Mechanism of Electrochemical Hydrogenation of Epitaxial Graphene

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Mechanism of electrochemical hydrogen adsorption on epitaxial graphene (EG) was observed to be dependent on defects in EG as observed by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and Raman spectroscopy. To determine the material dependence on electrochemical hydrogenation, a set of different EG samples (Si-face EG [∼2 ML], C-face EG [∼10 ML], M-plane EG [∼25 ML], defective Si-face EG [∼50 ML]) and a graphite disk [∼500 ML] were characterized using a home built electrochemical cell developed in previous work, dilute perchloric acid (HClO4 solution, silver/silver chloride (Ag/AgCl) reference electrode in saturated KCl (0.198 V vs. NHE) and potentiostat. The Nyquist plots obtained from EIS of epitaxial graphene with low defect density showed only one semicircle covering the entire frequency range attributed to adsorption of hydrogen at the relatively chemically inert basal plane surface and further supported by lack of hydrogen peaks in the CV. Samples with high defect density showed an additional semicircle at the intermediate to high frequency ranges linked to adsorption and charge transfer of hydrogen to graphene. The increased presence of point defects in epitaxial graphene augments the surface area of the material resulting in increased diffusion of hydrogen ions though the graphene lattice allowing for hydrogen to adsorb to additional sites within the lattice.© The Author(s) 2015. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.0191504jes] All rights reserved.

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Carbon materials are commonly used as electrodes due to their relatively low cost, chemical inertness, hardness and good electrical conductivity compared to expensive catalytic metals. Modifications, coating with catalytic metals, carbon coatings and carbon activation have been used to increase electrical conductivity, surface area and overall performance of carbon electrodes, though preparation of such electrodes require costly materials and/or equipment, making these techniques difficult to scale up from a manufacturer standpoint. Carbon electrodes like carbon nanotubes (CNT) and graphene are ideal in fuel cell and double layer capacitor electrodes having both high electrical conductivity and surface area.1–5

Graphene is a single atomic layer of carbon atoms arranged in a hexagonal lattice. Another way to look at this 2D carbon is as the planer version of 1D carbon nanotubes (CNT), and a single layer of bulk 3D graphite.13 Because of this 2-dimensionality, graphene also has an exceptionally high surface area of 2630 m² g⁻¹ due to every atom in the layer being exposed to the environment. This is compared to bulk graphite which is much lower at <10 m² g⁻¹ and CNT at half the surface area of graphene at 1315 m² g⁻¹.13 Graphene also has high electrical and thermal conductivity, high room temperature mobility (>15,000 cm²/V s)14 and high tensile strength due to the C-C bond.15–17 Characteristics that make it an appealing material for electrodes18–23 and ultra-sensitive sensors.24,25

An electrochemical cell using a dilute acidic solution as electrolyte was used to observe proton chemistries where atomic hydrogen is attracted to a negatively biased graphene electrode. Incorporation of hydrogen into the graphene lattice was not only possible by electrochemistry but also electrochemically reversible26 as observed by Raman spectroscopy, giving possibilities of not only inducing a substantial bandgap in the material, as supported by theory, but implications of graphene as a stable electrode and hydrogen storage medium.

Degree of hydrogenation was suspected to be either dependent on the underlying SiC, more specifically on the off-cut angle in the 11–20 direction, or on the quality of starting EG, where hydrogenation may be due at least partially to defects.26 To further understand this dependence, the electrochemical characteristics of these electrodes are studied. To test the electrochemical characteristics of the graphene electrodes and further understand the nature of graphene for its use as an electrode material, Raman spectroscopy, cyclic voltammetry and electrochemical impedance spectroscopy will be used. Cyclic voltammetry (CV) is used to determine the potential(s) of oxidation and reduction displayed as extrema points, where electron transfer mechanisms as well as adsorption processes between the working electrode and the analyte are observed.26 Electrochemical impedance spectroscopy (EIS) is used to not only acquire information regarding the electrolyte/electrode interface but kinetics and reactions that take place with the electrode.27 To determine the material dependence on electrochemical hydrogenation four different EG samples (Si-face EG [∼2 ML], C-face EG [∼10 ML], M-plane EG [∼25 ML] and defective Si-face EG [∼50 ML]) and a smooth graphite disk [∼500 ML] were characterized by Raman spectroscopy, CV and EIS.

Experimental

Growth of EG (Si-face, C-face and M-plane EG) was prepared by thermal decomposition of Si from SiC from different substrates in vacuo, <10⁻⁵ Torr, using an RF furnace previously described in more detail.30 Defective Si-face EG was grown using a vertical hot-wall CVD reactor using SiF₄ to grow defect engineered graphene (DEG).39

10 × 10 mm² 6H SiC semi-insulating samples were chemical-mechanical polished (CMP) and thoroughly cleaned using standard RCA clean (Trichloroethylene [TCE], acetone, methanol) and HF to remove any native oxide.

Raman spectroscopy was used to determine the defect density of grown EG. Raman was performed using a micro-Raman setup with laser excitation wavelength at 632 nm and a spot size of ∼2 μm. The system was calibrated using the known Si peak at 520.7 cm⁻¹. Reference blank SiC substrate spectra were scaled appropriately and subtracted from the EG/SiC spectra to show only the graphene and functionalized graphene peaks.31,32 All the spectra shown are difference Raman spectra obtained in this manner. There are three peaks associated with graphene: The D peak (∼1345 cm⁻¹) corresponds to disorder and presence of defects in the material, The G peak (∼1595 cm⁻¹) corresponds to the in plane vibration of the graphene lattice and the 2D peak due to double resonance.32 Defect density of each sample was calculated using the relation
\[ n_D (\text{cm}^{-2}) = (1.8 \times 10^{22}/\lambda^4) \ast (I(D)/I(G)), \]

where \( \lambda \) is the excitation wavelength of the Raman and \( I(D)/I(G) \) is the ratio between the peak intensity of the D and G peak.

Electrochemical measurements were carried out in 1.84 M HClO4 using a three electrode home-built electrochemical cell where a 99.6% Pt wire and exposed EG (approximately a 4 mm diameter circular area) were used as the anode and cathode, respectively with an Ag/AgCl saturated in KCl (0.198 V vs. NHE) reference electrode. A potentiostat (Series GTM 300, Gamry Instruments, Warminster, PA, USA) was used for CV and EIS measurements. CV was performed to determine oxidation and reduction potentials at a scan rate of 50 mV s\(^{-1}\). Spectra from EIS were measured over frequencies ranging from 300 kHz down to 0.1 Hz as a function of time and potential with a perturbation signal of 10 mV. Since system stability is important for obtain accurate data, impedance measurements were taken after reaching a system steady state after holding the potential constant.

**Results and Discussion**

Figures 1a–1d and 2a–2d shows Raman and CV data respectively obtained from various carbon materials, bulk graphite, C-face graphene, Si-face graphene and defective Si-face graphene. In the Raman, Figure 1, defect density was extracted from \( I(D)/I(G) \) ratio. In the CV, Figure 2, hydrogenation peak position decreased with increasing defect density from -125 mV with the Si-face EG (Figure 2c) to -275 mV in graphite disk (Figure 2a) followed by -300 mV observed in the defective Si-face EG (Figure 2d) vs. Ag/AgCl.

Oxidation and hydrogenation peaks observed in the CV of the graphite disk, Figure 2a, were not well defined. With defect density of \( 10^{11} \text{ cm}^{-2} \) as derived from an \( I(D)/I(G) \) ratio of 0.89 from Figure 1a, EIS spectra of the graphite disk, Figure 3a, indicated high diffusion in the intermediate frequencies but the lack of semicircle in the high frequency, Figure 3b, showed no significant features most likely due to ion inaccessibility to the bulk graphite layers. To test this hypothesis further, we look at a sample with very low defect density.

C-face EG CV, Figure 2b, showed an absence of hydrogenation peak most likely due to the lack of point defects in the material as \( I(D)/I(G) \) was measured at 0.001, Figure 1b, with a resulting defect density of \( 9 \times 10^9 \text{ cm}^{-2} \). This suggests inaccessibility of hydrogen ions through the basal plane of graphene and that grain boundaries in the material are not as electrochemically active as vacancies as previously thought and that functionalization is dependent instead on the presence of point defects in the material. This is further supported by a straight line in the high frequency regime in the EIS Nyquist plot, Figure 4b, showing surface adsorption of hydrogen to the graphene electrode but little charge transfer, or C-H bonding, similarly observed with closed carbon nanotubes. The large charge transfer resistance observed in EIS showed the system as being kinetically slow, likely due to inaccessibility of hydrogen ions through the chemically unreactive basal plane of graphene.

Si-face EG CV, Figure 2c, showed a sharp hydrogenation peak most likely due to point defects present in the material, \( I(D)/I(G) \sim 0.08 \) and a defect density an order of magnitude greater than C-face EG at \( 9 \times 10^9 \text{ cm}^{-2} \) as shown in Figure 1c. This is further supported by the plateau observed in the high frequency regime in the EIS Nyquist plot, Figure 5b showing charge transfer from hydrogen ions to the graphene electrode. The large charge transfer resistance shown in the EIS, Figure 5a however, shows the system is kinetically slow.

Defective Si-face EG, Figure 6b, with an \( I(D)/I(G) \) ratio of 1.7 and defect density of \( 1.92 \times 10^{11} \text{ cm}^{-2} \) obtained from Raman in Figure 1d, further supports dependence on the presence of defects...
Figure 2. Cyclic voltammetry of (a) graphite disk, (b) C-face EG, (c) Si-face EG and (d) defective Si-face EG. No hydrogenation peak was observed for C-face EG (b). Hydrogenation peaks were present with peak position decreased with increasing defect density from $-125$ mV with the Si-face EG (c) to $-275$ mV in graphite disk (a) followed by $-300$ mV observed in the defective Si-face EG (Figure d) vs. Ag/AgCl.

Present in the material, as the system revealed a second semicircle in the high frequency regime along with the first semicircle, Figure 6a. The diameter of the semicircle revealed a kinetically fast system with ample sites for hydrogen to diffuse and adsorb within the graphene lattice. This conclusion is maintained by the CV, Figure 2d, showing a hydrogenation peak at $-300$ mV vs. Ag/AgCl. This data suggests that there may not be a substrate to substrate dependence in electrochemical functionalization but a dependence on the quality of the EG film grown on it, with more defective EG ideal for electrochemical hydrogenation. To obtain quantitative information regarding the EIS data, an electrochemical model was designed to accurately model the resistive and capacitive nature of the electrochemical cell.

Based on oxidation and reduction points observed in CV, we suspect hydrogen to be the only adsorbed species in the system. For a single adsorbed species, in our case hydrogen, we modeled the electrochemical cell from the equivalent circuit for the case of one adsorbed species. A Warburg element was added to take into account diffusion of ions in the electrolyte through the graphene lattice. In the electrochemical impedance model in Figure 5, $R_s$ represents the solution resistance; $C_{dl,CPE}$ is the double layer capacitance as a constant phase element to account for surface roughness and nonuniform distribution of reaction sites in the electrode; $R_{ct}$ is the charge transfer resistance; $W$ is the Warburg element; $R_{ad}$ is the resistance formed by adsorbed species on the working electrode; $C_{ad}$ represents the adsorption pseudocapacitance of the adsorbed species; $R_s, R_{ad}, C_{ad}$ represent non-idealities in the electrochemical cell manifested as additional time constants in the electrochemical reaction. The complete model is shown in Figure 7. As shown by the red fit lines in Figures 3–6 the Nyquist plots of the electrodes agree with this model.

The resulting charge transfer and adsorption resistance obtained from the EIS model fit was plotted as a function of electrode defect density, Figure 8. A dependence on charge transfer and adsorption and
Figure 4. Electrochemical impedance spectroscopy of (a) full Nyquist plot of low defect C-face EG with impedance model fit. C-face EG showed surface adsorption as evident by the semicircle in the low frequency but the lack of ion diffusion as shown in the intermediate frequency and (b) linearity of the Nyquist plot in the high frequency regime.

Figure 5. Electrochemical impedance spectroscopy of (a) full Nyquist plot of Si-face graphene with impedance model fit with a semicircle in the low frequency attributed to hydrogen adsorption. In the high frequency regime (b) charge transfer of hydrogen ions are apparent by a plateau before the adsorption semicircle in the low frequency regime.

Figure 6. Electrochemical impedance spectroscopy of (a) full Nyquist plot of defective Si-face graphene with impedance model fit showing the second semicircle in the intermediate and low frequency regime (b) high frequency Nyquist range of defective Si-face graphene with impedance model fit showing the first semicircle in the high frequency regime.
defect density is established, with increasing defect density resulting in decreases in both resistances. This can be attributed to better ion diffusion through defects over pristine EG resulting in additional sites for hydrogen to adsorb and form C-H bonds as compared to the inert basal plane of EG.

This hypothesis is further supported by increases in Warburg impedance suggesting higher diffusion in more defective electrodes in Figure 9. Additional adsorption sites for hydrogen are supported by increases in double layer capacitance with increasing defect density as shown in Figure 10. With more ions on the electrode as shown with the Warburg and double layer capacitance, one would expect the resulting adsorption capacitance to also increase with defect density. The pseudocapacitance represents the capacitance formed by adsorption of ions on the electrode surface. As shown in Figure 11, an increase in adsorption capacitance is observed when defect density increased. When defect density is increased further, adsorption capacitance decreased by two orders of magnitude. This is caused by an increase in internal surface area greater than the external surface area, where defects at as micropores allowing ions access to underlying monolayers of graphene. This, however, results in an increased contribution from double layer capacitance as observed in Figure 10. To see this effect further, total capacitance of the electrochemical cell, capacitance derived from CV and specific capacitance was calculated.

Specific capacitance, or capacitance per unit weight, was calculated by integrating under the curve obtained from cyclic voltammetry for each electrode, then dividing by the scan rate and the electrode weight. Since graphene is grown on an insulating SiC substrate,

Figure 8. Adsorption and charge transfer resistance extracted from EIS impedance model showing a dependence on defect density where increasing defect density resulted in decreases in both resistances.

Figure 9. Warburg impedance normalized to a single graphene monolayer with diagram of ion diffusion into graphene. Diffusion is shown to increase with increasing defect density.

Figure 10. Double layer capacitance normalized to a single graphene monolayer with diagram of charges separated by small space on the order of angstroms. Double layer capacitance increased with increasing defect density with access to more hydrogen ions from the solution through the defects in the material.

Figure 11. Adsorption capacitance normalized to a single graphene monolayer with diagram of adsorbed surface charges forming a pseudocapacitance capacitance between surface charges and the graphene surface. Adsorption capacitance increased with increasing defect density. The sharp decrease in adsorption capacitance observed at high defect density corresponds directly to a sharp increase in double layer capacitance.
only the weight of the graphene is considered. Capacitance obtained from cyclic voltammetry was found to be in close agreement with the effective capacitance of the electrodes obtained from fits of the EIS model data for electrode. As observed in Table I, specific capacitance increases with increasing defect density, further evidence that graphene’s performance as an electrode and the degree of hydrogenation electrochemically are dependent on defect density.

**Conclusions**

Mechanism of hydrogen adsorption of epitaxial graphene was observed to be dependent on point defects in the material as observed by cyclic voltammetry, electrochemical impedance spectroscopy and Raman spectroscopy. Cyclic voltammetry revealed a dependence on point defects in the appearance of a hydrogenation peak, who’s existence and position is dependent on defect density. A secondary peak at 325 mV vs. Ag/AgCl was also observed though this peak is most likely attributed to number of carbon layers as it was only observed with bulk graphite (>500 ML) and defective Si-face EG (>50 ML) An impendence model of the electrochemical cell was derived from EIS measurements which allowed for resistance and capacitance parameters to be extracted. Increasing defect density revealed decreases in charge transfer and adsorption resistances and increases in diffusion of ions (Warburg) and double layer capacitances. High defect density ultimately revealed a sharp decrease in adsorption capacitance or pseudocapacitance as a result of an increase in internal surface area of the electrode higher than that found externally caused by defects and higher diffusion of ions into the electrode. Capacitances obtained by the EIS model, effective capacitance, matched closely with capacitances obtained by CV, integrated capacitance and calculated specific capacitance (F/g) was found to increase with increasing defect density. Engineering defects EG layers presents a new pathway to the formation of hydrocarbons and its use in supercapacitors, batteries and fuel cell electrodes.

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