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# Graphene cryogel papers with enhanced mechanical strength for high performance lithium battery anodes

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# Graphene cryogel papers with enhanced mechanical strength for high performance lithium battery anodes

## Abstract

A porous graphene paper was prepared by pressing a graphene cryogel, followed by thermal reduction at 220 °C. The cryogel was formed by freeze-drying a solution containing chemically reduced graphene and graphene oxide (CRG/GO). The formed graphene cryogel papers deliver a much higher discharge capacity and rate capability than that from conventional graphene papers fabricated by filtration. These new structures have a discharge capacity higher than 400 mA h g<sup>-1</sup> at a current density of 2000 mA g<sup>-1</sup> in sharp contrast to 229 mA h g<sup>-1</sup> at 50 mA g<sup>-1</sup> obtained from conventional graphene papers. These greatly improved electrochemical properties may be attributed to the porous structure and the concomitant high surface area. The mechanical properties may be tuned with the CRG/GO ratio. At a CRG/GO mass ratio of 2:1 the graphene paper has a Young's modulus nearly 9 times greater than an equivalent paper made from pure GO.

## Keywords

anodes, performance, graphene, cryogel, battery, papers, lithium, enhanced, mechanical, strength, high

## Disciplines

Medicine and Health Sciences | Social and Behavioral Sciences

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Shu, K., Wang, C., Wang, M., Zhao, C. & Wallace, G. G. (2014). Graphene cryogel papers with enhanced mechanical strength for high performance lithium battery anodes. *Journal of Materials Chemistry A*, 2 (5), 1325-1331.

# Graphene Cryogel Paper with Enhanced Mechanical Strength for High Performance Lithium Battery Anode

Kewei Shu, Caiyun Wang\*, Meng Wang, Chen Zhao, Gordon Wallace\*

A porous graphene paper was prepared by pressing a graphene cryogel, followed by thermal reduction at 220°C. The cryogel was formed by freeze-drying a solution containing chemically reduced graphene and graphene oxide (CRG/GO). The formed graphene cryogel papers deliver a much higher discharge capacity and rate capability than that from conventional graphene papers fabricated by filtration. These new structures have a discharge capacity higher than 400 mAh g<sup>-1</sup> at a current density of 2000 mA g<sup>-1</sup> in sharp contrast to the 229 mAh g<sup>-1</sup> at 50 mA g<sup>-1</sup> obtained from conventional graphene papers. These greatly improved electrochemical properties may be attributed to the porous structure and the concomitant high surface area. The mechanical properties may be tuned with the CRG/GO ratio. At a CRG/GO mass ratio of 2:1 the graphene paper has a Young's modulus nearly 9 times greater than an equivalent paper made from pure GO.

## 1. Introduction

Nowadays, increasing interests is being aroused in portable electronic devices including roll-up display, implantable and wearable medical devices.<sup>1-3</sup> As the indispensable components, flexible energy conversion and storage units with high energy and power density are required.<sup>4, 5</sup> The electrodes used in such energy system should possess the superior electrochemical properties along with the mechanical flexibility. Free-standing paper-like materials are the promising electrodes of interest, which normally include carbon-based and electrically conducting polymers (ECPs) based material.<sup>5, 6</sup> They are flexible and mechanically strong, which can be easily moulded and shaped into the desired structures. Also they can be used directly without the use of low capacity conducting additives and insulating binder, thus leading to high energy and power density.

Free-standing carbon nanotube (CNT) buckypaper can be easily fabricated by filtration method from its dispersion. It demonstrates promising electrochemical properties as either a battery or supercapacitor electrode due to its porous structure formed with the entangled nanotubes facilitating the efficient ion transport.<sup>7-10</sup> In addition, ECPs<sup>11</sup> and metal oxides<sup>12, 13</sup> are introduced to form CNT composite papers to further improve its charge capacity. The flexible ECPs or ECPs composite paper electrode has also been extensively studied for flexible energy storage application.<sup>14, 15</sup>

Compared with CNTs and ECPs, graphene possesses the advantages of high specific surface area and excellent electronic transport properties. It has been extensively investigated as battery or supercapacitor materials offering excellent electrochemical properties – high energy and power densities.<sup>16-19</sup> The flexible graphene or graphene oxide (GO) paper can also be easily fabricated by flow-directed graphene nanosheets assembly,<sup>20, 21</sup> and superior electrochemical properties are expected as that from the graphene powder.<sup>16-19, 22</sup> However, its performance was far from satisfactory. It delivered a very low reversible discharge capacity of 84 mAh g<sup>-1</sup> at a current density of 50 mA g<sup>-1</sup>, and the reversible capacity increased to 301 mAh g<sup>-1</sup> after removing some oxygen-contained functional group in our previous report.<sup>23</sup> It can be explained that the aggregation or restacking of the graphene nanosheets due to the strong  $\pi$ - $\pi$  stacking and van der Waals forces, which limits the available surface area and retards its electrochemical properties.

To obtain a porous/uncompact graphene paper with high charge capacity, several strategies such as leavening, template-directed assembly and cavitation-chemical oxidation are applied.<sup>24-26</sup> The “wet” graphene paper with solvents as the spacer preventing the graphene nanosheets restacking<sup>27</sup> delivered a specific capacitance of 156.5 F g<sup>-1</sup> at an ultrafast charge-discharge rate of 1080 A g<sup>-1</sup>. Graphene paper with open pores can also be formed with the cavity due to gas release during the chemical reduction of GO paper. Such paper delivered a greatly improved

1 specific capacitance of  $110 \text{ F g}^{-1}$  at  $0.5 \text{ A g}^{-1}$  in comparison  
2 with that of  $17 \text{ F g}^{-1}$  for highly packed graphene paper.<sup>24</sup>  
3 By using polymer microspheres as the template, a  
4 macroporous graphene paper with controlled pore size was  
5 fabricated by flow-directed self-assembly method. The  
6 macroporous graphene paper exhibits an electrochemical  
7 capacitance of  $49.2 \text{ F g}^{-1}$  at  $3.0 \text{ A g}^{-1}$ .<sup>26</sup>

8 More recently, a folded structure graphene paper was  
9 made from a freeze-dried GO cryogel and the subsequent  
10 thermal reduction. It presented significantly improved  
11 performances in lithium batteries compared to the  
12 graphene paper by filtration method, which can maintain  
13 reversible capacity of  $568 \text{ mAh g}^{-1}$  at  $100 \text{ mA g}^{-1}$  after 100  
14 cycles.<sup>28</sup> However, this paper was brittle and fragile due to  
15 its loose-packed layered structure. The thermal reduction  
16 of such GO cryogel paper further deteriorates its  
17 mechanical properties.

18 In this work, we introduce chemically reduced  
19 graphene (CRG) into the GO dispersion as the precursor  
20 solution for making the graphene cryogel. CRG possesses  
21 much less functional groups than GO. The introduction of  
22 CRG can decrease the entrapped water content associated  
23 to H bond in the formed graphene cryogel, which are  
24 expected to result in cryogel with better mechanical  
25 properties. The rationale is that the mechanical properties  
26 of graphene paper were essentially controlled by H-bond  
27 networks which strength can be enhanced with decreased  
28 water content within the interlayer cavities.<sup>29</sup> Our results  
29 clearly demonstrate that the mechanical properties of the  
30 graphene paper are remarkably enhanced with the  
31 increasing ratio of CRG. In addition, those CRG/GO  
32 hybrid papers all display excellent performance as anode in  
33 lithium ion battery, especially at high current densities.

## 34 2. Experimental

### 35 2.1 Material synthesis

36 Graphite oxide was synthesized from natural graphite  
37 flakes by the modified Hummels method.<sup>30, 31</sup> Exfoliation  
38 of graphite oxide to graphene oxide (GO) was achieved by  
39 ultrasonication of the dispersion using a Brandson Digital  
40 Sonifier (S450D, 30% amplitude, 2s on, 1s off) for 30 min.  
41 Chemically reduced graphene (CRG) aqueous solution was  
42 prepared by reduction of GO solution using hydrazine in  
43 presence of ammonium solution,<sup>32</sup> and it is described  
44 briefly as follows.  $168 \mu\text{L}$  of ammonium solution (28 wt%)  
45 and  $216 \mu\text{L}$  of hydrazine solution (35% in water) were  
46 added into  $40 \text{ mL } 1.5 \text{ mg mL}^{-1}$  GO dispersion while  
47 stirring. The resultant mixture was then stirred at  $95^\circ\text{C}$  for  
48 1h to complete the reduction. The as-prepared CRG  
49 solution was diluted to give a  $1 \text{ mg mL}^{-1}$  and  $0.4 \text{ mg mL}^{-1}$   
50 solution. The CRG/GO precursor hybrid solution was  
51 obtained by directly stir-mixing the GO and CRG solution.  
52 The CRG/GO mass ratio used in this work is 1:5, 1:2 and  
53 2:1. The resultant hybrid solution was transferred into a 50  
54 mL beaker and subjected to a freezing-dry process to form a

56 cryogel, which included an 8 h frozen at  $-30^\circ\text{C}$  and a 36 h  
57 freeze-drying. The hybrid (CRG/GO) papers were obtained  
58 by pressing the cryogels at 20 MPa, and named as GO-  
59 CRG-0.5, GO-CRG-2 and GO-CRG-5 according to the  
60 mass ratio of GO to CRG. The graphene (rGO) papers  
61 were obtained using the thermal reduction of the GO or  
62 hybrid papers at  $220^\circ\text{C}$  in air for 2h. Correspondingly, they  
63 are named as rGO-CRG-0.5, rGO-CRG-2 and rGO-CRG-  
64 5, respectively. A pure rGO paper was also prepared using  
65 the same method for comparison. In addition, graphene  
66 paper was also prepared by filtration of  $60\text{mL } 0.4 \text{ mg mL}^{-1}$   
67 CRG solution.

### 68 2.2 Material characterization

69 Conductivity measurements were carried out on a  
70 JandelRM3 Conductivity Meter using a four-point probe  
71 method. The morphology was investigated using a field-  
72 emission scanning electron microscope (FESEM, JEOL  
73 JSM7500FA). XRD measurements were performed on an  
74 Australia GBC Scientific X-ray diffract meter (Cu  $K_\alpha$   
75 radiation,  $\lambda=1.5418 \text{ \AA}$ ) with a scan rate of  $2^\circ \text{ min}^{-1}$ .  
76 Raman spectra were obtained using a confocal Raman  
77 spectrometer (Jobin Yvon HR800, Horiba) utilizing 632.8  
78 nm diode lasers. The thermal properties were characterized  
79 by TGA (Q500, TA instruments), and the measurements  
80 were tested under nitrogen with a ramp rate of  $5^\circ\text{C min}^{-1}$ .  
81 Uniaxial in-plane tensile tests were studied using a  
82 Shimadzu EZ mechanical tester. The samples with a  
83 dimension of approximately  $3 \times 15 \text{ mm}^2$  were used for  
84 mechanical testing at a cross head speed of  $1 \text{ mm min}^{-1}$ .

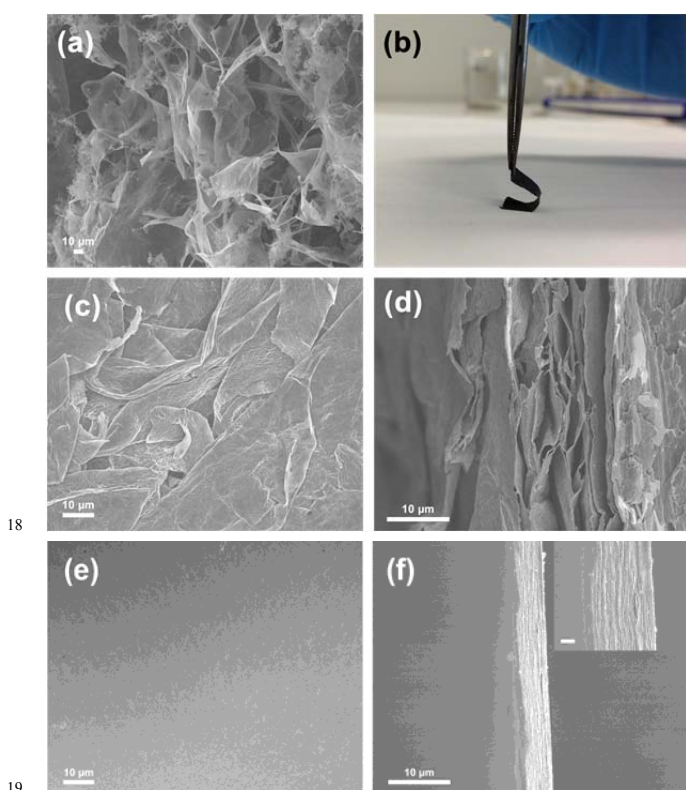
### 85 2.3 Electrochemical properties

86 The graphene papers were assembled into LR 2032  
87 type coin cells coupled with lithium metal anode for  
88 electrochemical properties testing. The electrolyte used  
89 was  $1 \text{ M LiPF}_6$  in 1:1 (v/v) ethylene carbonate/dimethyl  
90 carbonate. Galvanostatic charge/discharge tests were  
91 performed using a LAND CT2001A battery test system  
92 (Wuhan Jinnuo Electronics Co. Ltd. China) over a  
93 potential range of 0.005–3.0 V (vs.  $\text{Li/Li}^+$ ). Cyclic  
94 voltammetry of the cells was tested using a Solartron SI  
95 1287 and scanned between 0.0 to 3.0 V (vs.  $\text{Li/Li}^+$ ) at a  
96 rate of  $0.1 \text{ mV s}^{-1}$ . Electrochemical impedance  
97 spectroscopy (EIS) measurements were performed using a  
98 Gamry EIS 3000 system, and the frequency range spanned  
99 from 100 kHz to 0.01 Hz with amplitude of 10 mV at open  
100 circuit potential.

## 101 3. Results and discussion

102 The as-prepared cryogel shows an interconnected  
103 three-dimensional porous network (Fig. 1a) with the pore  
104 wall composed of graphene sheets. The pore is formed due  
105 to the sublimation of ice crystal during the freeze drying  
106 process, and its size is in the range of tens of micrometers  
107

1 to submillimeters. The graphene cryogel paper can be  
 2 easily obtained by pressing the cryogel at 20 MPa, and  
 3 followed by thermal annealing at 220°C for 2h in air. The  
 4 thickness of all the graphene papers is around 20  $\mu\text{m}$  with  
 5 a conductivity of approximately 2-5  $\text{S cm}^{-1}$ . For all the  
 6 cryogel papers have the similar structure (i.e. similar  
 7 surface morphology and cross-sectional view), only that of  
 8 the rGO-CRG-0.5 cryogel paper is presented here. Figure  
 9 1c shows the surface morphology of the graphene paper.  
 10 Different from the smooth surface of that graphene paper  
 11 fabricated by flow-directed filtration (Figure 1e), our  
 12 graphene paper exhibits a rough surface containing  
 13 graphene folds with random size (Figure 1c). A loosely-  
 14 packed layered structure can be observed through the  
 15 cross-sectional view of our graphene paper (Figure 1d), in  
 16 comparison with the compacted graphene layers structures  
 17 for graphene paper formed by filtration (Figure 1f).

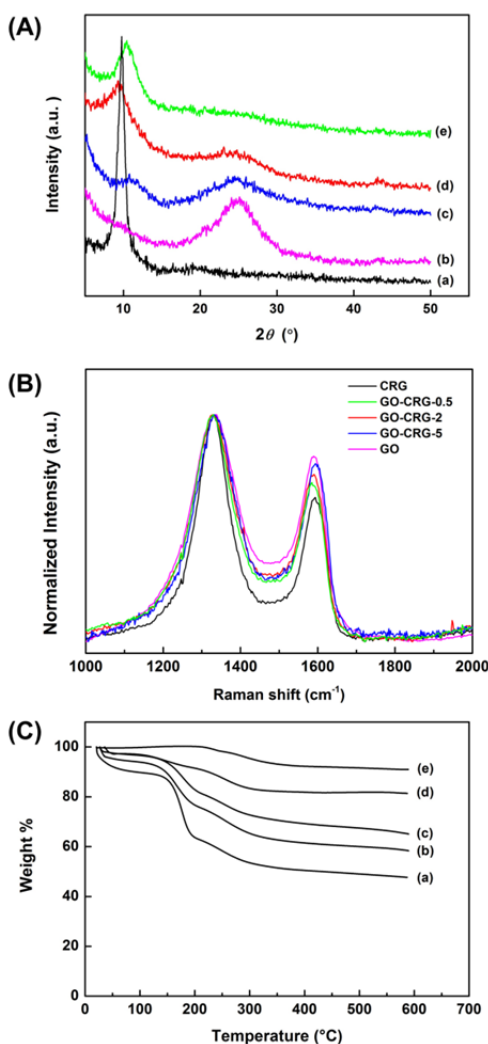


18 Figure 1 (a) FESEM image of rGO-CRG-0.5 cryogel; (b)  
 19 Photograph of rGO-CRG-0.5 paper demonstrating its flexibility.  
 20 FESEM images of the surface morphology and cross section of  
 21 rGO-CRG-0.5 paper (c, d) and CRG paper by filtration (e, f).  
 22 (Inset, cross-sectional view of f at higher magnification. Scale  
 23 bar: 1  $\mu\text{m}$ .)  
 24  
 25

26 X-ray diffraction (XRD) patterns of the hybrid  
 27 paper and GO paper before and after reduction are shown  
 28 in Figure 2A. GO paper displayed a strong and sharp peak  
 29 at  $9.8^\circ$  ( $2\theta$ ), as reported for GO solids and GO paper.<sup>33, 34</sup>  
 30 This strong diffraction derives from the interspacing  
 31 between the stacking layers of GO sheets, which  
 32 corresponds to a d-spacing of  $\sim 0.91$  nm. After thermal  
 33 reduction, a broad peak at  $24^\circ$  ( $2\theta$ ) is presented for rGO

34 paper, which corresponding to an average interlayer  
 35 spacing of 0.37 nm. Compared to GO paper, the hybrid  
 36 papers displayed two peaks, close to  $10^\circ$  and  $24^\circ$ . The  
 37 former belongs to (0 0 2) diffraction of GO and the latter  
 38 can be ascribed to (0 0 2) diffraction of rGO. The (002)  
 39 peak intensity decreased correspondingly with the  
 40 decreased GO content in this hybrid. For GO-CRG-5  
 41 paper, there is no pronounced rGO peak due to its low  
 42 content. The Raman spectra of CRG, GO-CRG-0.5, GO-  
 43 CRG-2, GO-CRG-5 and GO paper with normalized  
 44 intensity is shown in Figure 2B. They all display a typical  
 45 G band ( $1588 \text{ cm}^{-1}$ ) and D band ( $1334 \text{ cm}^{-1}$ ),  
 46 corresponding to the first order scattering of the  $E_{2g}$  mode  
 47 (G band) and disordered structures (D band),  
 48 respectively.<sup>35</sup> The D/G intensity ratio is 1.22 for GO, and  
 49 then increases to 1.59 after chemically reduction (CRG).  
 50 The change of D/G ratio can be attributed to the decrease  
 51 in the average size of the  $\text{sp}^2$  domains upon reduction  
 52 process.<sup>36</sup> The new graphitic domains in CRG are  
 53 increased in number but smaller in size. The D/G ratio for  
 54 GO-CRG-5, GO-CRG-2, GO-CRG-0.5 is 1.29, 1.35 and  
 55 1.45 respectively, which agrees well with the CRC ratio  
 56 increase.

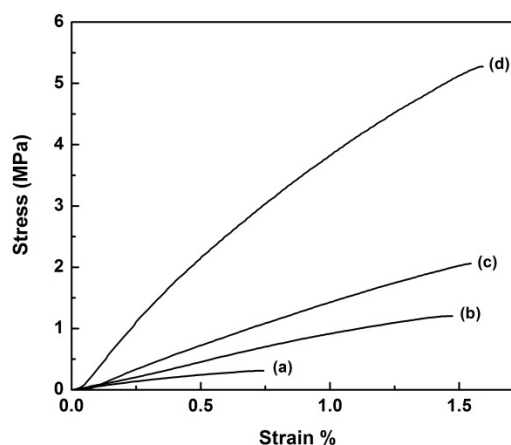
57 The TGA curves of the graphene paper with  
 58 different CRG/GO ratio are shown in Figure 2C. The  
 59 weight loss below  $100^\circ\text{C}$  can be attributed to the  
 60 evaporation of absorbed water. The hydrophilic GO paper  
 61 demonstrated a substantial loss of approximately 10% in  
 62 this temperature range. The major weight loss of the GO  
 63 paper occurs near  $150^\circ\text{C}$ , which may be caused by  
 64 pyrolysis of oxygen-containing groups from the GO  
 65 surface.<sup>34</sup> In the temperature range between  $100$ - $200^\circ\text{C}$ ,  
 66 which is mainly the decomposition of oxygen-containing  
 67 groups on GO in those hybrid papers, the weight loss are  
 68 25%, 17%, 13% and 7% for GO, GO-CRG-5, GO-CRG-2,  
 69 GO-CRG-0.5. Such decreased weight loss in this  
 70 temperature range agrees with the decreased content of GO  
 71 in the hybrid papers. For all of the papers, the weight loss  
 72 in the temperature range between  $200^\circ\text{C}$  and  $500^\circ\text{C}$   
 73 is about 10%, which probably due to the decomposition of  
 74 some residual oxygen-containing groups.<sup>21</sup> The total  
 75 weight loss between  $100^\circ\text{C}$  to  $600^\circ\text{C}$  for rGO, GO-CRG-  
 76 0.5, GO-CRG-2, GO-CRG-5 and rGO are 9%, 14%, 30%,  
 77 35% and 53%.



1  
2 Figure 2 (A) XRD patterns of GO paper (a), rGO paper (b),  
3 hybrid papers of GO-CRG-0.5 (c), GO-CRG-2 (d) and GO-CRG-  
4 5 (e). (B) Raman spectra of all graphene papers with normalized  
5 intensity. (C) TGA curves of graphene papers with different  
6 CRG/GO ratio: (a), pure GO; (b), GO-CRG-5; (c), GO-CRG-2;  
7 (d), GO-CRG-0.5; and (e) rGO.

8 The mechanical properties were tested in uniaxial  
9 tension of our graphene papers strips. The stress-strain  
10 response of graphene papers with different CRG/GO ratio  
11 is shown in Figure 3. These curves show straightening  
12 behavior at the beginning followed by roughly linear  
13 behavior and then plastic deformation behavior, similar to  
14 graphene paper fabricated by filtration method.<sup>20</sup> The  
15 ultimate tensile strain for the hybrid graphene papers is 1.5  
16 %, twice as much as the value of rGO paper (0.75 %). The  
17 Young's modulus can be calculated from the initial slope  
18 of the stress strain curve, and it was 58, 92, 179 and 510  
19 MPa for rGO, rGO-CRG-5, rGO-CRG-2 and rGO-CRG-  
20 0.5, respectively. It can be clearly seen that the mechanical  
21 properties of our graphene papers are improved with the  
22 increasing aspect ratio of CRG. The increase of mechanical  
23 strength is resulted from to lower water content integrated  
24 with the hydrophobic CRG sheets compared with

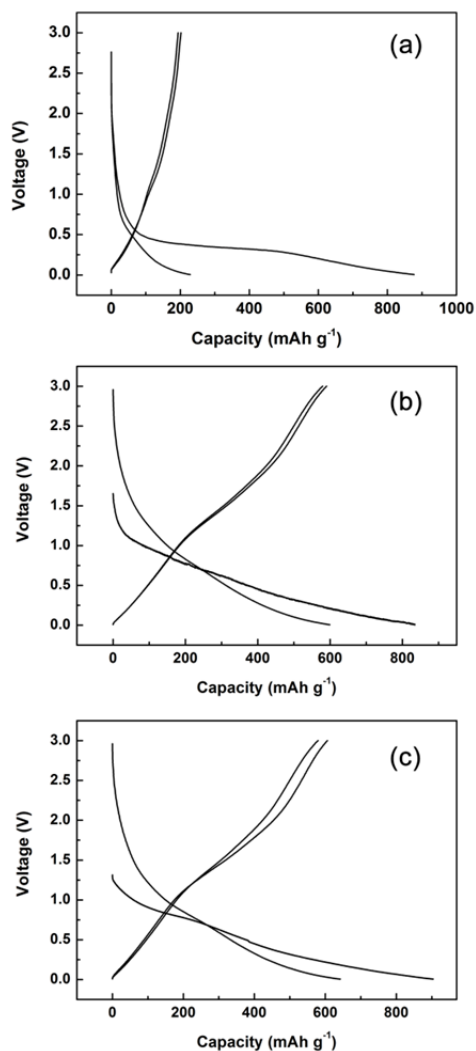
25 hydrophilic GO sheets. It is believed that lower water  
26 content in graphene papers leads to better H-bond  
27 networks making the graphene paper stiffer.<sup>29</sup> In addition,  
28 the hybrid paper with higher GO content may also suffer  
29 from the structural destruction caused by pyrolysis of  
30 oxygen-containing groups from the GO during thermal  
31 reduction, resulting in poorer mechanical properties. We  
32 should also point out that our graphene paper presents  
33 much lower modulus compared to flow-directed assembled  
34 graphene paper,<sup>20</sup> which can be ascribed to their loosely  
35 packed structure.



36  
37 Figure 3 Stress-strain curves of graphene papers with different  
38 CRG/GO ratio: (a) rGO; (b) rGO-CRG-5; (c) rGO-CRG-2; and  
39 (d) rGO-CRG-0.5.

40 The electrochemical properties of our graphene  
41 papers as binder-free electrode for lithium batteries are  
42 evaluated by galvanostatic charge/discharge in the  
43 potential range from 0.005 to 3.0 V. All of the graphene  
44 cryogel papers exhibit much similar performance, so here  
45 we only present rGO, rGO-CRG-0.5 cryogel paper and  
46 filtrated CRG paper for easy comparison. They all  
47 presented an irreversible capacity between the first and  
48 second discharge cycle. The irreversible capacity near  
49 0.5V is attributed to the formation of a solid electrolyte  
50 interface (SEI) layer in the first cycle. The reversible  
51 capacity below 0.5 V should be due to the lithium binding  
52 on the basal plane of the graphene sheets. While the  
53 capacity between 0.5-1.5 V may be ascribed to the  
54 faradic capacitance on the surface or on the edge sites  
55 of graphene sheets.<sup>19</sup> The first and second cycle  
56 charge/discharge profiles of hybrid paper electrode rGO-  
57 CRG-0.5 at current density of 50 mA  $\text{g}^{-1}$  are shown in  
58 Figure 4a. It delivers a first discharge capacity of 903 mAh  
59  $\text{g}^{-1}$ , then the discharge capacity drops to 642 mAh  $\text{g}^{-1}$   
60 on the second cycle. The Coulombic efficiency of our  
61 graphene papers is about 60-70% during the initial  
62 charge/discharge cycle similar to the performance of  
63 graphene powder.<sup>23, 33, 37</sup> This hybrid graphene cryogel  
64 paper exhibits a much higher reversible capacity compared  
65 to other paper based carbon materials. The reversible  
66 capacity of our graphene cryogel paper is at least 10 times

1 higher than that of flexible graphite foil, only 50 mAh g<sup>-1</sup>  
 2 obtained at C/20 rate (18.6 mA g<sup>-1</sup>).<sup>38</sup> Also it is even higher  
 3 than that of 6-15 layered graphene nanosheets, which  
 4 shows a 540 mAh g<sup>-1</sup> at the same current density.<sup>19</sup> The  
 5 graphene paper obtained by filtration shows second  
 6 discharge capacity of 229 mAh g<sup>-1</sup> at the same current  
 7 density (Figure 4b), only half the value compared to our  
 8 cryogel paper. The porous and loose-packed structure in  
 9 our graphene paper may prevent the restacking of the  
 10 graphene nanosheet, also provides more lithium insertion  
 11 active sites thus leads to a higher reversible capacity. The  
 12 rGO-CRG-0.5 paper shows equivalent performance to that  
 13 of rGO cryogel paper (Figure 4c), which has a second  
 14 discharge capacity of 600 mAh g<sup>-1</sup>, indicates the  
 15 electrochemical performance of the cryogel paper is not  
 16 affected by introduction of CRG.



17  
 18 Figure 4 First and second charge discharge curves of graphene  
 19 papers: (a) rGO-CRG-0.5 (b) CRG by filtration (c) rGO.

20 Figure 5a, 5b presents the charge/discharge  
 21 profiles of graphene cryogel papers at higher current  
 22 densities. The performance of graphene paper (filtration)

23 electrode at higher current densities is not shown here due  
 24 to its very low discharge capacity even at a low discharge  
 25 current density of 50 mA g<sup>-1</sup>. As can be clearly seen from  
 26 the figure, such graphene papers possess high rate  
 27 discharge/charge capability. For rGO-CRG-0.5 paper  
 28 (Figure 5b), at the current densities of 200, 500, 1000,  
 29 2000 and 3000 mA g<sup>-1</sup>, the corresponding reversible  
 30 capacity can reach 622, 557, 485, 405 and 355mAh g<sup>-1</sup>  
 31 respectively. The performance of rGO-CRG-0.5 is very  
 32 close to that of rGO paper, which shows reversible  
 33 capacity of 596, 537, 471, 403 and 357mAh g<sup>-1</sup>,  
 34 respectively (Figure 5a). The high rate discharge/charge  
 35 properties are likely to originate in the easy accessibility  
 36 and transportation of electrolyte into the host position of  
 37 the graphene sheets due to the folded and porous structure  
 38 of our graphene paper. They also displayed a good cyclic  
 39 performance and reversibility (Figure 5c, 5d). After 100  
 40 cycles at a current density of 2000 mA g<sup>-1</sup>, the rGO-CRG-  
 41 0.5 paper and rGO paper still maintains a specific capacity  
 42 of 395 mAh g<sup>-1</sup> and 394 mAh g<sup>-1</sup>, 98.7% and 98.9% of the  
 43 initial capacity.

44 The cyclic voltammograms (CV) of the rGO-  
 45 CRG-0.5 cryogel paper, rGO cryogel paper and graphene  
 46 paper are shown in Figure 6a, b and c. They all exhibit  
 47 much similar current responses in electrochemical window  
 48 of 0.0 V to 3.0 V versus Li/Li<sup>+</sup>. The cathodic peak around  
 49 0.5V indicates the formation of SEI. A large irreversible  
 50 cathodic peak corresponds to lithium intercalation  
 51 appeared around 0.0 V, which became weaker after the  
 52 first cycle due to the lithium intercalation reaction being  
 53 partially reversible. The cathodic peak at about 1.5 V is  
 54 attributed to lithium interactions with the residual  
 55 functional groups on the surface or on the edge sites of  
 56 graphene sheets. The shape of the CV curves matches well  
 57 with the discharge/charge profiles.

58 Electrochemical impedance spectroscopy was  
 59 used to evaluate the filtrated graphene paper and the  
 60 graphene cryogel paper electrodes after several cycles  
 61 (Figure 6d) in the Nyquist plot. The semicircle in the  
 62 medium frequency region is related to the charge-transfer  
 63 reaction of lithium intercalation into graphene sheets, and  
 64 the inclined line at an approximate 45° angle to the real  
 65 axis corresponds to the lithium-diffusion process within  
 66 carbon electrodes.<sup>39</sup> It can be clearly seen from the EIS  
 67 curves, the diameter of the semicircle at the medium  
 68 frequency region of the graphene cryogel papers is  
 69 significantly reduced compared to the graphene paper  
 70 obtained by filtration, indicative of a lower charge-transfer  
 71 resistance in the graphene cryogel papers. The reduced  
 72 charge transfer resistance might be induced by the easy  
 73 accessibility and transportation of electrolyte in the loose  
 74 packed structure.

75  
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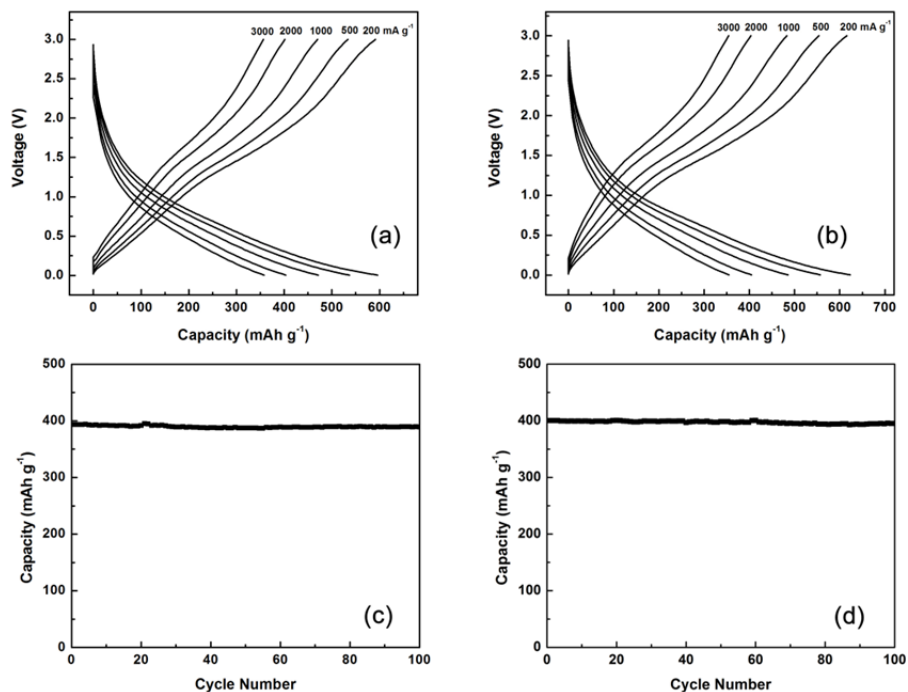


Figure 5 Charge discharge curves of graphene papers at different current densities: (a) rGO (b) GO-CRG-0.5. Capacity versus cycle number at 2000 mA g<sup>-1</sup>: (c) rGO (d) rGO-CRG-0.5.

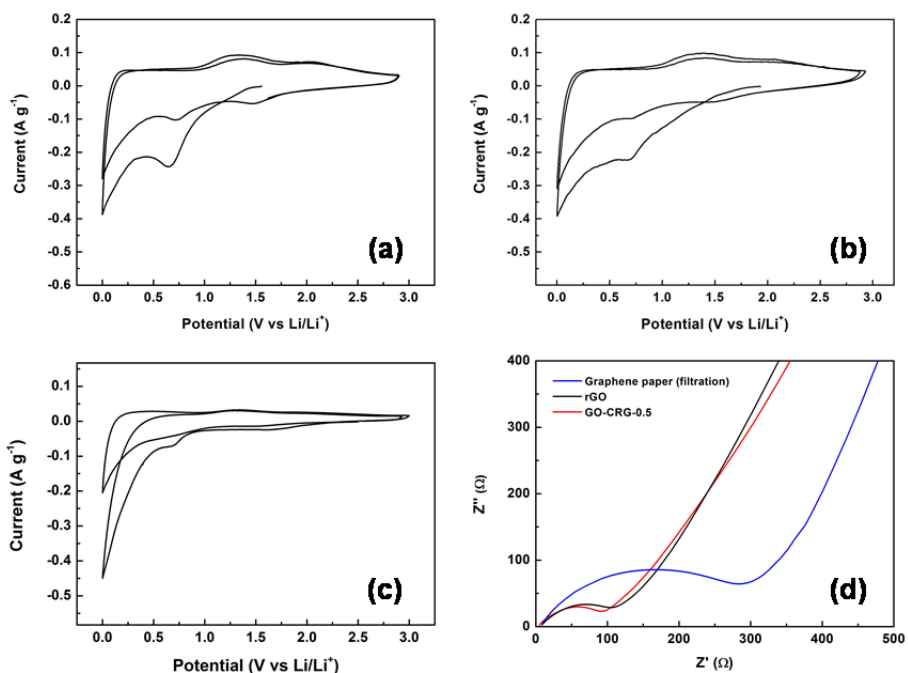


Figure 6 Cyclic voltammograms obtained for graphene papers using a scan rate of 0.1 mV s<sup>-1</sup>: (a) rGO-CRG-0.5 (b) rGO (c) graphene paper. (d) Nyquist plots of graphene cryogel papers and the graphene papers (filtration).

1

2

### 3 Conclusions

4 In summary, flexible graphene paper with a porous  
 5 structure has been fabricated by mechanically pressing a  
 6 graphene cryogel, prepared from a precursor solution

7 containing different CRG/GO ratios. The mechanical  
 8 property of such graphene papers was significantly  
 9 enhanced with the increase of the CRG/GO ratio in the  
 10 precursor solution. The introduction of CRG in the  
 11 precursor solution resulted in a strong graphene paper



1 without sacrificing electrochemical performance. All  
2 electrodes prepared exhibited enhanced electrochemical  
3 properties (high discharge capacity, good rate capability  
4 and cycling stability) compared to that graphene paper  
5 fabricated by filtration. The improved performance is  
6 attributed to the easy accessibility and transportation of  
7 electrolyte in the loose packed structures. This novel  
8 flexible/bendable graphene electrode should find use in  
9 flexible energy storage devices.

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## 24 Notes and references

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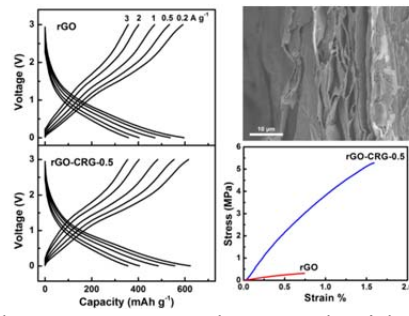
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## Graphitic Abstract



The mechanical properties of graphene paper can be tuned with CRG/GO ratio, demonstrating high performance in lithium batteries.