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Electronic Supplementary Information

Designing high-performance electrochemical energy storage nanoarchitectures to balance rate and capacity

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Experimental Methods

Chemicals

Resorcinol (Aldrich), formaldehyde (37%, Aldrich), sodium carbonate (Aldrich), sodium sulfate (Aldrich), sodium permanganate monohydrate (Aldrich), and lithium sulfate (Alfa Aesar) were used as received. All solutions were prepared with ultrapure water from an in-house water purification system (> 18 MΩ cm).

Preparation of carbon–fiber-supported carbon nanofoam papers

Carbon fiber and glass slide preparation

Carbon fiber paper (Lydall) was cut into 4 × 4 cm^2 squares and plasma etched for 45 min in the presence of air and an ice chip to humidify the gas (Harrick radio-frequency glow-discharge plasma cleaner; 30-W setting). Glass slides (VWR, 5 cm^2) were cleaned by soaking in a NaOH/ethanol base bath for 16 h, rinsed thoroughly with ultrapure water, and then heated in static air at 500 °C for 2 h in a muffle furnace (Thermolyne 47900).

Fabrication of carbon nanofoams

Carbon-paper-supported carbon nanofoams derived from resorcinol–formaldehyde (RF) precursors were prepared as previously described.[S1] The pore size was tuned by varying the RF weight percentage and/or resorcinol-to-catalyst ratio (Table S1). For all nanofoam formulations, a resorcinol–formaldehyde (RF) sol was prepared and stirred at 250 rpm for 30 min followed by a 3-h resting period at room temperature. Then, plasma-etched carbon fiber papers were placed in a dish containing the oligomerized RF sol, infiltrated under vacuum, and soaked for 1 min. The RF-infiltrated carbon fiber paper was removed from the RF sol and sandwiched between two glass slides, which were secured into place with mini-binder clips. Each assembly was wrapped in individually in duct tape. After the desired number of samples were assembled, all are placed in a single Al foil pouch containing ~2 mL of water and left for 12 h at room temperature to begin the initial curing process. The pouch is then placed in a pressure cooker (Nesco 3-in-1, Target) set to steam on “slow” cook (~88–94 °C) for 9.5 h then “warm” cook (~80 °C) for 14.5 h. The Al pouch was then removed from the pressure cooker and the duct tape was removed from each sample. The RF nanofoam was removed from the glass slides and soaked in ultrapure water for 1 h, followed by a 1-h soak in acetone, and subsequently dried in ambient laboratory air for 1 h. The RF nanofoams were then pyrolyzed to yield carbon nanofoams in a tube furnace (Thermo Scientific Lindberg Blue M) by ramping to 1000 °C at 1 °C min^{-1} and holding at 1000 °C for 2 h under flowing argon.

Electroless deposition of MnO*x*

Self-limiting deposition of conformal coatings of birnessite-like $Na_{\delta}MnO_2 \bullet xH_2O$ (designated MnO*x*) with the carbon nanofoam papers used a previously reported procedure.[S2] Briefly, carbon nanofoams were vacuum infiltrated with 0.1 M Na_2SO_4 and soaked under vacuum at room temperature for ~10 h. Then, the 0.1 M Na_2SO_4 solution was decanted and exchanged for 0.1 M $NaMnO_4 \cdot H_2O$ + 0.1 M Na_2SO_4. The carbon nanofoam was vacuum-infiltrated with the MnO_4^- solution 3× per hour for the first 5 h and then left to soak under vacuum for an additional 15 h. After 20 h of exposure to the MnO_4^- solution, the carbon nanofoams were removed, rinsed well and vacuum infiltated with ultrapure water, and soaked for 1 h. The H_2O rinse/vacuum infiltrate/soak steps were repeated two more times. The MnO*x*–carbon nanofoams were dried for 12 h under flowing N_2 at 50°C.

Materials Characterization

Electron Microscopy

Bare and MnO*x*-coated carbon nanofoam samples were prepared by cutting small sections with a fresh razor blade. The samples were mounted on flat and 90° Al stubs (Ted Pella) with conductive carbon tape and examined with a scanning electron microscope (Carl Zeiss Supra 55, 20 kV).

Porosimetry

Surface area and pore volume of bare and MnO*x*-coated carbon nanofoams were determined by nitrogen-sorption porosimetry (Micromeritics ASAP2010). All samples were degassed at 150 °C for 24 h prior to characterization. Pore size distributions were calculated from adsorption isotherm data using Micromeritics DataMaster software. Data were fitted with Micromeritics DFT Plus® software, using a density functional theory (DFT) model for a cylindrical geometry and Halsey curve thickness.

Electrochemistry

Electrochemical measurements were made using a PGZ 301 Voltalab potentiostat/galvanostat (Radiometer Analytical) or a Gamry REF600 potentiostat. All MnO*x*–carbon nanofoam electrodes were constructed by contacting pre-weighed pieces (typically 0.6 cm × 0.6 cm) to a nickel flag (Alfa Aesar Ni foil 0.1-µm thick, 99.5 %) with nickel print (MG Chemicals). The electrodes were vacuum-infiltrated with 2.5 M Li_2SO_4 and soaked under vacuum for 1 h. Symmetric cells were assembled using two MnO*x*–carbon nanofoam electrodes separated by an electrolyte infiltrated polyethersulfone membrane (130-µm thick, 1.2-µm pores, Sterlitech™). The MnO*x*–carbon nanofoam||separator||MnO*x*–carbon nanofoam cell was secured with Teflon tape. The symmetric cell was then placed in a vial containing electrolyte, infiltrated under vacuum, and soaked for 1 h. A beaker-cell was used for all electrochemical measurements. All electrochemical impedance spectroscopy was performed at +0.4 V.

Sheet Resistivity

The thickness of all samples was measured with a digital micrometer. Nanofoams were cut into 0.6 cm × 0.6 cm squares and adhered to a glass microscope slide with double-sided tape. Each corner of the nanofoam was electronically contacted with nickel print/ copper wire and the contacts were secured with epoxy (Loctite Hysol 1C). A potentiostat (PGZ 301 Voltalab, Radiometer Analytical) was used to measure voltages at 1, 5, and 20 mA and the voltages were measured with a multimeter.

Supplementary Tables

Table S1. RF sol recipes

Recipe	Resorcinol (g)	Formaldehyde (g)	Na_2CO_3 (g)	Water (g)
RF 50 R/C 500	10	14.74	0.0193	6.17
RF 50 R/C 1500	10	14.74	0.00254	3.13
RF 40 R/C 500	10	14.74	0.0177	13.9
RF 40 R/C 1500	10	14.74	0.00254	10.9

Table S2. MnO*x* weight loadings, sheet conductivity, and density of bare and MnO*x*–carbon nanofoams

Nanofoam	Wt% MnO*x*	Sheet conductivity (S cm^{-1})	Density (g cm^{-3})
one-ply 50/500	N/A	47	0.45
one-ply 50/500	60	28	1.4
one-ply 50/1500	N/A	47	0.54
one-ply 50/1500	57	33	1.8
one-ply 40/500	N/A	35	0.35
one-ply 40/500	60	26	1.2
one-ply 40/1500	N/A	31	0.41
one-ply 40/1500	41	25	0.93
three-ply 50/500	N/A	----	0.57
three-ply 50/500	59	33	1.2
three-ply 50/1500	N/A	----	0.49
three-ply 50/1500	54	34	1.2
three-ply 40/500	N/A	----	0.48
three-ply 40/500	52	27	0.73
three-ply 40/1500	N/A	----	0.43
three-ply 40/1500	33	27	0.54

Table S3. Electrochemical properties of one- and three-ply MnO*x*–carbon nanofoam symmetric devices

Nanofoam substrate	Specific capacitance [a] "$C_{s,cell}$" (F g^{-1})		Footprint capacitance [b] "$C_{f,cell}$" (F cm^{-2})		Volumetric capacitance [c] "$C_{v,cell}$" (F cm^{-3})		Total electrode loading (mg cm^{-2})	MnO*x* electrode loading [d] (mg cm^{-2})
	5 mV s^{-1}	50 mV s^{-1}	5 mV s^{-1}	50 mV s^{-1}	5 mV s^{-1}	50 mV s^{-1}		
50/500 one-ply	29	13	0.63	0.28	31	14	12	7.2
50/500 three-ply	29	8	1.7	0.48	36	10	32	19
50/1500 one-ply	30	14	0.65	0.31	36	17	12	6.8
50/1500 three-ply	27	8	1.6	0.44	32	9.1	30	16
40/500 one-ply	33	23	0.48	0.34	27	19	9	5.4
40/500 three-ply	30	18	1.2	0.7	22	13	22	11
40/1500 one1-ply	17	11	0.21	0.14	10	6.4	8	3.3
40/1500 3-ply	17	13	0.54	0.4	9.3	7.0	18	5.9

* Data derived from cyclic voltammetry of symmetric MnO*x* devices in 2.5 M Li_2SO_4

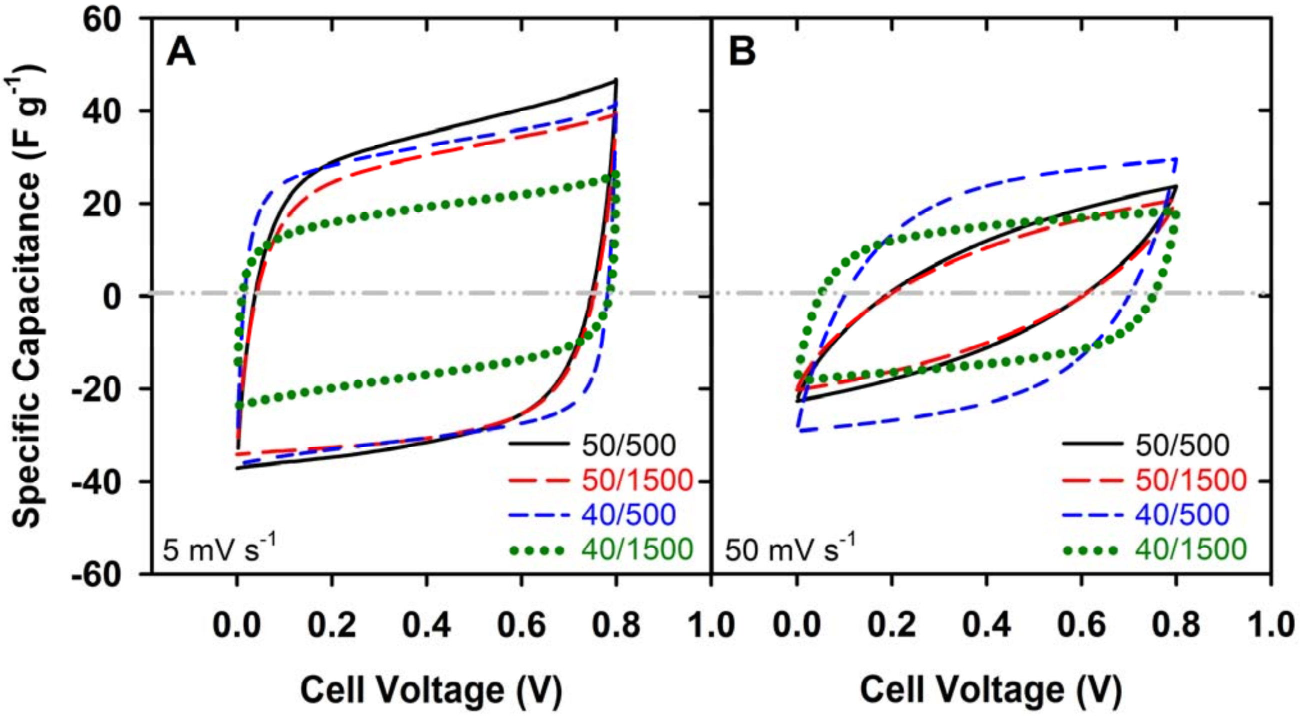
[a] Capacitance normalized to the mass of both electrodes (excluding metal foil current collectors and separator)

[b] Capacitance normalized to the footprint of the MnO*x* symmetric cell

[c] Capacitance normalized to the volume of both electrodes (excluding metal foil current collectors and separator)

[d] Normalized to mass of MnO*x* as determined gravimetrically

Supplementary Figures



5 **Fig. S1.** Specific capacitance versus cell voltage in 2.5 M Li_2SO_4 at (A) 5 mV s^{-1} and (B) 50 mV s^{-1} for symmetric cells comprising three-ply MnO*x*–carbon nanofoams of the following formulations: 50/500 (——), 50/1500 (– – –), 40/500 (- - -), and 40/1500 (• • •).

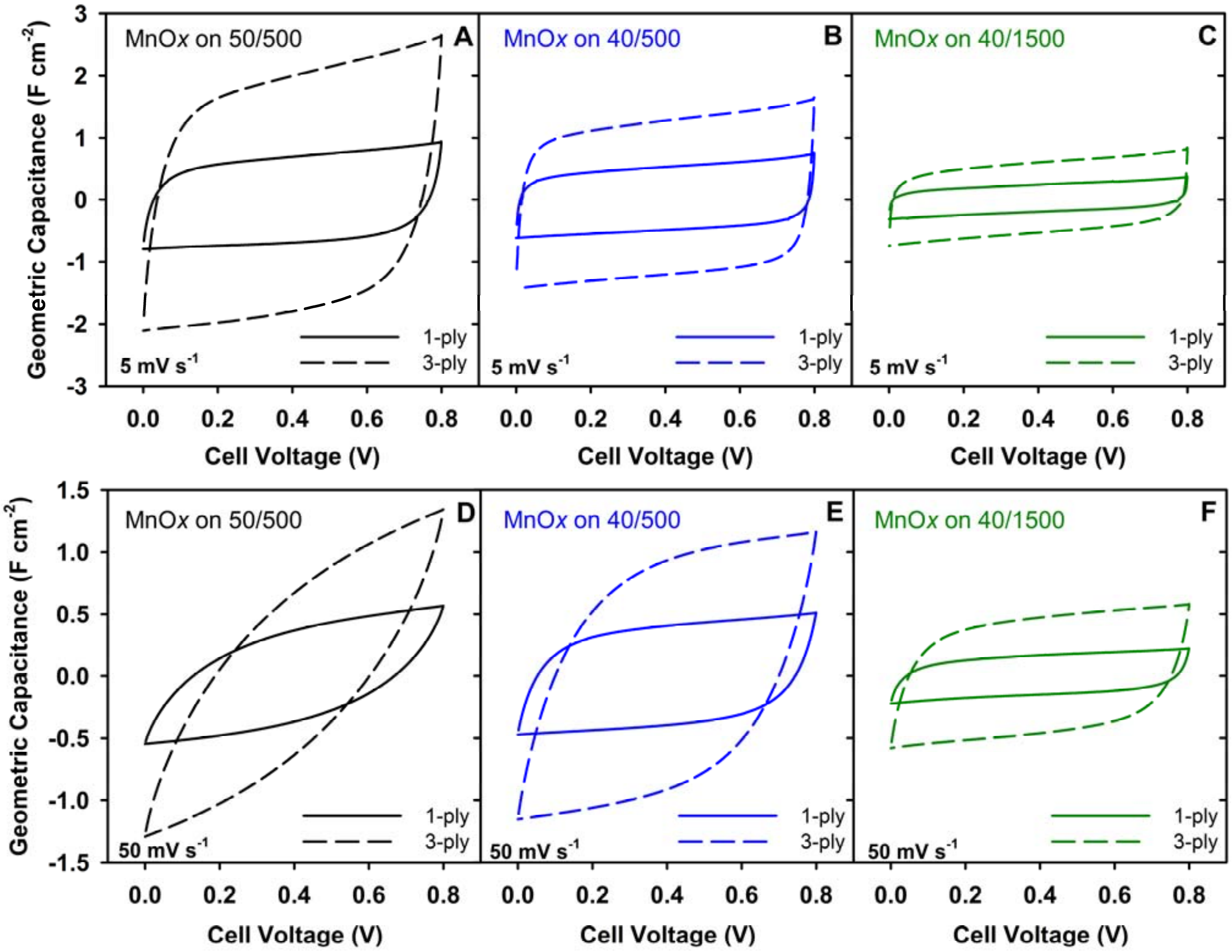


Fig. S2. Geometric capacitance versus voltage in 2.5 M Li_2SO_4 for symmetric cells at 5 mV s^{-1} (top row) and 50 mV s^{-1} (bottom row) with one-ply (——) and three-ply (– – –) MnO*x*-modified carbon nanofoam papers in which the nanofoam formulation varies from (A, D) 50/500, (B, E) 40/500, and (C, F) 40/1500.

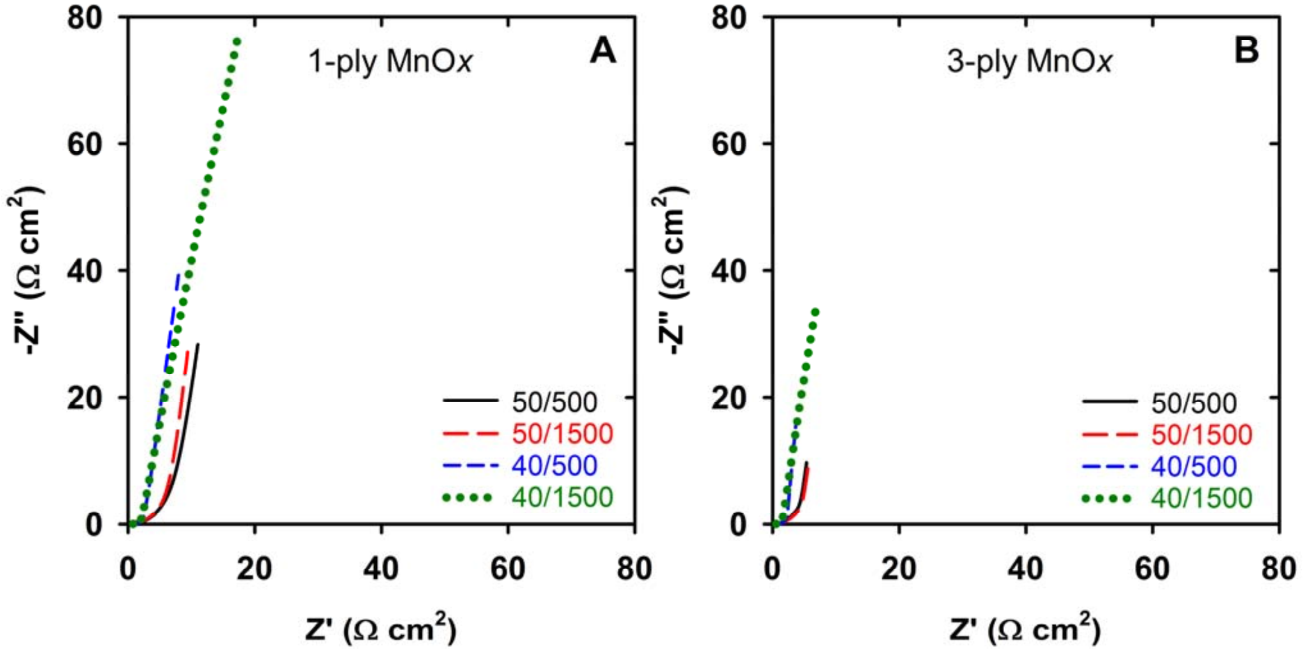


Fig. S3. Nyquist plots at 400 mV as normalized to the device footprint for symmetric cells with MnO*x* on 50/500 (——), 50/1500 (– – –), 40/500 (- - -), and 40/1500 (• • •) carbon nanofoams (A) one-ply and (B) three-ply.

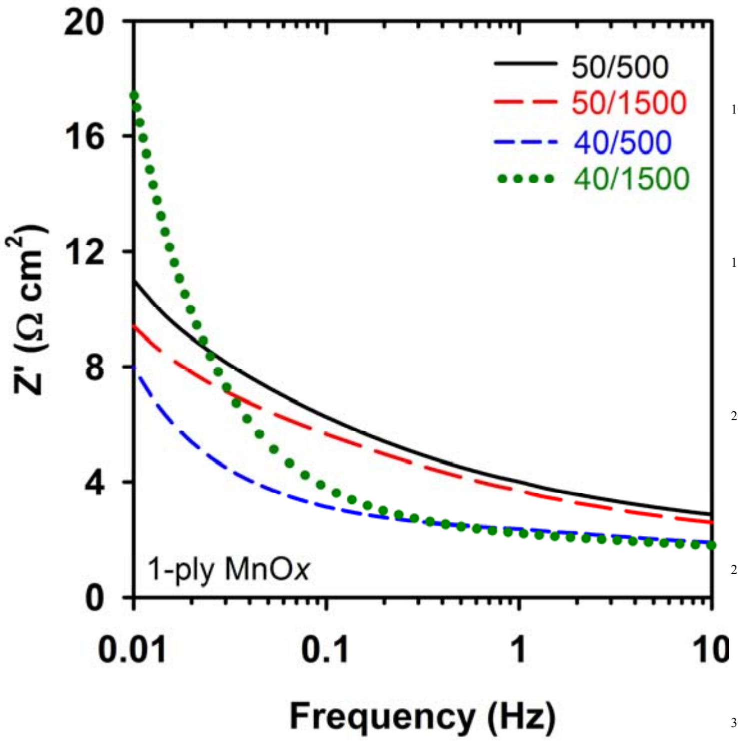


Fig. S4. Zreal versus frequency of one-ply symmetric cells with MnO*x* on 50/500 (——), 50/1500 (– – –), 40/500 (- - -), and 40/1500 (• • •) carbon nanofoams at +0.4 V.

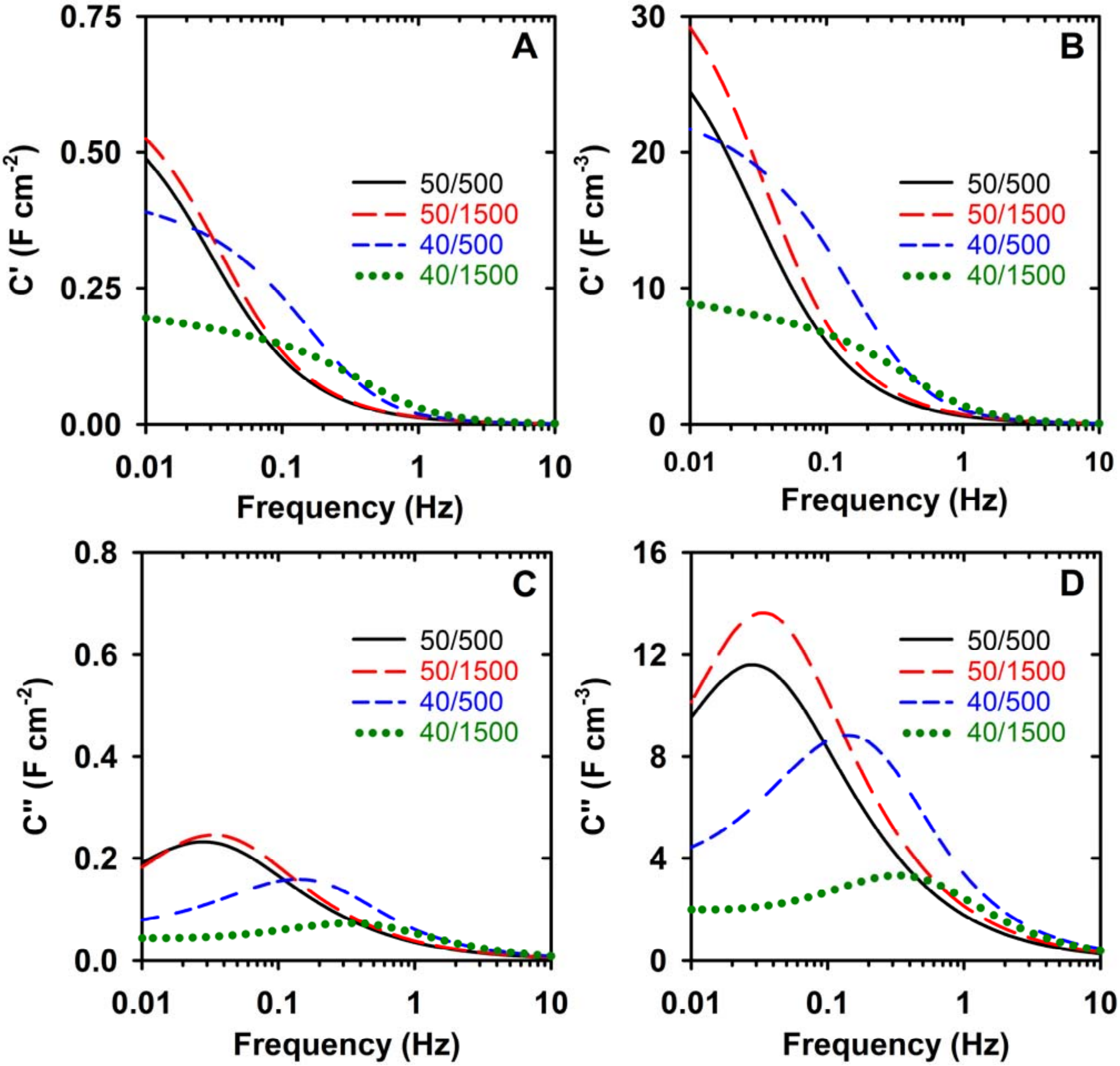


Fig. S5. The Bode plots as normalized for either geometric footprint or volume of the device of the real (top row) and imaginary (bottom row) components of capacitance for one-ply MnOx symmetric cells with 50/500 (—), 50/1500 (– – –), 40/500 (- - -), and 40/1500 (• • •) MnO*x*–carbon nanofoams at +0.4 V.

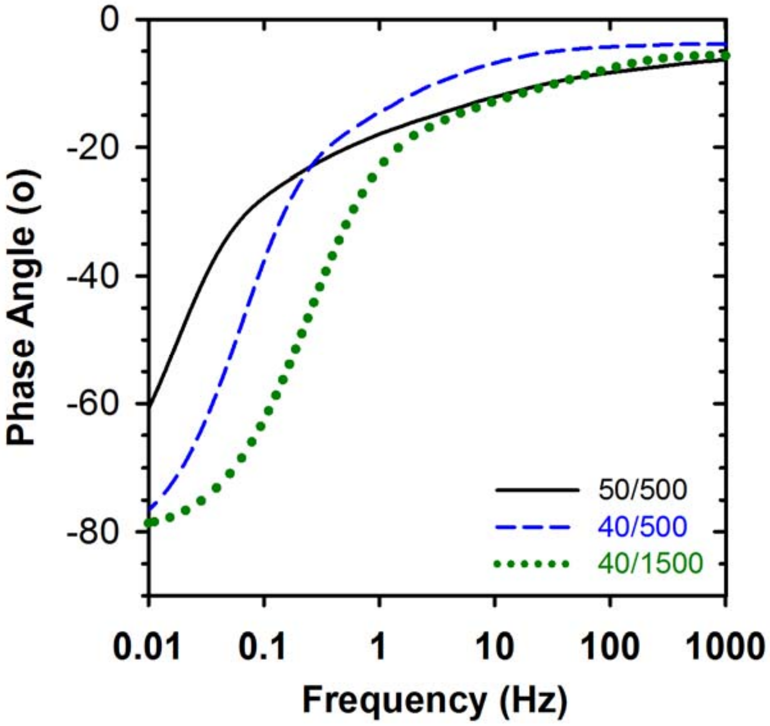


Fig. S6. Phase angle versus frequency for symmetric cells comprising three-ply MnO*x*–carbon nanofoams of the following formulations: 50/500 (——), 50/1500 (– – –), 40/500 (- - -), and 40/1500 (• • •).

Notes and references

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