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Electrochemically Exfoliated Graphene Electrode for High-Performance Rechargeable Chloroaluminate and Dual-Ion Batteries

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Supporting Information

ABSTRACT: The current state-of-the-art positive electrode material for chloroaluminate ion batteries (AIBs) or dual-ion batteries (DIBs) is highly crystalline graphite; however, the rate capability of this material at high discharge currents is significantly reduced by the modest conductivity of graphite. This limitation is addressed through the use of graphene-based positive electrodes, which can improve the rate capability of these batteries due to their higher conductivity. However, conventional methods of graphene production induce a significant number of defects, which impair the performance of AIBs and DIBs. Herein, we report the use of a defect-free graphene positive electrode, which was produced using the electrochemical exfoliation of graphite in an aqueous solution with the aid of Co^{2+} as an antioxidant. The Co-treated graphene electrode achieved high capacities of 150 mAh g^{-1} in DIBs and 130 mAh g^{-1} in AIBs with high rate capability for both batteries. The charge–discharge mechanism of the batteries is examined using in situ Raman spectroscopy, and the results revealed that the intercalation density of $[\text{AlCl}_4]^-$ or $[\text{PF}_6]^-$ increased from a dilute staging index graphite intercalation compound (GIC) to a stage 1 GIC within the operating voltage window. The simple production method of high-quality graphene in conjunction with its high performance in DIBs should enable the use of graphene for DIB technologies.

KEYWORDS: electrochemical exfoliation, Co^{2+} antioxidant, graphene, dual-ion battery, chloroaluminate ion battery, in situ Raman spectroscopy

INTRODUCTION

Rechargeable lithium-ion batteries (LIBs) are the leading energy storage devices for consumer electronics and electric vehicles. LIB negative electrodes are typically made from graphite, while the positive electrodes consist of lithium-containing transition-metal oxides. The current state-of-the-art positive electrode materials contain cobalt and nickel oxides in their structure. The cost of these transition metals has increased substantially over the recent years, and, at the current rate of consumption, the reserves of these materials will not meet future demand.¹ Therefore, there is a need to either replace the positive electrode material with less expensive, more abundant elements while maintaining the performance or redesign the battery chemistry.

Aluminum-based batteries (AIBs) have emerged as an attractive alternative to conventional LIBs because of their high volumetric capacity, ultrafast charge–discharge processes, and use of an abundant base material (Al).^{2–4} The most common negative and positive electrodes in AIBs are aluminum metal and carbon-based materials, respectively. The electrolyte is typically a nonflammable room-temperature ionic liquid (RTIL) that is formed by mixing 1-ethyl-3-

methylimidazolium chloride or triethylamine hydrochloride with aluminum chloride (AlCl_3).^{5–7} The mixture of the two salts produces the redox-active chloroaluminate anions ($[\text{AlCl}_4]^-$ and $[\text{Al}_2\text{Cl}_7]^-$) that are involved in the electrode reactions. The chemistry of AIB comprises reversible electrochemical intercalation/deintercalation of the tetrachloroaluminate at the carbon-based positive electrode and reversible electrochemical deposition and dissolution at the aluminum negative electrode during the charge–discharge process.²

There are several fundamental issues, however, facing AIB technology, which need to be addressed. The first one is associated with the chloroaluminate electrolyte, which is highly corrosive toward conventional current collectors and battery packing materials.⁸ This has been addressed by the use of an aluminum salt (AlClO_4) dissolved in an organic solvent although the energy density is substantially lower when compared to the chloroaluminate electrolyte.⁹ Furthermore, the development of a solid-state electrolyte based on the

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introduction of chloroaluminate to polymeric matrices has also been proposed to enhance the safety, stability, and flexibility of AIBs.¹⁰ The second is the fact that the AIB voltage output is about half that of LIBs and so the energy density is low. Finally, the high volumetric capacity of the Al negative electrode is not fully utilized as the overall capacity of the battery is profoundly limited by the anion intercalant positive electrode materials.⁸ The voltage and corrosion issues can be addressed by combining an Al metal negative electrode with another ion to construct a dual-ion battery (DIB). In DIBs, the electrolyte is the traditional carbonate-based organic electrolyte containing a Li salt (LiPF₆) and the electrodes are Al metal as the negative electrode and graphitic carbon as the positive electrode.^{11–13} For example, during the charging processes in DIBs, the anions ([PF₆][−]) are intercalated into the graphite positive electrodes (eq 1), while the cations (Li⁺) react with the Al negative electrodes (eq 2).¹⁴ Aside from increasing the cell voltage to over 4.0 V and eliminating the corrosive chloroaluminate electrolytes, DIBs also potentially replace the expensive lithium-containing transition-metal oxide positive electrode with cheap graphitic carbon. The state-of-the-art positive electrode material for DIB at present is highly crystalline graphite, which produces a discharge capacity of ~120 mAh g^{−1} at a low discharge current (0.1 A g^{−1}).¹²

Recent research revealed that the structure of the graphite and its degree of graphitization significantly impacts the performance of batteries based on anion intercalation. In general, the graphitic carbons that are commonly used for LIBs are unsuitable for AIBs or DIBs because of their low degree of crystallinity and the existence of defects in their structure.^{15,16} The presence of a defect in the graphitic structure obstructs fast anion insertion, reduces the number of active sites, and lowers the electrical conductivity of the electrodes.^{17,18} The repulsive interaction between oxygen-containing functional groups and the electronegative halides in [AlCl₄][−] or [PF₆][−] increases the overpotential needed to overcome the activation barrier for anion insertion.¹⁹ Moreover, chemical defects or adatoms in the graphitic structure also act as catalytic sites for the decomposition of [AlCl₄][−] to Cl₂ gas.²⁰ It has been shown that graphene-based materials with large lateral flake area and defect-free basal planes are suitable for efficient anion intercalation in AIB.^{17–19} However, the production of such types of graphene requires complicated procedures and very high temperatures of up to ~3000 °C. The conventional process involves, first, the preparation of graphene oxide (GO) using the Hummers method, followed by annealing the GO at ~3000 °C under an inert atmosphere to heal the defects. The scalability of this process seems challenging in terms of environmental and safety issues (i.e., due to the use of hazardous chemicals and need for extensive washing in the Hummers method) and cost because of the associated high energy input (3000 °C). Therefore, the production of high-quality graphene through inexpensive and simple methods is required for further development of DIB technology.

In this work, we produce a high-performing Al-based dual-ion battery using high-quality graphene as the positive electrode material. The few-layer, high-quality graphene is obtained by the electrochemical exfoliation of graphite foil in water, using a Co²⁺ additive as an antioxidant.²¹ The Co-

treated graphene showed the highest capacity (150 mAh g^{−1}) reported for a carbon-based electrode to date with a high rate capability when used as a positive electrode in DIBs. The intercalation behavior of the [AlCl₄][−] and [PF₆][−] into this material was studied using in situ Raman spectroscopy, and the results revealed that the intercalation density increased from a dilute staging index graphite intercalation compound (GIC) to a stage 1 GIC within the operating voltage window. Finally, the use of this graphene as the positive electrode in the AIB and DIB is described and compared to the graphene obtained in the absence of Co²⁺ as an antioxidant during electrochemical exfoliation.

RESULTS AND DISCUSSION

We have previously shown that the addition of Co²⁺ efficiently acts as an antioxidant, against surface oxidation during the electrochemical exfoliation of graphite in aqueous solution, and produces high-quality nonoxidized graphene.²¹ The partitioned electrochemical cell with a glass membrane was redesigned to scale up the production of few-layer graphene from milligrams to grams by increasing the electrolytic volume from 0.1 L (in the previous cell version) to 1 L (Figure S1A). The partitioned cell was essential because it eliminates the contamination of the graphene flakes with the cathode product, Co(OH)₂. The addition of Co²⁺ into the exfoliation solution essentially eliminates the surface oxidation of the graphene product (EEG1), see Figure S1B,C, when compared to the graphene obtained in the absence of Co²⁺ (EEG2). The absence of significant sp³ carbon or defects in the EEG1 sample was also evident from analysis using Raman spectroscopy (Figure S1D). The intensity ratio of the D band to the G band (*i*_D/*i*_G) in EEG1 was 0.06 compared to 1 for EEG2, which suggests that the former sample had a near-negligible defect density compared to the latter. High-resolution transmission electron microscopy (TEM) was also used to observe the atomic level defects. The EEG1 sample showed very few defects (Figure 1A,B), whereas the presence of significant defects/holes in the EEG2 sample is apparent (Figure 1C,D). Moreover, representative scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM) micrographs of the EEG1 flake are shown in Figure 1E,F, and the lateral size measurement of 100 flakes indicated that the flake size varies between 3 and 7 μm, with the majority of the flakes being ~4 μm wide.

The high quality (in terms of oxygen content and defect density) of the exfoliated few-layer graphene motivated our application of it as a positive electrode material for AIBs and DIBs. For use as a DIB positive electrode, graphene slurries were cast on a carbon-fixed Al foil substrate. Representative SEM images of EEG1 electrodes are shown in the inset of Figure 2A, and the images show large flakes of randomly restacked few-layer graphene. Figure 2A shows the cyclic voltammograms (CVs) recorded at EEG1 and EEG2 positive electrodes in an electrolyte containing 2 M LiPF₆ in ethyl methyl carbonate (EMC) using Al foil as a negative electrode in a coin cell configuration. As the electrode potential was scanned in the positive direction using EEG1, one well-defined oxidation peak and three shoulder oxidation peaks were seen in the voltage range of 4.1 and 4.8 V due to staged intercalation of [PF₆][−].²² In the return scan, one well-defined reduction peak at 4.35 V and several other unresolved peaks were seen between 3.5 and 4.2 V, at several scan rates, and attributed to the extraction of [PF₆][−] (Figure S2A). This assignment is

Figure 1. High-resolution TEM images of EEG1 (A, B) and EEG2 (C, D), and SEM image of EEG1 (E) and STEM image of EEG1 (F).

made as the general shape of the CV agrees with that reported previously for intercalation and deintercalation of $[\text{PF}_6]^-$ at carbon-based electrodes.^{22,23} In contrast, the CVs recorded at EEG2 were characterized by much lower currents, a lower degree of reversibility, and a wide peak-to-peak separation (ΔE) when compared to those at EEG1. The ΔE for the intense current peak at EEG1 is 0.27 V, compared to 0.36 V for EEG2, indicating that the kinetics of $[\text{PF}_6]^-$ insertion at EEG1 is faster than that at EEG2.

Electrochemical impedance spectroscopy (EIS) was also used to gauge the electrochemical behavior of the EEG1 and EEG2 positive electrodes in the battery configuration. In each cell, EIS was collected after obtaining a stable response by cycling the battery device from 2.5 to 5.0 V several times. The EIS data was obtained by applying 4.8 V to each cell, and the data is shown in Figure S2B. The Nyquist plot showed two partially overlapped semicircles, and this observation was consistent with the reported EIS of LIBs.²⁴ The Nyquist plot was fitted to the equivalent circuit shown in Figure S2C, and the charge-transfer resistance (R_{CT}) of EEG1 was 47 $\Omega \text{ cm}^2$ compared with a value of 532 $\Omega \text{ cm}^2$ for EEG2. The R_{CT} value indicates that the kinetics of the charge transfer during $[\text{PF}_6]^-$ intercalation at EEG1 is significantly faster than that at EEG2, which agrees with the CV data. The substantial presence of carboxyl and hydroxyl functional groups in EEG2 can create repulsive interactions that increase the overpotential required to overcome this activation barrier during the intercalation of $[\text{PF}_6]^-$. In addition, the rate at which $[\text{PF}_6]^-$ diffuses into

Figure 2. (A) Cyclic voltammograms recorded at 0.5 mV s⁻¹ in 2 M LiPF₆ in ethyl methyl carbonate (EMC) using coin cells constructed from an EEG1 or EEG2 positive electrode and an Al foil negative electrode. The voltage was scanned between 1.9 V (initial potential) and 5.0 V. The inset shows the SEM image of EEG1 electrodes, and the scale bar in each case is 5 μm. In situ Raman spectral series for the first anion ($[\text{PF}_6]^-$) insertion during (B) the charge and (C) discharge reactions. The voltage at each spectral acquisition is labeled, and the cell contained EEG1/Al in a 2 M LiPF₆ electrolyte.

interlayer galleries could slow down because of the presence of functional groups.¹⁹

Raman spectroscopy has been widely used for monitoring charge-transfer processes during guest species' intercalation to graphitic materials.^{25–27} The E_{2g2} symmetry due to the in-plane vibration of sp² carbon atoms in graphitic materials appears in the Raman spectra as the G band (at ~1580 cm⁻¹).²⁸ The G band is very sensitive to any charge transfer and interlayer interactions during the formation of a graphite intercalation compound (GIC). Any changes in the graphene layer stacking due to the staging of the electrode will result in the splitting of the G band. The interior unintercalated layers will display the original E_{2g2i} mode at ~1580 cm⁻¹, and the bounding layers next to the intercalants will be at an upshifted E_{2g2b} mode.²⁵ The exact extent of upshift is dependent upon the stage index of the intercalation.

Figure 2B,C shows the in situ Raman spectra obtained for the EEG1 positive electrode during CV charge and discharge cycles with 2 M LiPF₆ in EMC electrolyte. The freestanding EEG1 film showed the characteristic G band at 1578 cm⁻¹ and 2D band at ~2700 cm⁻¹ (see Figure S3 for the full scan) at open-circuit potential (OCP). The i_D/i_G was also similar to the one reported in Figure S1D, which indicates that the ink formulation process did not introduce defects to the graphene film. The G band of the material splits into two Raman modes (E_{2G2i} and E_{2G2b}) when the battery was charged to 4.1 V. The eventual reduction and disappearance of E_{2G2i} signal were observed between 4.1 and 4.55 V due to the onset of ordered staging, respectively. The E_{2G2b} band (1604 cm⁻¹) on the other hand started to emerge as the voltage increased above the position of the first redox peak in Figure 2A. The intensity of this peak increases (and blue-shifted to 1615 cm⁻¹) as the charging voltage is increased and overtakes the intensity of E_{2G2i} above 4.3 V. The E_{2G2i} band completely vanished at 4.55 V, the voltage corresponding to the onset of the largest redox peak within the CV, which indicates the absence of unperturbed interior graphene layers and marks the formation of a stage 2 GIC.²⁹ As the voltage was increased further, the E_{2G2b} intensity begins to reduce and a new Raman band that increased in intensity was observed at 1630 cm⁻¹. The new band is 20 times more intense and has a narrow spectral width (FWHM = 13 cm⁻¹) compared to the original G band. The emergence of this new E_{2G2b} Raman band indicates the transition of the material from a stage 2 GIC to a stage 1 GIC. The presence of a full stage 1 GIC for the intercalation of [PF₆]⁻ into graphene was realized at the peak voltage of the most intense redox peak in the CV. The formation of a stage 1 GIC was also supported by the transformation of the flake color from gray to blue (Figure S4).³⁰

The 2D band position and intensity remained fairly constant until 4.3 V, and above this voltage, the intensity gradually decreased and red-shifted by 16 cm⁻¹ relative to the one obtained at OCP (see Figure S3 for the extended scan). Furthermore, the 2D band completely disappeared once a stage 1 GIC was formed due to the increased in-plane lattice expansion and electronic doping by the intercalant.²⁷ The weak D band observed at OCP also disappeared with an increase in the intercalation density. Moreover, multiple intercalation and deintercalation of [PF₆]⁻ did not introduce defects into the graphitic structure.

The reverse trends were observed during discharge, which involves the deintercalation of [PF₆]⁻ (Figure 2C). The gradual reappearance of E_{2G2i} and disappearance of E_{2G2b} were observed as the cell voltage decreased. The E_{2G2i} mode appears after the battery was discharged below 4.0 V, and its intensity grew as the voltage is decreased. The original graphitic structure was recovered when the cell was fully discharged to 3.2 V, indicating that the intercalation and deintercalation of [PF₆]⁻ did not alter the structure or introduce defects.

Figure 3A shows the CVs recorded at EEG1 and EEG2 positive electrodes in an electrolyte containing [EMIm][AlCl₄] and high-purity freestanding Al foil negative electrode in a coin cell configuration. Similar to the electrochemistry of [PF₆]⁻, the EEG2 positive electrode showed lower performance in terms of redox reversibility for the intercalation of [AlCl₄]⁻. This indicates that the presence of defects in general adversely impacts the intercalation of anions into graphite galleries. Three shoulder peaks and one well-defined oxidation peak were observed at EEG1 during the oxidative scan. In the

Figure 3. (A) Cyclic voltammograms recorded at 1 mV s⁻¹ in [EMIm][AlCl₄] using coin cells constructed from an EEG1 or EEG2 positive electrode and an Al foil negative electrode. The voltage was scanned between 0.1 V (initial potential) and 2.45 V. In situ Raman spectral series for the first anion ([AlCl₄]⁻) insertion during (B) charge and (C) discharge reactions. The voltage at each spectral acquisition is labeled, and the cell contained EEG1/Al in [EMIm]-[AlCl₄] electrolyte.

return scan, one well-defined reduction peak at 2.2 V and broad unresolved peaks were seen at ~1.8 V. There are controversies in the literature regarding the assignment of the redox peaks. Dai and co-workers attributed the first three oxidation peaks to the oxidation of graphite and the oxidation process at 2.4 V to the intercalation of [AlCl₄]⁻ anion.^{2,31} On the contrary, Childress et al. attributed the peaks to the various stages of [AlCl₄]⁻ intercalation.²⁰ As we also describe below using in situ Raman, those oxidation peaks are associated with the different staging of [AlCl₄]⁻ intercalation.

The in situ Raman spectra obtained for the EEG1 positive electrode during a CV charge–discharge cycle in [EMIm][AlCl₄] electrolyte are shown in Figure 3B,C. Overall, similar trends to the LiPF₆ electrolyte can be seen for the [EMIm][AlCl₄] in the Raman spectra during charge–discharge of the EEG1 positive electrode. During charging of the battery, no changes in the Raman signature were observed from the OCP until the first redox peak in the CV at 1.85 V. At this point, the

splitting of the G band into the E_{2g2i} and E_{2g2b} modes had occurred indicating the start of ordered staging within the material, rather than graphite oxidation as was initially suggested by Dai. The E_{2g2i} mode gradually decreased in intensity, while the E_{2g2b} mode gradually increased in intensity as the battery was charged from 1.85 to 2.25 V due to the continual intercalation of $[\text{AlCl}_4]^-$. The E_{2g2i} mode had disappeared from the Raman spectra along with the D and 2D bands at the starting voltage of the intense redox peak (Figure S5). This behavior is similar to the $[\text{PF}_6]^-$ intercalation process and indicates the formation of a stage 2 GIC. As the voltage is increased further, the second E_{2g2b} mode at 1630 cm^{-1} appears, which corresponds to a stage 1 GIC. The opposite trends were observed during discharge, which shows similar shifts and splittings to the Raman G band. All Raman bands were restored when the cell was fully discharged to 0.1 V, indicating that the intercalation of the $[\text{AlCl}_4]^-$ ions into the graphene positive electrode is reversible and did not introduce defects into the graphitic structure.

The in situ Raman of EEG2 in both electrolytes is included as Figure S6. Unlike EEG1, the maximum staging that was achieved with the intercalation of $[\text{AlCl}_4]^-$ from the $[\text{EMIm}][\text{AlCl}_4]$ electrolyte was stage 3 (Figure S6A). This suggests that the functionalities on the graphene surface block the intercalation of $[\text{AlCl}_4]^-$ into the graphite galleries. In contrast, the intercalation of $[\text{PF}_6]^-$ into EEG2 could form a stage 1 GIC within the working voltage of the battery. However, during discharge, the staging of the electrode never decreased below stage 2 even when the battery was discharged below 2 V, indicating that there is a strong interaction between the $[\text{PF}_6]^-$ and the surface functionalities on EEG2 (Figure S6B). This behavior partly explains the slow kinetics and high R_{CT} of EEG2 when compared to those of EEG1.

The inset in Figure 4B displays the representative galvanostatic charge–discharge (GCD) profiles of the DIB battery at 350 mA g^{-1} . The LiPF_6 electrolyte battery was cycled at various discharge rates ranging from 0.1 to 3 A g^{-1} over the potential window of 2.0–5.0 V. The typical galvanostatic profiles of the battery at these different discharge rates are displayed in Figure 4A. It can be seen that the battery displayed repeated plateaus associated with $[\text{PF}_6]^-$ anion intercalation into the EEG1 in the GCD profiles for all rates. Significantly, unlike other carbon-based positive electrodes, the EEG1 positive electrode showed the highest reported capacity of 150 mAh g^{-1} with no loss in the capacity as the discharge current was increased to 3 A g^{-1} (Figure 4A). Various positive electrode materials have been proposed as anion intercalant materials including graphitic materials,^{12,32} metal–organic frameworks,³³ polycyclic aromatic hydrocarbons,³⁴ and nitrogen-containing organics.³⁵ Most of these positive electrode materials (except for the graphitic materials) suffer from either fairly low operating voltage, low discharge capacity, or poor electrical conductivity. The current state-of-the-art positive electrode materials for DIBs are based on high-quality graphite materials that produce about 120 mAh g^{-1} at a relatively low discharge current (0.1 A g^{-1}).^{12,23,36–38} For example, Fang et al.¹² constructed Al-based DIBs using a graphite positive electrode of this type and obtained a discharge capacity of $\sim 120\text{ mAh g}^{-1}$ at a discharge current density of 0.1 A g^{-1} . This discharge capacity decayed by $\sim 35\%$ when the discharge current was increased to 1 A g^{-1} . Similarly, Wang et al. reported a capacity of 100 mAh g^{-1} at 0.1 A g^{-1} that decreased by $\sim 22\%$ at 2 A g^{-1} when using a graphite positive electrode.²³

Figure 4. Electrochemical performance of the EEG1 positive electrode and Al negative electrode battery using 2 M LiPF_6 in EMC electrolyte. (A) Specific capacity of the cell at indicated current density during charge–discharge and (B) discharge current density vs coulombic efficiency. The inset in (B) shows a galvanostatic charge/discharge curve at a current density of 350 mA g^{-1} .

(see Table 1 for various positive electrodes used in the literature). The fact that our graphene positive electrode produced a high discharge capacity of 150 mAh g^{-1} with an exceptional rate capability is attributed to the high conductivity and crystallinity of the EEG1 due to the reduction of defects present from the production method. Furthermore, the capacity of $\sim 150\text{ mAh g}^{-1}$ obtained for the EEG1 positive electrode is the highest reported to date for a DIB positive electrode material.

The coulombic efficiency of the battery, however, increased from 72 to 94% with increasing current density (Figure 4B). The low coulombic efficiency of DIBs has been seen previously for carbon-based positive electrodes and has been attributed to the continual formation of the solid layer interface (SEI).¹¹ The fact that the coulombic efficiency increased at higher charge–discharge rates implies that the time it takes to form an extensive SEI is too short and hence improves the coulombic efficiency. Therefore, optimization of the SEI-forming additive for the electrolyte is required to improve the coulombic efficiency of the DIBs at low discharge rates.³¹

Figure 5A displays the representative GCD profiles of the AIB battery at 350 mA g^{-1} . The $[\text{EMIm}][\text{AlCl}_4]$ -based battery was cycled at various discharge rates ranging from 0.1 to 2 A g^{-1} over the potential window of 0.1–2.45 V. The typical galvanostatic profiles of the battery at these different discharge rates are displayed in Figure 5B. The loss in rate performance at the EEG1 positive electrode is minimal as it only experienced a 10% loss in capacity when the current was increased from 0.1 to 2 A g^{-1} . This improved performance is due to the high conductivity and crystallinity of the Co-treated graphene. The capacity of $\sim 130\text{ mAh g}^{-1}$ and rate capability

Table 1. Data Comparing the Materials Used as Positive Electrodes in AIBs and DIBs

positive electrode	capacity (mAh g ⁻¹)		gravimetric current (A g ⁻¹)	refs
	electrolyte ([EMIm][AlCl ₄])	electrolyte (with [PF ₆] ⁻ intercalation)		
EEG1	120	151	2	this work
SP-1 graphite	45		0.8	15
rGO@3000 °C	120		10	17
solution exfoliated graphene	65		2	39
edge-rich graphene	128		2	40
carbon nanoscrolls	100		10	41
tellurium	300		2	42
CoSe ₂ /carbon nanodice@rGO	300		1	43
graphite		100	0.2	44
thianthrene polymer		66	0.073	45
amorphous carbons		6.6	0.036	46
metal–organic framework		100	0.14	33
polycyclic aromatic hydrocarbon		42	0.01	34
3D porous microcrystalline carbon		130	1	47

achieved are higher than those obtained with high-quality natural graphite.

Dai et al. reported a discharge capacity of 110 mAh g⁻¹ at 66 mA g⁻¹ using SP-1 graphite, which decreased by more than 50% when the current was increased to ~800 mA g⁻¹ due to the modest conductivity of graphite.¹⁵ In an attempt to improve the rate capability of AIBs, Chen et al. used defect-free graphene made by annealing graphene oxide at 3000 °C and obtained a capacity of 120 mAh g⁻¹ at high discharge currents (>1 A g⁻¹).^{17,18} However, unlike the reduced graphene oxide, our Co-treated graphene is formed via simpler and less extreme production techniques while possessing equivalent rate capability. Other reported positive electrode materials include cobalt sulfide/selenide and tin sulfide-based, which have the highest reported capacities, over 200 mAh g⁻¹ at low discharge currents (0.1 A g⁻¹).^{43,48–50} However, the rate capability of these materials is very low, 60% loss at 1 A g⁻¹, compared to that of EEG1. Furthermore, the discharge plateau voltage of these materials is half that of the graphene positive electrode reported in this work (see Table 1 for various positive electrodes used in the literature).

The importance of the low defect density and high crystallinity of the EEG1 positive electrode is also demonstrated in Figure 5C. It can be seen that the EEG2 sample, which was shown to have a higher defect density, had a significantly reduced performance. The overall specific capacity of EEG2 is much lower when compared to that of EEG1, and the EEG2 positive electrode lost over half of its capacity when the discharge current increased from 0.1 to 2.0 A g⁻¹. This demonstrates that the addition of Co²⁺ during the electrochemical exfoliation of graphite produces sufficiently high-quality graphene, which enables fast anion insertion and therefore high electrochemical performance.¹⁵

Finally, the cyclability of the EEG1 positive electrode was investigated for both the AIB and DIB chemistries. Figure 6A,B shows the cyclability of the graphene positive electrode in the AIB and DIB setups, respectively. The AIB has an ultrahigh cycle life and was able to reach over 3500 cycles at 1 A g⁻¹ without showing any loss in performance. This is due to the high coulombic efficiency of the AIB battery chemistry, which stayed above 98% for the entirety of the cycles. This long cycle life of the AIB has been seen before by Chen et al., in which their battery reached 250 000 cycles with little to no loss using few-layer graphene oxide that was reduced at 3000 °C.¹⁷

However, it is worth noting that the RTIL electrolyte is extremely corrosive to standard cell and electrode components such as stainless steel or the traditional poly(vinylidene difluoride) binder.³⁹ Therefore, to adopt the AIB battery chemistry for commercial purposes, these standard cell and electrode components would need to be made from nontraditional materials. Toward this goal, Wang et al. demonstrated the use of titanium nitride flexible current collectors for [EMIm] [AlCl₄]-based electrolyte.⁵¹ The TiN showed high oxidative stability in the ionic liquid with a near 100% coulombic efficiency.

The DIB showed a significantly lower cycle lifetime when compared to the AIB. The DIB using EEG1 positive electrode showed a ~13% loss in capacity over 500 cycles at 0.2 A g⁻¹. The coulombic efficiency of the DIB is also below 90% for the majority of the cycle life testing. The lower coulombic efficiency was not related to the inability to extract the fully intercalated [PF₆]⁻ or due to the positive electrode material degradation since in situ Raman spectroscopy data showed the structural and electrochemical reversibilities of the [PF₆]⁻ intercalation. It is surmised that the SEI formation was not efficient enough to block the cointercalation of solvent species that contributed to higher charge capacity. This was apparent when cycling the battery, which shows an initial increase in coulombic efficiency from 79 to 90% due to the formation of the SEI layer on the electrodes.³⁸ However, the decrease in coulombic efficiency after 200 cycles suggests the instability of the formed SEI layer. This shows the need for an improved SEI-forming additive or electrolytic solvent. Fluorinated solvents with a tris(hexafluoro-iso-propyl)phosphate additives exhibited better oxidative stability at a high cutoff voltage of 5.2 V,¹¹ and future work should consider the use of this electrolyte system using this novel graphene positive electrode.

CONCLUSIONS

A route to a viable positive electrode in an Al-based dual-ion battery is demonstrated via scalable electrochemical production of high-quality large flake graphene in an aqueous electrolyte, using a cobalt ion additive as an antioxidant. It is shown that defective carbon adversely impacts the intercalation of anions into graphite galleries and highlights the importance of producing graphene with a high degree of crystallinity. The graphene obtained by electrochemical exfoliation in the presence of Co²⁺ demonstrated the highest specific capacity

Figure 5. Electrochemical performance of a graphene positive electrode and Al negative electrode battery using [EMIm][AlCl₄] electrolyte. (A) Galvanostatic charge/discharge curve at a current density of 350 mA g⁻¹ using EEG1 positive electrode. (B) Specific capacity of the cell at indicated current density during charge-discharge using a EEG1 positive electrode. (C) Discharge specific capacity of EEG2 at current densities indicated.

of state-of-the-art carbon-based electrodes when used as a positive electrode in the Al DIB configuration. Furthermore, the material showed an insignificant deterioration of its rate capability over a broad range of current densities. In contrast, the graphene obtained in the absence of Co²⁺ displayed inferior specific capacity, rate capability, and electrochemical reversibility due to the presence of substantial defects. In situ Raman spectroscopy has given significant insight into the intercalation of the chloroaluminate and hexafluorophosphate anions into few-layer graphene. Stage 1 graphene intercalation compounds were achieved for both anions within the operating electrochemical window of the battery, which indicates the full occupation of the interlayer spacing. Also, the Raman spectra showed that the intercalation and deintercalation of the anions did not induce a structural change within the material. These results establish a simple, scalable, and inexpensive high-quality

Figure 6. Capacity retention and coulombic efficiency of an EEG1/Al cell cycled at (A) 1 A g⁻¹ using [EMIm][AlCl₄] electrolyte and (B) 0.2 A g⁻¹ using 2 M LiPF₆ in EMC electrolyte.

graphene production method, which should be readily applicable for graphene usage in other battery technologies.

EXPERIMENTAL METHODS

Materials and Apparatus. Graphite foil (>99%) was obtained from Gee Graphite Ltd. (U.K.). Dry 1-ethyl-3-methylimidazolium chloride ([EMIm]Cl), anhydrous aluminum chloride (99.99%), ethylene methyl carbonate (EMC, 99%), sodium alginate, CoSO₄, and Na₂SO₄ were obtained from Sigma-Aldrich and used as received. Molybdenum (99.95%) and aluminum foil (99.99%) were obtained from Alfa Aesar, and battery-grade LiPF₆ was obtained from Fluorochem. X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Axis Ultra DLD spectrometer with a monochromated Al K α X-ray source ($E = 1486.6$ eV, 10 mA emission). (S)TEM was carried out using an FEI Titan3 G2 60-300 operated at 80 kV. Image J software, a low-pass filter, and a Gaussian blur filter were applied to TEM and STEM images. A sample for (S)TEM was prepared by dispersing dried, composite sample into *N,N*-dimethylformamide and then the solution was drop-cast over a lacey carbon TEM grid. SEM analysis was carried out using an FEI Quanta 650 FEG environmental scanning electron microscope. Electrochemical measurements were performed using an Autolab potentiostat (model PGSTAT302N, Metrohm Autolab, The Netherlands). The charge-discharge battery test was carried out using a Basytec cell test system (GmbH, Germany) with 32 independent test channels.

Electrochemical Exfoliation of Graphite. An H-type electrochemical cell (in a 1 L volume beaker) was partitioned with a 1 cm thick glass membrane (see Figure S1A). The glass membrane was sealed to the beaker using a Silirub AC silicone sealant. Graphite foils were placed in each compartment and used as both the working and counter electrodes. The electrochemical exfoliation of graphite was carried out by applying 10.0 V to the graphite foil (anode compartment) using a power source for 2 h. The electrolyte consisted of 30 mM CoSO₄(aq) and 0.2 M Na₂SO₄(aq). For comparison, graphite exfoliation was also carried out in the absence of the CoSO₄ additive (sample EEG2). The exfoliated product was washed several times with water and dried in a vacuum oven at 80 °C.

Preparation of Ionic Liquids. 1-Ethyl-3-methylimidazolium chloride-aluminum chloride ([EMIm][AlCl₄]) was made by mixing

[EMIm]Cl (>98%, dry) with anhydrous AlCl_3 (99.99%) in an argon-filled glovebox. The mixture was then stirred for 2 h at room temperature. The molar ratio of AlCl_3 to [EMIm]Cl was 1.3. The Raman data shows that the amount of $[\text{AlCl}_4]^-$ is approximately twice that of $[\text{Al}_2\text{Cl}_7]^-$ (Figure S7).

Electrode Preparation. Graphene slurries were prepared using 900 mg of EEG1 (electrochemically exfoliated graphite in the presence of 30 mM CoSO_4) or EEG2 (electrochemically exfoliated graphite in the absence of CoSO_4) and 100 mg of sodium alginate binder in a sufficient volume of deionized water. The slurry was stirred overnight and coated over a Mo (99.95%) substrate or a carbon-fixed Al foil with an Al_4C_3 (Toyal Carbo, Toyo aluminum K.K.) substrate using doctor blading. The graphene/Mo current collector was used for the RTIL-based electrolyte battery, while the carbon/Al/ Al_4C_3 current collector was used for the LiPF_6 organic electrolyte system. The cast electrodes were dried in a vacuum at 80 °C overnight. The cast electrodes were punched into small disks of 1 cm diameter for use in a coin cell. The mass loading of the graphene electrode ranged from 1 to 2 mg cm^{-2} .

Battery Assembly. For the construction of the ionic liquid ([EMIm][AlCl_4]) electrolyte-based coin cell, graphene coated on Mo was used as the positive electrode, where the Mo foil was a current collector, a glass microfiber filter (Whatman, ~400 μm thick) was used as a separator, and an aluminum foil was used as a negative electrode. The coin cells were constructed in an Ar-filled glovebox by applying 50 μL of [EMIm][AlCl_4] to the separator. Nickel foam was used as a spacer to minimize the corrosive nature of the RTILs toward the stainless steel. For dual-ion coin cells, the electrolyte was 2 M LiPF_6 with 2 wt % AlF_3 and 3 wt % vinylene carbonate in an ethyl methyl carbonate solvent.¹² The coin cell was assembled in an Ar-filled glovebox and consisted of a graphene electrode as the positive electrode, an Al foil as the negative electrode, a glass microfiber filter as the separator, and 150 μL electrolytes. For each electrolyte, coin cell assembly was prepared in the standard CR2032 coin cell hardware, and the coin cell was sealed using a hydraulic crimper (MSK-160D) located in the Ar-filled glovebox.

In Situ Raman Spectroscopy Measurement. Raman spectra were obtained using a Renishaw inVia microscope with a 532 nm excitation laser operated at a power of 0.274 mW with a grating of 1800 lines per mm and a 50 $\times$ long working distance objective. The in situ Raman cell was obtained from ECC-Opto-Std/El-Cell, which was airtight to study nonaqueous electrochemical measurements in atmospheric conditions. The cell was composed of a freestanding graphene (EEG1) positive electrode and an aluminum foil negative electrode with a glass microfiber separator. An aluminum current collector, which contains a small hole in its middle (diameter ca. 1 mm), was used as a current collector for the positive electrode. For the preparation of the freestanding EEG1 film, first, the graphene slurry (containing a 10% sodium alginate binder) was cast on a copper substrate and dried in an oven for 12 h at 80 °C. Then, the dried material was punched into small disks and immersed in 2 M FeCl_3 (aq) to etch away Cu. The resulting freestanding EEG1 disc was dried under vacuum at 80 °C. The exciting laser beam was shone onto the rear of the freestanding EEG1 film through a small hole in the center of the Al metal foil. Spectral scans were collected in a backscattering configuration through the thin glass window onto the graphene electrode that was visible through the hole in the current collector. The Raman measurements were collected at various voltages as the cell charged and discharged at 1 mV s^{-1} from 0.1 to 2.45 V for ionic liquid electrolyte and from 2.5 to 5.0 V for the organic electrolyte.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b06528.

Electrochemical cell, survey scan XPS, Raman spectroscopy data of [EMIm][AlCl_4], electrochemical impedance spectroscopy of graphene in 2.0 M LiPF_6 in EMC,

and Raman spectroscopy and optical images of graphene flakes during charging (PDF)

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Notes

The authors declare the following competing financial interest(s): A patent application has been filed in related area by the University of Manchester.

The University of Manchester has filed a patent application in the area of the electrochemical exfoliation and functionalization of graphene.

Source data files can be obtained from <http://www.mub.eps.manchester.ac.uk/robert-dryfeelectrochemistry/>.

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