Supporting Information:

Multifunctional High Strength and High Energy Epoxy Composite Structural Supercapacitors with Wet-Dry Operational Stability

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Detailed Experimental Procedures:

Synthesis of carbonized porous Si electrodes: Nanoporous silicon was synthesized from silicon wafers (.01-.02 Ω cm^{-1}) using an electrochemical etch with an electrolyte of 3:7 v/v HF (50% H_2O by volume) and ethanol at 45mA/cm^2 for 180s in an AMMT etching system. This yields a porous layer mechanically tethered to bulk silicon that exhibits approximately 75% porosity and is 4.5μm in thickness. A passivating carbon coating was then applied to the porous Si using chemical vapor deposition using a ramp procedure where a mixture of acetylene, hydrogen and argon were flowed over the sample in a ratio of 1:20:100, with two consecutive temperature ramps for 10 minutes each of 650-750 °C and 750-850 °C. Further details on this ramp procedure and the electrochemical stability of passivated nanoporous silicon materials can be found elsewhere, including representative microscopy images and material analysis.[38, 39]

Synthesis of epoxy-IL electrolyte and full devices: Epoxy-IL electrolytes were developed by first dissolving $LiBF_4$ into $BMIBF_4$ in a ratio of 1:4. Next, Super Sap CCR epoxy resin (Entropy Resins) and its corresponding CCS slow hardener (Entropy Resins) were mixed together in a 2:1 ratio via a 2 stage mixing process in a Thinky ARE 250 Planetary and Centrifugal Mixer with an initial planetary mixing step for 6 minutes at 2000rpm, followed by a centrifugal mix for 2 minutes at 2100rpm to degas the mixture. The SuperSap CCR epoxy is made up of epoxidized pine oils, bisphenol A/F type epoxy resin, benzyl alcohol, and proprietary reactive epoxy diluents, and the CCS slow hardener is polyoxypropylenediamine. The epoxy mixture was then combined with $LiBF_4$/$BMIBF_4$ with varying epoxy-IL ratios ranging from 70% epoxy and 30% IL to 40% epoxy and 60% IL. The final uncured epoxy-IL electrolyte was then poured into the desired shape and placed in an oven at 40-45 °C and allowed to cure overnight. Full devices were synthesized by pouring the same uncured epoxy-IL electrolyte mixture over the passivated nanoporous silicon electrodes and placing

them in a vacuum oven under vacuum at 50°C for approximately 20 minutes to remove the excess air from the porous Si electrodes before placing in the oven for the overnight cure.

Mechanical testing of bulk epoxy-IL electrolyte: Mechanical testing of the bulk epoxy-IL electrolyte was performed using an Instron 5944 single column load frame at a rate of 2 mm/s with a 2kN load cell.

Electrochemical testing of bulk epoxy-IL electrolyte and devices: Ionic conductivity was determined by placing steel disks on the either side of a bulk epoxy-IL electrolyte (~1cm by 1cm) and performing electrochemical impedance spectroscopy (EIS) from 1 MHz to .1 Hz with a sinusoidal wave pattern of amplitude 10 mV around 0V. EIS, cyclic voltammetry, and galvanostatic charge discharge measurements were performed using a portable Autolab potentiostat/galvanostat. Energy density was calculated from galvanostatic discharge curves by numerical integration according to the following equation $E = \int_0^t IV dt$ where I represents the current, and V the voltage and t is the total discharge time. This notably yields the exact energy density; this number is lower than the energy density obtained using the more conventional approximate $E = 1/2CV^2$ relation which assumes a perfectly linear discharge current.[25, 38, 39] Specific Capacitance was calculated from both the CV and galvanostatic charge discharge curves. In order to calculate the specific capacitance from the CV curves (C_{sp}), the area under the positive and negative sides of the CV curve was averaged and then divided by the scan rate (R), the weight (m), and the total voltage range (ΔV) according to the following equation:

$$C_{sp} = \frac{1}{m\Delta V R}\int_{V_b}^{V_a} I(V)dV$$

Specific capacitance was calculated from galvanostatic discharge curves by fitting a line to the discharge curve to find a slope which is equivalent to the change in Voltage over time or $\Delta V/\Delta t$. The current was then divided by this slope and by the device mass. Or equivalently

$$C_{sp} = \frac{I\,\Delta t}{m\,\Delta V}$$

In-situ mechano-electrochemical tests: In order to perform simultaneous mechanical and electrochemical measurements, we first built custom-designed grips with a flat top surface that clipped into the Instron testing system. The top of these grips, and the outer surfaces of the supercapacitor electrodes were both roughened using 100 grit sandpaper and a diamond scribe respectively, after which a pure low viscosity MAS epoxy resin (MAS Epoxies), with the corresponding MAS slow hardener (MAS Epoxies), was applied and cured as an adhesive layer between the grips and the devices. The outer edges of the device electrodes were then used as electrical contacts allowing for simultaneous tensile and electrochemical measurements. In order to ensure that the measured tensile load was essentially the same for any single electrochemical measurement the tensile stress was applied at the relatively slow rate of .0008 mm /s.

Wet-dry testing: Wet-dry testing of the bulk epoxy-IL electrolyte tensile samples was performed by synthesizing two identical tensile specimens with the same batch of epoxy-IL electrolyte. One of the specimens was then immersed in water for two hours, and then quickly tested after removal from the water, while the other was tested in its pristine condition.

The electrochemical wet-dry testing of the devices was performed using galvanostatic charge discharge tests under 1.2V on the same device first in the pristine condition, then while immersed in water after soaking for 2 hours, and finally after drying for over 3 days.

Supporting Figures:

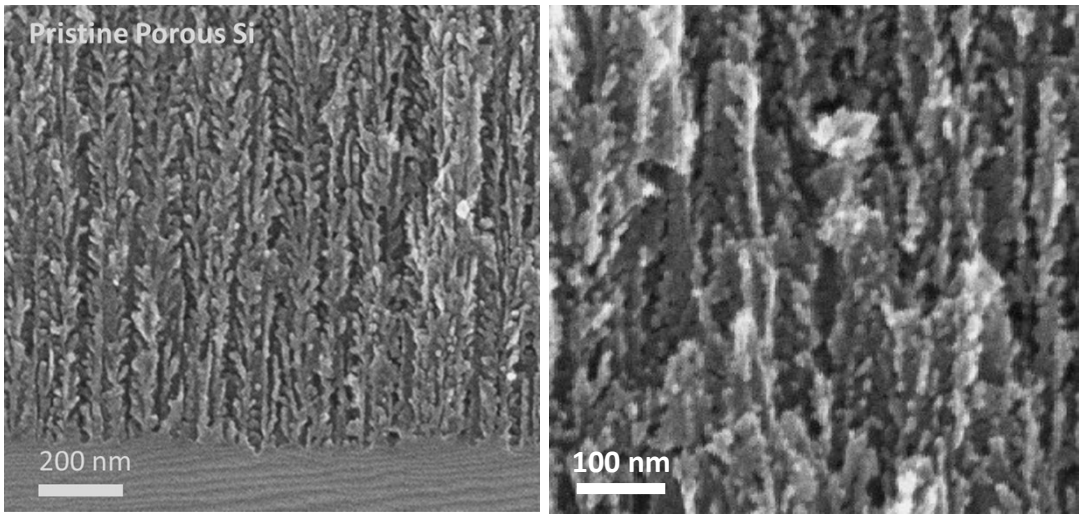

Figure S1: SEM images of pristine porous Si showing the detailed pore structure

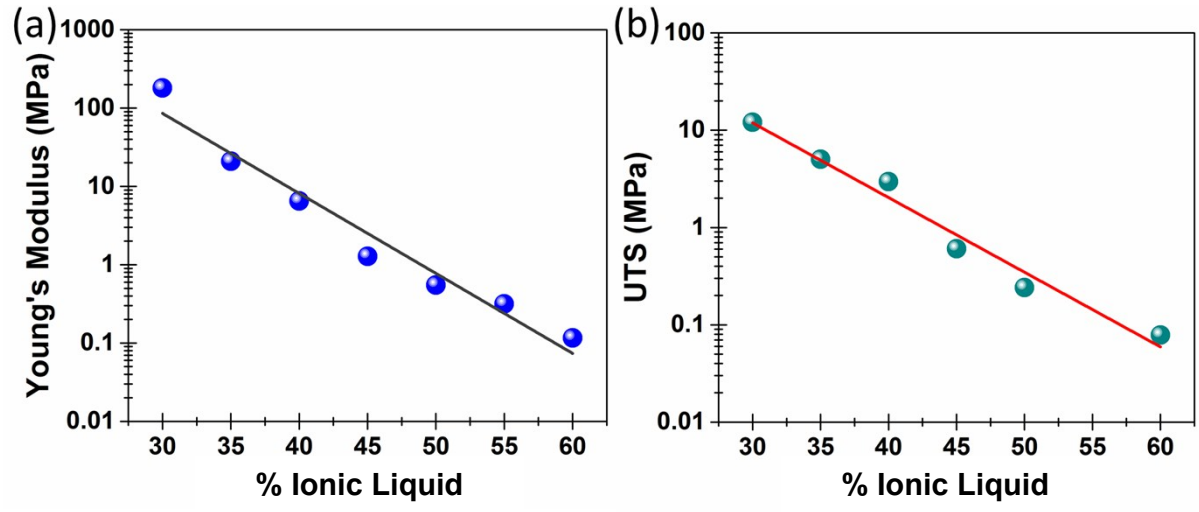

Figure S2: a) Young's Modulus as a function of IL loading. b) Ultimate tensile stress (UTS) as a function of IL loading.

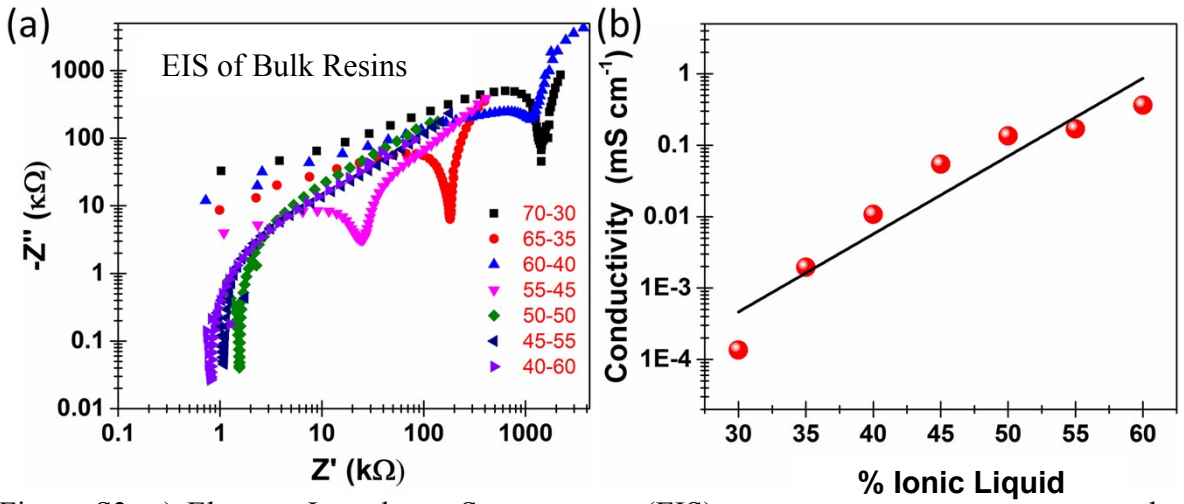

Figure S3: a) Electron Impedance Spectroscopy (EIS) curves of bulk epoxy-IL electrolytes placed on a log scale to enable comparisons. b) Ionic conductivity as a function of IL loading as measured from EIS curves.

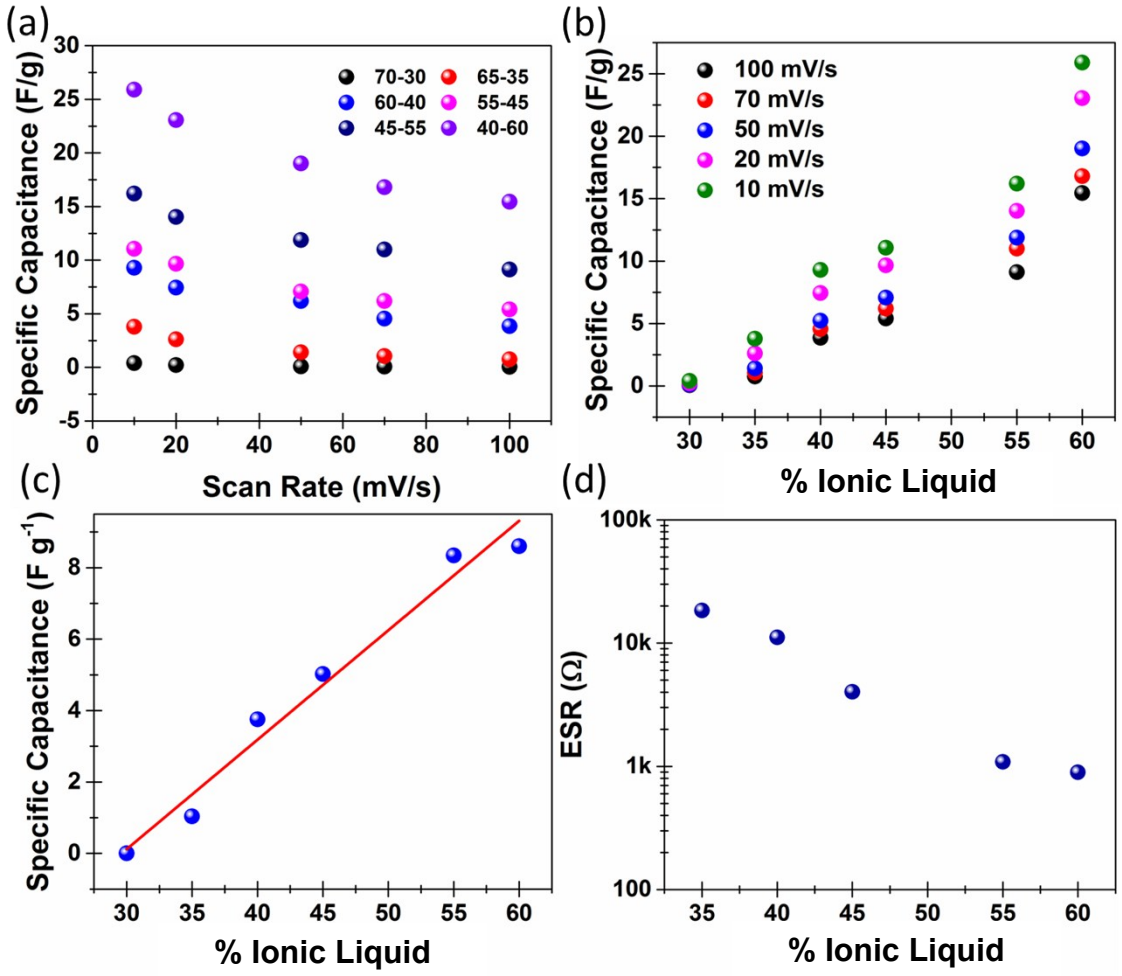

Figure S4: a) Specific capacitance as a function of scan rate as measured by cyclic voltammetry (CV) for various epoxy-IL ratios. b) Specific Capacitance as a function of IL loading measured from CV curves. c) Specific Capacitance as a function of IL loading as measured from galvanostatic discharge curves. d) Equivalent series resistance (ESR) as a function of IL loading from galvanostatic discharge curves.

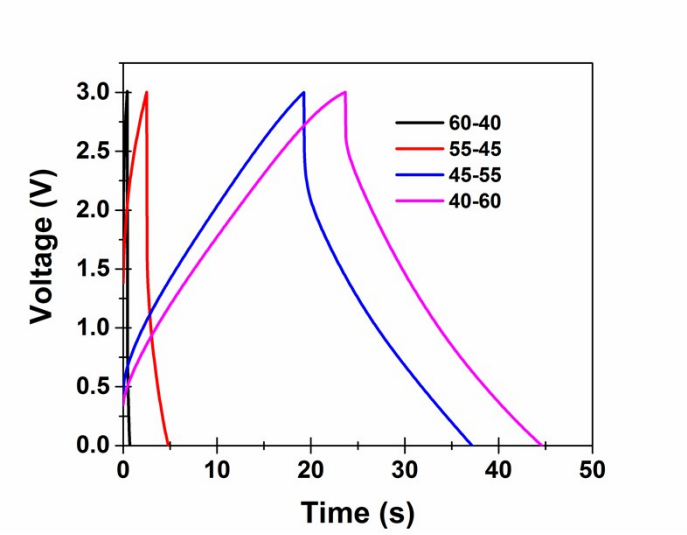

Figure S5: Comparison of Galvanostatic charge discharge curves of the devices with various Epoxy Resin-IL ratios at 1 A/g.

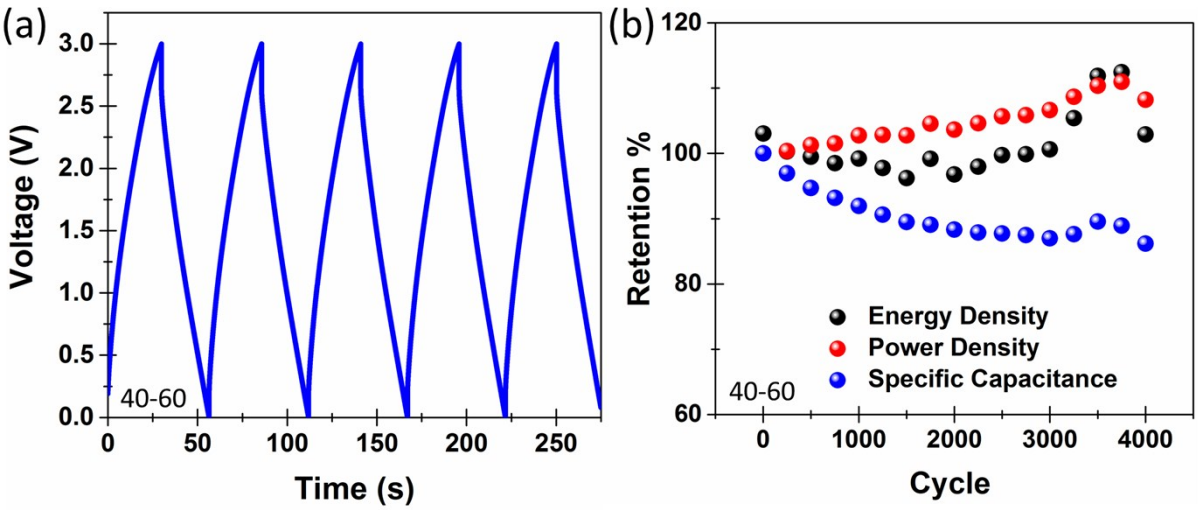

Figure S6: a) Consecutive charge discharge curves for a device with epoxy-IL electrolyte ratio of 40-60. b) Cycling performance over 4000 cycles.

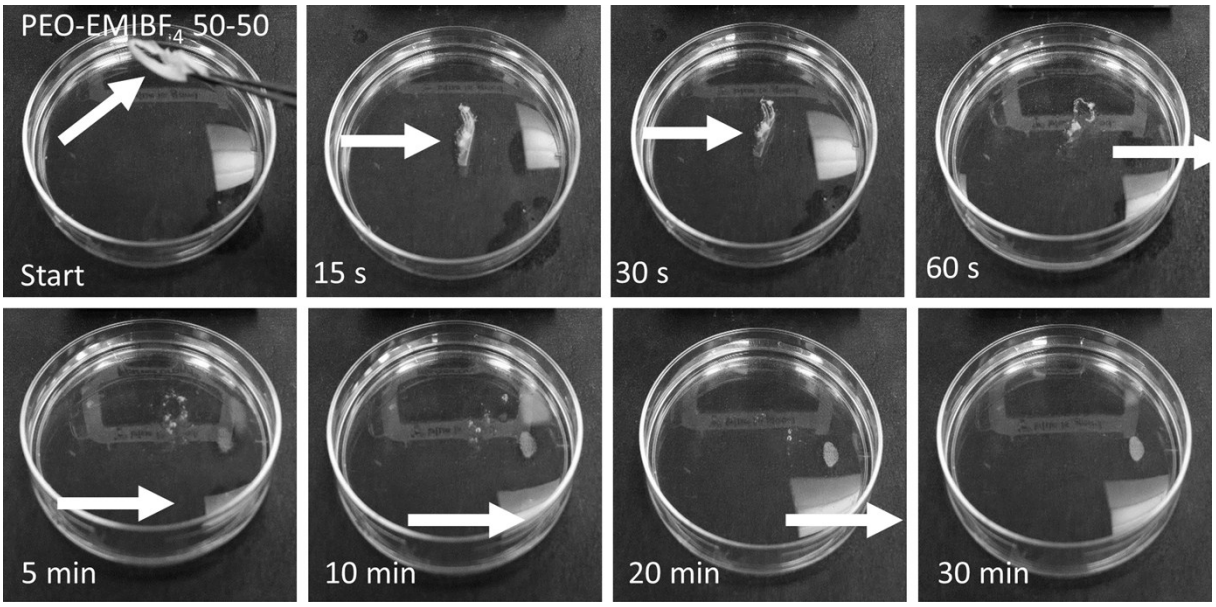

Figure S7: A series of photographs showing the dissolution of a polyethylene oxide (PEO) / 1-ethyl 3-methyl imidizolium tetra fluoroborate ($EMIBF_4$) polymer electrolyte in water.

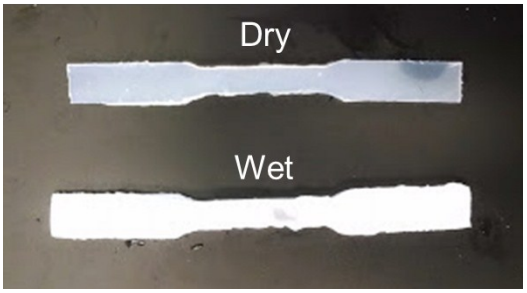

Figure S8: Picture of the epoxy-IL composite electrolyte in the initial (dry) state and after being immersed in water for 2 hours (wet).

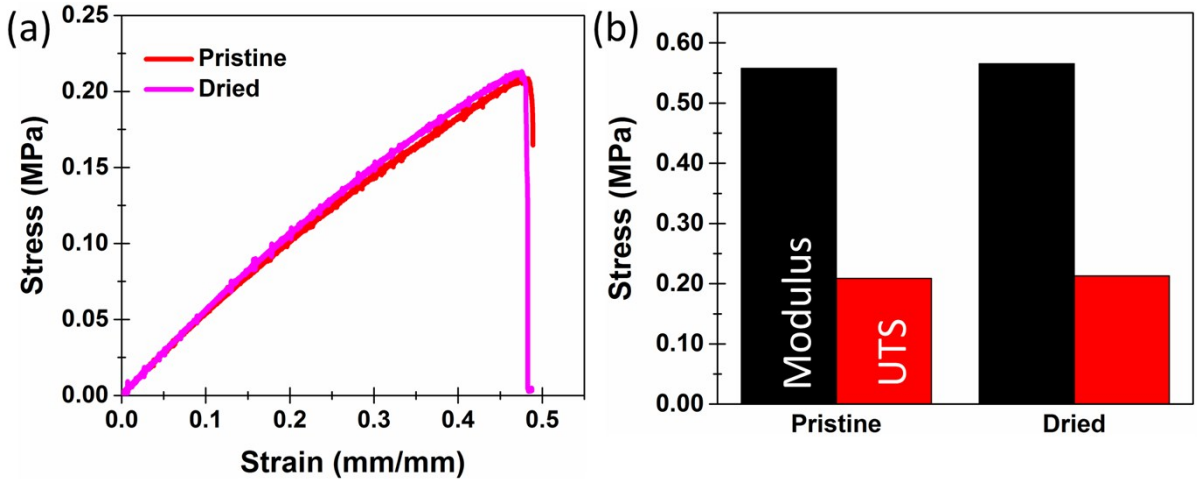

Figure S9: a) Stress/strain measurement for bulk epoxy resin electrolytes with epoxy-IL ratio of 45-55 in the pristine condition and after both a 2 hour soak in water and subsequent drying. b) Young's modulus and the ultimate tensile strength (UTS) for the pristine and dried samples as measured from Figure S6a.

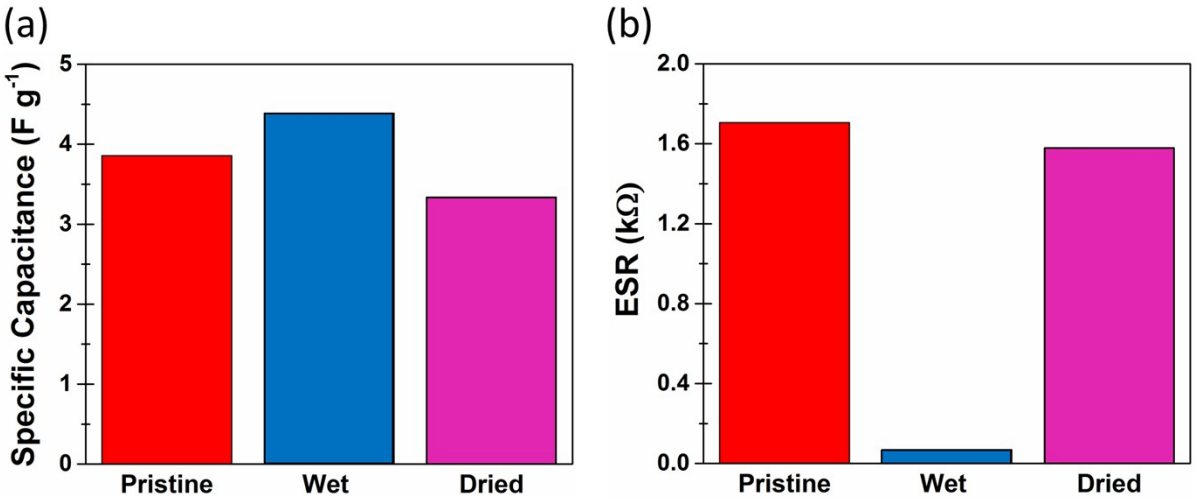

Figure S10: a) Actual numerical values for the specific capacitance for the galvanostatic charge discharge curves in figure 3d, and reported in figure 3e. b) Actual numerical values of the equivalent series resistance (ESR) for the galvanostatic charge discharge curves in figure 3d, and reported in figure 3e.

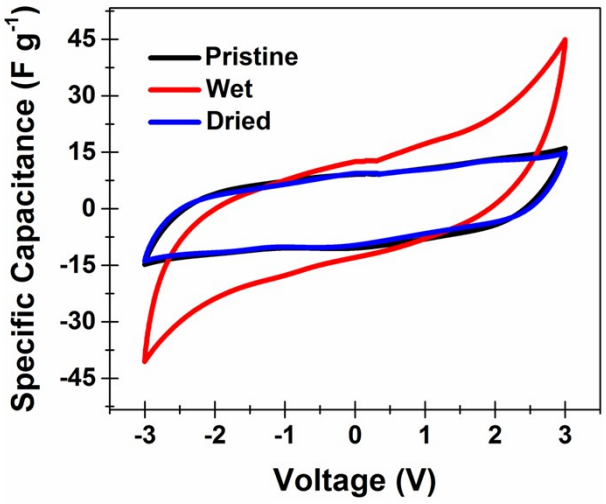

Figure S11: Cyclic Voltammetry curves of a full device in its pristine condition, tested while underwater after a 2 hour soak, and after the device had been completely dried.