Investigation of the Differential Capacitance of Highly Ordered Pyrolytic Graphite as a Model Material of Graphene

Yuqin Zou,† Alex S. Walton,‡,§ Ian A. Kinloch,§ and Robert A. W. Dryfe*†

†School of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, U.K.
‡Photon Science Institute, University of Manchester, Oxford Road, Manchester M13 9PL, U.K.
§School of Materials, University of Manchester, Oxford Road, Manchester M13 9PL, U.K.

Supporting Information

ABSTRACT: A study of the differences among the capacitances of freshly exfoliated highly ordered pyrolytic graphite (HOPG, sample denoted FEG), HOPG aged in air (denoted AAG), and HOPG aged in an inert atmosphere (hereafter IAG) is presented in this work. The FEG is found to be more hydrophilic than AAG and IAG because of the aqueous electrolyte contact angle (CA) increases from 61.7° to 72.5° and 81.8° after aging in Ar and air, respectively. Electrochemical impedance spectroscopy shows the FEG has an intrinsic capacitance (6.0 μF cm⁻² at the potential of minimum capacitance) higher than those of AAG (4.3 μF cm⁻²) and IAG (4.7 μF cm⁻²). The observed changes in the electrochemical response are correlated with spectroscopic characterization (Raman spectroscopy and X-ray photoelectron spectroscopy), which show that the surface of HOPG was doped or contaminated after exposure to air. Taken together, these changes upon atmospheric exposure are attributed to oxygen molecule, moisture, and airborne organic contaminations: high-vacuum annealing was applied for the removal of the adsorbed contaminants. It was found that annealing the aged sample at 500 °C leads to partial removal of the contaminants, as gauged by the recovery of the measured capacitance. To the best of our knowledge, this is first study of the effect of the airborne contaminant on the capacitance of carbon-based materials.

Electrical double-layer capacitors (EDLCs), also known as supercapacitors or ultracapacitors, represent a unique class of electrical energy storage devices, which have attracted much attention in recent years because of their high power density, fast charge–discharge rate, and long cycle life. Carbon-based materials have been extensively used as electrode materials for EDLCs because of the extremely short charge separation length. Graphene is a promising material for EDLCs because of its high conductivity and large theoretical surface area. However, the factors that influence the capacitance of graphene and the optimal parameters for EDLCs constructed from graphene materials are not thoroughly understood. A few studies have been conducted in this area. For instance, Ji et al. discussed the effect of the number of layers on graphene capacitance. Zhang et al. studied the effect of heteroatom content on graphene capacitance, and the relationship between graphene composition and capacitance has been reviewed.

As the precursor “bulk” material to graphene, understanding the capacitance of highly ordered pyrolytic graphite (HOPG), where the basal plane is formed from many individual graphene layers, is also relevant. Graphene films grown on different support materials by chemical vapor deposition (CVD) or epitaxial growth have been described; however, the capacitance of such graphene films might be affected by the substrate properties, defects, or inhomogeneous deposition of graphene. On the contrary, as HOPG is composed of stacks of multiple layers of highly ordered graphene layers, a full understanding of the electrochemical properties of HOPG under controllable conditions is a useful benchmark from which the intrinsic properties of graphene can be understood.

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Additionally, insights into the capacitance of HOPG provide insight into the density of states of the material, which in turn can be used to rationalize the electron transfer kinetics observed at graphitic electrodes.18

Although graphite is often regarded as a chemically inert material, some reports have discussed the changes between freshly exfoliated HOPG and “aged” HOPG, i.e., samples exposed to the air. A recent report from this laboratory found that the electron transfer kinetics of freshly cleaved HOPG are 2 orders of magnitude faster than those of an atmosphere-aged sample.19 Similarly, Patel et al. reported the time-dependent changes in the voltammetry of common aqueous phase redox couples on HOPG.20 Nioradze et al. applied scanning electrochemical microscopy (SECM) to demonstrate quantitatively that the electroactivity of the HOPG basal surface can be lowered by the adsorption of adventitious organic impurities from both ultrapure water and ambient air.21 A number of nonelectrochemical studies of the effect of contaminants on graphite surfaces have also appeared recently. Li et al. conclude that the surface of fresh HOPG is relatively hydrophilic, and the water contact angle (WCA) of HOPG increased from 64.4° to 80° after exposure to ambient air.22 Kozbial et al. have also discussed the effect of airborne hydrocarbon contamination on the wettability of graphite: ellipsometric measurements indicated that adsorption occurs on exfoliated HOPG, and attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) was used to identify the contaminants as hydrocarbons.23 Furthermore, Ashraf et al. explored different methods of cleaning the aged surface and evaluated the efficiency of those methods on the basis of spectroscopic analysis.17 Capacitance measurements are a sensitive probe of surface state and the presence of adsorbates on a conducting surface. Although the effect of contaminants has been mentioned in the context of earlier work on the capacitance of graphite,24–26 we are unaware of any prior work devoted to this specific topic. The purpose of this work is therefore to study the influence of air exposure on the specific capacitance of HOPG. The detailed investigation of this topic should provide a fundamental principle for the design of carbon-based electrode materials for electroanalysis and EDLCs.

To address this important issue, herein, a series of studies of freshly exfoliated HOPG (FEG), HOPG aged in air (AAG), and HOPG aged in an inert atmosphere (IAG) have been investigated through the change in electrolyte contact angle (CA), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and electrochemical impedance spectroscopy (EIS). The EIS results show that the FEG has an intrinsic capacitance higher than that previously reported at the potential of zero charge (PZC); moreover, the value found is larger than that of the AAG and IAG samples. This capacitance change is correlated with our findings showing that the FEG is more hydrophilic than AAG and IAG, evidenced by the increase in CA for the aqueous electrolyte after aging for 24 h in an inert-atmosphere glovebox or air. Raman and XPS results confirm that the surface of HOPG was doped by contaminants after exposure to air.

**EXPERIMENTAL SECTION**

**Chemicals.** Potassium chloride (99%) and lithium chloride (99%) were purchased from Sigma-Aldrich. The chemicals were used as received, and aqueous solutions were prepared using ultrapure water (18.2 MΩ cm at 25 °C, Milli-Q Direct 8, Merck Millipore). The total organic content of the water is estimated to be 10 ppb. The HOPG used in this study is commercially available from SPI supplies (grade SPI-1, supplied via Aztech Trading). The argon source used for the IAG sample was 99.998% pure Ar (BOC, “Pureshield”).

**Experimental Setup.** Cyclic voltammetry (CV) and EIS measurements were performed with a three-electrode configuration using a potentiostat (PGSTAT302N, MetrohmAutolab B.V.) in 6 M LiCl. A silver/silver chloride (Ag/AgCl) wire served as the reference electrode, which was made by oxidation of a silver wire (Advent Material, 99.999%, 0.15 mm diameter) in 1 M KCl. All potentials are quoted with respect to this reference. The counter electrode was made from platinum mesh (Aldrich, 52 mesh, area of 1 cm × 1 cm). The HOPG samples were electrically contacted and fixed with silver paint (RS Components Ltd.) on a glass slide, and a copper wire was stuck to the silver paint to make an external electrical contact.

The capacitance of the compact electrolyte layer on a Pt surface in 6 M LiCl (aqueous) was measured by cyclic voltammetry. First, the real surface area of a commercial Pt electrode (CH Instruments, Inc., CHI102) was measured in 0.1 M H2SO4 (aqueous). Second, by combining these results with cyclic voltammetry results in 6 M LiCl (aqueous), we calculated the capacitance of the compact layer from the following equation:

\[
C = \frac{1}{2\pi A \Delta V} \int_{V_0}^{V_0 + \Delta V} i \, dV
\]

where \( \nu \) is the scan rate, \( A \) is the real surface area of the Pt electrode, \( \Delta V \) is the potential window, which is 1 V in this work, \( i \) is the current, and \( V_0 \) and \( V_0 + \Delta V \) are the starting potential. This treatment led to a value for the capacitance of the compact layer of 16.3 μF cm⁻², which is consistent with the reported value in aqueous solution.

EIS measurements were taken by applying an ac voltage with a 10 mV amplitude over a frequency range from 100 Hz to 100 kHz in a potential range from −0.4 to 0.6 V. Following the approach of Hirschron et al.,27 we obtained the effective capacitance of the working electrode from

\[
\alpha = \frac{d \log(Z_f)}{d \log(f)}
\]

\[
C_{eff} = \sin\left(\frac{\alpha \pi}{2}\right) \frac{1}{Z_f \times \frac{\alpha \pi}{2} Z_{eff}^{\alpha}}
\]

where \( \alpha \) is the constant phase element exponent, \( Z_f \) is the imaginary part of the impedance, \( f \) is the frequency, and \( C_{eff} \) is the effective capacitance. The capacitance value at each potential used in this study is the average value within the frequency range from 100 Hz to 10 kHz. The capacitance—frequency curve is shown in Figure S1.

Three different treatments of the HOPG surfaces were used in this study. The first was the FEG sample, which was cleaved with Scotch tape in an Ar-filled glovebox (Innovative Technology, Inc., 13-069-A, PureLab HE 2GB, initial oxygen content of <0.1 ppm, with the pump disconnected during the acquisition of electrochemical data) to reveal a fresh surface for study. The second one, which was aged in air (AAG), was cleaved with Scotch tape and then left in air for 24 h. The third one was aged in the glovebox (IAG), having been cleaved with Scotch tape (in the glovebox) and left in the glovebox for 24 h.

**Cells for Electrochemical Measurement of HOPG.** In this study, a PTFE cell was used to measure the capacitance instead of the cell that was used in Yeager’s work.24–26 Some important issues should be addressed during the measurement. The first is the exposure of the material in the electrochemical cell such that only the basal surface is exposed without strain or distortion. Because it was reported that the interaction between the layers is very weak and even tiny pressures can cause cleavage and damage,27 pressing the HOPG sample into a cell to expose a defined area to the electrolyte can change the sample. This is because the capacitance measurements need a precise surface area; here the cell resulted in a well-defined HOPG circle 3 mm in diameter being exposed to the electrolyte. To study the capacitance over the full potential window, the capacitances were measured as a function of potential. Evaporation of the solution in an electrochemical experi-
ment with a droplet might have been problematic over this time period. However, the volume of the electrolyte used with the PTFE cell combined with the high-concentration electrolyte used in this study solves this issue. Finally, the PTFE cell can be transferred so that the experiment can be performed in different environments, for example, the glovebox.

The schematic of the electrochemical cell is shown in Figure 1. The electrically connected HOPG was placed on a glass slide and fixed with silver paint. The PTFE cell has outer cylindrical dimensions of 8 mm (diameter) \(\times\) 6 mm (height) (the volume is 300 \(\mu\)L). At the bottom, there is a smaller cylindrical diameter of 3 mm (width) \(\times\) 4 mm (height). At the beginning, single-side Scotch tape was gently pressed onto the HOPG surface and then peeled off to remove the top layers. Then the PTFE cell was gently positioned on the HOPG surface. After the counter and reference electrodes were placed in the cell, it was filled with \(\sim 300\ \mu\)L of 6 M LiCl. Capacitance measurements were taken 30 min after contacting each sample with the electrolyte to eliminate deviation among the three samples, particularly for the FEG sample, which was found to show a time-dependent change in capacitance (Figure 2a). The electrolyte was placed in a glovebox for more than 30 min, so that it was degassed with Ar.

**Characterization.** Static CA testing was conducted using 1 \(\mu\)L droplets of a 6 M LiCl aqueous solution in a glovebox. The results were recorded by camera (Lumeneva, model INFINITY2-1RC, serial number 0196920), and analysis was performed using ImageJ. X-ray photoelectron spectroscopy (XPS) measurements were performed using a SPECS NAP-XPS system, comprising a monochromated Al K\(\alpha\) source (1486.6 eV) and a SPECS Phoibos 150 NAP hemispherical analyzer. Survey spectra were recorded at a pass energy of 60 eV and detailed spectra at 20 eV. All measurements were performed at a 20° takeoff angle to maximize surface sensitivity. HOPG was cleaved in vacuum in the entrylock of the XPS instrument using a wobblestick coated with double-sided adhesive tape. The pressure during cleavage was \(\sim 1 \times 10^{-8}\) mbar. The sample was then immediately transferred into the analysis chamber (\(\sim 1 \times 10^{-9}\) mbar or better) and measured to check its cleanliness. This process was repeated as many times as necessary until a pristine spectrum was recorded, typically three or four times. For the IAG sample, the sample was then transferred into the entrylock of the system that was then vented to atmospheric pressure with argon. The entrylock was then sealed and left overnight (approximately 16 h). It was then evacuated and the sample transferred into the analysis chamber for measurements. For the AAG sample, the sample was completely removed from the system and left to age in the ambient environment of the laboratory overnight. It was then reinserted into the chamber for analysis.

**Figure 1.** Schematic of the electrochemical cell used for HOPG electrochemical experiments.

**Figure 2.** (a) Time-dependent capacitance of the FEG sample at a potential of 0 V. (b) Time-dependent capacitance of the IAG sample at a potential of 0 V. (c) Time-dependent capacitance of the AAG sample at a potential of 0 V. (d) Capacitance–potential curves of the FEG sample over various potential windows.
RESULTS AND DISCUSSION

To investigate the effect of aging on HOPG, EIS was used to measure the differential capacitance of three samples. Figure 2a presents the time-dependent capacitance of FEG after filling the PTFE cell with the electrolyte. The capacitance measured at a fixed potential of 0 V decreased from 6.7 to 5.5 μF cm⁻² over the first 30 min. This phenomenon was observed in other studies. For example, in Yeager’s work, the capacitance value of stress-annealed pyrolytic graphite (SAPG) was observed to decrease by 3% within the first 15 min when the electrode was peeled off in solution. These observations suggest that the capacitance change is due to the adsorption of species from the aqueous solution, despite being prepared with ultrapure water, can adsorb on the HOPG surface following its exposure to solution. This is consistent with the recent report from Yamaguchi and co-workers, who quoted a “typical” level of organic contaminants found in ultrapure water (20 ppb), which caused changes in the Faradaic electrochemical response of HOPG, as measured using SECM. The samples studied by Yamaguchi had been exfoliated in the laboratory ambient before immersion; therefore, their assumption was that the contamination arising from the water added to the initial air-based contamination. In their work on the time-dependent change in CA, Kozbial et al. have shown that the transition to the larger equilibrium contact angle, seen on exfoliation occurs after exposure to the laboratory atmosphere for ~15 min. A much slower transition in CA, with a small initial change (~5°) over 40 min, followed by a quasi-steady CA for several hours, was subsequently reported by the same group when the graphite was immersed in aqueous solutions; it was therefore concluded that the water layer was able to protect the graphitic surface from organic contamination from the ambient environment. The capacitance change reported here, with an initial decrease over 30 min, indicating adsorption of organic contaminants, is consistent with the CA-based work of Li et al. All subsequent measurements were taken after a 30 min exposure, as it is assumed that the capacitance has decayed to a quasi-static value at this time after contact with the electrolyte. In contrast, it should be noted that the capacitance of the IAG and AAG samples, although lower, did not show the same initial decay following immersion in the electrolyte (see Figure 2b). This suggests that the surfaces have already reached a quasi-steady state, in terms of surface contamination, due to the adsorption of species from the atmosphere. The capacitance of FEG as a function of potential was recorded over various potential ranges, as shown in Figure 2d. All the data collected on three different pieces of HOPG, and the error bars in Figure 2d (and also Figures 3 and 7), are the standard deviation of data. The shape and values of the capacitance–potential curves are quite reproducible in the potential window from −0.4 to 0.6 V (vs Ag/AgCl). However, the capacitance value fluctuated if the potential range was extended below −0.4 V (vs Ag/AgCl). Similar behavior has been observed previously by Yeager et al. and interpreted in terms of reduction of a residual surface oxide at negative potentials. In previous literature, the anodic scanning direction was chosen and quite negative potentials (~0.8 V vs NHE, corresponding to ~0.6 V vs Ag/AgCl) were applied to reduce the oxide, so that repeatable data were achieved. Here we have chosen to focus on the intrinsic capacitance of the substrate. Considering that the experiments were performed in a glovebox, the surface oxide content should be low and should reflect the intrinsic properties of the HOPG. Thus, subsequent EIS experiments were performed in the potential window from −0.4 to 0.6 V (vs Ag/AgCl) to minimize any potential-induced change in surface composition.

The capacitance–potential curve measured at the HOPG electrode displays a minimum for FEG, IAG, and AAG, as shown in Figure 3. First, the shape of the capacitance–potential curve of IAG and AAG is nearly symmetrical with respect to the minimum, as has been widely observed on various carbon materials, such as glassy carbon (GC), functionalized graphene sheets, N-doped carbon nanotubes, and SAPG in aqueous solution, although the minimum is much less pronounced in the AAG case. Second, the measured minimum capacitance value of FEG is 6.0 μF cm⁻² (at −0.2 V vs Ag/AgCl). The differential capacitance of a semimetallic species such as graphite can be treated as three series components, which are the capacitance of the space charge layer within the semimetal due to its relatively low carrier density, that of the compact double layer, and that of the diffuse ionic layer of the electrolyte. Considering the high concentration of the electrolyte used in this work, the capacitance of the diffuse ionic layer is large, which means its contribution to the total capacitance is negligible. Using the value obtained for the capacitance of the compact layer, C₀, of 16.3 μF cm⁻² in 6 M LiCl, as mentioned above, the measured capacitance is largely dictated by the space charge component within the graphite. The theory of semiconductor electrodes indicates that the capacitance of the space charge layer in a pure intrinsic semiconductor should have a minimal value given by the expression below:

\[
C_0 = \left( \frac{2\varepsilon_0 \varepsilon \varepsilon_r}{kT} \right)^{1/2}
\]

(4)

where \(\varepsilon\) is the relative permittivity, taken to be 3 for graphite; \(\varepsilon_0\) is the permittivity of free space; \(\varepsilon\) is the absolute value of electronic charge; \(\varepsilon_r\) is the electronic charge density (a value of 11 × 10⁻¹⁸ carriers cm⁻³ was used); \(k\) is Boltzmann’s constant; and \(T\) is the absolute temperature, which is 293 K in this work. The theoretical minimum capacitance is 4.5 μF cm⁻², and this compares with a value of 4.4 μF cm⁻², calculated from...
where $C_{\text{exp}}$ is the experimental value of the minimum capacitance and $C_s$ is the space-charge capacitance of HOPG. This value compares with reported experimental minimum values for the HOPG electrode in an ionic liquid (3.0 $\mu$F cm$^{-2}$) and an aqueous solution (2.6−4.0 $\mu$F cm$^{-2}$). Third, the potential of the minimum capacitance of FEG shifts from −0.2 to 0.3 V (vs Ag/AgCl) after the aging process. The shift is indicative of n-doping of the solid, which should shift the flat band potential to potentials more positive than those of the undoped sample. Previous reports have used ATR-FTIR spectroscopy to identify the airborne contaminants. The spectra showed two major peaks, assigned to the symmetric and asymmetric stretching of the methylene group derived from airborne contaminants. Fourth, the obtained minimum $C_{\text{exp}}$ value of IAG (4.7 $\mu$F cm$^{-2}$ at 0.3 V) is larger than that of AAG (4.3 $\mu$F cm$^{-2}$ at 0.3 V), indicating that oxygen molecules and moisture in air cause a decrease in capacitance larger than that caused by the purely hydrocarbon (or other organic) adsorption that is assumed to occur in the IAG case. We hypothesize that a layer of contamination was adsorbed on the HOPG surface, derived from either the water that was used to prepare the electrolyte or the laboratory atmosphere after a fresh surface was exfoliated. The XPS results are used (see below) to quantify the level of contamination arising from each aging treatment. Fifth, the slope of the “wings” in this work is 2.4 $\mu$F cm$^{-2}$ V$^{-1}$, which is higher than the reported value (1.6 $\mu$F cm$^{-2}$ V$^{-1}$) at the SAPG electrode in a 0.9 M NaF aqueous solution. However, it is lower than the theoretical calculated slope of differential capacitance of graphite with respect to potential. The capacitance data indicate that after exposure to air or argon (which is the main component of the glovebox), a physical modification of the graphite surface took place through adsorption with oxygen, moisture, and other chemicals present in the air and/or adsorption of contaminant molecules, and functional groups on the surface.

The CA values of FEG, AAG, and IAG were each measured using 1 $\mu$L droplets of 6 M LiCl (aqueous) in a glovebox, as shown in Figure 4. The CA measurements were performed on five different regions on each sample, with the reported data being the average. After exfoliation in a glovebox, the CA measured on a freshly cleaved HOPG is 61.7°, which is slightly smaller than the CA of 64.4° reported for pure water in air on HOPG. After exposure to ambient air for 24 h, the sample shows a significant increase of CA to 81.8°. Statistical information about the CA data is provided in Table S1. This phenomenon was observed in previous literature and has been attributed to ambient contamination affecting the properties of HOPG. To investigate the role of these factors in the aging process, freshly exfoliated HOPG was also aged in an inert atmosphere (IAG). The CA values of two aged samples are larger than that of the FEG sample. Moreover, the CA measured on IAG (72.5°) is smaller than that of AAG (81.8°), which leads us to suggest that exposure to the glovebox atmosphere leads to the adsorption of different organic molecules compared to the AAG case, which would lead to different effects on the properties of graphite surface: this observation has not been considered in previous literature.

Further conclusions about surface composition were drawn from the XPS data, which were analyzed using CASA XPS. A Shirley background was fitted to the C 1s peak and a linear background to the O 1s. Relative atomic percentages were determined using the peak areas of the strongest photoelectron peaks for a given element, using the Scofield relative sensitivity factors. Figure 5 shows the survey scans taken from the three samples. The FEG sample shows only the presence of the carbon photoelectron and Auger peaks, with a trace amount of oxygen and silicon. All other samples show a substantial increase in the O 1s peak, indicating the presence of oxygen-containing species on the surface. Furthermore, the IAG and the electrolyte-exposed sample show a marked increase in the level of silicon contamination of the surface. The IAG sample also shows a small amount of fluorine, and the AAG sample shows a small amount of phosphorus. The entire text includes detailed analysis and discussion of the experimental results and conclusions.
the FEG sample was 99%, and it was only 95% in the AAG sample. Moreover, the oxygen content of the FEG sample was <0.5%, reflecting the very small amount of oxygen-containing species on the surface of freshly exfoliated graphite. However, the oxygen content in the AAG sample was 4%, indicating a much increased level of oxygen-containing species on the graphite surface after aging in air.

The C 1s peaks for all samples were fitted to the same fit, comprised of an asymmetric Lorentzian line shape for the sp² carbon and standard Gaussian−Lorentzian product peaks for the sp³ carbon, C−O carbon, and the π−π* shakeup. The line shape for the sp² peak was determined by the best fit to the data for the pristine FEG sample. The same line shape was then used for all other samples. The area ratio between the π−π* peak and the sp² peak was measured for the FEG sample and then used as a fitting constraint for all the other fits. Spectra were charge-compensated such that the sp² component of the C 1s peak is 284.5 eV. Detailed scans of the C 1s peak reveal significant differences among the three samples (Figure 6). The FEG sample is dominated by the sp² carbon in graphite, which has a characteristic asymmetric shape and a satellite feature at 292 eV corresponding to the excitation of the π−π* transition by the outgoing photoelectron. The other two samples show a significant reduction in the sp² component in favor of an sp³ peak at 284.8 eV, corresponding to aliphatic carbon in an adventitious carbon overlayer. A third peak at 286.5 eV is also present, particularly in the AAG sample. This is assigned to carbon bound to oxygen, consistent with the increase in the intensity of the oxygen signal observed in Figure 5.

In all samples except FEG, it can be seen from Figure 6 that sp³ carbon and C−O make up approximately 25% of the total carbon signal. The surface coverage of this adventitious carbon overlayer can be estimated by considering the sampling depth of the XPS measurements. For the Al Kα source used, the C 1s photoelectrons have a kinetic energy of around 1200 eV. The inelastic mean free path of 1200 eV electrons in graphite is calculated at 3.01 nm. Given the interlayer spacing in HOPG is 0.335 nm, at normal emission (with the sample surface at 90° to the analyzer), the top nine layers of the HOPG are being sampled. In these measurements, the spectra were taken from the sample at grazing emission, with the sample surface at 20° to the analyzer. This increases the surface sensitivity by a factor of 3, meaning the sampling depth is reduced to the first three layers of the graphite crystal. Assuming that all the sp³ carbon detected is on the surface and neglecting attenuation from this carbon overlayer, it can be estimated that the surface coverage of adventitious carbon is approximately 75% of a monolayer for all samples except the freshly exfoliated graphite. In particular, the relative atomic percent of C−O is 2% in the IAG sample while it is 7% in the AAG sample, indicating more oxygen-containing species in the AAG sample.

Given that the XPS analysis has shown significant contamination of the graphite surface by ambient organic materials, a high-vacuum annealing treatment was explored to remove the adsorbed impurities as has been reported previously for graphene and graphite surfaces. In this study, different temperatures were used to clean the AAG sample under high vacuum (~10⁻⁵ mbar). The results are shown in Figure 7.
black curve represents the capacitance value of FEG; the red one represents the capacitance value of AAG, and the orange, yellow, green, blue, and purple curves represent the capacitance values of AAG annealed at 100, 200, 300, 400, and 500 °C, respectively. First, when the annealing temperature is lower than 400 °C, capacitances that were lower than those of the fresh surface were measured, indicating that these treatments cannot fully restore the surface to its initial state, but when the annealing temperature is 400 °C, the PZC shifts to a more negative potential, close to that of FEG, indicating that a significant fraction of the organic contaminations was desorbed at this temperature. Second, compared with other samples, it was found that annealing the AAG sample under high vacuum at 500 °C increases its capacitance to 5.4 μF cm⁻² (at PZC) and the PZC shifts close to that of FEG, which suggests that 500 °C is a more effective temperature for the removal of the contamination from the air.

CONCLUSION

In conclusion, a series of studies on the differences among FEG, AAG, and IAG have been presented in this work. First, the EIS results show the FEG samples have an intrinsic capacitance (6.0 μF cm⁻²) higher than those of AAG (4.3 μF cm⁻²) and IAG (4.7 μF cm⁻²), a change attributed to oxygen, moisture, and, most importantly, airborne organic contaminants. To the best of our knowledge, this is the first study of the effect of the airborne contaminants on the capacitance of carbon-based materials. Second, our findings show the FEG is more hydrophilic than AAG and IAG, as evidenced by the increase in the WCA from 61.7° to 72.5° and 81.8° after prolonged exposure to argon and air, respectively. Third, the XPS results show the surface of HOPG was doped by organic contamination after exposure to the atmosphere. Finally, high-vacuum annealing treatment was applied to remove these adsorbed contaminants; it was found that annealing at 500 °C of the aged samples partly removed the contaminants.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.6b02910.
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