Electronic Supplementary Information

Self-assembled fullerene additives for boosting capacity of activated carbon electrodes in supercapacitors †

Deepak Sridhar, ^a Kaushik Balakrishnan, ^b Tony J. Gnanaprakasa, ^c Srini Raghavan^{a, c} and Krishna Muralidharan ^{c*}

^a Chemical and Environmental Engineering, ^b College of Optical Sciences, ^cMaterials Science and Engineering The University of Arizona, Tucson, AZ

Experimental Procedure

Electrode Preparation:

E-AC: One gram of AC (Sigma Aldrich C5510) was combined with 100 μ l Nafion[®] perfluorinated resin solution (5 wt %, Sigma Aldrich) and the resultant mixture was sonicated in a glass vial along with 10 ml of ethanol for 30 minutes. Next this mixture was drop-casted on 25 μ m thick 99.999% pure 1x1 cm copper substrates (Alfa Aesar) to form films of thickness equaling about 130 μ m which were allowed to dry under a fume hood for 8 hours. Here, copper serves as the current collector.

E-ACC60: A solution consisting of C₆₀-fullerenes dissolved in toluene (2mg/ml) was sonicated for two hours and then drop-cast on copper substrates, followed by a directed stream of N₂ at 2 psi for one minute to ensure the removal of toluene as well as accelerate the formation of fullerene self-assemblies (FSA). This step was repeated for four times resulting in a uniform coverage of the copper substrate with fullerene self-assemblies (total mass inclusive of both the electrodes was about 80 µg). An X-ray diffraction (XRD) analysis revealed that the FSA structure was face center cubic (FCC) with a lattice parameter equalling 1.58 nm. The XRD pattern is given in Fig. S1.

For both systems, prior to the electrode preparation step, the copper substrates were pre-cleaned using 2N acetic acid (Fisher Scientific) at 60° C for ten minutes; this was followed by rinsing the copper substrates in ispropyl alcohol (Sigma Aldrich) and dried under an N_2 stream. The cleaned copper substrates were then placed in a quartz tube within a horizontal furnace and annealed at 1050° C for forty minutes under a H_2 atmosphere.



Fig. S1 XRD pattern of FSA on copper



Fig. S2 Schematic illustration of the electrode synthesis for the supercapacitors. A copper substrate is coated with fullerene molecules followed by jet drying allowing control over the shape of the fullerene assembles. Subsequently AC is coated on top of the FSA to achieve composite carbon electrodes.

Fig. S2 shows the schematic of the electrode preparation. The AC-Nafion mixture was then drop-cast as discussed above, resulting in an AC-fullerene-copper sandwich structure, where the AC-fullerene serves as the active electrode material, while the copper substrate serves as the current collector. In order to see if the addition of the AC-Nafion mixture had any effect on the fullerene self-assemblies' morphology, a film of PMMA was spin-coated on the electrode, followed by an etching step using dilute mixture $H_2SO_4-H_2O_2$ in DI water (1:1:30) to remove the underlying copper substrate (Fig. S3).



Fig. S3 SEM image of the FSA rods after the AC coating was added. (Image is taken in the opposite direction after copper was etched away using dilute mixture H_2SO_4 and H_2O_2)

Supercapacitor Assembly:

Symmetric supercapacitors consisting of either E-AC or E-ACC60 were assembled within a two-electrode split-cell setup (MTI corp.) *Whatman* filter papers (number 1) were used as separators, while 6M KOH served as the electrolyte. The filter paper was wetted by 80 μ L of the 6M KOH solution prior to the electrode assembly step.

Performance Metrics Analysis:

The equations employed for the calculations of the performance metrics of the supercapacitors For both CV and CD measurements, *forty* cycles were performed before the first reading was recorded, in order to stabilize the system and get consistent results. Specific capacitance was estimated from both CV (Equation 1) ^{1,2} and from the discharge curve (Equation 2) ^{3–5} to ensure consistency.

$$C_{s} = \frac{4\int IdV}{m \times \Delta V \times S}$$
(1)
$$C_{s} = \frac{4i}{m\frac{dV}{dt}}$$
(2)

where C_s is the gravimetric specific capacitance, $\int IdV$ represents half the integrated area under the CV curve (i.e. either the positive or the negative voltage sweep), S is the CV scan rate, ΔV represents the voltage window (=1V in our studies) for the CV experiments, m is the mass of the active material in both the electrodes, i is the discharge current and dv/dt is the slope of the discharge curve (after the potential drop).

For each system (i.e. E-AC and E-ACC60), a minimum of ten trials were carried out to ensure repeatability as well as provide statistical bounds for capacitance evaluation. In addition to specific

capacitance, energy density (E) and maximum power density (P_{max}) were also calculated from Equation 3 $^{6-8}$ and Equation 4 $^{9-11}$

$$E = \frac{1}{2}C_s \Delta V^2$$
 Equation 3
 $P_{\text{max}} = \frac{\Delta V^2}{4m(ESR)}$ Equation 4

Here, ESR is the equivalent series resistance calculated from Nyquist plots and t is the total discharge time in hours (from charge discharge curves).



Fig. S4 CV curves obtained at different scan rates for E-AC



Fig. S5 CV curves obtained at different scan rates for E-ACC60



Fig. S6 Model circuit used to fit the experimental EIS data



Fig. S7 EIS plots for both E-AC and E-ACC60 systems.

Table S1 Values of ESR and Ri for E-AC and E-ACC60 as estimated from using the circuit given in Figure S6.

Electrode	ESR	Ri	ESR	Ri	χ^2 of the fit
	experimental	experimental	model	model	
	(ohms)	(ohms)	(ohms)	(ohms)	
E-AC	1.8	2.1	1.7	2.0	0.001
E-ACC60	1.5	1.7	1.5	1.6	0.001



Fig. S8 Galvanostatic charge-discharge curves for E-ACC60 electrode at three different current densities.



Fig. S9 Effect of fullerene wt % on specific capacitance (obtained from CV plots carried out at 20 mV/s)

References

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