Electromechanical Properties of Reduced Graphene Oxide Thin film on 3D Elastomeric Substrate

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ABSTRACT: Electrically conducting, 3D elastomeric composite foams are fabricated successfully using multiple cycles of infusing polyurethane foams with graphene oxide sheets followed by reduction, to form coatings of reduced graphene oxide up to ~1260 nm thick. The reduced graphene oxide coating increases the compression modulus of the composite and lowers the electrical resistance significantly compared with polyurethane foam, the extents of which increase with increasing coating thickness. The electrical resistance of the coated foams varies by as much as three order of magnitude for coating thickness between ~150 and ~1200 nm, whereas the capacitance varies by one order of magnitude. Both the stress-strain and the resistance-strain behavior are highly repeatable with compression cycles performed up to 70% strain. Both SEM and X-ray tomography characterization show that deformation is mostly by bending of the pore walls up to about 20% strain, collapse of pore opening to about 60% strain, and densification beyond that. Micro-fractures also develop on the coating during the first few cycles of compression, but no obvious structural changes can be detected afterwards.

1. Introduction

Effective energy storage is critical for any mobile electronic device. For applications where the ability to withstand elastic deformation is essential, such as wearable electronics, surgical implants that naturally integrate with human functions, and systems with conformal formats, it is highly desirable that the energy storage components are stretchable, compressible, and bendable in all three dimensional axes. Electrodes are integral to any energy storage device. Thus, deformable electrically conducting materials that can be used to form electrodes will be critical

enablers of high performance deformable electronic devices. The known approaches such as the use of metallized plastic and stretchable conducting material bonded onto elastomeric sheets and engineered into patterns [1], such as waves [2], mesh [3, 4], and buckled configuration[5] are not easily amenable to forming three-dimensionally deformable material, especially deformation by compression. Other approaches include embedding carbon fiber, nanotube mats and crumpled sheets into an elastomeric matrix, and sandwiching them between elastomeric layers and forming 2D elastomeric electrodes [6, 7]. While excellent electrochemical performance has been reported for some of these 2D designs, their applications are limited due to the limited degree of deformability. To obtain a higher degree of conformal flexibility and increase active material loading, the current 2D electrodes have to be extended into freestanding 3D configurations.

One approach to 3D electrically conducting material is to use graphene foams and carbon nanotube/graphene foams, which can be made compressible and elastomeric [8-10]. Since their electrical conductivity and mechanical properties both depend on the stacking of the graphene sheets and the nature (type, size) and density of defects of the sheets, they cannot be independently varied, and the material properties depend rather sensitively on the preparation procedure.

Another approach is to decouple the physical/mechanical and electrical properties by forming a composite of an elastomeric material, such as polyurethane that are highly deformable in three-dimensions, with an embedded electrically conducting network of, e.g. carbon nanotubes or graphene sheets. However, because of the vastly different elasticity between conducting carbon and the polyurethane, typically only a few weight percent of conducting carbon can be uniformly dispersed into the elastomer without significantly adversely affecting its mechanical properties. At such low loadings, it is difficult to achieve a highly conductive composite material. Thus, in

spite of the relative ease of preparation and the advantage of 3D deformability, reported applications of these composites are currently limited to utilizing their dielectric [11, 12] and mechanical properties [13] for sensors [14] and actuators [15, 16].

For the purpose of high electrical conductivity, stacking and overlapping of the conducting component that provides a continuous path is more desirable than distributing it uniformly within the elastomeric matrix. That is, it is desirable to coat the walls (both interior and exterior) of a porous elastomeric matrix with a conducting, electrochemically active layer than dispersing the conducting material in the matrix. Because the two phases are physically distinct in such a composite, their individual properties could be tuned independently to generate a highly conductive, electrochemically active, and deformable 3D material. In previous reports of such coated material using reduced graphene oxide (rGO) as the conductive phase and porous polyurethane (PU) foam as the elastomeric supporting matrix [14, 17, 18], the electrical resistance of the composite was found to be very high, in the range 10^3 - 10^6 ohms [19-21]. We conjectured that this was because the rGO coating was too thin and/or the inherent conductivity of the rGO layers was too low due to insufficient reduction. Thus, by increasing the thickness and the degree of reduction of the rGO coating, we should be able to generate elastomeric materials of higher electrical conductivity. In order to achieve this, a preparation procedure needs to be devised that is compatible with the hydrophobic rGO and the hydrophilic PU, while ensuring good adhesion between these two phases and maintaining electrical continuity of the conducting phase in the composite. Here we report our successful preparation of such a composite, its mechanical and electrical properties, and its application as an electric double layer capacitor electrode after subjecting it to severe deformation upon applied mechanical strain. The

deformation led to the formation of surface defects that had not been observed previously in graphene-based 2D electrode systems.

After completion of our work, a recent article appeared that employed a similar approach of coating a polyurethane foam with reduced graphene oxide layer for use as a pressure-sensitive electrode for a battery [21]. Similar to the earlier reports [10, 14], because only one coating of limited thickness was applied, the electrical conductivity of the material in the relaxed state was low and insulating, it could not function as an electrode without reaching compressive strain as high as 80%. The conductivity increased drastically upon compression, such that the material functioned as an effective cathode support for electron transfer sites in a Zn-air battery. This drastic change in conductivity made the material unsuitable for use as a flexible electrode for energy storage, which requires high electrical conductivity at any strain.

2. Experimental

2.1 Preparation of PU-rGO.

Pieces of polyurethane (PU) foam, $2.5 \times 2.5 \times 2.5 \text{ cm}^3$, were cut from larger stock pieces obtained from BJB Enterprises (Tustin, CA, Type TC-266(50/100), IR spectrum shown in Figure S1) and used as received. An aqueous suspension of 0.5 wt.% graphene oxide (GO) was prepared using the modified Hummer's method as described previously [22], starting with graphite flakes (Asbury Carbons, 230U Grade, High Carbon Natural Graphite 99⁺). The procedure used for the fabrication of elastomeric, electrically conductive, and electrochemically active composite is shown schematically in Figure 1. A piece of PU foam was submerged in 60 mL of the GO suspension for 2 h under high vacuum, which served to remove trapped air within the porous structure. The soaked foam was removed carefully so as to retain as much of the entrapped liquid as possible, and then dried in vacuum overnight at 70 °C. The dried sample was placed on a

stainless mesh screen above a 20 mL aqueous solution of ethylenediamine (1 mg mL^{-1} , Sigma Aldrich) in a sealed 40 mL Teflon autoclave vessel. The setup was then heated to 100°C for 4 h to initiate hydrothermal reduction of the GO coating. This coating process, from the initial vacuum dip-coating to the ethylenediamine-assisted hydrothermal reduction, could be repeated a number of times to obtain GO coatings of different thicknesses. After the desired number of coating cycles was completed, the sample was then submerged in 60 mL 65 wt.% aqueous hydrazine monohydrate solution (Sigma Aldrich) for 3 h at 80°C for further reduction to form the reduced graphene oxide (rGO) coating. The sample was then gently washed with distilled deionized water and then vacuum dried overnight at 80°C .

Figure 1. Scheme showing steps employed to form a PU-rGO foam sample.

2.2 Characterization.

Scanning electron microscopy images were collected with a high-resolution field emission scanning electron microscope (FESEM, Hitachi SU8030). In order to facilitate locating the interface for the rGO coating thickness measurement, some of the PU foams were first sputter-coated with a thin Pd metal film. Then the sample surface was ion-milled by FEI Helios Nanolab

SEM/FIB to obtain a clear cross-sectional image of the PU bulk material with the rGO coating, the thickness of which was then measured digitally with a ImageJ software. No significant differences were detected with data collected from samples with and without Pd coating. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Scientific ESCALAB 250Xi (Al K α , 1486.6 eV). The stress-strain relationships were determined with a mechanical tester (MTS Sintech 20G), using a compression and rebound speed of 5 mm s⁻¹.

For electrical resistance measurements, aluminum foils serving as electrical contacts (Alfa Aesar, 0.025mm, 99.99%) were pasted with silver conducting paste onto two opposing faces of a PU-rGO foam piece to improve electrical contact. A voltage ramp from 0 to 3 V was applied across the current collectors using a potentiostat/galvanostat system (Arbin Instruments BT2000), which recorded the current passing through the foam piece.

Electrochemical tests of a foam piece were carried out in a three electrodes setup, with PU-rGO composite as the working electrode, Ag/AgCl (CH Instruments) as the reference electrode, and Pt foil (Alfa Aesar, 0.025mm, 99.9%) as the counter electrode. An aqueous solution of K₂SO₄ (0.5 M, Sigma Aldrich, 99% ACS) was the electrolyte. Using an electrochemical workstation (Autolab PGSTAT128N), current at densities of 0.05 A/g, 0.1A/g, and 0.5 A/g, based on the weight of the active materials in the foam pieces, was applied to charge and discharge the sample over a voltage range of -0.2 to 0.6 V. Cyclic voltammetry (CV) was performed with a scan rate of 5 to 100 mV s⁻¹ for a voltage scan of 0 to 1 V using a potentiostat/galvanostat system (Arbin Instrument BT2000).

3 Results and discussion

3.1. Structural characterization

The as-received PU foam had open, spherical, and interconnecting pores that averaged 500 μm in diameter (Figure 2a), that were packed tightly and separated by thin PU walls. The openings (necking) connecting adjacent pores were $>100\text{ }\mu\text{m}$ in size on average. Three types of samples, with 1, 3, or 5 coatings of rGO, labeled PU-rGO-1, PU-rGO-3, and PU-rGO-5, respectively, were synthesized. Their weight % loadings of rGO materials were ~ 2 , ~ 5 , and ~ 7 , respectively and repeatable to within 15%, as determined by comparing the weights of pristine PU samples and PU-rGO samples after processing. PU-rGO-1 (Figure 2c, d) showed a thin but rough coating, PU-rGO-3 (Figure 2e,f) showed a smoother coating $\sim 600\text{ nm}$ thick as estimated from SEM images of FIB milled (Figure S5), and PU-rGO-5 (Figure 2g,h) also showed a rather rough coating $\sim 1200\text{ nm}$ thick (Figure S6) with evidence of some loosely bound rGO flakes on the surface.

Subjecting the PU substrate through the mild reduction step with ethylenediamine did not change its structure or chemical composition significantly, as judged by the SEM images and XPS results (Figures S2, S3). However, treatment with hydrazine resulted in slight reduction in the C-O peak intensity at 286.7 eV in the XPS spectrum (Figure S3c), although its mechanical (compression) behavior was unaffected (Figure S7).

Coating of PU with rGO did not change the open pore structure of the PU substrate (Figure 2c, e, g), although the interconnecting pores were partially blocked by the rGO coating. The rGO coatings on all samples adhered well to the PU and showed no obvious signs of delamination even after repeated high-strain compression.

Figure 4 shows the C1s XPS spectra of the PU-rGO samples. Relative to the C-C peak at 284.7 eV, the intensities of C=O (286.8 eV) and, more significantly, C-O (284.7 eV) peaks were reduced after the two-step ethylenediamine plus hydrazine reduction (Figure 4a, b, c). The C/O ratio increased from 1.88 for the original GO to 6.5 and 6.2 for PU-rGO-1 and PU-rGO-5, respectively. Most of the reduction occurred at the hydrazine stage, as the C/O ratio after ethylenediamine reduction remained high at 2.2 (Figure 2d). Small amounts of N were also detected in the PU-

(Figure S4).

Figure 2. SEM images of: (a, b) pristine PU foam; (c, d) PU-rGO-1; (e, f) PU-rGO-3; inset in e is cross-sectional image obtained using FIB, with the rGO layer highlighted by arrows. From additional images (Figures S5), the thickness was estimated to be 570 ± 185 nm; and (g, h) PU-rGO-5; inset in g is cross-sectional image with rGO layer highlighted, and the thickness was estimated to be 1260 ± 220 nm (Figure S6).

Figure 3. Compressive stress-strain (S-S curves) of PU, PU-rGO-1, -3, and -5 foams. Overlapping data from multiple cycles (up to 200 cycles) are shown.

Figure 4. High-resolution XPS C1s spectra of: (a) GO before reduction treatment, (b) PU-rGO-1, and (c) PU-rGO-5 samples after ethylenediamine and hydrazine hydrothermal reduction, and (d) PU-rGO-1 after ethylenediamine but before hydrazine hydrothermal reduction.

Figure 5. XRD patterns of sample (a) PU-rGO-1 single coated composite sample after only ethylenediamine hydrothermal reduction, (b) PU-rGO-1 single coated composite sample after ethylenediamine and hydrazine hydrothermal reduction.

The average interlayer spacing between rGO sheets in the coating was determined for PU-rGO-1 by XRD, using a piece of the rGO coating removed from the external surface of the sample with Scotch tape. The data, shown in Figure 5, indicated that the interlayer stacking separation was slightly smaller for the sample reduced with both ethylenediamine and hydrazine than with ethylenediamine only, probably due to more extensive reduction and thus stronger attractive interaction between rGO sheets.

3.2. Mechanical properties

The compressive strain-stress (S-S) curves of PU and PU-rGO foams are shown in Figure 3. The PU foam was highly deformable with a low Young's modulus up to 50-60% strain, after

which the elastic modulus increased rapidly due to densification of the porous material. The compression behavior was highly reversible, and no permanent changes could be detected after many repeated (>1000) cycling. The S-S curves for all PU-rGOs followed a similar behavior except that the elastic modulus increased systematically with increasing coating thickness. The behavior of all coated samples was also highly repeatable after the first 5-10 cycles, when a few loose flakes of rGO broke off the foam.

Structural deformation of the PU-rGO composites under compression was investigated by SEM, and the data for PU-rGO-3 foam are shown in Figure 6. Up to about 20% strain, the deformation was mostly due to bending of the pore walls (Figure 6a-c). This corresponded to the linear region in the S-S curve in Figure 3. Between 20-60% strain (Figure 6d-f), collapse of pore openings began to occur, which corresponded to the plateau (or more gently sloping) region in the S-S curve. At high strain (>60%) (Figure 6g, h), the composite underwent densification and began to exhibit a modulus approaching that of solid bulk material. These structural changes were similar to those observed based on reconstructed 3D images from X-ray tomography (Figure S8), and consistent with literature findings on the deformation mode of porous polyurethane foam [23]. Importantly, there was no obvious detachment of rGO coating from the PU matrix throughout the cycling process.

The S-S behavior of the samples can be described adequately with the classical model for open-cell foams [24] after extension to account for the effect of coating layer (see SI). Using the experimental moduli, the model predicted the ratio of coating thickness of PU-rGO-5 and PU-rGO-3 to be ≈ 1.45 , close to the measured ratio of about 1.6.

Figure 6. SEM images of PU-rGO-3 foam at different compressive strain (vertical compression): (a) 0%, (b) 10%, (c) 20%, (d) 30%, (e) 40%, (f) 50%, (g) 60%, and (h) 70%. The scale bar is 300 μm .

3.3. Electrical properties

The electrical conductivities of the composite samples were determined from I-V scans at different compressive strains. In all cases, the current across the foam increased linearly as the applied voltage increased, as exemplified by the behavior of PU-rGO-3 (Figure S10). Figure 7a shows the resistance of PU-rGO-3 at various levels of strain up to 70% during repeated cyclic deformation. The overall resistance of the sample stabilized after first few (~ 10) cycles of deformation when loose pieces of rGO fell off. Figure 7b shows the dependence of resistance on coating thickness. PU-rGO-1 with the thinnest coating exhibited the highest resistance, $\sim 20 \text{ k}\Omega$, three orders of magnitude larger than the other samples. Before compression, the resistance was $\sim 470 \text{ }\Omega$ for PU-rGO-3 and $\sim 140 \text{ }\Omega$ for PU-rGO-5. All three samples exhibited decreasing resistance with increasing compressive strain. As shown in the SEM (Figure 4) and X-ray

tomography images (Figure S9), compression led to gradual closing of the open pores, which in turn generated new electrically conductive pathways and lower resistance. Although these resistance values were slightly higher than those of graphene or graphene-CNT composites [25, 26], which is expected as the majority of the composite consists of insulating PU, the relatively low resistance of these composite foam suggested very efficient use of the graphene.

Figure 7. (a) Resistance of a PU-rGO-3 foam at different compressive strain after 2, 50, and 100 repeated cycles of compression; (b) Resistance of PU-rGO-1, -3, and -5 samples as a function of applied compressive strain after 100th cycle of compression.

Figure 8. (a) Capacitance of a PU-rGO-5 foam electrode as a function of compressive strain; (b) Its EIS data at corresponding compressive strain, with illustration of equivalent circuit used for obtaining the fitted resistance values.

The capacitance and impedance of PU-rGO-5 were measured as a function of compressive strain (Figure 8) in a configuration shown in Figure S11 which also shows the CV curves. The impedance data were fitted with the equivalent circuit shown in the figure. The resulting series resistance (R_s), which corresponded to the sum of the resistances from electrode-Pt contact, the bulk electrolyte, and the electrode material, decreased slightly with increasing compressive strain (Table 1). This was expected based on the behavior of the electrical resistance with compression shown earlier. The charge transfer resistance (R_{ct}), which represented movement of charges within the Helmholtz double layer and charge transfer at functional groups of the rGO surface, decreased significantly from 30 to 50% strain and then increased again at higher strain. Such behavior was observed in capacitance as well. At the higher current densities of 0.1 A/g and 0.05 A/g, the capacitance increased from 30% to 50% strain, then decreased at 70% strain. At a low

current density of 0.05 A/g, the decrease at 70% strain was replaced by a slight increase. These electromechanical behaviors were reproducible even after many compression cycles.

Table 1. EIS fitting results of PU-rGO-5.

Strain	R_s (Ω)	R_{ct} (Ω)
30%	0.458	70.85
40%	0.440	19.07
50%	0.437	8.94
70%	0.431	23.02

There were two major contributing structural factors to the observed electromechanical behavior. One was closing of the open pores as described earlier, the other was creation of open facial micro-fractures under high strain. This is shown schematically in Figure 9. In the first few compression cycles, the tension on the stretched surface of a bent pore wall of the macroporous PU under compression led to the creation of facial micro-fractures on the rGO coating, which was evident in the SEM images. After these fractures were developed, the capacitance of the electrode increased when the compression strain was increased from 30 to 50%, because the compression opened the fractures, and the exposed rGO edge planes provided additional charge storage sites as well as exposed surfaces to allow infiltration of electrolyte into the interlayer spacing between graphene sheet stacks, which resulted in the increased capacitance. It has been reported that newly exposed edge planes of fractured rGO have up to 4 orders of magnitude higher specific capacitance than that of basal planes of stacked rGO [27]. When the strain was

released, closing of the micro-fracture opening decreased the accessible interfacial area and exposed edge sites, returning the sample to its original state, and the capacitance decreased. The macrostructure of PU-rGO began to undergo significant deformation under increasing compressive strain higher than 50%. This led to closing of macropores within the porous matrix of the composite, which in turn reduced the areas that were accessible to fast transport of electrolyte ions. Such effect of closing of macropores off-set the effect of fracture and exposed edge planes. Thus, the rate of increase of capacitance with increasing compression strain slowed at low currents. At high currents, the fast ion transport limited the effective interfacial areas to only those readily accessible. Thus, macropore closing mechanism dominated the capacitance behavior, and a decrease in capacitance and an increase in R_{ct} were observed with increasing strain.

Figure 9. (a) Schematic cross-sectional diagrams of a coating of stacked graphene layers (black) on a PU substrate (yellow) and (b and c) after bending due to compression, showing tension-induced formation of micro-fracture. (d) SEM image of PU-rGO-3 under 70% compression strain, exhibiting facial micro-cracks of the rGO coating.

CONCLUSIONS

A 3D, porous, electrically conducting elastomeric composite foam was successfully fabricated that was suitable for use as flexible electrical conductors and electrodes for electrical energy storage devices. The material, consisting of an elastomeric PU foam coated with a conducting layer of rGO, was highly durable to repeated compression cycling. Good adhesion between the rGO coating and the supporting PU matrix resulted in highly repeatable behavior even though micro-fractures were formed by compression at high strain. The findings pointed to the beneficial effect of decoupling the component for electrochemical properties from the component for mechanical properties.

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Author Contributions

‡These authors contributed equally. They worked closely together to design and conduct experiments, prepared samples, and interpret data. Yeguang Xue and Yonggang Huang formulated and analyzed the descriptive model, Denis T. Keane designed and performed X-ray tomography measurements. Mayfair C. Kung and Harold H. Kung supervised the project and contributed to experiment design and data interpretation.

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Graphical Abstract

Highly stable, 3D elastomeric composite foams were successfully fabricated by coating polyurethane foams with graphene oxide sheets followed by reduction. The foams exhibit low electrical resistance and high capacitance.