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Transition metal-free graphene framework based on disulfide bridges as a Li host material

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A B S T R A C T

A graphene sulfide framework (GSF) is designed and synthesized via a hybridization of graphene and organic compounds for use in electrodes for high-performance Li-ion batteries (LIB). This electrode material is devoid of transition metal and features a layered framework structure that is constructed by the formation of covalent disulfide bonds between organic linker molecules and graphene sheets. This structure capitalizes on the advantageous properties of each of the components in an electrochemical reaction. The structures of GSFs are characterized by Cs-corrected transmission electron microscopy (Cs-TEM), field emission scanning electron microscopy (FE-SEM), and X-ray diffraction (XRD). Depending on current density, the GSF electrodes exhibit two different types of electrochemical behavior during Li incorporation/extraction process, indicating the involvement of multiple Li-incorporation mechanisms. Various types of dithiol organics as linker components are incorporated in the GSF to evaluate the effect of length or structure on the electrochemical properties. The linker-dependent Li storage mechanism is explained based on the results of differential capacity analyses and electrochemical impedance spectroscopy (EIS). The GSF proposed in this study shows promise as an electrode material for a high-performance energy-storage system that is inexpensive and free of transition metals.

1. Introduction

The exploitation of Li chemistry has resulted in great progress in the field of electric energy storage systems, and large-scale electric devices (electric vehicles and grid-energy storage systems) are now operated using Li-ion batteries (LIBs). Despite the advantageous power and energy density of LIBs over other energy storage systems, the surging demand for ever-higher levels of performance drives the continuous development of advanced electrode materials for LIBs. Current LIBs are mainly composed of two types of materials: either graphite or inorganic crystals containing transition metal (TM) species. Among these, the TM-based electrodes feature greater levels of energy density and cyclic stability, which has attracted intensive research on this electrode material [1–17]. However, most TM-based materials have the disadvantageous aspect of gravimetric capacity due to inherently high atomic mass. In addition, detrimental effects on eco-systems and low cost-effectiveness have increased concerns about the use of TM-containing materials [18–20]. Consequently, the development of a TM-free electrode material is highly anticipated for a variety of aspects.

Graphene has been investigated for use as a TM-free electrode material due to its high capacity [21–41]. Although the theoretical capacity of graphene as LIB anodes is usually calculated as high as 744 mAh g⁻¹, which is simply double the value of graphite, many studies have reported that more than 1000 mAh g⁻¹ can be achieved via the chemical modification of graphene. The most widely used method for improving the electrochemical activity of graphene involves heteroatom doping with compounds such as nitrogen, boron, and sulfur [21–24]. However, the doping processes usually require high reaction temperatures of approximately 800 °C that demands a high use of energy at great cost. Recently, several studies showed that graphene materials can be functionalized under mild conditions (< 100 °C) using simple synthetic methods (e.g. thiolation, acylation, and Grignard reaction) that are common in the field of organic chemistry [42–44]. Therefore, the introduction of such synthetic methods could be useful for the construction of high-performance graphene-based electrode material at a lower production cost. Recent important researches on the simple organic molecules as LIB electrode material has provided great potential for their synergism with functionalized graphene [45–48].

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In the present study, we developed a graphene sulfide framework (GSF) with graphene sheets connected by disulfide bridges that can act as a TM-free and high-performance anode material for LIBs. We adopted functionalized graphene and organic compounds to serve as building blocks for a GSF. An understanding of the structure-property relationships of the GSF is necessary to achieve the optimized electrochemical performance of a GSF. The gap between graphene layers should be emphasized, as it determines Li ion mobility inside the material and the amount of surface area available for Li adsorption. The introduction of organic compounds for bridging the gap between graphene sheets enables one to control the inter-sheet distance and prevent the undesired restacking of individual sheets. Two essential design criteria include the presence of structural diversity and the existence of functional groups located at both ends of the organic linkers. Those functional groups are supposed to be responsible for the potential-sensitive redox reaction of Li, which affects the voltage profile during Li incorporation/extraction into/from synthesized material. To investigate the effects of the structure of a linker component on electrochemical performance, 1,2-ethanedithiol (EDT), 1,4-benzene-dithiol (BDT), biphenyl-4,4′-dithiol (BPDT), and p-terphenyl-4,4′-dithiol (TPDT) were used as functional organic linkers in the GSF. The synthesized GSFs showed distinctive electrochemical performance, which depends on linkers that feature reversible cleavage/formation of disulfide bonds upon lithiation/delithiation [49,50]. The optimized GSF exhibited a specific capacity of more than 1000 mAh g⁻¹ and stable cyclability during 100 charge-discharge cycles.

2. Materials and methods

2.1. Synthetic method

Graphene oxide (GO) was synthesized using the improved Hummer’s method reported by Marcano et al. [51] The pre-treatment of GO with a base solution and the synthesis of thiol-functionalized graphene oxide (SHGO) were in reference to procedures reported by Thomas et al. [52].

2.1.1. Pretreatment of graphene oxide with base solution

500 mg of GO was dispersed in 500 ml of deionized water by sonication for 30 min. Under gentle stirring conditions, 10 ml of a 1.25 M NaOH solution was slowly added until a dark brown color had formed. The solution was stirred at 70 °C for 1 h. The base-treated GO samples were collected by centrifuge at 12,500 rpm for 30 min. After washing with deionized water, the samples were re-dispersed in 500 ml of a 0.05 M HCl solution, and re-stirred at 70 °C for 1 h. After centrifuge and washing by the previously mentioned procedure, the resultant sample was dried under 0.1 Torr vacuum at 60 °C for 12 h. The obtained base-washed GO (bwGO) sample was collected and grinded.

2.1.2. Synthesis of thiol-functionalized graphene oxide (SHGO)

200 mg of bwGO in 50 ml DMSO solution was sonicated for 1 h. The dispersed solution was sealed and then moved into an Ar-filled glove box. After adding 20 mg of potassium thioacetate (CH₃COSK), the solution was tightly sealed and reacted at 50 °C for 5.5 h. After cooling to room temperature (RT), 10 ml of a 1 M HCl solution was added and then centrifuged at 12,500 rpm for 30 min. The sample was washed according to the following procedure: acetone (20 min, 3 times), diethyl ether (10 min, 2 times) and deionized water (2 h, 3 times). The SHGO was finally obtained after drying the sample under 0.1 Torr vacuum at RT.

2.1.3. Disulfide-linking between SHGO and linker molecules

The disulfide bond formation method reported by M. Kirihara et al. was adopted [53]. First, 100 mg of SHGO was dispersed in 30 ml ethyl acetate (CH₃CO₂C₂H₅, EtOAc). After dispersion by intensive sonication (duty cycle: 50 %, output: 60 W) for 10 min, the solution was cooled at RT. The amounts of added linker molecules were calculated.

Fig. 1. Graphical images, TEM and SEM images of (a) SSGO, (b) GSF/EDT, (c) GSF/BDT, (d) GSF/BPDT and (e) GSF/TPDT.
as follows: 20.5, 31.5, 42.4, and 13.6 mg of BDT, BPDT, TPDT and EDT, respectively. After a linker was added, the SHGO/linker mixed solution was stirred for 10 min. After adding 3 mg NaI with stirring for 10 min, 0.22 ml of 30% H2O2 was added, and was stirred for 24 h at room temperature. The synthesized sample was membrane-filtered and washed with 10 ml EtOAc, 20 ml ethanol, and 10 ml acetone. After drying under 0.1 Torr vacuum at 60 °C for 12 h, the resultant GSF samples were obtained. A schematic diagram of the synthetic procedures for SHGO and GSF is shown in Fig. S1.

2.2. Electrochemical measurements

All of the electrodes for the electrochemical performance measurement were fabricated by mixing active material: Super P:poly(vinylidene difluoride) (PVdF, Sigma-Aldrich) in an 8:1:1 weight ratio. The mixed components were dispersed homogeneously in a few drops of N-methyl-2-pyrrolidone (NMP) in an agate mortar. The dark-greyish slurry mixtures were uniformly caste onto Cu foils via doctor-blading and dried under 0.1 Torr vacuum at 60 °C for 12 h. Then the electrodes were roll-pressed, cut into 1 cm² round discs, and assembled into a button-type coin cell (CR2032). Li foil (0.75 mm thickness, Alfa Aesar) and 1.15 M LiPF6 in a 2:4:4 volumetric ratio of ethyl carbonate/ethyl-methyl carbonate/dimethyl carbonate solution were used as counter electrode and electrolyte, respectively. Galvanostatic charge/discharge properties were characterized with multichannel battery cycling equipment (WBCS3000, WonATech). Electrochemical impedance spectroscopy (EIS) was conducted using potentiostat equipment (ZIVE SP2, WonATech). The electrochemical parameters of the equivalent circuit were obtained using ZMAN software.

2.3. Characterizations

The gap distances of the GSFs were analyzed via Cs-corrected Transmission electron microscopy (Cs-TEM, JEM-ARM200F). Also, field-emission scanning electron microscopy (FESEM, AUGIRA) was used to analyze the surface morphology. To analyze the elemental components and chemical states of the samples, X-ray photoelectron spectroscopy (XPS, Sigma Probe, Thermo) was performed. An X-ray

![Fig. 2. XRD patterns of SSGO, GSF/EDT, GSF/BDT, GSF/BPDT and GSF/TPDT from 5° to 35°. Raw data are expressed as hollow dots and solid lines indicate smoothed values. Adjacent-averaging was utilized for smoothing, and the point of windows was set as 50.](image)

![Fig. 3. XPS spectra and deconvoluted peaks for C1s and S2p of (a) SHGO, (b) SSGO and (c) GSF/BDT.](image)
differential diffractometer (XRD, Rigaku, D/max-2200, Cu Kα1 radiation) was used to investigate the diffraction patterns of the synthesized samples. BET surface areas were measured using a Micrometrics ASAP 2010 instrument.

3. Results & discussion

Fig. 1 shows a graphical image of the GSFs with different linkers along with their TEM and SEM images. As a control sample, a GSF without a linker was also prepared for comparison, and is referred to as SSGO. As shown in the TEM images, the gaps between the graphene layers became wider as longer linker molecules were incorporated in the GSFs (SSGO = 0.37 nm, GSF/EDT = 0.42 nm, GSF/BPTD = 0.45 nm, GSF/BPTD = 0.49 nm, GSF/TPDT = 0.52 nm). The observed gap distance values of the GSFs showed differences in the molecular length of the adopted linkers. The bonding angle of -S-S- was 103°, so the linkers were attached between graphene layers in an inclined configuration, rather than in a straight-standing form. In SEM analysis, all of the samples showed highly porous morphologies, which means that restacking between graphene sheets was prevented during the synthesis processes for all samples.

Fig. 2 shows the XRD patterns of the GSFs. The main peak positions of SSGO, GSF/EDT, GSF/BPTD, and GSF/TPDT, and GSF/EDT appeared at 23.7°, 22.0°, 21.3°, 20.8°, and 19.5°, respectively. These results correlated well with TEM analysis showing that the gap distances widened as longer linkers were used. The diffraction patterns at 23.7° corresponded to GSF/BPTD and GSF/TPDT because of the partial nature of the disulfide bond formation between SHGOs when there was no insertion of either linkers or unreacted thiols. As described above, the main diffraction peak of SSGO was observed at 23.7°. However, this unspecific formation of a disulfide bond was observed neither in GSF/EDT nor in GSF/BPTD. Diffraction patterns of other intermediate materials such as graphite, GO, bwGO, and SHGO are also shown in Fig. S2.

XPS analysis was used to observe the chemical state of carbon and sulfur before and after the disulfide formation reaction. Fig. 3(a), (b), and (c) show the Cls spectra of SHGO, SSGO and GSF/BPTD, respectively. Each of the deconvoluted peaks in these spectra represent commonly known functional groups on GO such as C-C bonds (284.2 eV), hydroxyls (285.4 eV), carbonyls (286.8 eV), and esters (288.7 eV). The Cls spectra of SHGO and SSGO show no remarkable difference in either peak position or intensity, which means that disulfide bond formation had a negligible effect on the chemical state of the carbon-containing functional groups on SHGO. In GSF/BPTD, however, a higher peak intensity of C-C was observed compared with that of the other two materials, which was due to the incorporation of aromatic ring-containing linker molecules. Fig. 3(d), (e) and (f) are the results of the S2p analyses of SHGO, SSGO and GSF/BPTD, respectively. To distinguish the peaks corresponding to -SH (163.1 and 164.3 eV) and -S-S- (162.1 and 163.0 eV), normalized S2p peaks of these 3 materials from 161 to 166 eV are compared in Fig. S3. A slight shift in the peak positions of SSGO and GSF/BPTD to a lower binding energy verified that even -SH was dominant from among all three materials, and that a disulfide bond was partially formed in SSGO and even more so in GSF/BPTD. Therefore, the peak deconvolution was proceeded based on this observation. The results of S2p analysis were also utilized to quantify the sulfur content in SHGO. The atomic ratio of sulfur in SHGO was calculated as 4.2%. Based on this value, we determined the amount of linkers required for the construction of GSFs in order to acquire a molar ratio of 1:1 for the thiol groups in SHGO and linkers.

To evaluate the Li storage performances of the synthesized samples, half-cell Galvanostatic charge/discharge tests were carried out using Li metal as an anode. Fig. 4(a) shows the first cycle charge/discharge profiles of samples at a current density of 0.05 A g⁻¹, and a potential window from 0.01 V to 3.0 V. Discharge capacities of 703, 1055, 778, 725, and 892 mAh g⁻¹ during the first cycle were recorded for SSGO, GSF/BPTD, GSF/TPDT, and GSF/EDT, respectively. All samples showed analogous profiles and a sloped potential plateau below 1.0 V during charge and discharge. The electrochemical behavior of disulfide bonds with Li ions have been well established in previous reports, and the overpotential between oxidation and reduction is relatively high (~1.6 V) due to the low reaction kinetics. Considering this effect, the discharge plateau that appeared at 1.0 V was due to the lithium-sulfur bond formation. The redox behavior of disulfide was observed in differential analysis (Fig. 5(a) and (b)). In the first cycle, all samples showed a low level of Coulombic efficiency (52.8 – 68.8%). The ex-situ XPS revealed that the formation of Li2CO3, with a main component composed of a solid electrolyte interphase (SEI), on the GSFs during charge/discharge cycles (Fig. S4). Therefore, a high irreversible capacity among all materials during the first cycle was due to the formation of SEI. After the first cycle, the highly reversible nature of liathiation and delithiation was maintained. The charge/discharge profiles of samples at various current densities are presented...
in Fig. S5, and the initial charge/discharge profiles and rate capability of graphite, bwGO, and SHGO are shown in Fig. S6.

Charge/discharge testing was performed at various current densities to evaluate the rate capability of the GSFs (Fig. 4(b)). The GSFs with long linkers, GSF/BPDT and GSF/TPDT, showed a relatively lower capacity in all ranges of current rates due to the higher amount of electrochemically inactive weight of the aromatic rings in the linker molecules. At relatively low current densities, 0.05 and 0.1 A g\(^{-1}\), GSF/BDT showed the highest specific capacity, followed by GSF/EDT, GSF/BPDT, GSF/TPDT, and SSGO. As current density increased by more than 0.25 A g\(^{-1}\), however, the specific capacity of GSF/EDT began to overtake that of GSF/BDT. Also, GSF/BPDT and GSF/TPDT showed values that were even lower than those of SSGO. Details of these results will be discussed later.

Fig. 4(c) indicates the long cyclic stability of the SSGO and GSFs. The cells were first cycled at 0.05 A g\(^{-1}\) for 2 cycles to promote stabilization, and were then cycled repeatedly at 0.25 A g\(^{-1}\). After 100 cycles, GSF/BDT, GSF/BPDT, and GSF/TPDT retained 78.1, 74.0, and 75.8% of their initial capacities, respectively. However, the reversible capacity of GSF/EDT was quickly degraded in the first 10 cycles, which could be attributed to the innate structural instability of EDT compared with other linkers containing aromatic rings.

As described above, the rate performances differed among the GSFs depending on current density, particularly between GSF/BDT and GSF/EDT. To clarify the Li storage mechanisms that depended on current rates, \(N_2\) adsorption and desorption analyses were first carried out to measure the BET surface area (Table S1). There were no remarkable differences in the surface areas between the GSFs, and it could be assumed that the discrepancies in the Li storage performances of GSFs were not significantly affected by the differences in surface areas. Note that no morphological differences were found among the materials, as discussed in SEM analysis (Fig. 1). Fig. 5(a) and (b) represent differential capacities during delithiation at 0.05 A g\(^{-1}\) and 0.25 A g\(^{-1}\), respectively. At 0.05 A g\(^{-1}\), cathodic peaks corresponding to disulfide bond formations (-SLi + LiS- → -S-S- + 2Li+) were observed, while the peaks were significantly attenuated at 0.25 A g\(^{-1}\). We speculated that a threshold of current density exists between 0.05 and 0.25 A g\(^{-1}\), which could be related to the accessibility of Li ions toward the interior of GSF structures when thiol redox moieties are present.

To obtain more evidence on linker-dependent Li storage mechanisms, we performed XPS analyses with 4 types of GSF/BDT which include the electrodes charged and discharged at low (0.05 A g\(^{-1}\)) and high (0.25 A g\(^{-1}\)) current densities. Fig. S7 shows the S2p spectra of the prepared electrodes. Even at a low signal-to-noise ratio, we were able to find the signal corresponding to an S-Li bond (near 160 eV) from the electrode that was discharged at 0.05 A g\(^{-1}\) (Note that the low signal-to-noise ratio of XPS data is due to the low atomic concentration of sulfur in GSF). However, there were no noticeable signals in other samples. The XPS data indicates that the formation of S-Li bonds by Li oxidation occurred only within the electrode discharged at low current density. Considering that disulfide bridges exist between the graphene layers in GSFs, this result supports the idea that Li diffusions through interstitial graphene layers and subsequent redox reactions are prominent at low current density. This phenomena is also well-correlated with the previous reports on graphene anode materials for LIBs, whereby the Li storage mechanism of graphene varies depending on the current density [33,34].

Electrochemical impedance spectroscopy (EIS) analyses were carried out to analyze the detailed resistive factors in the GSF structures. Fig. S5(c) and (d) represent the acquired Nyquist plots of SSGO and GSFs, respectively, for application of the equivalent electrochemical circuit model. The simulated parameters are shown in Table 1, where \(R_c\) is the equivalent series resistance, \(R_{ic}\) is the charge transfer resistance.
resistance between intercrystallites. Because the electrochemically active part in GSF is graphene layers, $R_{ic}$ is assigned as charge transfer resistance between graphene sheets across the linker molecules. $R_{ct}$ is the charge transfer resistance between an electrode and its active material, and $A_w$ is the Warburg coefficient which represents the mass transfer resistance, which is defined as follows:

$$A_w = \frac{RT}{\pi n^2 F^2 \theta C D}$$

where $R$ is the gas constant, $T$ is the temperature, $A$ is the diffusion area, $n$ is the valency, $F$ is the Faraday constant, $C$ is Li ion concentration, $D$ is the diffusion coefficient of Li ion, and $\theta$ denotes the fraction of the reduced and oxidized species present.

The high $R_{ic}$ that is obvious in GSF/EDT could be attributable to a linker molecule without a conjugated aromatic structure. However, considerable values for $R_{ic}$ were also observed in GSF/BPDT and GSF/TPDT. As explained above, during the synthesis of the GSF, the slow reaction kinetics of BPDT and TPDT with SHGOs created a small population of linker pillars between the graphene layers in GSF/BPDT and GSF/TPDT. Consequently, the reduced amount of organic linker resulted in loosely packed structures for GSF/BPDT and GSF/TPDT. The $R_{ct}$ in GSF/BDT had the highest value among the samples. It is possible that the lower graphene content in GSF/BDT, compared with that in SSGO and other GSFs, induces distinctive surface properties (e.g. hydrophobicity, wettability). As the molecular length of the linkers increased, the $A_w$ values tended to decrease, however, there was a negligible difference between GSF/BDT, GSF/BPDT and GSF/TPDT.

To summarize the EIS results, GSF/BDT was favorable in terms of inter-sheets charge transfer and mass transfer, whereas GSF/EDT had the most favorable level of charge transfer between active material and electrode.

Based on the differential analysis, EIS and XPS observations, multiple Li ion storage mechanisms were proposed for the GSFs (Fig. 6). Li adsorption on the inner and outer surfaces of graphene and redox reactions with disulfides are possible mechanisms. Both Li adsorption on the inner surface and redox reactions with disulfides should be based on the precondition that the Li ions can diffuse into the graphene layers. Thus, these mechanisms can be categorized into two forms: Li insertion between layers and adsorption on the surface. At low current densities, Li insertion between layers and either the subsequent redox reaction or adsorption occupies a large portion of the overall Li storage. The lower specific capacities of GSF/BPDT and GSF/TPDT are due to the higher content of the electrochemically inactive mass within linker molecules, as discussed above (Fig. 3(b)). By contrast, although BDT has a higher molecular weight than EDT, the specific capacity of GSF/BDT surpasses that of GSF/EDT. As presented in the EIS analyses, GSF/EDT shows $R_{ic}$ and $A_w$ values that are higher than those of GSF/BDT, which indicates that the shorter molecular length and structural instability of EDT increases the electron/mass-transfer resistance within GSF/EDT. Therefore, at low current density, GSF/BDT represents the optimized structure of the GSF by means of the structural stability of the aromatic linker molecules and moderate amounts of electrochemically inactive elements. The lowest specific capacity of SSGO can also be explained by the fact that, without linker molecules, it is possible to store only small amounts of Li between the graphene layers of SSGO. On the other hand, adsorption of Li ions on the outer surface of materials becomes dominant at relatively high current density. Under this condition, the amount of Li insertion between the layers decreases, and, consequently, the weights of electrochemically inactive elements determine the specific capacities of materials. Therefore, GSF/EDT showed a higher value of specific capacity compared with that of GSF/BDT. The SSGO was relatively less affected by increases in the current density, which enabled it to exhibit superior specific capacities over GSFs within a high current domain (> 0.25 A g$^{-1}$).

### Table 1

Resultant parameters of EIS data by fitting simulations.

<table>
<thead>
<tr>
<th>Material</th>
<th>$R_e$</th>
<th>$R_{ic}$</th>
<th>$R_{ct}$</th>
<th>$A_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSGO</td>
<td>5.89</td>
<td>35.00</td>
<td>6.37</td>
<td>$5.96 \times 10^2$</td>
</tr>
<tr>
<td>GSF/EDT</td>
<td>4.15</td>
<td>67.69</td>
<td>5.69</td>
<td>$3.52 \times 10^2$</td>
</tr>
<tr>
<td>GSF/BDT</td>
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<td>24.46</td>
<td>42.35</td>
<td>$2.90 \times 10^2$</td>
</tr>
<tr>
<td>GSF/BPDT</td>
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<td>55.82</td>
<td>16.44</td>
<td>$2.96 \times 10^2$</td>
</tr>
<tr>
<td>GSF/TPDT</td>
<td>2.79</td>
<td>54.06</td>
<td>35.65</td>
<td>$2.79 \times 10^2$</td>
</tr>
</tbody>
</table>

![Fig. 6. Schematic illustrations explaining the Li⁺ storing mechanisms with various GSF materials at different current rates.](image_url)
4. Conclusions

In the present research, a GSF electrode was proposed as an advanced type of graphene-based electrode material with enhanced Li electroactivity. The synthesized GSF showed a specific capacity of more than 1000 mAh g$^{-1}$ at 0.05 A g$^{-1}$ of current density. Considering its economic feasibility, eco-friendly, and excellent performances, GSF electrodes provide competitive Li storage performance compared with those of graphene-based anode materials reported previously (Table S2). When evaluating the performance of GSF/BDT and GSF/EDT had the highest structural stability and a minimized electrochemically inactive mass of linker molecules, and will be valued greatly for the Li storage performance of a GSF. This research marks the first attempt to design GSF material for use in Li host materials. We believe that further optimization of the GSF could strengthen its candidacy as an advanced TM-free electrode material. For example, the large amount of thiol functionalization on the graphene surface enables a higher population of linker molecules, and will be valued greatly for the further enhancement of Li storage performance. In addition, the use of nano-sized functional graphene and the additional functionality of organic linkers would also be beneficial to the GSF. Now that graphene is used as electrode material for other energy storage systems such as Na-ion batteries and supercapacitors, the GSF and its structural tunability could be useful in achieving desired performances in such systems.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ensm.2018.04.007.

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