Supporting Information

Hall-Effect Measurements of the Double-Layer Capacitance of the Graphene-Electrolyte Interface

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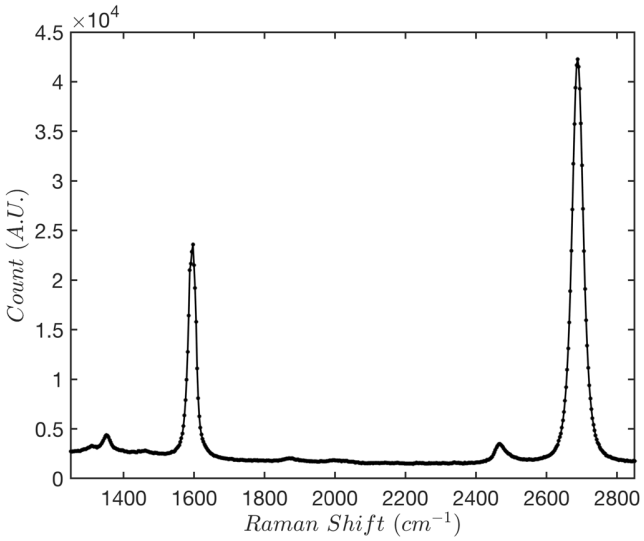

Figure S1. Characteristic microRaman spectrum obtained from the graphene device. The ratio of the 2D peak to G peak intensity is ~ 2, confirming single layer graphene.[S1] There is a small peak associated with defects (located at ~1350 cm^{-1}).[S1] MicroRaman spectra were obtained from multiple locations on the graphene after completing device fabrication. The laser wavelength was 532 nm and the spot size was ~ 1 μm.

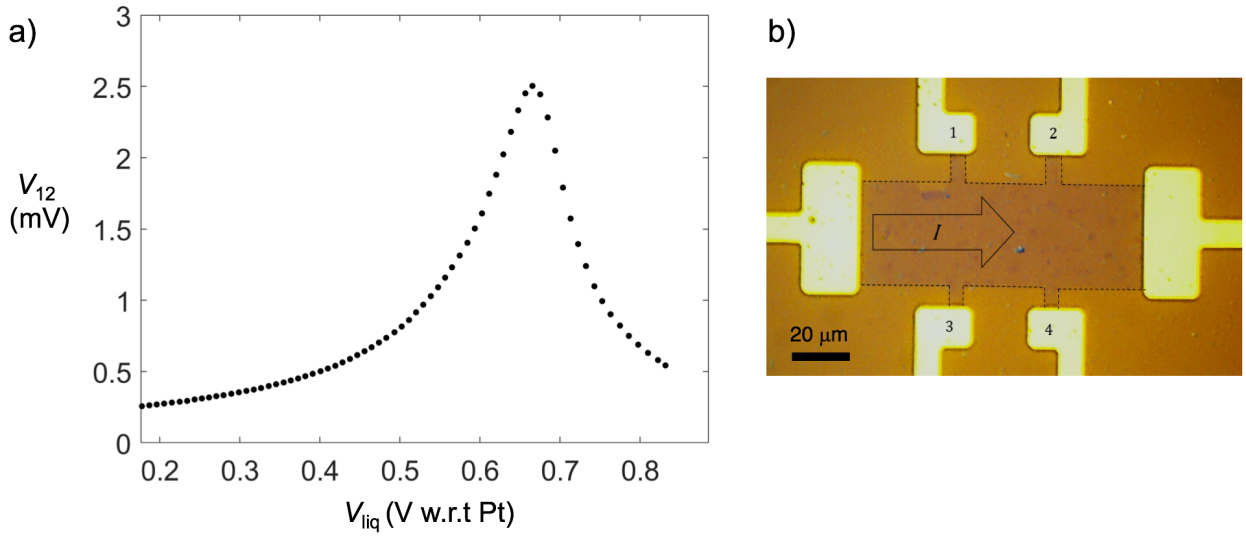

Figure S2. Graphene sheet resistance. (a) Voltage drop in the direction of current flow (I = 5 µA). The minimum sheet resistance is ~ 50 Ω/sq and the maximum sheet resistance is ~ 500 Ω/sq. The electrolyte gate is 600 mM NaCl. (b) The experimental geometry showing contacts 1 and 2 used to measure V_{12}.

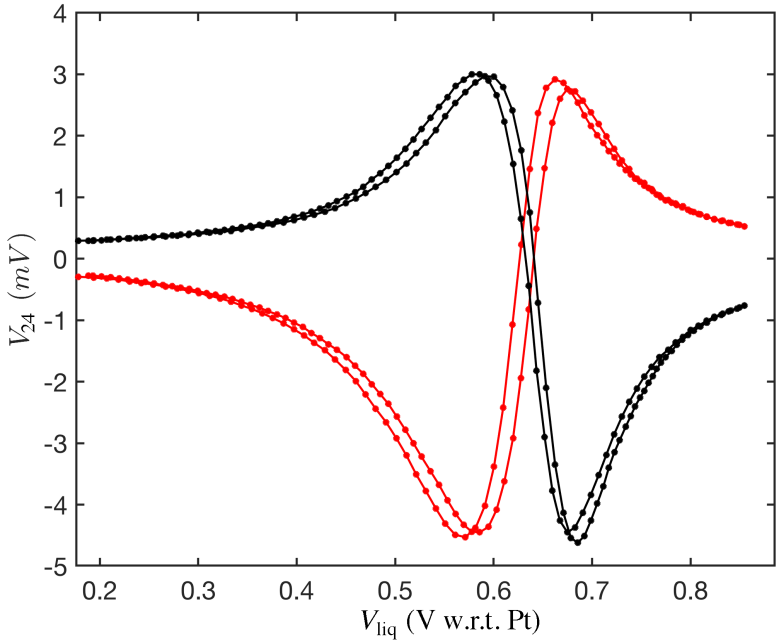

Figure S3. A typical Hall-effect measurement showing forward and backward sweeps of V_{liq}. The electrolyte solution is 600 mM NaCl. The sweep rate is 6 mV/s. The hysteresis is approximately 10 mV.

Expressions for quantum capacitance and the band filling potential

Figure S4 shows the density of states, $D(E)$, predicted by the tight-binding model for graphene's electronic structure.[S2] In this plot, electron energy, E, is measured relative to the highest occupied state in charge-neutral graphene. For small $|E|$ we have

$$D(E) = \frac{2|E|}{\pi\hbar^2 v_F^2} \qquad \text{(S1)}$$

where v_F is the Fermi velocity.

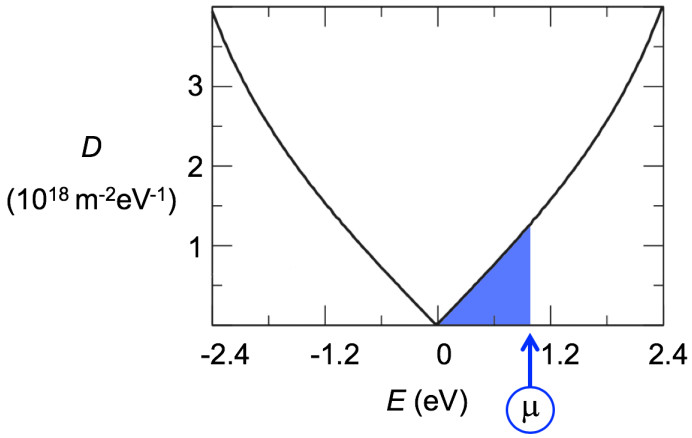

Figure S4. The density of electronic states in pristine graphene, $D(E)$. The chemical potential μ is positive when the graphene is charged with electrons. Conversely, μ is negative when the graphene is charged with holes. The blue shaded area corresponds to the sheet density of free carriers.

The number of electrons per unit area on the graphene is related to $D(E)$ via the integral

$$n = \int_0^{\mu} D(E)\, dE \approx \frac{\mu^2}{\pi\hbar^2 v_F^2} \quad \text{when } \mu > 0, \qquad \text{(S2)}$$

where μ is the chemical potential in the graphene. A similar integral describes the number of holes per unit area when $\mu < 0$.

In a real graphene sample, there is spatial inhomogeneity in the local electrostatic potential. We describe this situation using a position-dependent energy offset. At a given position (x, y), the magnitude of the offset is $\epsilon(x, y)$, where ϵ is sampled from a probability density function, $P(\epsilon)$. The spatially-averaged free-carrier concentrations are then

$$n(\mu) = \int_{-\mu}^{\infty} P(\epsilon) \frac{(\mu + \epsilon)^2}{\pi\hbar^2 v_F^2} d\epsilon \qquad \text{(S3a)}$$

$$p(\mu) = \int_{-\infty}^{-\mu} P(\epsilon) \frac{(\mu + \epsilon)^2}{\pi \hbar^2 v_F^2} d\epsilon \qquad \text{(S3b)}$$

In our work, we assume a normal distribution $P(\epsilon) = (1/\sqrt{2\pi\sigma^2})\exp(-\epsilon^2/2\sigma^2)$ where σ is the standard deviation. The integrals S3a and S3b can be found by numerical integration (see Fig. 2b in the main text).

The integrals (Eq. S3a and S3b) have a simple closed-form solution when $|\mu| \gg \sigma$. We find

$$n(\mu) = \frac{\mu^2}{\pi \hbar^2 v_F^2} + n^* \qquad \text{for } \mu \gg \sigma \qquad \text{(S4a)}$$

$$p(\mu) = \frac{\mu^2}{\pi \hbar^2 v_F^2} + p^* \qquad \text{for } \mu \ll -\sigma \qquad \text{(S4b)}$$

where

$$p^* = n^* = \frac{\sigma^2}{\pi \hbar^2 v_F^2}.$$

The closed-form solution (Eq. S4b) is used in the main text to find the expression for the quantum capacitance C_Q and the band filling potential V_Q. First, consider the band filling potential $V_Q = \mu/e$. Rearranging Eq 4b we find

$$V_Q = \frac{\mu}{e} = \frac{\hbar v_F}{e} \sqrt{\pi (p - p^*)} \qquad \text{for } \mu \ll -\sigma. \qquad \text{(S5)}$$

Next consider the quantum capacitance, $C_Q = e^2 dp/d\mu$. Differentiating Eq. S4b we find

$$\frac{dp}{d\mu} = \frac{2\mu}{\pi \hbar^2 v_F^2}. \qquad \text{(S6)}$$

Then, multiplying by e^2 and writing μ in terms of p, we find

$$C_Q = e^2 \frac{dp}{d\mu} = \frac{2e^2}{\sqrt{\pi} \hbar v_F} \sqrt{p - p^*} \qquad \text{(S7)}$$

Analysis of Hall-Effect Data from Ye et al. (2011)

Ye et al. (2011) used an ionic liquid (1-allyl-3-butylimidazolium bis-(trifluoromethanesulfonyl)-imide) to reach high carrier density in single-layer graphene.[S3] These authors used the Hall effect to determine charge density as a function of voltage. For single-layer graphene, the largest value of the differential capacitance reported was $e(dn/dV) = 0.038$ F/m^2 (see Fig. 2d in Ye et al.). This differential capacitance was found in the electron doped regime with $n = 3.6 \times 10^{13}$ m^{-2}.

Using these numbers, we can estimate C_{DL} for the interface between graphene and the ionic liquid. From Eq. S7 we find $C_Q \approx 0.15$ F/m^2 when $n = 3.6 \times 10^{13}$ m^{-2}. We then use Eq. 4 from the main text to find $C_{DL} \approx 0.05$ F/m^2.

References for Supporting Information

(S1) Ferrari, A. C. Raman Spectroscopy of Graphene and Graphite: Disorder, Electron–Phonon Coupling, Doping and Nonadiabatic Effects. *Solid State Commun.* **2007**, *143*, 47–57.

(S2) Castro Neto, A. H.; Guinea, F.; Peres, N. M. R.; Novoselov, K. S.; Geim, A. K. The Electronic Properties of Graphene. *Rev. Mod. Phys.* **2009**, *81*, 109–162.

(S3) Ye, J.; Craciun, M. F.; Koshino, M.; Russo, S.; Inoue, S.; Yuan, H.; Shimotani, H.; Morpurgo, A. F.; Iwasa, Y. Accessing the Transport Properties of Graphene and Its Multilayers at High Carrier Density. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, *108*, 13002–13006.