Dynamics of the Electric Double-Layer in Electrolyte Gated Graphene FETs

T. J. Badcock, J. Kuleshova, A. Nikolaenko, M. Tyler, V. Curto, N. Conway and J. Tingay
Paragraf, 7-8 West Newlands, Somersham, Cambridgeshire, PE28 3EB, UK.
t.badcock@paragraf.com

Field-effect gating forms the operational basis for most of the applications of graphene electronic devices. When using thin/high-k dielectrics, Fermi-level shifts of 100s meV are possible and allow charge densities $>10^{13}$ cm^{-2} to be accumulated in the graphene channel with less than 1V of gate bias. A particularly useful example of this property can be seen in aqueous electrolyte gated graphene FETs, due to the > µF/cm^2 gate capacitance that results from the spontaneously formed electric double layer (EDL) at the graphene/liquid interface. FET biosensing is reliant on controlling this complex interaction, yet generally only dc electrical techniques are employed, thus crucial information on the relevant processes is lost. To address these limitations, we study the EDL of fabricated graphene FETs in the time/frequency domain over a range electrolyte concentrations (c_{ion}) ($1 < c_{\mathrm{ion}} < 150$ mM) (Fig.1). From impedance data, the measured, effective gate capacitance is modelled, using the graphene quantum capacitance (including a residual charge $< 1\mathrm{x}10^{12}$ cm^{-2}) in series with a bias-independent EDL capacitance (C_{EDL}), itself a series combination of Stern (C_{St}) and diffuse layer (C_{diff}) capacitances (Fig.2). A core tenet of FET biosensor principles is the notion that the Debye 'screening length', determined by c_{ion}, also controls C_{EDL} and therefore the potentiometric sensitivity of the device. In contrast to this assumption, our measured data is consistent with a model in which C_{EDL} is independent of c_{ion}, suggesting that the inner 'Stern' layer of the EDL is controlling the charge coupling of the channel (Fig.2) [1]. The electrical bandwidth of the FETs is then studied via a single-source mixing technique [2] (Fig.3), again as a function of c_{ion} (>1 mM). It is seen that the -3dB cut-off frequency of the FET transconductance can be described by a single-pole RC filter fit in which only the solution + graphene resistance is varying (C_{EDL} is constant). The transient dynamics of the EDL are examined via electrically pulsed gating, revealing that the time required to reach a steady-state current in the channel increases as c_{ion} reduces, ranging from ~10 µs (x1 PBS=150 mM) to ~1 ms in de-ionised water, timescales that are complementary to the cut-off frequencies (Fig.4). The only electrical fingerprint of the diffusive Debye layer is found in the observation of the long transients measured at very low c_{ion}, suggesting an EDL 'formation time' compatible with standard theory [3]. Nevertheless, once the EDL charge plane is fully established, the capacitive coupling between the EDL and the graphene channel is similar over orders of magnitude variation in c_{ion}, as evidenced by the c_{ion} invariant dc transconductances of the FET.

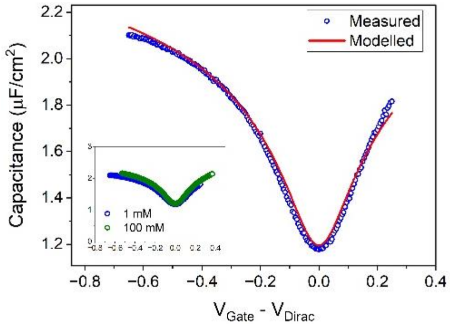

Fig.1. Gate capacitance as a function of c_{ion}. The form of the C-V curve does not depend on c_{ion} (inset)

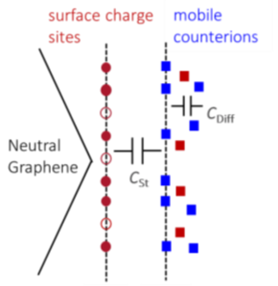

Fig.2. Schematic of EDL depicting charge planes of inner fixed (C_{St}) layer and outer (C_{Diff}) Debye) layer

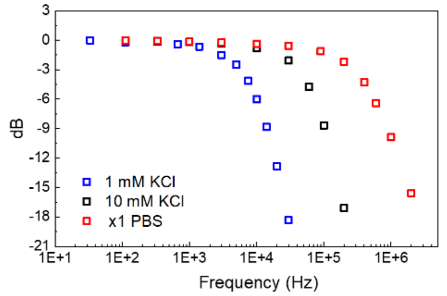

Fig.3 FET transconductance vs mixing frequency with varying c_{ion}

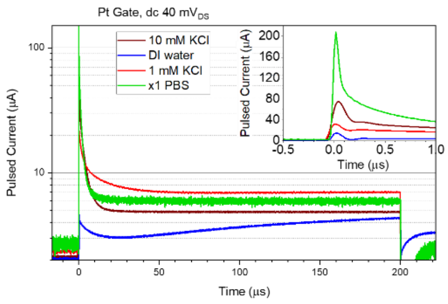

Fig.4. Channel current under pulsed excitation with varying c_{ion}

References

[1] Dankerl *et al*. PRL 106, 196103 (2011)
[2] Kulkarni *et al*. Acc. Chem. Res 2016, 49, 11, 2578
[3] Bazant *et al*. Phys. Rev. E 70, 021506 (2004)