PAPER

Interfacial capacitance of single layer graphene

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The interfacial capacitance of large area, single layer graphene was directly measured with electrolyte accessing both sides of the graphene sheet. PMMA and photoresist patterns were used as supports to suspend the CVD grown graphene in electrolyte during electrochemical testing. Both one and two sides of single layer graphene films were measured and compared. The results show that the area normalized charge that can be stored simultaneously on both sides is significantly lower than could be stored on just one side of single layer graphene, consistent with charge storage having a quantum capacitance component. These measurements are also consistent with the specific capacitance of graphene materials as previously measured in supercapacitor cells and provide a basis for the further understanding and development of graphene based materials for electrical energy storage.

Introduction

Supercapacitors based on electrochemical double-layer capacitance (EDLC) are electrical energy storage devices that store and release energy by nanoscopic charge separation at the electrochemical interface between an electrode and an electrolyte.[1] While the energy density of supercapacitors is very high compared to electrostatic and electrolytic capacitors, it is much lower than batteries and fuel cells. Coupling with batteries (or another power source) is still required for supplying energy for longer periods of time. Thus, there is a strong interest, *e.g.*, as enunciated by the U.S. Department of Energy, for increasing the energy density of supercapacitors to be closer to the energy density of batteries.[2] A supercapacitor's energy density is primarily determined by the cell's electrode material and oper-

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ating voltage. An electrode material's storage capacity in turn is based on its interfacial double-layer capacitance (uF/cm^2) and its surface area (m^2/g). There is thus an interest in developing very high surface area electrode materials. Graphene has a theoretical surface area of 2630 m^2/g, and various graphene derived materials have been reported for supercapacitor electrodes, specifically: chemically reduced graphene oxide,[3] graphene oxide reduced in propylene carbonate,[4] microwave exfoliated graphite oxide,[5] and a novel carbon produced by the chemical activation of graphene.[6]

For very high surface area materials such as graphene, it is critical to understand the components that affect interfacial capacitance and the resulting charge that can be stored. It has been reported that interfacial capacitance for high surface area carbons has a space charge component[7,8] and, with the application of graphene and ultrathin layers of other carbons to supercapacitors, it may be a primary factor in describing the energy storage capacity of these new classes of materials. Indirect calculations of the interfacial capacitance of multilayer graphene[9] and the direct measurement of the interfacial capacitance

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Broader context

Energy storage is one of the major challenges to efficiently capturing, storing and utilizing energy from various renewable energy sources. It is also the major constraint to widespread adoption of hybrid electric vehicles. Supercapacitors and secondary batteries are two main devices for storing electricity. A supercapacitor electrode's interfacial capacitance and its surface area determine its energy storage capacity. Graphene, with a theoretical surface area of 2630 m^2/g, is a promising material with a rapidly increasing volume of research in recent years investigating its use for supercapacitor electrodes. To date, the primary focus has been on developing graphene materials with increased surface area. In this study we measure, for the first time, the interfacial capacitance of both sides of single layer graphene and show that in addition to surface area, graphene's electronic properties play a crucial role in its storage capacity. Understanding of the components that affect interfacial capacitance and the resulting charge that can be stored is critical to the future development of graphene for electrical energy storage applications.

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on one side of single layer graphene supported by a SiO$_2$ surface[10] have been reported. This latest study by Xia, *et al.* reported that as graphene materials become thinner, with the limit being single layer graphene, the interfacial capacitance is dominated by the quantum capacitance of the solid side of the interface. However, to fully utilize graphene's available surface area in a super-capacitor electrode, the electrolyte should simultaneously access both sides of single atom thick sheets, and to our knowledge, direct interfacial capacitance measurements of graphene in this configuration have yet to be reported. In this study, the interfacial capacitance with both sides of large area graphene accessed by the electrolyte, as would be the configuration that maximizes the surface area of graphene in an actual supercapacitor electrode, was measured.

Experimental

Graphene growth and transfer to electrochemical cell

Large area single layer graphene was grown by chemical vapor deposition (CVD) on a Cu substrate. The growth method is given in detail elsewhere[11] but briefly the graphene films were grown on 25 um thick copper foil (Alfa Aesar, item No. 13382, cut into 1 cm strips) in a hot wall furnace consisting of a 22 mm inside diameter fused silica tube heated in a split tube furnace. The process flow is 1) load the fused silica tube with the copper foil, evacuate, back fill with hydrogen, heat to 1000 °C and maintain a H$_2$ (g) pressure of 40 mTorr under a 2 sccm flow; 2) stabilize the Cu film temperature at 1000 C, and introduce 35 sccm of CH$_4$ (g) for 30 min at a total pressure of 500 mTorr; and 3) after exposure to CH$_4$ (g), the furnace is cooled to room temperature.

For electrochemical testing, the graphene must be transferred from the Cu growth substrate to an electrochemical cell without compromising the film. The schematic of the process flow is shown in Fig. 1. As stated above, two cell configurations were used for capacitance measurements. The first was with the electrolyte accessing just one side of the graphene sheet, the second with both sides of the graphene exposed simultaneously to the electrolyte. To form a single sided graphene working electrode, a continuous film of PMMA was used to cover each edge and one side of the graphene coated copper foil. PMMA powder (M$_w$ 996000, Sigma Aldrich) was dissolved in chlorobenzene (Sigma Aldrich) and the resulting PMMA solution (100 mg/ml), was applied to the edges and backside of the graphene coated copper foils by dipping the foil edges into the solution and by dropping

a thin coating of the solution onto the top of the foil, respectively, and allowing it to dry in ambient. The copper that was not covered by PMMA was then etched away by immersing the foil in a bath of ammonium persulfate (0.1 M, Sigma Aldrich). Upon the removal of the copper, the ammonium persulfate was exchanged with DI water without removing the PMMA supported graphene from the liquid to prevent disruption of the graphene film due to capillary forces. Finally, sulfuric acid was added to form 4 M electrolyte along with the insertion of Ag reference and Pt mesh counter electrodes to form the three-electrode cell for electrochemical testing.

To form the two-sided graphene working electrode, a graphene coated copper foil was taped along its edges to a flat silicon substrate for photo resist patterning. Aluminum foil spacers were placed between the copper and silicon substrate to elevate the graphene/copper surface above the edges of the tape. The surface was treated with HMDS and spincoated (5000 rpm, 35 s) with a 7 um thick film of photoresist (AZ 9260). The resist was patterned with an array of 8 um square windows (Karl Suss MA6 mask aligner, chrome mask from Colorado Nanofabrication Lab, AZ 726 MIF developer). To ensure complete removal of the photoresist from the open areas, the resist was "overexposed" and "overdeveloped" by increasing the process times approximately 20% above nominal values. Fig. 2 shows a photo of the patterned graphene/copper foil taped onto the Si substrate and Fig. 2 (inset) shows an optical microscope image of the photo-resist pattern. The area of the graphene that is open (not covered by photo resist) is 55% as verified by high-resolution scanning electron microscope measurements. After patterning, the graphene/copper foil was removed from the silicon support, the edges trimmed and coated with PMMA and the Cu was etched away by the same processing as for the single sided graphene electrode.

A graphene sample from the same CVD batch was transferred directly to a glass substrate for Raman analysis. A second graphene/Cu foil sample was subjected to the full photo resist process as described above with the photoresist then removed with acetone and also transferred to a glass slide. Fig. 3 shows typical Raman spectra (WiTec Alfa 300 Micro-Raman, 532 nm) of the two graphene samples. Both have features typical of monolayer graphene with an approximately 0.5 G to 2D band
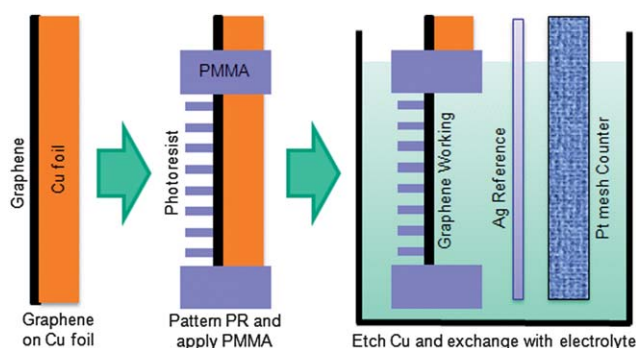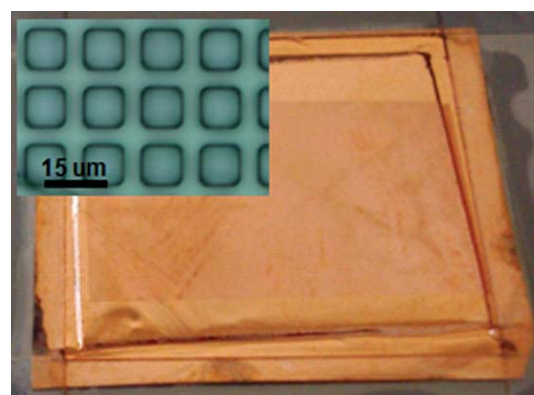

Fig. 1 Graphene electrode process flow.

Fig. 2 Graphene/Cu foil mounted on Si substrate and (inset) optical microscope image of photoresist pattern.
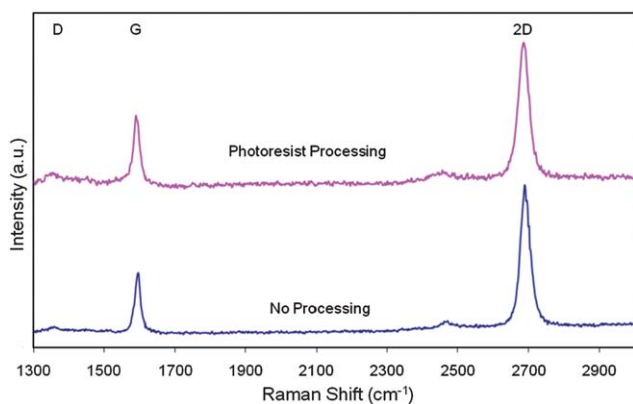
Fig. 3 Raman spectra of graphene subjected to full photoresist process (top) and as grown with no processing (bottom).

intensity ratio and a symmetric 2D band centered at ∼2680 cm⁻¹ with a full width at half maximum of ∼34 cm⁻¹.

Electrochemical measurement

Electrochemical measurements were performed with an Eco Chemie Autolab PGSTAT100 potentiostat equipped with the FRA2 frequency response analyzer module and GPES/FRA software. Cyclic voltammograms were first performed with each electrode to verify the lack of any non-linearity that would indicate the presence of contamination or non-faradic activity. The interfacial capacitance was measured using electrical impedance spectroscopy (EIS). EIS was done using a sinusoidal signal with amplitude of 10 mV over a frequency range of 100 kHz to 1 Hz. Capacitance values at each potential were determined by fitting the EIS spectra to an R(RC) equivalent circuit using Nova analysis software (version 1.5, Eco Chemie). The specific capacitance reported is the capacitance divided by the graphene surface area exposed to the electrolyte. The baseline capacitance was also measured on a smooth Pt surface to determine the background interfacial capacitance contribution from the electrolyte side of the solid/liquid interface.

Results and discussion

The capacitance behavior of a solid with a limited density of mobile charge carriers can be represented by a series of two capacitors, one representing the quantum capacitance of the solid, in this case graphene, the other the electrolyte capacity consisting of the Helmholtz double layer C_H, and the diffuse double layer C_{Diff}. The total capacitance for the interface (or the capacitance that is measured experimentally) is then given by.[12]

$$1/C_{Interface} = 1/C_Q + 1/C_H + 1/C_{Diff} \quad (1)$$

In concentrated electrolytes, $C_{Diff} \gg C_H$ and therefore C_{Diff}^{-1} in eqn (1) can be neglected. The quantum capacitance of mechanically exfoliated graphene was recently studied using a three electrode electrochemical cell with ionic liquid and the results supported that the interfacial capacitance for graphene-based electrodes does have a quantum origin.[10] For bulk metal electrodes, the liquid side of the interface dominates the
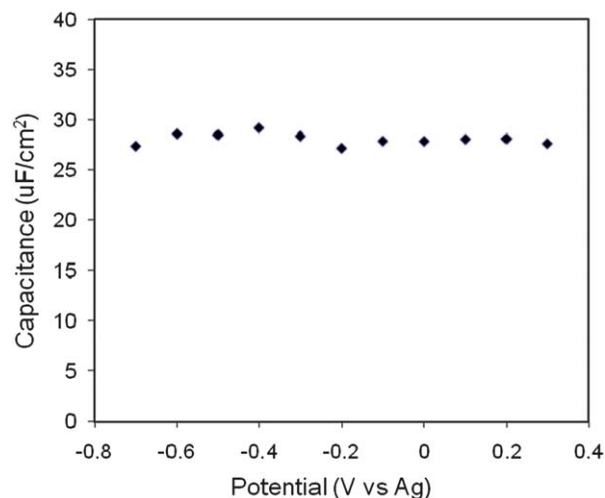

Fig. 4 Measured interfacial capacitance for Pt surface.

interfacial capacitance. To get a baseline for the liquid side, the capacitance of a smooth Pt surface was measured using the same electrolyte, Ag reference, and Pt mesh counter electrodes that were used for the graphene electrochemical measurements. As shown in Fig. 4, the capacitance values have an average of about 28 uF cm⁻², are relatively independent of the electrode potential, and are in good agreement with similar experiments in the literature.[13] The quantum capacitance of single layer graphene can be given by

$$C_Q \approx e^2 \frac{2}{\pi} \frac{eV_{ch}}{(\hbar v_F)^2} = \frac{2e^2}{\hbar v_F \sqrt{\pi}} \sqrt{n} \quad (2)$$

where $\hbar$ is the Planck constant, e is the electron charge, $V_{ch} = E/e$ is the potential of graphene, k_B the Boltzmann contant, $v_F \approx c/300$ the Fermi velocity of the Dirac electron, and n is the charge carrier concentration.[10] The quantum capacitance has a minimum value that is close to zero at the Dirac point, and as shown in Fig. 5, the capacitance increases linearly with potential with a slope of about 23 uF cm⁻¹ V⁻¹ on each side of the Dirac point.
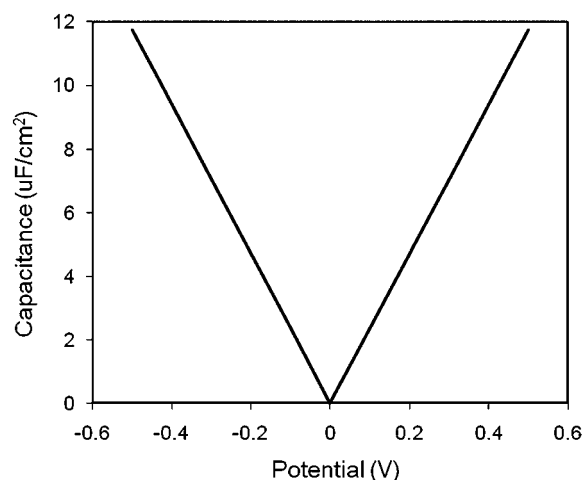

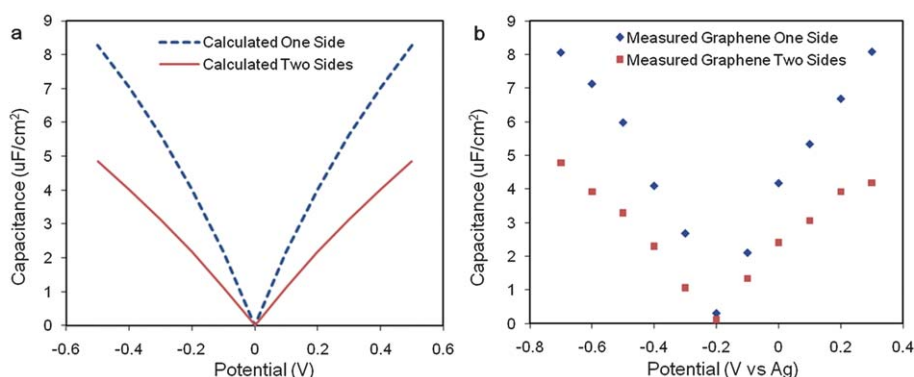**Fig. 5** Quantum capacitance for single layer graphene.

Fig. 6 (a) Calculated interfacial capacitance for one and two sided graphene, and (b) measured interfacial capacitance for one and two sided graphene.

Fig. 6a shows the interfacial capacitance calculated using eqn (3) using the measured interfacial capacitance for Pt for C_H and the quantum capacitance for graphene from eqn (2). The capacitance was calculated separately for electrolyte on one and two sides of the graphene; for two sides C_{H1} was set equal to C_{H1} and for one side C_{H2} was set equal to zero.

$$1/C_{Interface} = 1/C_Q + 1/(C_{H1} + C_{H2}) \qquad (3)$$

Fig. 6b shows the experimentally measured interfacial capacitance for one and two sides of the single layer graphene film. The experimental results correspond very closely to predicted curves in Fig. 6a. The overall magnitudes, as well as the slopes of the curves, match very closely. Both graphs show a similar dependence on the electrode potential with distinct minima. The potential of the measured values are shifted with the potential of zero charge at approximately −0.2 V which is consistent when using an Ag reference electrode.[14] This correlation supports that the capacitance is governed significantly by the electronic properties of the graphene, in addition to the properties of the solution side of the interface. The results show the interfacial capacitance becomes increasingly limited by the quantum capacitance as the graphene surface area is increased. These results are consistent with reported results from the literature that show that even large increases in surface area for graphene based materials have not yielded a corresponding linear increase in energy storage capacity. In 2008, graphene based electrodes with 705 m²/g surface area yielding 99 F/g in organic and 135 F/g in aqueous electrolyte were reported.[3] More recently, electrodes made from activated graphene material with 3100 m²/g surface area and a capacity of 155 F/g in organic electrolytes were reported.[6] We also measured the same activated graphene electrode material with aqueous electrolyte and obtained capacities of 200 F/g. While the measurement methods for these bulk materials differ from those used in this study, the surface area measured using N_2 gas adsorption and the capacitance measurements with two electrode test cells, in each case the capacitance measurements were performed with a best practice methodology which has been shown to correspond closely to fundamental values.[15] For the 705 m²/g surface area graphene material, the calculated specific capacitance is 19 uF/cm² and 14 uF/cm² for aqueous and organic electrolyte, respectively. For

the 3100 m²/g surface area activated graphene derived material, the calculated specific capacitance is 6 uF/cm² and 5 uF/cm² for aqueous and organic electrolyte, respectively. Clearly, another factor, such as quantum capacitance, is limiting the energy storage capacity as surface areas are increased.

Conclusion

We report, for the first time, the direct measurement of the interfacial capacitance for one and two sides of single layer graphene. The results show that the electronic density of states or quantum capacitance plays a significant role in the interfacial capacitance. When applying graphene materials in a supercapacitor for electrical energy storage, increasing the surface to access both sides of a graphene sheet as compared to just one side does not yield a corresponding doubling in storage capacity. Our results show that the quantum capacitance increasingly becomes a factor with the result being a reduced increase in capacitance, not the linear increase with surface area as would be expected for bulk conductive materials. As high surface area graphene materials are applied to supercapacitors, an understanding of the components of capacitance is critical for future development of this promising class of materials. These results indicate that the development of higher surface area graphene materials alone will not be sufficient for the further increases in performance; the modification of the electronic properties will also be required.

Acknowledgements

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