_i + (n - 1)d_g)$$

Our measured XRD patterns are consistent with $d_i$ values of 5.8 and 5.7 Å for stage index 5 and 6, respectively, in agreement with previous experimental results (5.7 Å). As shown in Figure 4c, our XRD data indicate $n$ values of 6 for PG, 5 for FLG@PG, and a combination of 5 and 6 for FLG/CNT@PG. To verify these results, we simulated XRD spectra with various conditions and confirmed that $d_i$ of 5.7 Å with $n = 6$ and $d_i$ of 5.8 Å with $n = 5$ reproduce the experimental XRD patterns of PG and FLG@PG, respectively (see Figures S8 and S9 in Supporting Information). We also find that larger h values of 8.8 Å that have been suggested in previous theoretical studies are inconsistent with our experimental XRD patterns. Significantly, these data show that the increased capacity (Figure 4b) upon combining FLG with PG arises from a decreased stage index from 6 to 5. We ascribe this improved staging performance to the increased availability of the host material to chloroaluminate ions because of the more loosely packed graphene layers in FLG@PG (Figure 3h). To understand these staging behaviors, we also performed a modeling study based on density functional theory (DFT) (see Methods in Supporting Information). Our DFT studies suggest that the inability to proceed to even lower stages may be a result of the high energy cost and volumetric expansion that is required to reach lower intercalation stages (see Figures S10 and S11 in Supporting Information). Thus, the addition of both FLG and CNTs to PG, which appears to create an even more porous structure (Figure 3i−k), produces.
a more significant increase in charge and discharge capacities over PG alone, that is, about 23% and 17%, respectively, notwithstanding a less complete transformation of the staging performance. We surmise that FLG acts as a host for chloroaluminate intercalation, while CNTs improve battery performance by preventing graphene layers from restacking, buffering volume changes during intercalation/deintercalation, and, as we will show, improving ion diffusion, as reported for LIBs.25–28

Isolating the Performance of Few-Layer Graphene and Carbon Nanotube Cathodes and Electrochemical Measurements of Chloroaluminate Diffusion. Since the gravimetric specific capacities of the FLG@PG, and FLG/CNT@PG electrodes are calculated from the total weight of all active materials, including PG, we sought to deconvolute the direct contribution of FLG and FLG/CNT to the specific capacity of the AIB from that of the PG substrate. To this end, FLG and FLG/CNT electrodes were prepared on Mo foil because the Mo foil cannot participate in the intercalation reaction. Representative cyclic voltammetry and charge/discharge curves of AIBs with these cathode materials are displayed in Figure S5a,b, respectively. The cyclic voltammetry profiles of FLG and FLG/CNT electrodes exhibit similar behavior showing four anodic peaks at ∼1.87, ∼2.01, ∼2.17, and ∼2.32 V. However, the reduction peaks of FLG and FLG/CNT electrodes are slightly different. (Figure S12 in Supporting Information) The FLG electrodes exhibit three cathodic peaks at ∼1.65, ∼2.02, and ∼2.22 V, whereas the FLG/CNT electrodes exhibit those at ∼1.65, ∼1.88, and ∼2.22 V. The reduction peaks occur at a lower voltage compared to the corresponding oxidation peaks. Analysis of the potential difference between the oxidation and reduction peaks (∆E_{peak} = E_{peak} - E_{red}) revealed that all coupled redox processes were of a quasi-reversible nature.29 For the higher voltage (∼2.3 V/∼2.2 V) couple, ∆E_{peak} was 300 (2.4 V/2.1 V), 100 (2.32 V/2.22 V), and 100 (2.32 V/2.22 V) mV for PG, FLG, and FLG/CNT, respectively. The larger separation between the coupled peaks of PG compared to those of FLG and FLG/CNT suggests hysteresis in the equilibrium voltage and/or a large activation overpotential.29 At a current density of ∼2640 mA g⁻¹ (∼40 C rate), the FLG and FLG/CNT composite electrodes exhibited respective discharge capacities of 82 and 94 mAh g⁻¹ with Coulombic efficiency values of 97% and 96%, respectively, confirming that FLG and FLG/CNT serve as highly effective host materials for AlCl₄⁻ intercalation with capacities exceeding that of PG-based cathodes. Importantly, these capacities are very close to the values we extract from measurements of mesoscopic devices (Figure 1). AIB cells using these FLG/CNT composite cathodes could be charged and discharged at a current density up to 19800 mA g⁻¹ (∼300 C rate) while retaining capacities of ∼70 mAh g⁻¹ and Coulombic efficiency of ∼99% (Figure 5c). To evaluate cycling stability, we subjected these AIBs to 4000 charge-discharge cycles at a rate of 2640 mA g⁻¹ (40 C) and found no decay in specific capacity and Coulombic efficiency of ∼98% (Figure 5d).

We use the galvanostatic intermittent titration technique (GITT) to investigate the intercalation and diffusion coefficient of AlCl₄⁻ in PG, FLG@PG, and FLG/CNT@PG as shown in Figure S13a and summarized in Figure S13b in Supporting Information. The average diffusion coefficients are 7.8×10⁻⁹, 1.37×10⁻⁹, and 1.94×10⁻⁹ cm² s⁻¹, respectively, in agreement with previous theoretical predictions.26 The diffusion coefficients of FLG@PG and FLG/CNT@PG obtained in this study are about 1–2 orders of magnitude higher than those of graphite-based LIBs measured using analogous electrochemical techniques30 and close to those of exfoliated TiS₂ electrodes used in MgCl²⁺ batteries,31 demonstrating the excellent rate capabilities of these composites as AIB cathodes. Nevertheless, the diffusion coefficients from these GITT measurements in bulk-scale electrodes remain 2–3 orders of magnitude lower than those we obtain from mesoscopic devices of single crystal graphite (Figure 2). This significant discrepancy points to the role that defects, additives, and binders may be playing in hindering chloroaluminate diffusion in macroscopic battery electrodes.

CONCLUSION

Understanding the underlying electrochemical processes in battery materials is essential to improving battery performance. Charge transport measurements were performed to gain insight into the electrochemistry of AlCl₄⁻ intercalation into few-layer graphene and thick graphite flakes. These measurements uncovered the intercalation behavior of the 2D limit of the chloroaluminate–graphite intercalation compound and allowed estimations of the limiting capacity that might be expected from AIBs comprising graphitic cathodes. Transport of AlCl₄⁻ within thin graphite crystals was revealed by optical microscopy, leading to a quantitative determination of the chloroaluminate diffusion coefficient as 9.6×10⁻⁹ cm² s⁻¹ at 320 K. Against the backdrop of the insights gained from these mesoscopic devices, we find that when combined with PG, FLG, and FLG/CNT mixtures substantially improve the performance of PG cathodes in terms of capacity (up to 20% improvement over PG alone) and ion diffusivity (2–3-fold increase). Our results thus establish that controlling the nanoscale morphology of graphitic cathodes will be especially important to optimize the performance of AIBs. These studies also provide a mesoscopic device framework for probing the fundamental physicochemical phenomena underlying the operation of practical battery devices and exemplify how to make connections between these approaches and more conventional electrochemical measurements.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.1c04832.

Experimental details, Figures S1–S13 showing additional discussions (fabrication schematics of micro-electrochemical cell, diffusion study of chloroaluminate anion intercalation into few-layer graphene and graphite via optical microscopy, simulated XRD data, DFT calculation data) (PDF)

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References


(27) Hu, Y.; Li, X.; Wang, J.; Li, R.; Sun, X. Free-standing graphene-carbon nanotube hybrid papers used as current collector and binder free anodes for lithium ion batteries. J. Power Sources 2013, 237, 41–46.