Supporting Information For:

Battery/Supercapacitor Hybrid via Non-Covalent Functionalization of Graphene Macro-Assemblies

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Contents:

GMA synthesis:

Graphene macro-assemblies were prepared in a similar manner to what has been previously reported by our group.[1] Graphene oxide (GO, 1-2 layer, 300-800 nm diameter sheets) was purchased from Cheaptubes and used as received. GO was dispersed in Milli-Q H_2O (20 mg/mL) by ultrasonication for 24 h, and ammonium hydroxide catalyst (211 µL/g) was added to the resulting suspension. The GO suspension/catalyst mixture was cast into disk shaped molds, sealed, and placed in a 75 °C oven for 72 h for crosslinking/gelation. The monolithic disks were washed in water, followed by acetone, and dried with supercritical CO_2. The disks were then carbonized at 1050 °C for 3 h under flowing N_2 to remove oxygen functionality (final O content <2 at.%). The resulting GMA disks are approximately 1 cm in diameter by 250 µm thickness, weigh ~1 mg, have density of ~0.07 g/cm^3, and have a BET surface area of ~1300 m^2/g.

Experimental details for Figure 4 (Ragone plot).

In order to calculate specific energy and power for the Ragone plots in Figure 4, we ran a series of galvanostatic charge/discharge experiments (1.2V window) at different currents (e.g., 2 mA, 6 mA, 10 mA, 20 mA, etc.). Integration of the discharge curve (c.f., Figure 3), performed in the Bio-Logic EC-Lab software, gives V•s, which is multiplied by discharge current (A) and divided by 3600*total mass of electrodes (or working electrode, in kg) to give W•h/kg. To get W/kg, divide Wh/kg by the discharge time at each current.

Theoretical calculations:

The calculations were performed using the Quantum-ESPRESSO code[2] with the van der Waals-corrected vdW-DF functional[3] and the reference exchange term derived from the revPBE functional.[4] A plane-wave cutoff of 80 Ry was used. Periodic boundary conditions were imposed in all directions, with images perpendicular to the basal plane separated by 20 Å. To sample the densities of states (DOS), a 16 × 16 in-plane **k**-mesh and electronic smearing width of 0.005 were used. From the DOS, we calculated the differential quantum capacitance within the rigid-band approximation according to **Equation 2**.[5]

$$C_q(V) = \frac{\partial Q}{\partial V} = e^2 \times DOS(-Ve) \tag{2}$$

This quantity was then integrated starting from the Fermi level to obtain the capacity curve for the half-cell.
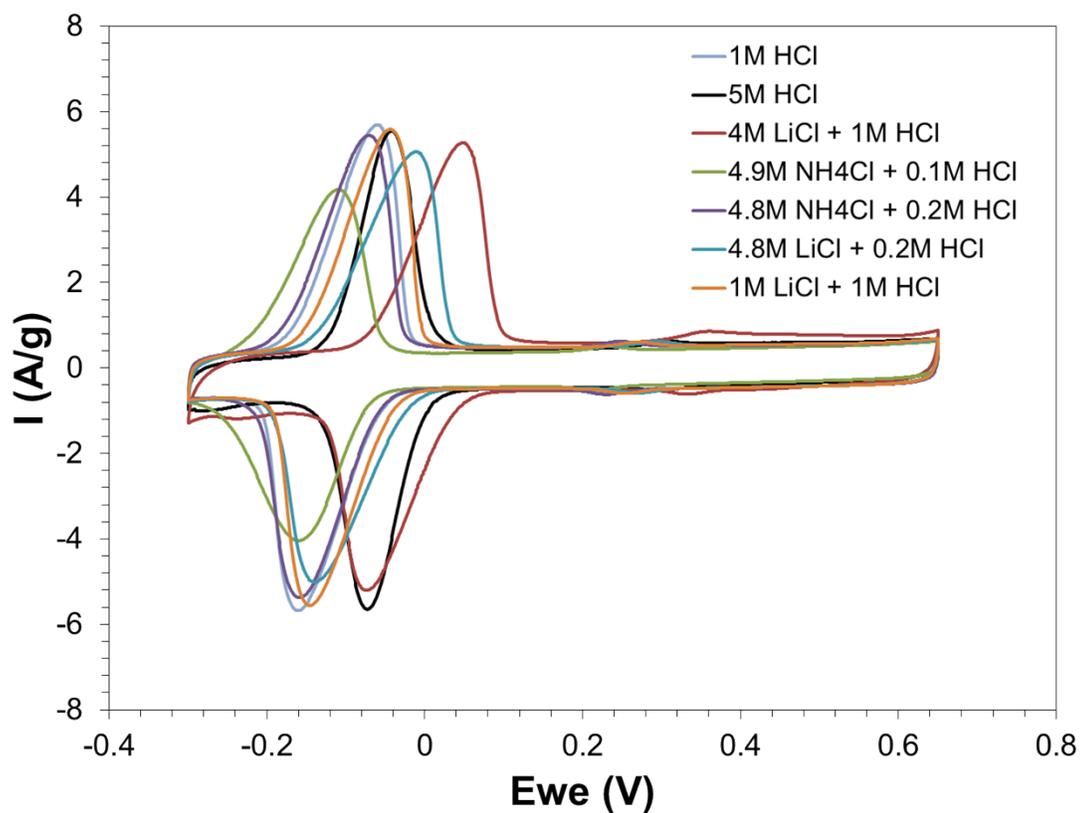
Figure S1: Tunability of AQ redox potential by altering electrolyte composition and/or pH. All CVs performed using 250 µm thick AQ-GMA working electrodes with 10-14 wt% AQ, 5 mV/sec, 3-electrode cell with SCE reference electrode and Pt counter electrode.
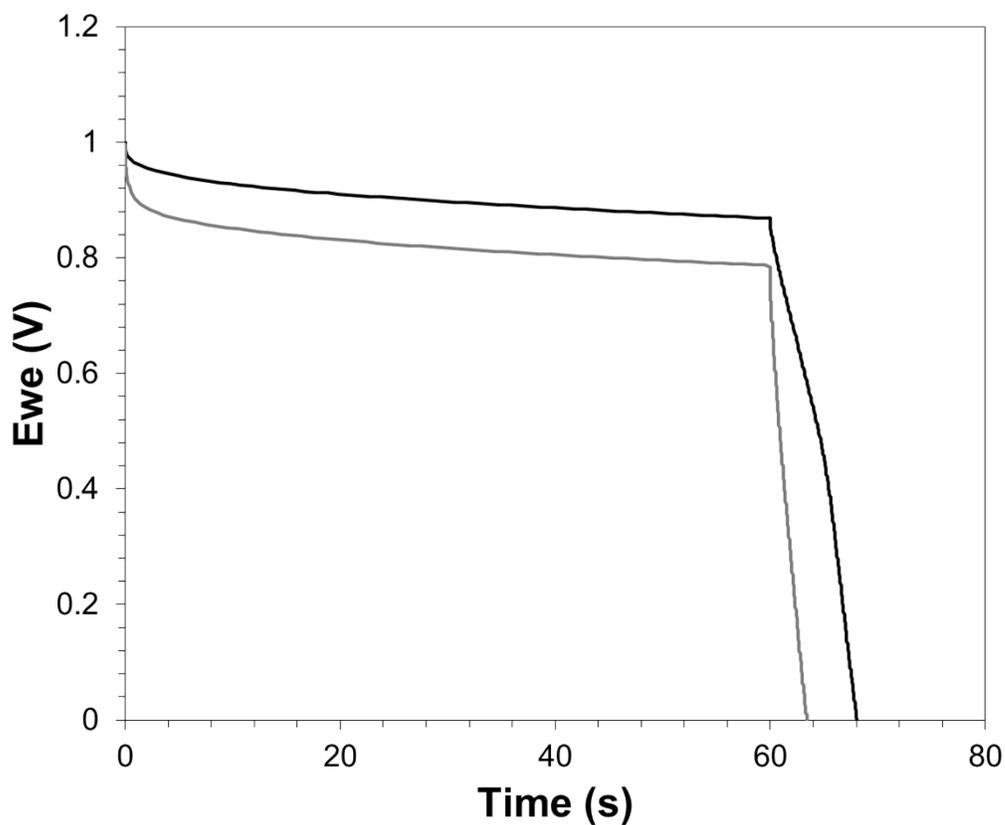
Figure S2: Self-discharge behavior of 11% AQ-GMA/500 UCE cell (black line) and untreated reference cell (gray line) in 1 M HCl. During 60 s rest period after charging to 1 V, the AQ-GMA self-discharged 0.14 V and the untreated GMA reference cell self-discharged 0.2 V. The redox feature on the discharge curve (10 A/g) remains apparent for the AQ-GMA electrode pair, which suggests that the AQ remains in contact with the GMA substrate and does not diffuse away when charged.
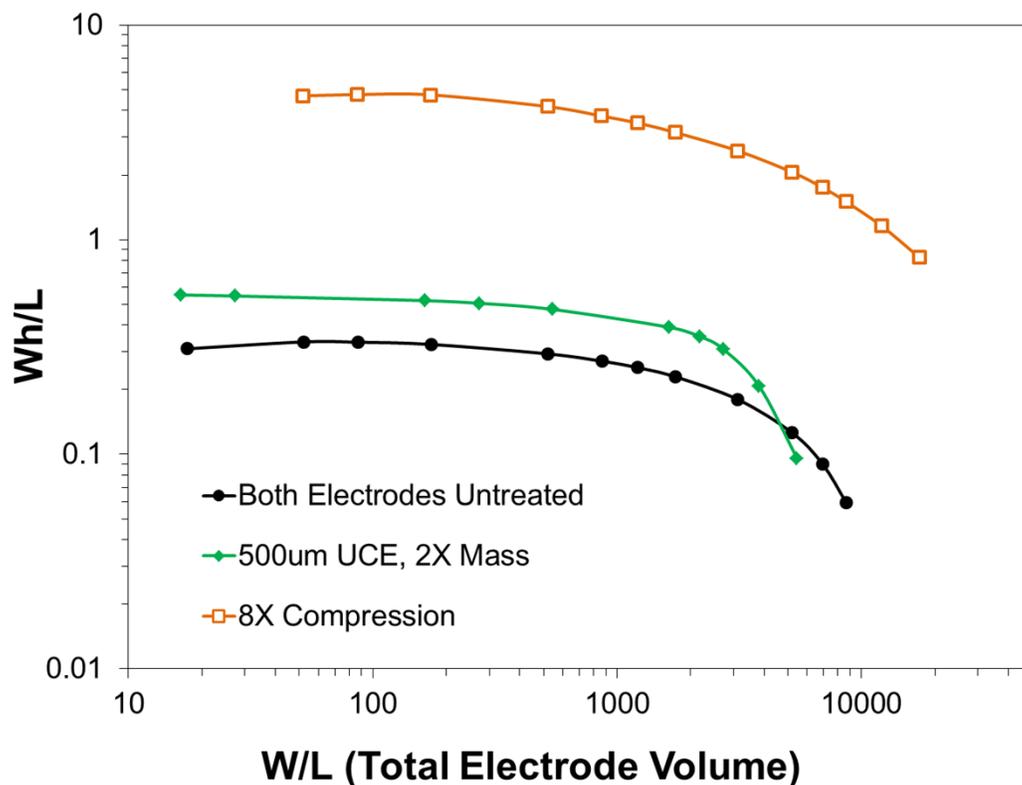
Figure S3: Ragone plot for 8X compressed AQ-GMA electrode with 13 wt.% AQ loading paired with UCE of 2X mass (orange line). Two electrode cell assembled using 1,000 μm AQ-GMA coupled with a 2,000 μm counter electrode of twice the mass. Both electrodes were mechanically compressed 8X in the cell by using silicone gasket spacers of 125 and 250 μm, respectively. Uncompressed, untreated (black line) and AQ-GMA paired with 500 μm UCE (green line) are presented for comparison. 8X compression yields the expected 8X increase in energy density, even at moderate to high power.
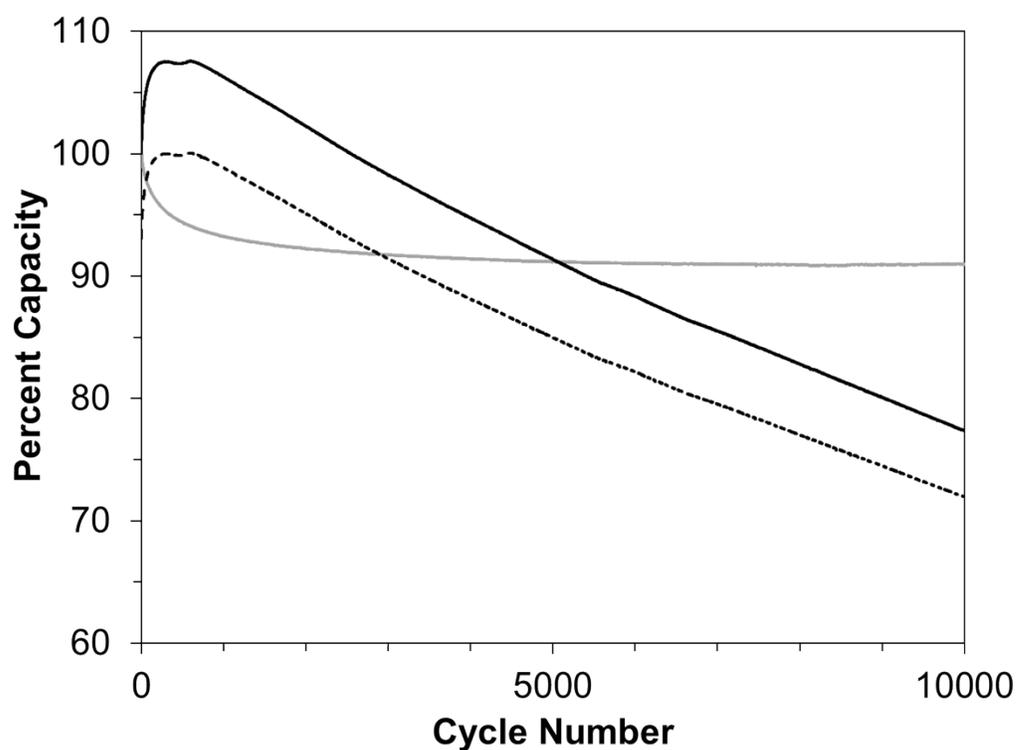
Figure S4: Long-term stability study for a 250 μm thick AQ-GMA electrode with 10 wt.% AQ paired with a 500 μm UCE (black line, dashed line is the same curve normalized to 100% at peak capacity) and stability of untreated GMA electrode (gray line). Two-electrode cell, 10 A/g, 1 V window, 1.5 M HCl. After 10,000 cycles AQ-GMA maintains 77% of original capacity and stores 2X more energy than the untreated electrode.
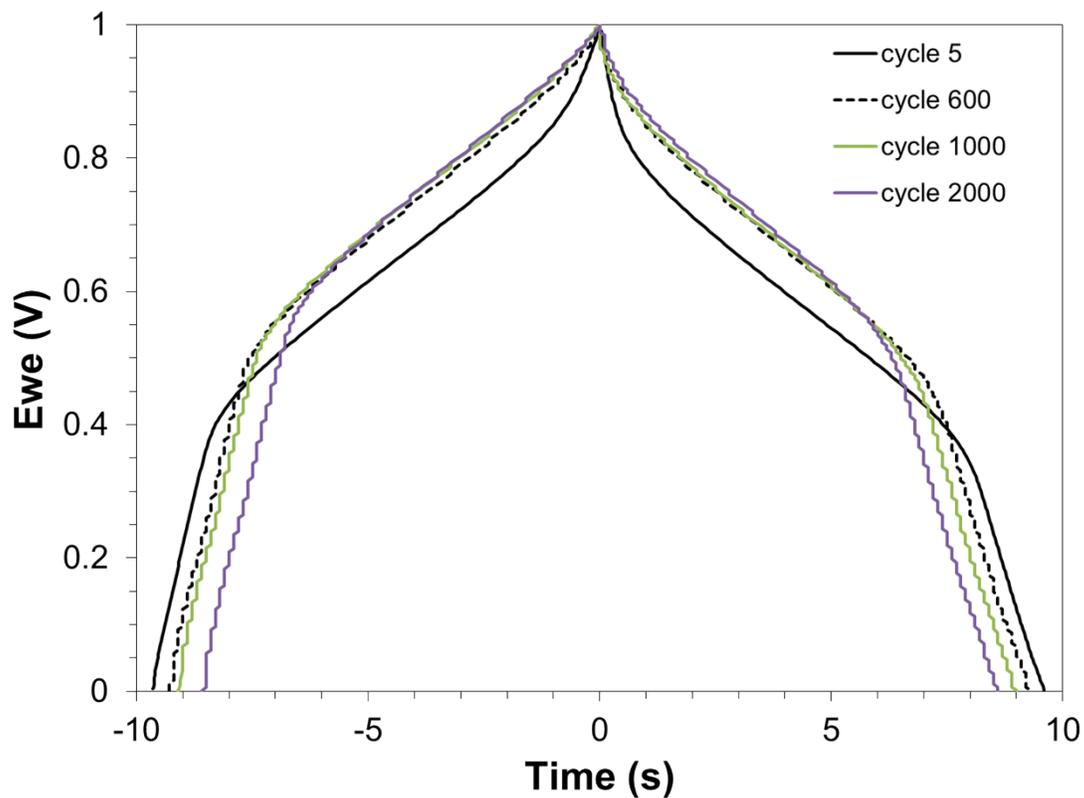
Figure S5: Evolution of charge-discharge curve of AQ-GMA electrode with 10 wt.% AQ (1.5M HCl, 1V window, 10 A/g). AQ redox peak shifts to higher potential (thus higher energy) as cycling progresses while total coulombs stored do not increase (as indicated by the reduced charge-discharge time at constant 10 A/g).

References:

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