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Reduced Graphene Oxide Hydrogels Deposited in Nickel Foam for Supercapacitor Applications: Toward High Volumetric Capacitance

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ABSTRACT

Graphene hydrogels have been considered as ideal materials for high-performance supercapacitors. However, their low volumetric capacitance significantly limits its real application. In this study, we report an environment-friendly and scalable method to prepare high packing density, electrochemically reduced graphene oxide hydrogels (ERGO) for supercapacitor application by the electrophoretic deposition of graphene oxide onto nickel foam, followed by the electrochemical reduction and hydraulic compression of the deposited materials. The as-prepared ERGO on nickel foam was hydraulic compressed up to 20 tons, resulting in an increase of the packing density of ERGO from 0.0098 to 1.32 g cm⁻³. Consequently, the volumetric capacitance and volumetric energy density of ERGOs greatly increased from 1.58 F cm⁻³ and 0.053 Wh cm⁻³ (as-prepared ERGO) to 176.5 F cm⁻³ and 6.02 Wh cm⁻³ (ERGO compressed at 20 tons), respectively. The ERGOs also exhibited long-term electrochemical stability with a capacitance retention in the range of approximately 79–90 % after 10,000 cycles. We believe that these high packing density ERGOs are promising for real-world energy storage devices for which scalable, cost-effective manufacturing is of significance and for which space constraints are paramount.

Keywords: Reduced graphene oxide, hydrogel, electrophoretic deposition, electrochemical reduction, supercapacitor.

1. INTRODUCTION

Supercapacitors, a class of electrochemical energy storage devices with superior power density and long cycling life, have attracted significant attention for the last decade due to their widespread application in energy back-up systems, portable devices, power tools, and hybrid electric vehicles.¹⁻³ According to their storage mechanisms, supercapacitors can be classified as electrochemical double-layer capacitors (EDLCs) and pseudocapacitors. EDLCs store energy through reversible ion adsorption at the electrode/electrolyte interface, whereas pseudocapacitors store energy chemically through fast surface redox reactions of the associated electrodes.¹⁻² For EDLCs, the specific surface area and the electrical conductivity of the electrode material are crucial to ensure satisfactory performance. Carbon materials, including activated carbon, carbon nanotubes, carbon aerogels and graphene, are the most commonly employed EDLC electrode materials.⁴ Among them, graphene has been considered as the ideal supercapacitor electrode material due to its large surface area, superior electrical conductivity, good chemical stability, and high mechanical strength.²⁻⁵ The theoretical specific capacitance of graphene is as high as $\sim 550 \text{ F g}^{-1}$.⁶ Assembling graphene sheets into three-dimensional interconnected porous microstructures, namely graphene hydrogels, has been considered the most effective approach to achieve high specific capacitance.⁷⁻⁹ Li et al. first demonstrated that the graphene hydrogel, prepared by vacuum-assisted filtration of reduced graphene oxide (RGO) solution, exhibited a specific capacitance of 156.5 F g^{-1} at an ultrahigh current density of 1080 A g^{-1} .^{10,11} The unique three-dimensional, interconnected networks with continuous porous structure and large surface area that constitute graphene aerogels can provide efficient ionic transportation and adsorption, leading to notably high performance for supercapacitors.⁹ Moreover, entrapped water within the graphene hydrogel acts as a spacer, preventing the restacking of individual graphene sheets.

Suppressing the sheet restacking yields a highly open and porous structure that creates continuous ion transport networks and allows electrolyte solutions to access to the surface of individual graphene sheets easily. Further, this allows graphene-based hydrogel supercapacitors to operate at ultrafast charge–discharge rates. Similarly, graphene hydrogels prepared by the hydrothermal, chemical, and electrochemical reduction of graphene oxides also exhibit superior specific capacitances at high current densities.¹²⁻¹⁶ However, graphene hydrogels consist of a large amount of water, up to 99 wt. %, resulting in very poor graphene packing density. Therefore, the volumetric capacitance of graphene hydrogels tends to be very poor, limiting their practical application, especially for increasingly lightweight, low form factor mobile devices.¹⁷ Attempts have been made to improve the volumetric capacitance of graphene hydrogels.^{11,14} Li et al. reported using the vacuum evaporation method to remove water selectively in graphene hydrogels, resulting in dramatically increasing the graphene packing density and nearly maintaining the outstanding electrochemical capacitive performance of graphene hydrogels.¹¹ Graphene hydrogels were first immersed in ratio-controlled volatile/non-volatile miscible solution (water/H₂SO₄ 5M or water/1-ethyl-3-methylimidazolium tetrafluoroborate) to exchange solvents, following by a vacuum treatment to remove volatile solvent (water). By using this approach, the packing density of graphene hydrogels increased from 0.069 to 1.33 g cm⁻³, corresponding to an increase of the volumetric capacitance from 18.0 to 255.5 F cm⁻³ in an aqueous electrolyte. Duan et al. recently demonstrated a facile method to increase the packing density of graphene hydrogels through compression under 150 MPa at a rate of 0.5 cm min⁻¹.¹⁴ The packing density of the graphene hydrogel increased ~ 60 fold, up to 0.71 g cm⁻³, resulting in a volumetric capacitance of 212 F cm⁻³.

Another challenge is that graphene hydrogels have very low mechanical strength, making them quite fragile during electrode processing. To prepare an electrode, the graphene hydrogel must be well-attached to the underlying metal current collector with low contact resistance. This challenge can be solved by directly “growing” RGO hydrogels atop the current collector.^{12,16} Shi et al. deposited RGO hydrogels inside the micropores of nickel foam by filling the porous structure of nickel foam with GO solution via the dip-casting method, followed by the chemical reduction of graphene oxide with ascorbic acid.¹² In our previous study, we reported a facile method to grow RGO hydrogel onto a stainless steel mesh substrate by electrochemical deposition.¹⁶ By directly depositing RGO hydrogel onto a current collector, no need exist for further processing to prepare the electrode. Moreover, the binding between RGO hydrogels and the current collector also significantly improves and, thus, produces an electrode with very low resistance.

In this study, we report a scalable method to prepare high packing density graphene hydrogels by the electrophoretic deposition (EPD) of graphene oxide (GO) on nickel foam (NF), followed by an electrochemical reduction. The obtained, electrochemically reduced graphene oxide hydrogels (ERGO) on nickel foam were hydraulic compressed by up to 20 tons of force, resulting in an increase in the packing density of ERGO from 0.0098 to 1.32 g cm⁻³. In a two-electrode symmetric supercapacitor test, using a 6M KOH electrolyte, ERGO exhibited excellent performance with a volumetric specific capacitance up to 176.5 F cm⁻³ at a current density of 1 A g⁻¹. Moreover, ERGO exhibited favorable cycling stability with a retention in range 79–90 % after 10,000 cycles, as a function of the packing density of ERGO.

2. EXPERIMENTAL

2.1 Preparation of ERGO

GO was prepared by the modified Hummers method using microwave-assisted expanded graphite as the starting material.¹⁸ The as-synthesized GO was diluted to a concentration of 6.0 mg mL⁻¹ and sonicated for 1 hour. The EPD of GO on NF was performed using a home-built system consisting of a Keithley 2410 Sourcemeter controlled by a home-designed Labview program. To increase its wetting characteristics, thus facilitating the penetration of the GO solution into the interior porous structure, the nickel foam was treated in 1M HCl solution for 10 min, following by copiously washing with D.I. water and drying at 100 °C. For the EPD experiments, the anode nickel foam sheets (0.16 x 1.5 x 4.0 cm, MTI Corp.) were mounted parallel to identically sized 316 L stainless steel (McMaster Carr) counter cathodes; the cathodes and anodes were separated by a 1.0 cm gap. A DC voltage of 5.0 V was applied after fully dipping the electrodes into the GO solution; the voltage was maintained until after the electrodes were fully withdrawn from the solution. The GO was electrophoretically deposited on the anode, whereas nothing deposited on the cathode. The electrodes were then dipped into 1M KOH electrolyte, and a reversed bias was applied across them. The electrochemical reduction of GO was performed by applying a reversed bias of 2.5 V across the two electrodes for 10 min. The obtained ERGO on NF was then immersed in a 6M KOH electrolyte for 12 hours. Finally, the prepared electrode was hydraulically compressed to prepare the supercapacitor electrode.

2.2 Characterizations

The morphologies of the surface and the cross-section of the ERGO were characterized by scanning electron microscopy (SEM, Hitachi 4800). X-ray photoelectron spectroscopy (XPS) analysis was performed on an X-ray photoelectron spectrometer (SPECS Phoibos 100 MCD

analyzer) using a non-monochromatized Al-K α X-ray source (SPECs XR 50). Thermogravimetric analysis (TGA) was performed on a thermogravimetric analyzer (Perkin Elmer) under a nitrogen atmosphere at a heating rate of 10 °C min⁻¹. The thickness of the ERGO electrodes were determined by averaging five measurements at different positions using an electronic digital micrometer (Chicago Brand) with the accuracy of 1.27 μ m.

2.3 Electrochemical measurement

The NF and as-prepared ERGO were compressed between two stainless steel plates using a hydraulic press (Specac) under a compression force of 1.0–20.0 tons for 30 seconds during which the squeezed electrolyte was removed with a Kimwipe tissue. The resulting NFs and ERGOs were denoted as NF x and ERGO x , where x is compression force in tons, in the range 1.0–20.0. The two identical ERGO electrodes were separated by a cellulose filter paper separator (Fisherbrand™ grade P8) soaked with 6M KOH electrolyte. All the components were assembled into a layered structure and were tightly sealed in a supercapacitor test cell (EQ-STC split flat cell, MTI Corp.). Cyclic voltammetry measurements were performed on a potentiostat/galvanostat PARSTAT 2273 (Princeton Applied Research), and galvanostatic charge–discharge tests were conducted on an Arbin battery tester BT2000 (Arbin Instrument) in the potential range 0–1.0 V. Electrochemical impedance spectroscopy tests were performed over a frequency range from 0.01 Hz to 100 kHz at an open circuit potential with an AC perturbation of 10.0 mV. The gravimetric and volumetric specific capacitance, energy density, and power density were calculated according to the following equations:^{19,20}

$$C_{wt} = 4 \left(\frac{I \Delta t}{m \Delta V} \right) \quad (1)$$

$$C_{vol} = C_{wt} \times \rho \quad (2)$$

$$E_{wt} = \frac{1}{8} C_{wt} (\Delta V)^2 \quad (3)$$

$$E_{vol} = E_{wt} \times \rho \quad (4)$$

$$P_{wt} = \frac{E_{wt}}{\Delta t} \quad (5)$$

$$P_{vol} = P_{wt} \times \rho \quad (6)$$

where C_{wt} and C_{vol} are the gravimetric and volumetric specific capacitances; E_{wt} and E_{vol} are the gravimetric and volumetric energy densities; P_{wt} and P_{vol} are the gravimetric and volumetric power densities, respectively. I is the constant discharge current, Δt is the discharging time, m is the mass of two electrode, ΔV is the operating voltage (obtained from the discharge curve subtracted by the voltage drop), and ρ is the graphene packing density of ERGO.

3. RESULTS AND DISCUSSION

The deposition of RGO hydrogels inside the nickel foam could be performed by simply dip-coating the NF in the GO solution, followed by a chemical reduction.¹² However, by using this method, the loading mass of the RGO hydrogel inside NF would be limited by the concentration of the GO solution precursor. Shi et al. found that the loading mass of RGO hydrogels in the 0.1 cm thick NF increased from 0.1 to 0.25 and 0.33 mg cm⁻², corresponding to an increase of the concentration of GO solution precursor from 2.0 to 4.0 and 6.0 mg mL⁻¹, respectively.¹² The further increase of the concentration of the GO solution could have resulted in an ultrahigh viscosity, limiting the penetration of the GO solution into the micropores of the nickel foam. A low loading mass of RGO hydrogels in NF is undesirable for practical supercapacitor applications because of the severe limit in the energy density. To overcome this problem, we employed EPD, a well-known process to deposit GO on different metal substrates, to increase

the loading mass of the RGO hydrogel.²¹⁻²³ As illustrated in Fig. 1, the GO was first electrophoretically deposited on NF, followed by an electrochemical reduction and a subsequent hydraulic compression. By using this protocol, we increased the loading mass of the ERGO hydrogel to 1.92 mg cm^{-2} . The EPD of GO was achieved by applying a DC voltage of 5.0 V for 5.0 min. The negatively charged GO sheets were deposited on the anode, creating thick layers of GO hydrogel on the both sides of the NF and throughout its interstitial space, as shown in Fig. S2. The GO hydrogel was then converted into an ERGO hydrogel by electrochemical reduction. Taking advantage of the electrochemical system used for EPD, the electrochemical reduction of GO hydrogel was performed with the constant potential mode by simply changing the magnitude of the applied DC voltage and inverting the polarity of the electrodes, as seen in Fig. 1. Finally, the extant ERGO hydrogel on the surface of the nickel foam was injected into the interior micropores of the nickel foam during the hydraulic compression step (Fig. S2).

Fig. 1: Schematic diagram of the preparation procedure of an ERGO supercapacitor electrode.

Electrochemical reduction is a facile, fast, scalable, and environmentally benign method to reduce GO with desirable quality.²⁴⁻²⁶ The electrochemical reduction of GO is typically attained by applying a constant potential or variable CV techniques to reduce the GO. In the constant potential technique, the selection of both the appropriate cathodic reduction potential and the reduction time is crucial for the complete reduction of GO to ERGO. A more negative potential increases the GO reduction rate.²⁶ UV-Vis spectroscopy and TGA were used to investigate the effect of voltage and reduction time on the reduction of the GO hydrogel. Fig. 2a shows the UV-Vis spectra of GO and ERGO, reduced at applied voltage of 2.5 V, as functions of time. The spectrum of GO displays a strong absorption peak at 232 nm and a shoulder at ~ 300 nm, which are assigned to $\pi \rightarrow \pi^*$ transitions of aromatic C–C bonds and $n \rightarrow \pi^*$ transitions of C=O bonds, respectively.²⁷ The absorption peak of ERGO gradually red-shifted to 264 and 271 nm after 5 and 10 min reduction, respectively. Moreover, the absorption in the whole spectral region also gradually increased, indicating the restoration of conjugated C=C bonds.²⁸ The further increase of the reduction time up to 20 and 30 min resulted in a small increase in the absorption, suggesting that the reduction is almost saturated after 10 min. This result is consistent with TGA of ERGOs, as shown in Fig. S3. The TGA curve illustrates that the GO loses 54 wt. % by 550 °C. The primary mass loss that occurred between 150 °C and 250 °C can be attributed to the decomposition of labile oxygen functional groups, such as hydroxyl, epoxy, and carbonyl groups.²⁹ The thermal stability of ERGOs gradually increased with the reduction time and was saturated after 10 min. The TGA curves of ERGOs reduced in 10, 20 and 30 min were almost identical. The mass losses in range 150–250 °C were minor; the ERGOs still retained ~ 87 wt. % at 550 °C, indicating that most of the labile oxygen functional groups were removed upon the electrochemical reduction. We also conducted electrochemical reduction of GO hydrogels at

different applied voltages and found that the reduction was much slower at lower applied voltages (1.5 and 2.0 V). Notably, the reduction did not increase with higher applied voltage (5.0 V).

Fig. 2: (a) UV-Vis spectra of GO and ERGOs reduced as a function of reduction times; (b) XPS survey spectra; and (c) & (d) XPS C1s spectra of GO and ERGO reduced for 10 min, respectively.

The XPS was used to further characterize the electrochemical reduction of the GO hydrogels. Fig. 2b shows the survey spectra of GO and ERGO reduced for 10 min. The intensity of the C1s peak of GO clearly is much lower than that of the O1s peak, whereas the intensity of the C1s peak of ERGO is significantly higher than that of the O1s, implying that a substantial quantity of oxygen functional groups was removed during the electrochemical reduction. The deconvolution of the C1s spectrum of GO, depicted in Fig. 2c, indicates four distinct peaks assigned to four

types of carbon groups, including non-oxygenated ring carbon (284.7eV), carbon in C–O bonds (286.6 eV), carbonyl C (287.9 eV) and carboxylate C (289.1 eV).³⁰ The deconvolution of the C1s spectrum of ERGO also shows these peaks, but the intensity of oxygenated carbon peaks decreased greatly, especially the peak which was assigned to the epoxy and hydroxyl groups (Fig. 2d), implying that these oxygen functional groups were significantly removed. The elemental compositions of GO and ERGO, determined from XPS survey spectra, revealed that the C/O ratio increases from 2.2 of GO to 7.1 of ERGO, which is comparable to previous ERGOs.^{16,31,32}

Fig. 3: SEM images of (a) the surface of NF, (b) the surface of NF10 (c) the cross-section of NF10, (d) the surface of as-prepared ERGO, (e) the surface of ERGO10 and (f) the cross-section of ERGO10.

Fig. 3 shows the morphologies of the NFs and ERGOs, examined by SEM. The NF exhibits a skeleton-like structure with the micropores ranging from 100 μm to 500 μm . After hydraulic compression, the NF skeletons were deformed and tightly wedged against each other, creating a flattened surface. The surfaces of the compressed NFs were similar when the compression force was higher than 5 tons (Fig. S4). Since the porosity of the NFs greatly decreased upon compression, the density and the size of micropores inside of the NF structure significantly decreased. Fig. 3d shows the image of the surface of the as-prepared ERGO, in which ERGO fully covered the NF. The hydraulic compression pushed the ERGO on the surface of the NF into the interstitial micropores with the NF. Note that no difference in the thicknesses of compressed NFs and ERGOs exists at the same compression force, implying that the ERGO completely occupied the pores inside the NF. The thicknesses and the graphene packing densities of ERGOs as functions of compression force are shown in Table 1. The thicknesses of ERGO electrodes decreased by a factor of 15, 50, and 137 by applying a compression force of 1, 10, and 20 tons, respectively. This resulted in a corresponding increase in the graphene packing density. At a compression force of 20 tons, the graphene packing density of ERGO increased to 1.32 g cm^{-3} , which is nearly identical to that of CCG hydrogel (1.33 g cm^{-3}), the most compact graphene hydrogel ever reported.¹¹ Moreover, the graphene content in ERGO hydrogel also significantly increased with the compression force due to the extrusion of water during the compression, from 1.19 wt. % of as-prepared ERGO up to 81.84 wt. % of ERGO20.

The electrochemical performance of the ERGO electrodes was evaluated by cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), and electrochemical impedance spectroscopy (EIS) in two-electrode, full cell supercapacitors. Fig. 4 shows the CV profiles of the ERGOs in the potential range 0.0–1.0 V at scan rates of 20–200 mV s^{-1} . At a moderate scan

Table 1: The thicknesses and the graphene packing densities of ERGOs as functions of the compression force

	NF* + ERGO thickness (μm)	ERGO thickness (μm)	Graphene packing density (g cm^{-3})	Graphene content in ERGO hydrogel (wt.%)
As-prep. ERGO	2024.60 $\pm$ 18	1985.76 $\pm$ 18	0.0097 $\pm$ 0.000089	1.19
ERGO1	165.13 $\pm$ 0.9	126.29 $\pm$ 0.9	0.1521 $\pm$ 0.0011	14.26
ERGO5	78.74 $\pm$ 0.8	39.90 $\pm$ 0.8	0.4812 $\pm$ 0.0096	42.97
ERGO10	66.07 $\pm$ 0.6	27.23 $\pm$ 0.6	0.7059 $\pm$ 0.015	61.04
ERGO15	58.42 $\pm$ 0.5	19.58 $\pm$ 0.5	0.9806 $\pm$ 0.025	76.28
ERGO20	53.34 $\pm$ 0.6	14.50 $\pm$ 0.6	1.3241 $\pm$ 0.055	81.84

* The real thickness of the NF is 38.84 μm , which was calculated based on the areal density of NF (34.6 mg cm^{-2}) and the density of nickel (8.908 g cm^{-3}).

Fig. 4: (a) & (b) CV profiles of as-prepared ERGO and ERGO20; (c) & (d) CV profiles of ERGOs at scan rate of 50 mV s^{-1} and 200 mV s^{-1} , respectively.

rate of 50 mV s^{-1} , the CV profiles were nearly rectangular, indicating an approximate electrical-double-layer capacitive behavior. With an increase in the scan rate, the current response increased accordingly, and the CV profiles remained quasi-rectangular at a high scan rate of 200 mV s^{-1} , suggesting superior capacitance behavior, low equivalent series resistance (ESR), and fast diffusion of electrolyte ions throughout the ERGO electrodes. Note that the current density response of the ERGOs at the same scan rates slightly decreased with an increase of the graphene packing density of ERGOs, implying a slight decrease of the gravimetric specific capacitance. Moreover, the shape of the CV profiles ERGOs became more oblique with the increase of the graphene packing density at high scan rate, suggesting that the diffusion of electrolyte ions was less effective. The decrease in the gravimetric specific capacitance and the decrease in the efficiency in electrolyte ion diffusion of ERGOs with an increase in the graphene packing density can be explained by the fact that the ERGO pores significantly decreased during compression. According to Müllen et al., the macropores act as a bulk-buffering reservoir for the electrolyte to minimize the distance for diffusion into the interior surfaces of the pores.³³ Simultaneously, the mesopores provide a large, accessible surface area for ion transport/charge storage; the micropores continuously increase the charge accommodation. Moreover, the small fraction of ERGO sheets would be restacked due to the extraction of the electrolyte during compression, resulting in a decrease of the effective surface area and the electrolyte ion diffusion pathway.

The GDC curves of ERGOs measured in the current density range of $1.0\text{--}10.0 \text{ A g}^{-1}$ are shown in the Fig. 5 (a-c). All of the GCD curves were symmetrically triangular, which is another typical characteristic of ideal electrical-double-layer capacitive behavior. A very small voltage drop

Fig. 5: (a & b) GCD curves of the as-prepared ERGO and ERGO20 at various current densities; (c) GCD curves of ERGOs at current density of 1.0 A g⁻¹, and (d) Nyquist plot of ERGOs.

(~0.06 V) was observed at the beginning of the discharge even at a high current density of 4.0 A g⁻¹, which suggests low internal resistance for the ERGO electrodes. The low internal resistance of the ERGO electrodes were further confirmed by EIS analysis. Figure 5d shows Nyquist plots based on a frequency response analysis for frequencies ranging from 100 kHz to 10 mHz. The Nyquist plots exhibit a typical arc in the high-frequency region and a straight line in the low-frequency region. The vertical shape of the straight lines in the low-frequency region indicated that the ERGO electrode system closely resembles an ideal capacitor. The internal resistances (R_s), determined by the first intersecting point with the real axis in the high-frequency region, were particularly small, only ~0.25-0.4 Ω . This suggests a low contact resistance at the interface of ERGO–NF current collector, which could be attributed to the penetration of the ERGO within the micropores of the NF; this shortens the distance of charge transfer from the active material to

the current collector.¹² Note that the R_s slightly increased as a function of the ERGO's graphene packing density. The interfacial charge-transfer resistances (R_{ct}), calculated from the span of the single semi-circle along the x-axis from the high to low frequency region, were almost unchanged. On the other hand, the equivalent series resistances (ESR), determined by extrapolating the vertical portion of the plot to the real axis, significantly increased with the graphene packing density, especially for ERGOs having packing densities more than 0.15 g cm^{-3} . The ESR was 1.4, 1.7, and $\sim 2.2 \text{ } \Omega$ for as-prepared ERGO, ERGO1, and ERGO5-ERGO20, respectively. From the inset of the Fig. 5d, the Warburg-type line (the slope of 45° portion of the curve) can be seen to be significantly extended with the increase of the graphene packing density, implying the decrease in efficiency of electrolyte ion diffusion. As mentioned above, the decrease in the efficiency of the electrolyte ion diffusion of ERGOs as a function of increasing graphene packing density is due to the decrease in the pores in the high packing density ERGOs, resulting in a decrease in the electrolyte ion diffusion pathways.

The gravimetric and volumetric specific capacitances of ERGOs calculated from the slope of the discharge curves at various current densities are shown in Fig. 6 (a & b). The as-prepared ERGO exhibited highest gravimetric specific capacitance, up to 161.1 and 126.3 F g^{-1} at the current density of 1 and 20 A g^{-1} . The gravimetric specific capacitance of the ERGOs gradually decreased with increase of graphene packing density. At current density of 1 A g^{-1} , the gravimetric specific capacitance of ERGOs decreased approximately 8.2, 12.3, and 17.1 %, corresponding to an increase of the graphene packing density from 0.0097 ± 0.00089 to 0.48 ± 0.0096 , 0.98 ± 0.025 , and $1.32 \pm 0.055 \text{ g cm}^{-3}$, respectively. In contrast to the gravimetric specific capacitance, the volumetric specific capacitance of ERGOs greatly increased as a

Fig. 6: (a & b) gravimetric and volumetric specific capacitance, and (c & d) gravimetric and volumetric Ragon plots of ERGOs, respectively.

function of the graphene packing density. As shown in Fig. 6b, the as-prepared ERGO exhibited very low volumetric specific capacitance, only about $1.2 \pm 0.011 - 1.58 \pm 0.014 F cm^{-3}$ due to the low graphene packing density. As the graphene packing density increased up to $1.32 \pm 0.055 g cm^{-3}$, the volumetric specific capacitance increased correspondingly, up to $176.5 \pm 7.3 F cm^{-3}$, which is roughly comparable to the volumetric specific capacitance of CCG hydrogel, the best volumetric specific capacitance ever measured for graphene hydrogel (Table S3).¹¹ Note that the CCG hydrogel was prepared by vacuum filtration of CCG dispersion, following by a vacuum treatment to remove volatile solvent, which are time-consuming and not industrially scalable. In contrast, the reported ERGOs were prepared by electrophoretic deposition of GO directly on the current collector, followed by an electrochemical reduction and, then, hydraulic compression. All of these processes are fast, inexpensive, and industrially scalable. The Ragon plots in Fig. 6(c &

d) show that the as-prepared ERGO exhibited superior gravimetric energy densities, approximately 5.5 and 2.9 Wh kg⁻¹ at the gravimetric power densities of 260 and 4600 W kg⁻¹, respectively. The volumetric energy densities were rather low, less than 0.06 Wh L⁻¹ at volumetric power densities less than 50 W L⁻¹. As the graphene packing density increased to 1.32±0.055 g cm⁻³, both of the volumetric energy density and the volumetric power density increased more than 110 times, up to 6.0 and 2.9 Wh L⁻¹ at gravimetric power densities of 350 and 5400 W L⁻¹, respectively.

Fig. 7: Cycling stability of ERGOs at different graphene packing densities.

Cycling stability, a crucial property of supercapacitors for their practical applications, was evaluated using the galvanostatic charge–discharge technique at a current density of 2.0 A g⁻¹ for up to 10000 cycles. Graphs of the cycling stability of ERGOs with different graphene packing densities were shown in Fig. 7. The cycling stability of ERGOs gradually decreased with increasing graphene packing density. The capacitance retentions of as-prepared ERGO, ERGO10, and ERGO20 were 89.7, 87.2 and, 78.9 % of their initial capacitances, retained after 10,000 charge/discharge cycles. The decrease of cycling stability with increasing graphene

packing density could be attributed to the lack of bulk-buffering reservoir for electrolyte of high packing density ERGOs, which could tolerate the swelling and shrinkage of ERGOs during the various electrochemical processes. Although a decrease in the cycling stability was observed as a function of increasing graphene packing density, the capacitance retention of the high packing density ERGOs remained approximately 79 – 90 % after 10,000 cycles, indicating the long-term electrochemical stability.

4. CONCLUSIONS

We have demonstrated a wholly scalable method to prepare high packing density ERGO hydrogels integrated inside of a current collector for supercapacitor applications. Electrophoretic deposition of GO onto and within nickel foam, followed by an electrochemical reduction and volumetric compression of the electrode yielded graphene packing densities that increased from $0.0097 \pm 0.000089 \text{ g cm}^{-3}$ of as-prepared ERGO up to $1.32 \pm 0.055 \text{ g cm}^{-3}$ of ERGO compressed at 20 tons. Consequently, the volumetric capacitance and the volumetric energy density of ERGOs greatly increased from $1.58 \pm 0.014 \text{ F cm}^{-3}$ and $0.053 \pm 0.00047 \text{ Wh cm}^{-3}$ of as-prepared ERGO to $176.5 \pm 7.3 \text{ F cm}^{-3}$ and $6.02 \pm 0.25 \text{ Wh cm}^{-3}$ of ERGO20, respectively. The ERGOs also exhibited long-term electrochemical stability with capacitance retention of about 79–90 % after 10,000 cycles. Considering this environment-friendly, scalable preparation method and the outstanding volumetric performance, these high packing density ERGOs are promising for real-world energy storage devices where scalable, cost-effective manufacturing is of significance and for which space constraints are paramount.

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Supporting Information. Description of GO synthesis, EPD profile, photographs of ERGO on nickel foam, TGA, elemental composition of ERGO, morphologies of NFs and ERGOs, and XRD of ERGOs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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