Supplementary Information for

Optimizing Supercapacitor Electrode Density: Achieving the Energy of Organic Electrolytes with the Power of Aqueous Electrolytes.

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Experimental

The GMA electrodes were prepared in a manner similar to previous work [1]. A 2 wt% graphene oxide suspension (3 ml) was prepared in deionized water via ultrasonication. Concentrated ammonium hydroxide (500 μl) was added to the graphene oxide suspension. The reaction mixture was poured into appropriately sized molds to produce electrodes of approximately 0.15, 0.3, 0.6, and 1.2 mm thick. The molds were sealed and placed in an oven at 85 °C for gelation. The resultant discs were then washed in deionized water, which, then was exchanged against acetone, before undergoing critical point drying using liquid CO_2. Finally, the electrodes were thermally annealed at 1050 °C in N_2 to yield the monolithic GMA electrodes with a density of 0.144 g/cm^3. The density of the electrode was altered by compression to gasket-controlled thicknesses between insulated, ¼" steel plates in symmetric electrode setups.

Transmission electron microscopy (TEM) characterization was performed on a Phillips CM-300FEG electron microscope operated at 300 kV. Surface area determination and pore volume and size analysis were performed by Brunauer-Emmett-Teller (BET), Barrett-Joyner-Halenda (BJH), and density functional theory (DFT) methods with an ASAP 2010 Surface Area Analyzer (Micromeritics Instrument Corporation) [2]. Samples of approximately 0.1 g were heated to 300°C under vacuum (10^{-5} Torr) for at least 24 hours to remove adsorbed species. Electrical conductivity was measured using the four-probe method with metal electrodes attached to the ends of cylindrical samples. The amount of current transmitted through the sample during measurement was 100 mA, and the voltage drop along the sample was measured over distances of 3 to 6 mm. Seven or more measurements were taken, and results were averaged. Standard deviation error was within 5%. Bulk density was determined from the physical dimensions and mass of the GMA samples.

Electrochemical experiments were performed with a Bio-Logic VSP electrochemical workstation. Symmetric electrode setups were constructed by separating electrolyte-saturated electrodes with a 25 μm thick porous polypropylene separator (Celgard 3501). The electrode chambers were sealed with silicone gaskets (McMaster-Carr) between current collectors of 2 x 2 cm ZYH grade highly oriented pyrolytic graphite (HOPG, K-Tek Nanotechnology). The electrolyte's mass contribution to the two electrode, symmetric supercapacitor will dilute the gravimetric performance values by a factor of X_ρ. The X_ρ factor for graphitic electrodes can be calculated according to equation (S1), where $\rho_{electrode}$ is the electrode density, $\rho_{electrolyte}$ is the electrolyte density, and it has been assumed that the carbon's density is 2.27 g/cm^3 and that all of the electrode's void space has been filled with electrolyte.

$$X_{\rho} = \frac{\rho_{electrode}}{\rho_{electrode} + \rho_{electrolyte}\left(1 - \dfrac{\rho_{electrode}}{2.27\,{}^{g}\!/\!_{cm^3}}\right)} \tag{S1}$$

The 5 M KOH electrolyte's density is considered to be 1.28 g/cm³ and the 6 M LiCl + 1 M CsCl electrolyte's density is 1.42 g/cm³. The energy in units Wh, $E_{(Wh)}$, is calculated according to equation (S2), where C is capacitance and V is the maximum voltage bias.

$$E_{(Wh)} = \frac{1h}{2 \cdot 3600s} CV^2 \tag{S2}$$

The power in units W, $P_{(W)}$, is calculated according to equation (S3), where t is the discharge time of the symmetric, two-electrode setup.

$$P_{(W)} = \frac{3600s}{1h} \cdot \frac{E_{(Wh)}}{t} \tag{S3}$$

The capacitance of an individual electrode, C_{ind}, is calculated form the total capacitance of the symmetric, two-electrode setup, C_{tot}, according to equation (4), where one factor of 2 occurs by considering the mass of both electrodes and the other factor of 2 occurs by considering two equally sized capacitors in series [3].

$$C_{ind} = 4 \cdot C_{tot} \tag{S4}$$

Supporting Figures
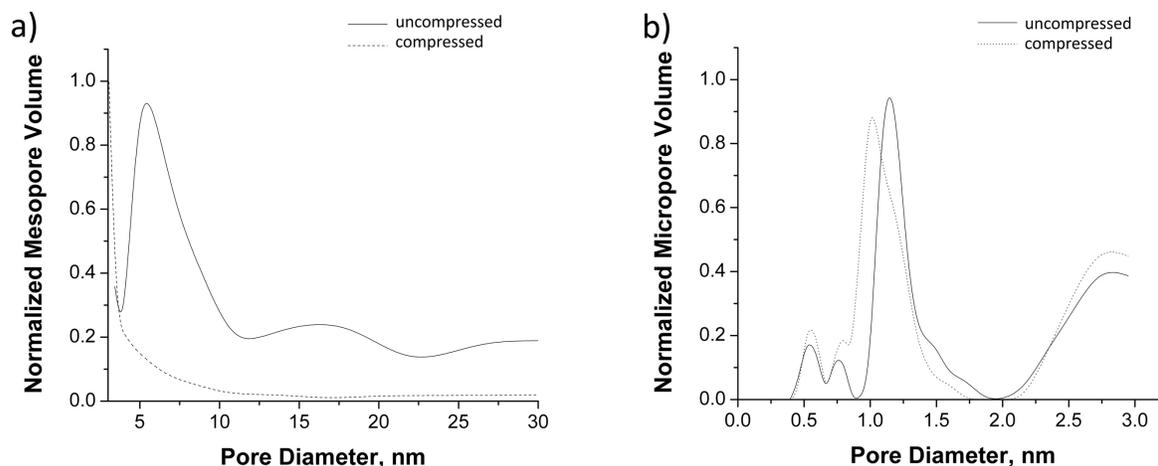
Figure S1.   Pore size distributions showing pore volume of the uncompressed and compressed GMA in the a) mesopore and b) micropore regimes.

Figure S1 illustrates how the pore size distribution may shift in the GMA upon compression. Practically speaking, we did not have the means to hold the highly elastic GMA in compression while we performed the nitrogen porosimetry. Therefore, a slightly different method was used to prepare the compressed GMA shown in Figure S1. Though the final GMA is highly elastic under compression and will spring back to its original form once load is removed, the pre-carbonized graphene aerogel is not. Before carbonization, deformation of the GMA is mostly plastic such that it remains in the compressed form when the load is removed.   So the compressed GMA in Figure S1 was compressed ~80% prior to carbonization, then carbonized, and characterized via nitrogen adsorption to determine the pore size distributions. Figure S1a shows that compression does produce the expected reduction in mesoporosity and macroporosity, effectively eliminating pores above 5 nm. However, pores below 5 nm remain intact (Figure S1b) allowing the GMA to show no loss in energy density with compression.
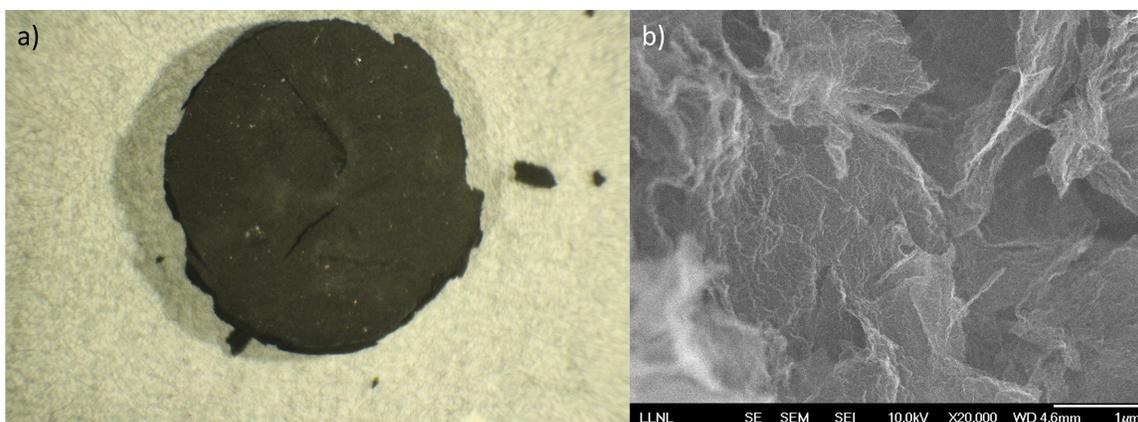
Figure S2. a) Macroscopic image and b) electron micrograph of GMA after compression. Diameter of GMA disc in a) is ~1 cm.

Figure S2 presents macroscopic and microscopic images of GMA after compression. The images show that on the macroscale (Figure S2a) after compression the GMA remains largely intact and unchanged, except for some surface fractures.   At the microscale, the compression event appears to have no effect on the GMA. The microstructure of the GMA after compression is identical to that of the pristine GMA.[1] This mechanical robustness during compression contributes to the ability of the GMA electrode to maintain its high performance during compression.

References

1.   M. A. Worsley, S. O. Kucheyev, H. E. Mason, M. D. Merrill, B. P. Mayer, J. Lewicki, C. A. Valdez, M. E. Suss, M. Stadermann, P. J. Pauzauskie, J. H. Satcher, J. Biener and T. F. Baumann, Chem Commun **48** (67), 8428-8430 (2012).
2.   S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity*, 2nd ed. (Academic, London, 1982).
3.   F. Béguin, V. Presser, A. Balducci and E. Frackowiak, Advanced Materials **26** (14), 2219-2251 (2014).