Free-standing Monolithic Nanoporous Graphene Foam as High Performance Aluminum-ion Battery Cathode

Xiaodan Huang, Yang Liu, Hongwei Zhang, Jun Zhang, Owen Noonan and Chengzhong Yu* * Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, Brisbane QLD 4072, Australia

*E-mail: c.yu@uq.edu.au (Chengzhong Yu)

Electronic Supplementary Information

Experimental Procedures

Material Synthesis:

Graphene oxide was synthesized from graphite flakes purchased from Sigma-Aldrich, by a modified Hummers' method. Typically, graphite flakes (5 g) was dispersed into H₂SO₄ (98 %, 200 mL) for 1 h with ice/water bath cooling. Then, KMnO₄ (30 g) was added very slowly into the suspension with stirring. After 3 days stirring at room temperature, the mixture was slowly diluted into distilled water (2 L) and kept stirring for another 12 h. After that, H₂O₂ (30 %, \sim 20mL) was added dropwise to dissolve insoluble manganese oxides. Graphene oxide can be obtained by centrifugation (4700 rpm, 30 min) and then washed with distilled water (4 times). The as-made graphene oxide was dried in 40 °C vacuum oven and then dispersed in to water with a concentration of (5 mg mL⁻¹).

Silica nanospheres (~100 nm diameter) were prepared by Stöber method. At room temperature, tetraethyl orthosilicate (TEOS) (23 mL), ammonia solution (28 wt%, 30 mL) and distilled water (10 mL) were added into ethanol (600 mL). Strong stirring was applied for 6 h. Then silica nanospheres were separated by centrifugation (10000 rpm, 15 min) and washed by ethanol for 3 times. Finally, silica nanospheres were dried in 100 °C oven overnight.

Results and Discussion

(I) Weight density determination by the measurements of mass and volume:

As NGF shows a well-defined pellet morphology (Figure S4), the weight density can be calculated based on the measurements of mass and volume by the following equation:

$$\rho = \frac{m}{t \times \pi (D/2)^2} \tag{1}$$

in which, ρ is the density, m is the weight of NGF pellet (9.09 mg), t is the thickness (1.07 mm) and D is the diameter (11.56 mm). Thus, the density was calculated to be 81.0 mg cm⁻³.

In the case of graphene foam monolith by conventional freeze-drying method (Figure S12a), the mass weight is 143 mg, the height is 3.8 cm, and the diameter is 2.5 cm. Thus the weight density was calculated to be 7.67 mg cm⁻³.

(II) Theoretical weight density determination by the Nitrogen adsorption/desorption results:

Graphene foam containing dense-packing and uniform spherical pores was adopted as the ideal model. Then the volume of pore voids can be calculated based on the surface area by the following equation:

$$V_{voids} = \frac{S \times (D_p/2)}{3}$$

(2)

where, V_{voids} is the specific volume of pore voids within graphene foam, S is the specific surface area, D_p is the diameter of the spherical pore.

Considering the graphene pore wall density, the weight density of graphene foam can be determined by equation:

$$\rho = \frac{1}{V_{voids} + 1/\rho_g} \tag{3}$$

in which, ρ is the weight density, V_{voids} is the specific volume of pore voids, and ρ_g is the density of graphite (2.2 g cm⁻³).

Combining equation (2) and (3), the correlation between theoretical weight density and pore diameter of porous graphene foam can be expressed as:

$$\rho = \frac{1}{\frac{S \times (D_p/2)}{3} + 1/\rho_g}$$
(4)

in which, ρ is the weight density, D_p is the diameter of spherical pore, S is the specific surface area (taking 762 m² g⁻¹ for the density comparison of NGF), and ρ_g is the density of graphite (2.2 g cm⁻³).

Plotting curve in the range between 30 and 100000 nm based on equation (4) yields a hyperbola (Figure 1). It is shown that when the pore size is in micron-size range the density will be very low, which agrees well with the density results of graphene foams from CVD method (~5 mg cm⁻³, ~850 m² g⁻¹ in ref. 10) and conventional freeze-drying methods (Figure S12 and ref. 12-13). When the pore size is decreased within 1000 nm, the theoretical weight density will be obviously increased. Decreasing pore diameters within 100 nm will dramatically improve the weight density. Monolithic NGF with 94.2 nm nanopore has an estimated density of 80.7 mg cm⁻³, consistent with the value from direct measurements (81.0 mg cm⁻³). Further decreasing nanopore size would result in even higher weight density. However, the formation of small graphene nanopores would require strong affinities to induce the bending of GO nanosheets. For example, using ~40 nm silica sphere templates in the hydrothermal hard-templating protocol failed to produce well-defined nanoporous structure (Figure S8), because of the weak hydrophobicity of silica templates induced by hydrothermal condition. Hydrophobic functional group modification enabled silica spheres as effective templates for nanoporous graphene material preparation (~30-120 nm, ref. 14). But this strong hydrophobicity interaction also led to severe GO sheets deformation, and resulted in only powder morphology (ref. 14b).



Figure S1. Schematic illustrations of the synthesis of free-standing NGF.



Figure S2. SEM images of (a) silica nanospheres with ~100 nm in diameter; (b) dried GO/silica suspension droplet, showing simply mixture form without interaction/assembly; (c) dried GO/silica hydrogel revealing the self-assembly process occurred during hydrothermal treatment; and (d) GO/silica composite after annealing in Ar.



Figure S3. Photographs of (a) GO/silica composite hydrogel; (b) free-standing NGF.



Figure S4. Photographs of free-standing NGF pellet electrode. (a) the diameter of a pellet; (b) the thickness, weight and the calculated density of NGF pellet. Calculated by the measured diameter and weight, the areal mass loading of this typical NGF cathode is 8.67 mg cm⁻².



Figure S5. Low magnification SEM image of free-standing NGF.



Figure S6. The wide-angle XRD pattern of free-standing NGF.



Figure S7. C1s XPS spectrum (a) and Raman spectrum (b) of free-standing NGF.



Figure S8. N₂ adsorption/desorption isotherms and the corresponding pore size distribution (inset) of free-standing NGF.



Figure S9. Photographs of coin cell inner surface before (a) and after (b) PEDOT coating.



Figure S10. SEM images of PEDOT coating peeled from a coin cell case.



Figure S11. Galvanostatic charge/discharge profiles of the coin cell without NGF cathode (blank cell). Only negligible capacity can be recorded by galvanostatic charge/discharge measurement (based on the weight of carbon felt, \sim 5 mg).



Figure S12. The coulombic efficiency of NGF cathode at different current densities.



Figure S13. Electrochemical performances of NGF cathode at 0°C. (a) charge/discharge profiles, and (b) cycling performance.



Figure S14. Structure characterizations of graphene foam prepared by conventional freeze-drying method. (a) Photograph of graphene foam (parameters are in weight density calculation part in this SI); (b) SEM images showing numerous micron size pores; (c) TEM image presenting no distinguished nanopore morphology; and (d) Nitrogen adsorption/desorption results giving low surface area.



Figure S15. Charge/discharge profiles of control electrode materials. (a) graphene foam by conventional freeze-drying method, and (b) commercial graphite paper.



Figure S16. XPS survey spectrum of glass fiber separators (fresh and after 100 cycles at 500 mA g⁻¹).



Figure S17. SEM images of Al foil anode. (a) fresh, and (b) after 100 cycles at 500 mA g⁻¹.

Cathode materials	Electrochemical performance			
	Reversible capacity	Discharge voltage	Cell configuration	Ref. ^[c]
V ₂ O ₅ nanowire ^[a]	273 mAh g ⁻¹ at 125 mA g ⁻¹ 1	~0.55 V	bare coin-cell	5b
VO ₂ ^[b]	116 mAh g ⁻¹ at 50 mA g ⁻¹	0.5 V	bare coin-cell	5a
Ni ₂ S ₃	60 mAh g ⁻¹ at 100 mA g ⁻¹	1.0 V	pouch cell using Ta foil	6
NiS	104.4 mAh g ⁻¹ at 200 mA g ⁻¹	0.9 V	pouch cell using Ta foil	7
CuS@C microsphere	90 mAh g ⁻¹ at 20 mA g ⁻¹	~1.0 V	pouch cell using Ta foil	8
Fluorinated graphite	225 mAh g ⁻¹ at 60 mA g ⁻¹	< 1.0 V, sloping	three electrodes in Teflon container	3
Carbon paper	84.55 mAh g ⁻¹ at 50 mA g ⁻¹	1.8 V	Teflon container using Mo foil	9b
Zeolite-templated carbon	157 mAh g ⁻¹ at 1 A g ⁻¹ ,	capacitive behaviour, no plateau	custom, tungsten electrochemical cells	4
3D graphene foam by CVD growth	~66 mAh g ⁻¹ at 100-5000 mA g ⁻¹	2.25-2.0 V and 1.9-1.5 V	pouch cell with polymer coated Ni foil; Swagelok cell using glass carbon current collector,	9a
Ar ⁺ plasma treated 3D graphene foam	148 mAh g ⁻¹ at 2000 mA g ⁻¹	1.9-1.65 V	pouch cell, Ni foil current collector	9d
3D graphene foam by chloroaluminate ion intercalation	~60 mAh g ⁻¹ at 2000- 12000 mA g ⁻¹	~1.8 V	pouch cell, glass carbon foil current collector	9c
Free-standing NGF	151, 133 and 116 mAh g ⁻¹ at 500, 1000 and 2000 mA g ⁻¹ , respectively	~1.9 - 1.5 V	PEDOT coated coin-cells	This work

 Table S1. A survey of electrochemical performances of Al-ion battery cathode materials.

[a] and [b] The high capacity and low discharge voltage were found to be ascribed to reactions of electrolyte and stainless steel coin-cell components (ref. 5). [c] Refs. here are references in main text.