The role of electrolyte acid concentration in the electrochemical exfoliation of graphite: Mechanism and synthesis of electrochemical graphene oxide

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Electrochemistry has emerged as a major route for graphene and graphene oxide synthesis from graphite. Anodic graphite oxidation is commonly used with dilute mineral acid or aqueous salt electrolytes. In this system, the electrolyte acid concentration appears to be a critical parameter. However, the effect of the acid concentration, particularly at low concentrations, is still not fully understood. To address this issue, we used a packed bed electrochemical reactor to synthesize seven different electrochemical graphene oxide (EGO) products in 2–16 M sulfuric acid. Detailed XRD, XPS, Raman, conductivity and optical microscopy analysis of the products was carried out. We found dilute acid (<10 M) graphite oxides were less crystalline and less oxidized than those produced in stronger acids. The oxygen evolution reaction at the graphite surface appears to affect the structural changes, oxidation mechanism, and electrochemical corrosion of the anode. EGO conductivity is also strongly affected by the electrolyte’s acidity. We show that well oxidized, yet reasonably conductive, single layer graphene oxide can be produced from 7.1 M acid. These results broaden our understanding of graphite electrochemistry and will serve to inform future electrochemical graphene synthesis efforts.

1. Introduction

Electrochemical exfoliation is one of a handful of potentially cost-effective and scalable methods for converting graphite to graphene [1–7]. As an essentially wet chemical approach, electrochemical methods have the advantage of being green (avoiding hazardous or energy intensive processes), using low-cost and readily available precursors, and allowing for a large degree of functionalization [1].

Although cathodic exfoliation is possible [8,9], oxidation of graphite anodes in dilute mineral acids or aqueous salt solutions is much more common [3]. Generally, highly positive potentials are applied to the graphite, causing intercalation of negatively charged ions and graphite expansion or exfoliation. The treated graphite can then be sonicated to single to few layer graphene. This paradigm allows for the synthesis of a range of functional products, from more pristine, high C/O ratio graphite [10–12] to heavily oxidized, electrochemically produced graphite/graphene oxide (EGO) [1,10,13–24]. For example, Pei et al. [17] and Cao et al. [13] developed a method where graphite is immersed in concentrated sulfuric acid, forming a first stage graphite intercalation compound (GIC); subsequent electrolysis in dilute sulfuric acid or ammonium sulfate electrolyte lead to rapid exfoliation of graphite oxide from the electrode. We have also recently demonstrated that flake graphite can be oxidized in a packed bed electrochemical reactor in a scalable, cost-effective fashion using 11.6 M sulfuric acid and sustained, low constant current charging [25]. Tian et al. [18] and Guržda et al. [21,22,26–28] have shown that graphite oxide can be produced via a similar route, varying the type of mineral acid.

This and other recent work has pointed to the electrolyte acidity as a critical factor which shapes the final graphene product [2]. However, our understanding of the role of the acid concentration is incomplete. Electrolyte acid concentration has been examined by early work in the 1970s onward looking at the “overoxidation” of graphite as a function of acid strength [5,29–32]. This work, however, tended to focus on relatively concentrated acids (>9 M) and the formation of GICs. More dilute acids were generally not examined, physical properties of the material (e.g. dispersibility and conductivity) were not assessed, and graphene was not produced. Studies that have examined more dilute electrolytes (namely 4.6 M perchloric acid) have not charged the graphite anodes to
On the other hand, there is a breadth of literature examining the transient response of carbon anodes in dilute (e.g. 1 M) mineral acids [34-37]. These studies employ in situ techniques such as AFM/STM [34,36,38] to understand how defects and cracks form on the carbon surface as charging begins. However, the product of prolonged oxidation in such dilute acids is not assessed. Pei et al. [17] considered the acid concentration in the second electrolysis step of the two-step synthesis previously mentioned. However, their study used a parallel plate configuration where graphite could easily exfoliate from the electrode. Thus, the results could be explained by this kind of premature exfoliation effect, as noted by the authors. There is therefore a gap in our understanding of how prolonged exposure of a graphite anode to dilute acids affects graphite properties as it relates to graphene oxide production.

In this study, we address this gap by characterizing in detail EGO produced from a broad spectrum of sulfuric acid dilutions. In order to get a clearer idea of the effect of electrolyte acidity, ideally the graphite should be held in contact with the electrode for a controlled amount of time. Our recently developed packed bed electrochemical reactor is ideal for this task [25]. We use this reactor to produce seven different EGO products using sulfuric acid electrolytes ranging in strength from 2 to 16 M. The samples are characterized using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, conductivity measurements, and optical microscopy. We find that when the acid concentration is below approximately 10 M, a less crystalline, less oxidized EGO is formed, relative to the higher acid concentration products. Oxygen evolution at the graphite surface appears to drive the phenomenon and likely plays a role in catalyzing graphite oxidation. To place our work in the context of the graphene literature, we show that this EGO with 80% single layer flakes can be exfoliated from the 7.1 M (50 wt %) acid. This EGO has a high conductivity for graphite oxide (~4400 S/m), given its degree of oxidation. This work should not only further our fundamental understanding of graphite oxidation, but also provide useful design criteria for future electrochemical graphene synthesis efforts.

2. Materials and method

2.1. Materials

Large, natural flake graphite used for synthesis was as received from Sigma Aldrich (Product Number 332461, particle size: +100 mesh). Sulfuric acid purchased from ChemSupply (Gillman, SA, Australia) was diluted with deionized water and used as the electrolyte. A 43 cm 0.25-mm-diameter platinum wire formed the counter electrode and was sourced from Goodfellow (Item 850-988-64, Cambridge, UK). The seal between the glass test tube making up the reactor and the boron-doped diamond (BDD) electrode was made up of three layers of Parafilm M (Bemis, Neenah, US) with a 13 mm hole punched in the center of the film. The BDD working electrode consisted of a 100 × 20 × 2 mm (length × width × thickness) niobium plate coated using CVD with a 12–18 μm thick polycrystalline BDD film (Diaccon GmbH, Fürth, Germany). The reactor consisted of the glass test tube as well as 3D printed plastic flanges used to clamp the tube onto the niobium plate. The flanges were printed using a MakerGear M2 or M3 3D printer (Beachwood, OH, US) using ABS filament (Verbatim Americas LLC, Charlotte, NC, US) and were attached to the glass test tube using epoxy resin. The graphite press was 3D printed with semi-transparent 1.75-mm-diameter PVD filament (Apium Additive Technologies, Karlsruhe, Germany). All 3D printed parts were designed in AutoCAD 123D Design. The separator between the graphite and the plastic press consisted of three thin, 13.5-mm-diameter glass fiber membrane discs cut from a larger membrane filter (pore size 0.7 μm, Whatman brand from GE Healthcare, Chicago, CAT No. 1825-047). Silicon wafers (item ID 785, P/B type, 525 μm thickness, (100) orientation) used for SEM imaging were sourced from University Wafer (Boston, USA).

2.2. Synthesis of EGO samples

The synthesis employed the same apparatus and method described in detail in our previous work [25]. A schematic of the reactor is shown in Fig. 1. Essentially, the reactor consists of a glass tube (inner diameter of 14 mm) which was pressed and sealed against a BDD plate, the anode. Note that it is important to use BDD as the working electrode, rather than a more active material such as platinum. As explored in Lowe et al. [25], in relatively concentrated mineral acids and at low current densities, the graphite oxidation voltage falls within the potential window of BDD. Using BDD thus ensures that most of the applied current flows through the graphite, rather than the anode substrate.

Flake graphite was poured through the opening at the top of the reactor, where it formed a packed bed at the bottom. Glass fiber membranes were placed atop the bed, and then the membranes and graphite were pressed into the BDD plate using a plastic press. The plastic press was hollow and contained large holes at the bottom to allow easy diffusion of gas and electrolyte. Inside the plastic press was a coiled platinum wire counter electrode (33 cm of the wire made up the spring-like coil), placed approximately 4 mm from the top of the graphite bed. The platinum wire was cleaned before each experiment with sonication in acetone, brief rinsing with ethanol and water, then with electrochemical cleaning in 0.1 M H2SO4, which included: −2.0 v. SCE for 2 min, followed by CV run between −0.23 and +1.10 V with a scan rate of 100 mV/s for 20 cycles, stopping at 1.1 V. A 0.5 kg weight was placed atop the graphite press, ensuring the graphite bed made intimate contact with the BDD. Electrolyte was then poured into the reactor. The BDD and platinum wire were connected to a Gamry Interface 1000 potentiostat (Gamry Instruments, Warminster, PA).

A positive current of 16 mA was then applied to the BDD/graphite electrode. The experiment was monitored to detect when the final voltage plateau was achieved and the slope had stabilized. The experiment was run until approximately 60 C of additional charge was transferred after the final slope stabilization point. This 60 C allowance was made to ensure that the final plateau had indeed been reached. At the end of the electrolysis, samples were removed from the reactor, rinsed of excess acid several times with DI water in a vacuum filter cup, and then stored in DI water in a refrigerator at 4 °C.

2.3. Characterization

Information about the characterization instrumentation is provided here. For information about the details of sample preparation, see the
Supplementary Information, Section 1. X-ray diffraction (XRD) employed a Bruker D8 Advance diffractometer, equipped with a graphite monochromator. Thin film samples were scanned in fixed sample illumination mode (5 mm illumination length) at a scan rate of 3°/minute. OriginPro 2018 was used for the peak fitting using a combination of Pseudo-Voigt and Gaussian-Lorentzian cross product functions.

X-ray photoelectron spectroscopy (XPS) was carried out on a Kratos Axis ULTRA incorporating a 165 mm hemispherical electron energy analyzer, and data were analyzed using Casa XPS.

Raman spectroscopy was conducted on a Renishaw inVia Raman Microscope equipped with a 532 nm laser and a 20× objective and 100× objective (the 100× objective was only used on the single graphite flake samples). Five measurements were collected for each sample to ensure the presented spectra were representative. Renishaw Wire 5.0 software was used for background correction and peak fitting.

SEM was performed on EGO spin coated onto a conductive Si/SiO2 wafer. SEM images were captured using a Joel JSM-7500FA with a 15 keV beam. ImageJ was used for particle size analysis of SEM images. Atomic force microscopy (AFM) images were captured with a Bruker Dimension Icon AFM with a ScanAsyst-Air probe operating in ScanAsyst mode. AFM images were assessed with Bruker Nanoscope Analysis Software, the height being measured with the depth tool. Optical microscope images were collected using an Olympus LEXT OLS5000 Industrial Laser Confocal Microscope in non-confocal mode.

A Jandel RM3000 four-point probe system with a linear arrayed head (probe spacing of 1 mm) was used for conductivity measurements, with roughly 30 measurements taken for each sample at the center and on both sides of a membrane compressed with 5 ton pressure using a hydraulic press. A digital outside micrometer with 1 μm accuracy was used to measure the sample thickness.

For the yield measurements, one third of the total product of the reaction was filtered using a vacuum filtration apparatus. The membrane was dried overnight in air at 80 °C. To determine the mass of the sample, and thus the product yield, the membrane was quickly removed from the oven and immediately weighed.

For the dispersibility tests, the material was freeze-dried and then redispersed in dimethylformamide (DMF) at a concentration of 0.1 mg/mL in a 50 mL centrifuge tube. The dispersion was bath sonicated for 1 h in an ice bath. To measure the concentration of the supernatant after 24 h sedimentation, almost all of the supernatant (typically around 40 mL) was pipetted up and vacuum filtered onto a pre-weighed 0.22 μm PTFE membrane (membrane without polypropylene support, Hawach Scientific, Xi’an City, China). The membrane was dried overnight in an 80 °C oven in air. After drying, the membrane was quickly removed from the oven and immediately weighed again. The sediment was also weighed in this manner (i.e. vacuum filtration with overnight oven drying). The reported mass retained in the supernatant was the mass of the supernatant over the mass of the supernatant and the sediment.

3. Results and discussion

Oxidations were carried out in a custom-made packed bed electro-chemical reactor [25]. In this reactor, a bed of graphite flakes (40 mg) with no binder or adhesive was pressed into a BDD working electrode with constant pressure (Fig. 1). The reactor has several advantages for this type of study. First, it ensures almost all of the graphite is in constant ohmic contact with the power supply. Further, the inactive nature of the BDD limits side reactions at the working electrode in the potential ranges under study. Finally, glass walls allow for visual observation of the graphite and gas evolution from the packed bed.

3.1. Charging curves and yield measurements

The graphite electrodes were charged with a constant current of...
The potential versus time curves for each experiment (Fig. 2b; magnification in Figs. S1 and S2) exhibit three typical regions, corresponding to an induction region, a long potential plateau where oxidation occurs, and finally a rise to a final voltage plateau, as marked on Fig. 2a. Early work has demonstrated that the initial, rising voltage period is associated with the formation of a GIC [30,39]. We have shown that during the oxidation plateau, the packed bed essentially reacts from the top/bulk solution down [25]. When the reaction front reaches the bottom and the unreacted graphite is used up, the voltage rises to the final plateau as the predominant reaction switches to water oxidation.

Here, we observe that the reaction time increases as the acid is diluted (Fig. 2c), as has been previously observed [29]. We attribute this effect to an increase in water oxidation/oxygen evolution at the graphite surface during the reaction. As the acid strength is decreased, the potential for water oxidation also falls and hence associated oxygen evolution increases. Accordingly, we visually observed nearly continuous bubbling.

Fig. 3. Images of the products and XPS and Raman results for the 2, 7.1, 11.6, and 16 M H₂SO₄ electrolyte conditions. (a–d) Photographs of the packed graphite beds taken when the bed height was at its maximum, before the final voltage rise. A gas bubble emerging from the side of the packed bed is marked in the 7.1 M condition photograph (b). (e–h) Optical microscope images of the as-synthesized and water washed graphite oxide flakes drop cast on glass. (i–l) High-resolution C 1s XPS spectra with peak deconvolutions. (m–p) Raman spectra (D and G band region) acquired using a 532 nm laser on bulk, freeze-dried material. The first column of Fig. 3 shows the data for the 2 M condition, while the second, third, and fourth columns show data for the 7.1, 11.6, and 16 M conditions, respectively. Images and spectra for the 5, 10, and 14 M conditions are shown in the Supplementary Information, Fig. S3, Fig. S4, and Fig. S5.
from the graphite bed at lower acid concentrations (less than or equal to 7.1 M; an example of such a gas bubble is highlighted in Fig. 3b). While bubbles can be seen in the more concentrated acid conditions, the bubbling rate is much slower. The bubbling at lower acid concentrations likely accounts for the dramatic bed expansion observed in these conditions (Fig. 3a and b; additional photographs of all acid conditions are shown in Fig. S3), as bubbles expand the graphite gallery and press upward on the plastic press. The diversion of current away from oxidation of graphite towards the oxygen evolution reaction (OER) slows the reaction front and lengthens the reaction time.

The graphite generally gains mass with the addition of oxygen during the reaction (Fig. 2d). To some extent, the magnitude of this mass increase reflects the degree of oxidation. However, at lower acid concentrations, the mass change in fact becomes negative. This may be due to carbon dioxide formation, as discussed in the section below on the mechanism.

### 3.2. XRD

XRD of the samples after washing and brief sonication shows a pronounced (002) reflection for graphite oxide in all conditions around 11 ± 0.3° 2θ (Fig. 4; full spectra in Fig. S8). The patterns also include a multi-component peak around 17–34°. Deconvolution of the peaks (Fig. 4) reveals that there are at least three components in each of the samples, which for convenience we label Peaks I, II, and III (full peak statistics in Table S3). The broad Peak II around ~23° most likely reflects the interlayer spacing of mildly oxidized, restacked graphene layers [40–42]. Peak III (~25–26°) is the (002) reflection of graphite. It may represent pristine unreacted graphite, or, more likely, graphite which has been reacted to form a GIC and then de-intercalated during workup [43]. There is also a very broad, weak peak around 52° in some of the samples, which we attribute to the (004) reflection of graphene or graphite. However, because it is difficult to distinguish from the background, it was not included in the peak analysis.

There are several trends in the XRD patterns as a function of concentration (Fig. 5a). The higher acid concentrations are characterized by a sharper Peak I, and a less pronounced Peak II. The relatively narrow FWHM of Peak I (Table S3) for the 10 and 11.6 M products, suggests increased crystallite size or reduced crystallite strain (based on the Scherrer equation).

The lower acid concentrations (2–7.1 M) are characterized by a very broad and intense Peak II around 24.5°, relative to the less intense Peak II around 22–23° for higher acid concentrations (Fig. 5a). The greater area for this peak (associated with less oxidized graphene) suggests that the more dilute acid samples are relatively less oxidized. This is not to say that these samples are unreacted graphite, however. At lower acid concentrations, the area associated with Peak III is very low, and even not discernible in the 7.1 M condition, suggesting most of the graphite has been converted to an at least partially oxidized form.

### 3.3. XPS

The XPS components and peak positions (Fig. 3i-l, Fig. S4, and Table S1) are congruent with those previously reported for graphite oxide [25,44]. As with the XRD, XPS suggests that the more concentrated acid products are more oxidized, evident in the lower proportion of sp² carbon (Fig. 5b). Further, the π-π* peak associated with intact conjugated structures is only discernible for lower acid concentrations (<10 M). XPS also shows trends in the types of functional groups. There is a prominent COOH peak with more dilute acid electrolytes and a less prominent C-OH peak, suggesting the oxidation mechanism may vary with acid concentration.

### 3.4. Raman spectroscopy

Raman spectra acquired on freeze-dried, bulk material were deconvoluted into 4 peaks using the graphene oxide (GO) fitting strategy described by Claramunt et al. [45] (Fig. 3m-p; full spectra and fitting details are in Fig. S5 and Table S2). This resulted in four fitted peaks, D, D’, G, and D’. In their GO synthesized from carbon nanofibers, Claramunt et al. observed a D* mode around 1150-1200 cm⁻¹ associated with disordered graphitic lattices, a peak initially reported for soot [46]. However, this mode was not later observed in GO chemically synthesized from natural flake graphite [47], nor was it observed here. Although the precise origin of the defect-related peaks has not been completely resolved, they can be activated by oxygen functionalization [48]. Raman analysis of both graphitic and amorphous carbon shows the D’ mode is also activated by the presence of amorphous phases and

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**Fig. 4.** XRD diffraction patterns with peak deconvolutions as a function of electrolyte sulfuric acid concentration. In all but the 7.1 M condition, three peaks can be identified, labeled Peaks I, II, and III.
These structural defects likely emerge from OER-related processes associated with dilute acids. Previous work has shown structural defects can emerge during oxidation in dilute acids. For example, graphite anodically exfoliated in 0.1 M ammonium sulfate at high voltage exhibits surface roughness, hole defects, and tears [53]. Likewise, the surface of HOPG shows blistering and cracks during lower voltage oxidation in dilute acids [34,54]. These processes are attributed to intercalation and gas formation. Similar processes likely occur here in the very dilute acid concentrations, leading to the elevated levels of defects.

3.5. Optical microscopy on graphite oxide flakes

After water washing, the graphite oxide solutions were drop cast onto glass slides and allowed to dry overnight. At the highest magnification, all the EGO samples are multicolored mosaics (examples provided in Figs. S11, S12, and S13). However, at lower magnifications, these colors can blend together to produce the dull brown colors observed in Fig. 3e–h and Figs. S9–S10.

GO is an inherently multicolored material. Colors are generated from islands of conjugate, aromatic domains (chromophores) which remain after the graphite basal plane has been oxygen functionalized or suffers from hole defects [55]. Different colors can be generated by the size of these islands and the presence of different oxygen functional groups (substituent effects), and observed colors are combinations of colors from multiple, overlapping sheets.

In this case, it does not appear that different colors within a given sample indicate fundamentally different materials. Raman spectroscopy performed on multiple, differently colored areas produces identical spectra (Fig. S7). This may be because structures that generate the colors do not change the Raman spectra or because each spectrum represents a statistical average of many different overlapping sheets.

The dilute acid conditions clearly have a greater fraction of light-colored graphite oxide. We presume that lighter colors can be observed when the graphite is partially exfoliated (otherwise, many stacked layers would create a brown color, as discussed). The physical expansion of the dilute acid graphite oxides (Fig. 3a and b) and their more amorphous structure likely render these samples more susceptible to self-exfoliation during water washing.

3.6. Dispersibility and conductivity

The stability in solution was measured by freeze-drying then redispersing the EGO in DMF at 0.1 mg/mL using 1 h bath sonication. After 24 h sedimentation, the fraction of the initial suspended material remaining in the supernatant was measured by filtering and weighing the supernatant and sediment. The solution stability of the products showed a negative parabolic trend with respect to concentration, with the 11.6 M acid producing the most stable EGO (Fig. 6a). The 11.6 M acid EGO is most dispersible presumably because of its high degree of oxygen functionalization. Interestingly, the 5 and 7.1 M samples were more stable than the 14 and 16 M samples, despite having a higher fraction of sp² carbon (Fig. 5b). We expect that increased ionizable COOH groups, as well as the in situ expansion discussed above, aided exfoliation of the lower acid products. Indeed, during sonication, the lower acid samples (<11.6 M) begin dispersing within seconds of immersion into the sonic bath, such that no graphite particles were visible after ~2 min. The more concentrated acid samples remained mostly as swollen graphite oxide particles for several minutes before eventually exfoliating.

The conductivity of thick (approximately 20 μm) vacuum filtered membranes was measured using a four-point probe (Fig. 6b). The trends in conductivity can be explained with reference to the degree of oxidation. The 11.6 M acid sample is the least conducting, consistent with it being most oxidized. Further, the trends in conductivity follow the trends in the sp² carbon content measured by XPS, reflective of the fact that electron transport relies on intact conjugated domains. The 7.1 M EGO was most conductive (4430 S/m). We believe 7.1 M acid is optimal for...
measured using a four-point probe (error bars represent the interquartile range). This process is relatively mild and less destructive towards the carbon lattice. The low acid conditions, on the other hand, are marked by significant and prolonged water bubbling. These bubbles cause the dramatic in situ graphite expansion, which mechanically strains the lattice, contributing to defects observed in the Raman spectra.

The above model, however, does not fully explain the clear downward trend in the graphite mass gain as the acid concentration is lowered (Fig. 2d). The graphite oxidized in 2 M acid actually experiences a slight mass loss of ~2%. Pei et al. also observed approximately 4% weight loss after their two-step oxidation process. This cannot be explained in terms of reduced oxidation, given that these samples are all reasonably well oxidized. We believe the mass loss is a consequence of carbon corrosion, which can occur via CO₂ gas formation and/or dissolution of the graphite into soluble small molecules. The anodic dissolution of carbon electrodes in acidic media is well known [56-58]; it has recently been studied for graphite anodes in conditions comparable to ours in the context of electrochemical advanced oxidation processes [59]. The mechanism for this reaction is [58,60]:

\[
\text{C} + \text{H}_2\text{O} \rightarrow \text{C-O}_\text{ad} + 2\text{H}^+ + 2\text{e}^- \\
\text{C-O}_\text{ad} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-
\]

Where O_ad refers to adsorbed oxygen species. Although the thermodynamic potential for this reaction is only 0.207 V vs. SHE, the reaction has a very high overpotential [60]. However, above around 1.65 V (the potential at which OER begins in earnest on graphite), significant carbon corrosion may be observed [56]. This reaction appears to be mediated by ROS generated during OER [56,57], namely adsorbed *OH, *O and *OOH. Yang et al. [56] have proposed a model where atomic oxygen initially hydroxylates aromatic rings, which are then (possibly electrochemically) converted to carbonyls and carboxylic acids. Finally, neighboring carboxyls or carboxylic acids are converted to carbon dioxide. The elevated levels of carboxylic acids we observed in the low acid concentration conditions may enable CO₂-formation via this decarboxylation pathway. OER-mediated CO₂ formation at lower acid concentrations can create edges and hole defects which would help explain the defect-induced Raman modes observed in the dilute acid samples. Such defects could also explain the downward trend in conductivity as the acid concentration is reduced from 7.1 M. Given the carbon corrosion reactions rely on a chemical oxidation of graphite by ROS, the findings suggest graphite oxygen-addition is in fact a combination of electrochemical and chemical oxidation processes.

3.8. AFM and SEM

In addition to improving fundamental understanding of graphite oxidation, our findings can inform future synthesis of graphene oxide using the electrochemical method. To illustrate this, we exfoliated and analyzed the 7.1 M product. The 7.1 M EGO appears promising in that it has good conductivity, complete reaction from the starting graphite (according to the XRD), a reasonably high yield and solution stability, and it can rapidly disperse in polar solvents. The 7.1 M graphite oxide pellets were exfoliated in DMF by two rounds of sonication (10 min) and low-speed shear mixing (10 min) in sequence. Optical microscopy of the EGO spin coated onto mica (Fig. S14) reveals a mixture of large, thick flakes, up to ~18 μm in diameter, as well as much smaller particles. AFM (Fig. 7a and c) and SEM (Fig. 7b and d) reveal most flakes are smaller (mean of 1.35 μm) and the vast majority (81%) are single layer. The single-layer sheets had a measured thickness of 1.7–2 nm, consistent with well-oxidized GO. Note the actual thickness is likely somewhat thinner, given that factors such as the cantilever force and residual solvent underneath the flakes can alter the measured height [61]. Regardless, these results show that predominantly few layer graphene oxide can be produced with more dilute acid. Compared to our previously reported EGO using 11.6 M acid [25], this EGO has the advantage of being orders of magnitude more conductive in its as-prepared state, and it demands milder synthesis conditions. The conductivity appears to be greater than
other reported forms of EGO [13,17,23], despite similar oxygen contents (~22.5% oxygen, according to the XPS survey spectrum).

4. Conclusion

In this study, we provide the first comprehensive analysis of graphite oxidation in a mineral acid electrolyte ranging in concentration from very dilute to very concentrated. Broadly, there are two qualitatively different EGO-forming regimes associated with low or high acid concentration. The low acid regime (less than or equal to 7.1 M H₂SO₄) is characterized by prolonged and elevated levels of oxygen evolution on the graphite electrode. Evolved oxygen most likely plays a role in oxidizing the carbon backbone, promoting CO₂ evolution, and mechanically straining the carbon lattice. This leads to a more amorphous graphite structure. Higher acid concentrations favor more thorough intercalation and oxidation by water, as well as maintenance of crystallinity. Interesting trends in conductivity were observed, with the 7.1 M electrolyte producing a relatively conductive yet well oxidized few-layer graphene product. The balance between intercalation and water electrolysis can in part explain the structural and compositional differences among samples. These results should help future optimization of the oxidation level, solution stability, conductivity, and other structural/chemical parameters of EGO. This can allow EGO properties to be matched to particular applications (e.g. more conductive graphene can be produced for conductive nanofillers applications). More generally, the findings here can help explain the mechanism and consequences of intercalation and OER in aqueous anodic graphite electrochemistry.

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Appendix A. Supplementary data

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