Electrochemical Behavior of Graphene in a Deep Eutectic Solvent

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ABSTRACT: Graphene electrodes and deep eutectic solvents (DESs) are two emerging material systems that have individually shown highly promising properties in electrochemical applications. To date, however, it has not been tested whether the combination of graphene and DESs can yield synergistic effects in electrochemistry. We therefore study the electrochemical behavior of a defined graphene monolayer of centimeter-scale, which was produced by chemical vapor deposition and transferred onto insulating SiO2/Si supports, in the common DES choline chloride/ethylene glycol (12CE) under typical electrochemical conditions. We measure the graphene potential window in 12CE and estimate the apparent electron transfer kinetics of an outer-sphere redox couple. We further explore the applicability of the 12CE electrolyte to fabricate nanostructured metal (Zn) and metalloid (Ge) hybrids with graphene by electrodeposition. By comparing our graphene electrodes with common bulk glassy carbon electrodes, a key finding we make is that the two-dimensional nature of the graphene electrodes has a clear impact on DES-based electrochemistry. Thereby, we provide a first framework toward rational optimization of graphene−DES systems for electrochemical applications.

KEYWORDS: graphene, deep eutectic solvent, electrochemistry, electrodeposition, zinc, germanium

INTRODUCTION

The electrochemical behavior of graphene is central to the many considered uses of graphene and related graphene-derived carbon materials as electrode materials in electrochemical energy storage including supercapacitors and batteries.1−4 Equally, graphene’s electrochemical properties are key when graphene is electrochemically produced or electrochemically coated to form functional graphene/metal(−oxide) hybrids.5−8 Graphene also serves as an ideal model system to fundamentally study electrochemical mechanisms for other carbon-based electrodes with a less defined and controllable crystalline structure, such as common glassy carbon electrodes.9

The electrochemical behavior of a given material is however not universal but critically depends on the choice of the employed electrolyte. While the electrochemistry of graphene has to date been mostly studied in conventional aqueous and nonaqueous electrolytes,1,2,10−17 novel electrolytes with enhanced properties are continuing to emerge. A particularly prominent example of such a novel class of electrolytes is deep eutectic solvents (DESs). DESs are ionic liquid-like fluids, which consist of a eutectic mixture of Lewis or Brønsted acids and bases that can encompass a variety of anionic and/or cationic species.18−20 DESs share many of the beneficial properties of ionic liquids, but additionally are inexpensive and environmentally friendly.18−20 Consequently, they have been a subject of intense interest in many fields of application including electroplating/metal processing,21,22 nanotechnology,23,24 organic synthesis,25 biomass processing,26 and electrochemical energy storage.27

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Whether the advantages of DESs can also be translated in the context of electrochemical applications of graphene remains however largely unexplored. While a few, mostly computational studies investigated DES/graphene interfaces, present only very limited experimental reports on the electrochemical behavior of graphene in DESs are available. So far, DESs were employed to electrochemically exfoliate graphene from graphite55−58 to covalently functionalize graphene(−oxide),59−62 and to explore the potential application of a DES as an electrolyte in graphene-based supercapacitors.63 Fundamental characterization of the electrochemical behavior of a defined graphene monolayer in a DES remains however missing. In addition, the applicability of DESs to produce graphene-based hybrid materials by electrochemical means has not been explored yet. Such hybrid materials have been suggested for corrosion protection44,45 of steel, for energy storage in the case of, for example, graphene/zinc (Zn), or as anode materials in Li-ion batteries in the case of, for example, graphene/germanium (Ge). All of these bulk composite materials have either been prepared in aqueous media or from the gas phase. While the former procedures may suffer from possible side reactions, for example, hydrogen evolution, which can affect the chemical integrity of graphene as well as the morphology of the composites, the latter method is highly involved and probably difficult to control in a scaled-up procedure. The feasibility of preparing such graphene composites by electrodeposition from cheap and environmentally friendly nonaqueous electrolytes such as DESs has not been explored to date. A detailed understanding of the reactivity of the graphene/DES interface is in this context crucial for a rational selection of fabrication strategies but remains completely missing in the literature.

To address this, we show here for the first time how centimeter-scale graphene electrodes made from graphene monolayer films49 that were produced by chemical vapor deposition (CVD) and transferred onto insulating SiO2/Si supports, interact with the common DES choline chloride/ethylene glycol of 1:2 molar ratio (12CE) under typical electrochemical conditions, including identification of the graphene/DES potential window and determination of apparent electron transfer kinetics. For comparison, we contrast the observed electrochemical behavior of our graphene electrodes with the behavior of widely used standard glassy carbon electrodes under the same conditions. We also explore how our graphene films can be decorated with metal (Zn) and metalloid (Ge) nanostructures by electrodeposition from DES electrolytes.48,53 We have chosen choline chloride/ethylene glycol (12CE) as an archetypal example of DES electrolytes. 12CE fulfills all criteria for technical applications. Its components are cheap and environmentally friendly, while the mixture is easy to prepare, and it shows the highest ionic conductivity at room temperature among such types of electrolytes. Consequently, 12CE probably is the most extensively studied DES for electrochemical applications.48 Moreover, also features of the double layer structure at carbon electrodes and some of its mechanistic implications, for example, for the electrodeposition of Zn, have been reported. The double layer structure of three choline chloride-based DESs showed similar features, and therefore, the resulting charge transfer behavior is highly likely to be similar as well, particularly for outer sphere redox probes, such as ferrocene.

Combined, our work here systematically explores for the first time the prospects and limitations of monolayer graphene−DES systems in electrochemical applications.

## METHODS

### Fabrication of Monolayer Graphene Electrodes

We fabricate monolayer graphene working electrodes using graphene monolayers of macroscopic size (∼ 2 × 1 cm), that were grown by CVD and transferred onto electrically insulating SiO2 (90 nm thermally grown) covered Si wafers (SiO2/Si). These working electrodes are immersed along half of their length into the DES electrolyte during the electrochemical experiments (Figure 1a,b). The graphene monolayer films are electrically contacted on their front via silver epoxy on their non-immersed end above the electrolyte meniscus. This geometry allows us to study the electrochemical response exclusively from the graphene avoiding interference of any electrically conductive support. Graphene films were grown via CVD using 25 μm thick Cu foil catalysts exposed to CH4/H2 at 12 mbar and 960 °C, resulting in high-quality polycrystalline (grain size tens of μm) monolayer graphene films. After CVD, graphene was transferred from the Cu catalyst onto the target SiO2/Si wafers via a widely used, standard polymer-assisted (poly(methylmethacrylate), PMMA) transfer process using a wet etch (FeCl3 in H2O) to remove the Cu catalyst. After
transfer onto the target SiO2/Si wafers, the PMMA scaffold was removed by soaking in acetone (> 8 h), followed by a final sample clean in isopropanol. See Figure 1c–e for the optical photograph/micrograph and a Raman spectrum56 of an as-fabricated, not electrochemically cycled graphene electrode. The as-fabricated graphene electrode is a continuous film on the SiO2/Si with only very small μm-sized holes, allowing an electrical conduction path along its entire length (Figure 1c,d). The Raman spectrum of the as-fabricated electrode is fully consistent with that of high-quality monolayer graphene produced by CVD (Figure 1e).56 It shows only very little defect-related D band intensity, and the observed 2D to G intensity ratio of ~ 2 confirms the monolayer nature of the graphene.56 It is known that the employed PMMA-transfer method leaves only few microscopic but a considerable amount of nanosize PMMA residues on the graphene support,57,58 which are inherent to state-of-the-art transferred graphene produced by CVD. Prior electrochemical studies have shown that these PMMA residues do not have a critical impact on the fundamental electrochemical behavior of graphene in a first approximation,59 allowing us to study the intrinsic electrochemical properties of graphene.

**Electrolyte Preparation.** The DES consisting of a 1:2 molar ratio of choline chloride and ethylene glycol (12CE) was prepared by first drying the choline chloride (99% Fluka) at 100 °C under reduced pressure (10⁻² mbar) in a Schlenk flask for 24 h. When the flask had cooled down close to room temperature, the flask was isolated from the vacuum pump and transferred to an argon-filled glovebox, where anhydrous ethylene glycol (99.8%, Aldrich) was added as supplied, without further drying. The mixture was stirred using a TFE-coated magnetic stir bar until a single, colorless liquid phase was obtained. Electrolytes containing ZnCl₂ were prepared similarly by adding predried powdered ZnCl₂ (99.999%, Aldrich, dried at room temperature at 10⁻² mbar for ≥ 24 h) to the 12 CE electrolyte. The solution was stirred until all of the salt had completely dissolved. Higher temperatures were avoided to limit reactions between ZnCl₂ and the hydroxyl group of the choline.

Karl–Fischer analysis was performed to determine the initial water content of the electrolytes using an automatic titrator (CA-100/VA-100, Mitsubishi Chemicals Corp.). Ethylene glycol contained 30 ppm water, and the freshly prepared and dried 12 CE electrolyte had 70 ppm water content.

Ferroene (≥ 98%) was purchased from Merck and used as received. Tetra(n-butyl)ammonium trichlorogermanate (TBAGeCl₃) was synthesized at the University of Southampton as published previously.39

**Electrochemical Measurements.** Electrochemical experiments were carried out in a three-electrode glass cell within a dry, argon-filled glovebox (MBraun, MB G-120) at 30 °C unless otherwise stated. The graphene on SiO2/Si was used as the working electrode with the graphene films immersed up to approximately half of their length. Because of the slightly varying immersion depths and slight variations in graphene film dimensions, the exact electroactive area and hence the absolute currents of the graphene electrodes used in this study vary to some extent. For reference, comparative measurements with a 3 mm diameter glassy carbon disk working electrode (Metrohm, 0.071 cm², polished to a mirror finish with an aqueous slurry of alumina powder) and with a zinc disk electrode of 5 mm diameter were also made. The zinc disk was machined from a rod (99.999%, Goodfellow Cambridge Limited, UK) and inserted into an interchangeable rotating disk electrode tip holder with a polyether ether ketone shroud (Pine Research Instrumentation Inc., USA). Working electrodes were rinsed with deionized water and acetone and dried in air prior to their transfer into the glovebox.

A zinc wire immersed in 0.3 M ZnCl₂ was used as a reference electrode (RE) separated from the bulk electrolyte in the Haber–Lugin capillary via a glass frit. In some measurements, a Ag/Ag⁺ (1 mM) RE separated from the bulk electrolyte in the Haber–Lugin capillary via a glass frit was used. The potentials in this paper are reported versus Zn/0.3 M ZnCl₂ to allow easy comparison to our previous studies of ZnCl₂ in 12CE. They can be converted to the AgAg⁺ (1 mM) potential scale by subtracting 1.033 V. Platinum mesh was used as the counter electrode (CE).

A Metrohm Echo Chemie Autolab PGSTAT100 potentiostat/galvanostat controlled by NOVA 1.10 software and hooked up to the glovebox was used for electrochemical measurements.

**Material Characterization.** The structural quality of the graphene films before and after all electrochemical measurements was assessed by Raman spectroscopy (all samples measured both in NT-MDT NTEGRA Spectra60 at 473 nm and in LabRAM HR at 633 nm laser wavelengths). Coverage and morphology of graphene films and, if present, Zn and Ge deposits before and after electrochemistry were studied by optical microscopy (Olympus), scanning electron microscopy (SEM, Zeiss Supra 55 VP, 2 kV, Everhart–Thornley secondary electron detector), and atomic force microscopy (AFM, Asylum Research Cyppher, tapping mode, Olympus OMCL-AC240TS-R3 tips). Additional chemical and structural characterization of Zn and Ge deposits employed energy dispersive X-ray spectroscopy (EDX, FEI Quanta 250 FE with EDAx SDD Octane Elite 55, 10 kV) and powder X-ray diffractometry (XRD, PANalytical Xpert Pro MPD, Cu-Kα at 0.154 nm, θ-θ Bragg–Brentano geometry) including qualitative phase analysis by comparison to the International Centre for Diffraction Data (ICDD) using HighscorePlus software.

### RESULTS AND DISCUSSION

**Cyclic Voltammetric Background Curves.** We first present in Figure 2a,c results of anodic and cathodic voltammetric background cycling experiments of our graphene electrodes in neat 12 CE and compare them to the behavior of common glassy carbon electrodes. In Figure 2b, we assess the effect of voltammetric cycling on the structural quality of the graphene via well-established Raman spectroscopy.36

For the as-fabricated graphene electrodes that are subjected to a first positive sweep, the current only starts to rise above +2.2 V and decreases again during the return sweep (Figure 2a, blue). This anodic behavior upon a first positive sweep is comparable to that of glassy carbon in 12CE (Figure 2a, gray dashed). The rise in current above +2.2 V is probably due to the anodic oxidation of the chloride ions,61 which limits the anodic stability of the DES. This occurs at the same potential for both types of carbon electrodes. In the case of glassy carbon, a peak for the reduction of the Cl₃⁻ ions, which form upon the oxidation of chloride ions, can be observed on the cathodic return sweep. This peak is missing in the case of graphene, where the chloride oxidation current is almost one order of magnitude lower than that in the case of glassy carbon. In Figure 1e above, the Raman spectrum of an as-fabricated, not electrochemically cycled graphene electrode has been shown in which the low defect-related D peak intensity and the intensity ratio of 2D/G of ~ 2 confirmed high-quality monolayer graphene. In comparison, Figure 2b shows the Raman spectrum of the once positively swept electrode (bottom blue). Notably, after anodic cycling up to +2.5 V, the Raman signature of the graphene electrodes remains virtually unchanged, suggesting that the graphene layer remains structurally fully intact during anodic cycling 12CE. Consistent with this, optical microscopy images of the graphene electrodes before and after anodic cycling show no observable change in terms of graphene film homogeneity and coverage from their as-prepared state as shown in Figure 1d.

In stark contrast to the anodic background sweep, the first sweep of a fresh graphene electrode to negative potentials shows a large cathodic peak with an onset at approximately −0.4 V (Figure 2a, red). After reaching its maximum at −1.25 V, a rather steep drop of the current is observed, which is in most cases discontinuous toward the cathodic switching potential.
We find that the cathodic peak shape is typical for the behavior of the monolayer graphene in 12CE, as in comparison glassy carbon electrodes show only a small increasing cathodic background current in the same potential range (Figure 2, gray dashed). Raman measurements in Figure 2b of the once negatively swept electrode (top red) reveal that the large cathodic peak is related to severe defect formation in the graphene as evidenced by a significant increase of D band intensity. The emergence of the D′ and the D + D′ bands in the spectrum is also indicative of this effect. The formation of defects in the graphene upon negative sweeps is also corroborated by further electrochemical observations in Figure 2c, where we study the effects of repeated cycling. First, when sweeping to the positive regime after initial cathodic sweeps, an anodic peak around +2.2 V is observed (Figure 2c, blue) which was absent in the first anodic sweep of as-fabricated, noncycled graphene (Figure 2a, blue). This suggests that the initial cathodic sweep has electrochemically activated the graphene toward anodic reactions. Electrochemical activity of graphene is known to be linked to defects, consistent with the defects observed in the Raman spectrum that formed during cathodic sweeps of graphene (Figure 2b, red). Second, repeated cycling to the negative switching potential consistently shows that the current drastically decreases from sweep to sweep (Figure 2c). This suggests that the graphene electrode is deactivated upon sweeping to negative potentials, which can be ascribed to diminishing electrical conductivity of the graphene layer. Because defects in graphene are known to drastically decrease the intrinsically high electrical conductivity of graphene, this observed electrode degradation can also be linked to the defect formation observed in the Raman spectrum. Finally, for graphene cycled to large cathodic potentials we also find strong signs of graphene film degradation and even delamination in optical microscopy by formation of voids and ruptured areas (Supporting Information Figure S1). This indicates that the detrimental impact of the cathodic sweep is not only microscopic, but also adversely affects the macroscopic homogeneity of the graphene film.

We suggest that the mechanism behind the cathodic degradation of the graphene in 12CE is linked to highly reactive radical electrolysis products of 12CE. Haerens et al. have studied the cathodic decomposition of 12CE and identified several products of the preparative electrolysers of 12CE. On this basis, they suggested possible reaction pathways for choline, whereby the initially formed choline radical decomposes into trimethylamine and an ethanol radical (Scheme 1A) or into dimethylamino-ethanol and a methyl radical (Scheme 1B). In both paths, radicals are generated that can easily bind covalently to graphene as known from electrografting. Covalent bonding of these radicals to graphene converts sp² into sp³-hybridized carbons and disrupts the delocalized π-electron system. Such types of defects result in a decrease of electronic conductivity and also lead to characteristic changes in the Raman spectrum of graphene. Corroborating this is also our observation during cyclic voltammetry that gas bubbles emanated on the graphene electrodes around the cathodic switching potential. This can be explained by the decomposition of choline to trimethylamine (Scheme 1A), although the formation of gaseous products, such as methane or ethane in reaction path B, cannot be ruled out. Bubble formation may also exacerbate the graphene film destruction via bubble-induced delamination from the...
substrate, which may account for the extensive void formation observed by optical microscopy for the fully cathodically cycled film (Supporting Information Figure S1). With respect to the proposed reaction scheme, the anodic peak around +2.2 V, which is observed only after the cathodic decomposition, points to the grafting of an oxidizable functional group such as the hydroxyl group in the ethanol radical generated also in path A.

Electrochemical background cycling has revealed the stability limits of graphene in 12CE, whereby we find that graphene is electrochemically stable at positive potentials up to +2.5 V, while at potentials negative from approximately −0.5 V versus Zn/Zn2+, graphene degradation via radical formation from 12CE decomposition readily occurs.

**Electron Transfer Kinetics.** Well-characterized redox couples are often used to study the electrochemical behavior of electrode materials in combination with a certain electrolyte. Here, we use the ferrocene/ferrocenium couple to compare the electrochemical behavior of the CVD graphene electrodes with that of glassy carbon in the DES. This couple is known to undergo an outer-sphere one-electron transfer, that is, without strong interaction (bond formation) with the electrode material and is thus well suited for comparing the heterogeneous charge transfer rate at different electrode materials. Typical features of the cyclic voltammograms of this redox couple, such as the peak potentials and peak currents and their variation with the scan rate, can be used as diagnostic criteria to estimate the rate of heterogeneous charge transfer. If the charge transfer is fast on the timescale of the experiment (reversible or Nernstian system), the peak potentials should be independent of scan rate, and a peak potential difference, $\Delta E_p$, of 59 mV is expected for the one-electron transfer of ferrocene. In this case, the reaction is diffusion controlled and the forward peak currents should be proportional to the square root of the scan rate. The linear regression of the corresponding plot should pass through the origin, and the diffusion coefficient can be calculated from the slope with the Randles–Sevcik equation (eq S1 in the Supporting Information). The cyclic voltammograms of 3.2 mM ferrocene between 0 and +2 V on the graphene electrodes in Figure 3 (blue traces) show peak potential differences, $\Delta E_p$, to vary between 145 and 446 mV at sweep rates $\nu$ from 10 to 500 mV s$^{-1}$ (Table 1). Such large values for $\Delta E_p$ and their strong dependence on the sweep rate indicate slow charge transfer at the monolayer graphene electrodes in 12 CE (quasi-reversible behavior), although some contribution to $\Delta E_p$ of the uncompensated ohmic resistance of the electrolyte and across the macroscopically large CVD graphene layer cannot be ruled out ($iR$ drop). A minimum value of $1.0 \times 10^{-4}$ cm s$^{-1}$ for the apparent heterogeneous rate constant of ferrocene at the CVD graphene electrode is estimated from the data in Table 1 via the work function by Nicholson. Prior literature has argued that the contribution at edges and defects to the heterogeneous electron transfer rate is much higher than that at the basal plane for graphene. We note, however, that our measurement provides a mean value for which contributions from graphene’s basal plane, edges, and point defects cannot be differentiated. In agreement with the background experiments above, the graphene electrodes are not degraded by cyclic voltammetry of ferrocene up to anodic potentials of 2 V vs Zn/Zn2+ as evidenced by the Raman spectrum in Supporting Information Figure S2, which does not show any indications for induced defects. The observation of slow charge transfer and the magnitude of the measured apparent heterogeneous rate constant are in line with prior reports in the literature for similar outer-sphere redox couples at monolayer graphene in other electrolytes. This behavior for outer-sphere redox probes such as ferrocene has been suggested to be linked to the low density of electronic states at the Fermi level of graphene and of the basal plane of highly ordered pyrolytic graphite (HOPG).

In contrast to the graphene electrode, glassy carbon in Figure 3 (gray traces) shows pairs of peaks with peak potential differences, $\Delta E_p$, between 66 and 71 mV at sweep rates from 10 to 500 mV s$^{-1}$ (Table 1). The much smaller $\Delta E_p$ values, as compared to those at graphene, and their negligible dependence on the sweep rate $\nu$ indicate that the electron transfer on glassy carbon is fast, that is, the reaction is diffusion controlled (electrochemically reversible or Nernstian behavior) with some $iR$ drop contributing to $\Delta E_p$. A series of cyclic voltammograms recorded at scan rates between 10 and 500 mV s$^{-1}$ is shown in Supporting Information Figure S3. A plot of the anodic peak current $i^{\text{p,ox}}$ versus the square root of the scan rate has a linear regression with a correlation coefficient larger than 0.9999 and an intercept close to zero (Supporting Information Figure S4). From the slope of this regression, a diffusion coefficient for ferrocene in 12CE of $1.9 \times 10^{-7}$ cm$^2$ s$^{-1}$ is calculated with the Randles–Sevcik equation. This value is almost one order of magnitude larger than that reported by Bahadori et al., who have however used the Randles–Sevcik equation without correction term for hemispherical diffusion to analyze cyclic voltammetric currents at a Pt ultramicroelectrode.

![Figure 3](https://doi.org/10.1021/acsami.0c11467)

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**Table 1. Cyclic Voltammetric Peak Potential Differences, $\Delta E_p$, of 3.2 mM Ferrocene at Graphene and Glassy Carbon Electrodes for a Range of Sweep Rates, $\nu$.**

| $\nu$ / V s$^{-1}$ | graphene $\Delta E_p$ / V | glassy carbon $\Delta E_p$ / V |
|-------------------|--------------------------|-----------------------------|
| 0.010             | 0.145                    | 0.066                       |
| 0.025             | 0.186                    | 0.069                       |
| 0.050             | 0.226                    | 0.065                       |
| 0.100             | 0.275                    | 0.071                       |
| 0.250             | 0.365                    | 0.071                       |
| 0.500             | 0.446                    | 0.069                       |
Electrodeposition of Zinc. After having established the potential window and electron transfer kinetics of graphene in 12CE, we now turn to using the DES as an electrolyte for metal (Zn) and metalloid (Ge) electrodeposition on the graphene.

We have recently studied the mechanism of zinc electrodeposition from ZnCl₂ in 12CE on various electrode materials including glassy carbon and Zn. It has been found that Zn deposition from ZnCl₂ in 12CE is a two-step process that first requires the formation of a reducible zinc species via ligand exchange with cathodic decomposition products of 12CE. In the second step, these newly formed zinc species are reduced during the anodic return sweep affecting zinc deposition. The explanation for this two-step process is that the otherwise dominating tetrachlorozincate ion [ZnCl₄]⁻ cannot be directly reduced within the potential window of 12CE. It was found that this process strongly depends on the electrode material and is additionally complicated by the blocking of the electrode at very cathodic potentials.

Typical cyclic voltammograms of ZnCl₂ in 12CE on graphene with variable cathodic switching potentials in Figure 4a show that graphene electrodes also generally conform to the above two-step process. A rather small current is observed on sweeping cathodically in ZnCl₂/12CE, which increases toward the switching potential (same as in the cathodic 12CE background curves in Figure 2a) during which the reducible Zn species is generated via 12CE decomposition. In the reverse anodic sweep in Figure 4a, a cathodic peak (“A”) is observed, which corresponds to Zn deposition from the in situ generated reducible Zn species. If samples are unloaded after this point, Zn deposition on the graphene is readily verified by SEM (Figure 4b), whereby additional EDX and XRD in Supporting Information Figure S5 confirm that the observed deposits are polycrystalline Zn. If, however, cycled further after cathodic Zn deposition (“A”), an anodic peak (“B”) appears, which corresponds to Zn stripping. Consistent with our prior cathodic background cycling in 12CE to such negative potentials (Figure 2a,b) also during the two-step potentiodynamic Zn deposition the graphene is severely degraded by generation of defects, as shown by the emergence of the defect-related D band in the Raman spectrum of a graphene electrode after Zn deposition in Figure 4c. At potentials negative from −0.5 V vs Zn/Zn²⁺, the 12CE electrolyte decomposes producing reactive radicals that attack the graphene. While the decomposition of the electrolyte is necessary for generating reducible zinc species, it also produces radicals that react with the graphene and thus decrease its conductivity.

An interesting observation we make from potentiodynamic Zn deposition (i.e., without anodic Zn stripping “B”) is that Zn exhibits a strong morphology gradient with respect to the distance from the electrolyte meniscus (Figure 4b, here shown for 10 voltammetric deposition cycles corresponding to Figure S5, see also Supporting Information Figure S6 for additional AFM and SEM data). Near the meniscus, a coherent, thick Zn coating on the graphene electrode is observed with an average thickness of about 1–2 μm (estimated from the side view SEM image in Supporting Information Figure S6). The SEM image at higher magnification and the AFM image in Supporting Information Figure S6 show that the coherent Zn coating is composed of an assembly of nanograins with an apparent average lateral size of about 100 nm, fully consistent with the polycrystalline nature of the deposits measured by XRD. With increasing distance from the electrolyte meniscus, the amount of deposited Zn drastically decreases. In the lower immersed third of the electrode, only individual Zn nanoparticles (≈ 100 nm lateral size and ≈ 50 nm height, Supporting Information Figure S6) on graphene can be observed. Given that the amount of deposited Zn decreases with increasing distance from the electrolyte meniscus (and also the nonimmersed graphene electrode’s silver epoxy contact), this points to a strong influence of an IR drop along the graphene layer during electrodeposition. The resistance of the graphene causes a potential drop along the graphene film that continuously

![Figure 4](image-url)
Figure 5. ZnCl$_2$ in 12CE: (a) Cyclic voltammograms with different cathodic switching potentials of 0.3 M ZnCl$_2$ in 12CE at a glassy carbon working electrode ($A = 0.07$ cm$^2$), $v = 10$ mV s$^{-1}$, Pt gauze auxiliary electrode, Zn/Zn$^{2+}$ RE. Arrow indicates sweep start in the cathodic direction. (b) Successive cyclic voltammograms of 0.3 M ZnCl$_2$ in 12CE on a graphene electrode ($A \approx 0.3$ cm$^2$) and on a zinc disk electrode ($A = 0.95$ cm$^2$), $v = 10$ mV s$^{-1}$, Pt gauze auxiliary electrode, Zn/Zn$^{2+}$ RE. Arrows indicate the sweep direction.

increases with the distance to the electrolyte meniscus/silver epoxy contact. This leads to a gradient of the local current density for metal deposition, which is reflected in the amount of deposited zinc decreasing with distance from the electrolyte meniscus. The situation is similar to the current density distribution in a Hull cell, which is caused by the inclined arrangement of the cathode. Similar results for inhomogeneous metal deposition on carbon electrodes have been achieved in bipolar electrochemistry. Furthermore, bipolar cathodic grafting of 4-bromobenzene on monolayer graphene films has produced similar results.

In our case, the gradient of the current density is the result of a combination of several factors. Initially, the internal resistance in the graphene layer (see the Supporting Information) causes an $iR$ drop with increasing distance from the connecting wire. This leads to a gradient for zinc deposited during the first cycle. This gradient then is enhanced from cycle to cycle, because, on the one hand, zinc will be deposited on zinc, which has an electric conductivity more than 5 times higher than graphene. On the other hand, the conductivity of the uncoated graphene is diminished by the chemical attack of radical species generated by the cathodic decomposition of the DES toward the rather negative switching potential of $-0.6$ V.

We note that on the lower third of the immersed graphene electrode below the electrolyte meniscus also signs of graphene delamination can be observed (Supporting Information Figure S7), again consistent with the Raman spectrum in Figure 4c pointing to severe graphene degradation during the sweeps to very negative potentials. The key impact of in situ graphene degradation during the negative sweeps is finally also corroborated, when observing that the amount of deposited zinc on graphene decreases with the cathodic switching potential becoming more negative, as shown in Figure 4a. The more negative the applied potential, the more the electrolyte is decomposed, which causes two opposing effects on the zinc deposition rate. On the one hand, the higher the decomposition rate of the electrolyte, the more reducible Zn species are formed from the decomposition products. A higher concentration of reducible Zn species will increase the Zn deposition rate during the anodic return sweep. The more reactive radical decomposition products are formed, on the other hand, the more defects are generated in the graphene, resulting in an increasing $iR$ drop. This in turn gradually decreases the effective overpotential of the electrode, slowing down both potential-dependent processes. As a result, the applied cathodic overpotential and the amount of Zn inversely correlate for graphene, as observed.

This behavior is in direct contrast to the electrochemical behavior observed on glassy carbon electrodes (Figure 5a). For the glassy carbon, the charge found for zinc deposition (and stripping) directly correlates with the cathodic overpotential. The more negative the switching potential on glassy carbon, the larger the extent of electrolyte decomposition, and thus the more zinc is deposited on the anodic return sweep. In contrast to graphene, glassy carbon electrodes are bulk electrodes in which the overall conductivity is not impeded by a possible defect-induced degradation of conductivity in the top-most atomic layer. The bulk of the electrode underneath can continue to transport sufficient charge for Zn deposition; that is, the overall conductivity of glassy carbon electrodes is hardly affected by defects in the first atomic layer. In contrast, for the truly two-dimensional graphene monolayers, defects in the top-most (and only) layer immediately decrease their overall conductivity. This shows that the two-dimensional nature of graphene has a key effect on its electrode properties in electrochemistry. While the general reaction pathway for zinc deposition upon variation of the cathodic switching potential for graphene and glassy carbon is found to be identical, the two-dimensional nature of graphene results in the two carbon materials showing opposite trends in terms of Zn deposition rate as a function of applied potential. This highlights that graphene can in principle be used to approximate the behavior of other graphitic carbon electrodes; however, graphene’s two-dimensional nature has to be kept in mind when doing so.

The unique impact of the two-dimensional nature of graphene on electrochemistry is also corroborated when considering that in our experiments the generation of defects in graphene monolayers did not improve their electrochemical activity. Although defects might increase the density of electronic states at the Fermi level and thus the rate of heterogeneous electron transfer, the decrease of conductivity in the 2D material negates this effect. This is in stark contrast to the commonly observed behavior for the graphene bulk analog HOPG, for which defect generation in the HOPG basal plane improves electrochemical activity.

Further insight into the build-up of the Zn layer on graphene can be obtained by studying the consecutive voltammetric cycles shown in Figure 5b, where the zinc is not anodically...
onto bulk Zn electrodes, where an exemplary cycling curve is shown in Figure 5b (green dashed). Thus, the data in Figure 5b evidence the changeover from a two-dimensional graphene to a three-dimensional Ge phase with increasing cycle number. In turn, also graphene degradation is less severe, and the graphene electrode can be cycled several times without diminishing current densities. In doing so, we find that the deposition current increases from cycle to cycle, and with increasing cycle number, a deposition peak is not only observed on the anodic return sweep, but increasingly also on the cathodic forward sweep. Moreover, these peaks residing on an increasing background current develop a pronounced triangular shape from cycle to cycle. Such a triangular shape was previously found for Zn deposition from ZnCl₂/12CE onto bulk Zn electrodes, where an exemplary cycling curve is also shown in Figure 5b (green dashed). Thus, the data in Figure 5b evidence the changeover from a two-dimensional graphene electrode that with increasing Zn coverage becomes increasingly more similar to a bulk Zn electrode in its electrochemical properties in agreement with the previous observations for the zinc gradient (Figure 4b). The shift of the peak maxima toward negative potentials with increasing peak current from cycle to cycle for the graphene electrode as shown in Figure 5b can be attributed to a slowly increasing iR drop from an increasing number of defects in the graphene with an increasing cycle number.

**Electrodeposition of Germanium.** Our results on Zn electrodeposition generally show that electrochemical deposition routes that require very negative potentials in 12CE are nonideal for monolayer graphene electrodes, because in parallel to metal deposition also graphene degradation readily occurs. Precursors in 12CE that require less negative potentials for deposition, however, may circumvent any graphene degradation. To test this hypothesis, we finally investigate deposition of Ge from TBAGeCl₃ in 12CE.

In Figure 6a (red) we find that for TBAGeCl₃ in 12CE on graphene, the onset of reduction is at 0.115 V versus Zn/Zn²⁺. This is by far less negative than that of Zn(II) and well within the above established potential window of graphene in 12 CE. No clear reduction peak for TBAGeCl₃ on graphene is observed (Supporting Information Figure S9), but only a steady increase of the cathodic current with a nucleation overpotential of about 150 mV. As shown by SEM in Figure 6b, this electrochemical behavior corresponds to successful Ge deposition on the graphene (here shown after potentiostatic Ge deposition at −0.3 V for 260 s). In contrast to the Zn deposition, no gradient in the amount of deposited Ge with respect to the macroscopic distance from the electrolyte meniscus is observed. Instead, we find the same Ge morphology near and far from the electrolyte meniscus. As seen in the SEM images in Figure 6b, the Ge is composed of individual islands with lateral sizes ranging from ≈ 100 nm to ≈ 800 nm while having a rather uniform height of ≈ 50 nm (AFM in Supporting Information Figure S8). These individual islands start to form a coherent layer at longer deposition times (Figure 6d, potentiostatic deposition at −0.3 V for 7000 s). Corresponding AFM data is plotted. (b) SEM image of a graphene electrode with potentiostatically deposited Ge. (c) Raman spectrum of a graphene electrode with potentiostatically deposited Ge. (d) SEM image of a graphene electrode with potentiostatically deposited Ge (−0.3 V for 7000 s).

in agreement with our hypothesis that electrodeposition from 12CE at moderate cathodic potentials can readily be carried out on graphene without degradation of the graphene quality. The absence of a gradient in the Ge deposit homogeneity along the electrode length, combined with the retained high graphene quality observed in Raman after Ge deposition, corroborates our above suggestion that the defect formation in graphene at strongly cathodic potentials (as observed for potentiodynamic Zn deposition) is the compounding factor to cause a large enough iR drop, which results in a macroscopic...
deposit gradient (as observed above for Zn). A second factor that affects the local current density during Ge deposition probably is the electric conductivity of germanium. In contrast to zinc, the conductivity of germanium is smaller by six orders of magnitude compared to that of the graphene monolayer.

As a result, the local current density on the uncoated graphene area increases during the deposition, favoring two-dimensional growth of Ge with uniform thickness (Supporting Information Figure S8) toward the formation of a coherent layer (Figure 6d).

The cyclic voltammogram for Ge electrodeposition on graphene (Figure 6a, red) shows a steady increase of cathodic current and a nucleation overpotential/loop. In contrast, on glassy carbon (Figure 6a, black) a clear reduction peak at 0.052 V vs Zn/Zn²⁺ without significant nucleation overpotential is seen. This difference between the two electrode materials suggests that nucleation is more difficult on the graphene compared to the glassy carbon. This could be related to a higher nucleation barrier on the structurally highly defined graphene basal plane compared to the less defined glassy carbon surface.

A close inspection of the Ge islands shown in Figure 6b and Supporting Information Figure S8 supports this hypothesis, as we find several examples (white arrows) where Ge nanoparticles nucleated preferentially over wrinkles in the graphene film instead of on the basal plane. Wrinkles are known to be preferred sites for nucleation of ad-deposits on graphene because of their higher electrochemical activity and surface energy compared to the graphene basal plane.

Thereby our observations confirm that also for a DES such as 12CE graphene’s higher reactivity sites such as wrinkles show variations in their electrochemical properties compared to the graphene basal plane, which translate to spatial differences in electrodeposition.

**CONCLUSIONS**

In summary, we have determined the potential limits of graphene monolayer electrodes in neat 12CE upon cathodic and anodic sweeps and elucidated apparent electron transfer kinetics of the outer-sphere ferrocene/ferrocenium couple. We suggest that the observed lower stability in the cathodic regime is linked to electrochemical formation of radicals during choline reduction, which attack and degrade the monolayer graphene. By comparison to common glassy carbon bulk electrodes, we have found that the two-dimensional nature of our graphene electrodes critically impacts DES electrochemistry. For potentiodynamic Zn deposition from ZnCl₂ in 12CE, for instance, a significant iR drop over the length of the graphene electrode, which is enhanced by the aforementioned radical attack, resulted in spatially graded amounts of deposited Zn. The spatial inhomogeneity of the zinc deposits and the graphene degradation are interrelated via graphene’s two-dimensional nature in which defects generated in the topmost (and only) layer decrease the overall electrode conductivity. This is in stark contrast to bulk carbon electrodes such as glassy carbon or HOPG for which the overall conductivity is hardly affected by defects in the topmost atomic layer and for which generated defects might even increase their electrochemical activity. For graphene in DESs, both the graphene degradation and the spatial inhomogeneity of deposits can however be avoided by potentiostatic deposition at less cathodic potentials. This was demonstrated by uniform electrodeposition of Ge from TBAGeCl₂ in 12CE onto graphene monolayer electrodes without any degradation of the graphene. Combined, our work highlights that while some aspects of the electrochemical behavior of graphene in 12CE are similar to those of bulk carbon materials such as glassy carbon or HOPG, other aspects in the graphene/12CE system are unique, because of graphene’s two-dimensional nature. These findings merit consideration for processing of graphene and related carbon (composite) materials in choline chloride-based DESs and for the application of these materials in such electrolytes.

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**ASSOCIATED CONTENT**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c11467.

Calculation of iR drop, optical microscopy, cyclic voltammograms with Randles–Sevck plot, Raman and EDX spectra, X-ray diffraction patterns, additional SEM data, and AFM data (PDF)

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**Notes**

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