

Supporting information

A graphitic foam framework with hierarchical pore structure as self-supported electrodes of Li–O₂ batteries and Li ion batteries

Guangyu Zhao, Li Zhang, Jixian Lv, Changle Li, Kening Sun*

Academy of Fundamental and Interdisciplinary Sciences, Harbin Institute of Technology, Harbin 150001, (China)

E-mail: keningsunhit@126.com

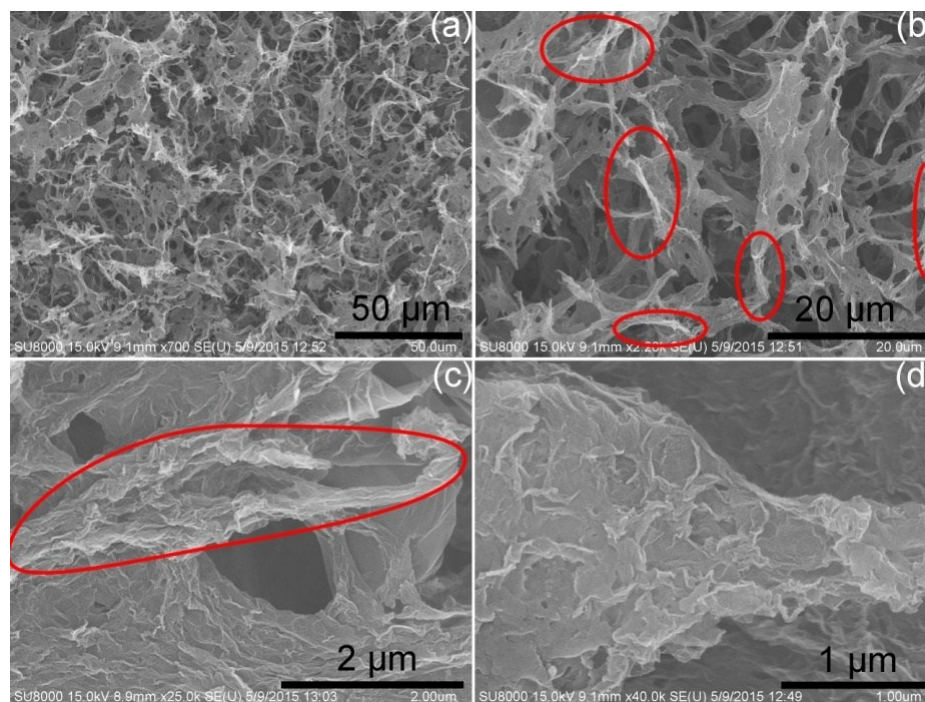


Figure S1. SEM images of the graphitic foam obtained from 1:2 rate of charge.

SEM images of the sample prepared from 1:2 rate in Figure S1 reveal the ridges and its role clearly. The porous graphitic sheets are connected by the ridges, as seen from the low magnification images of Figure S1a and b. The higher magnification images show the ridges are formed by GOs folding or stacking, as shown in Figure S1c and d. The GO stack can be seen clearly from the image of a typical ridge in Figure S1d, which results in a “skeleton” of the graphitic framework.

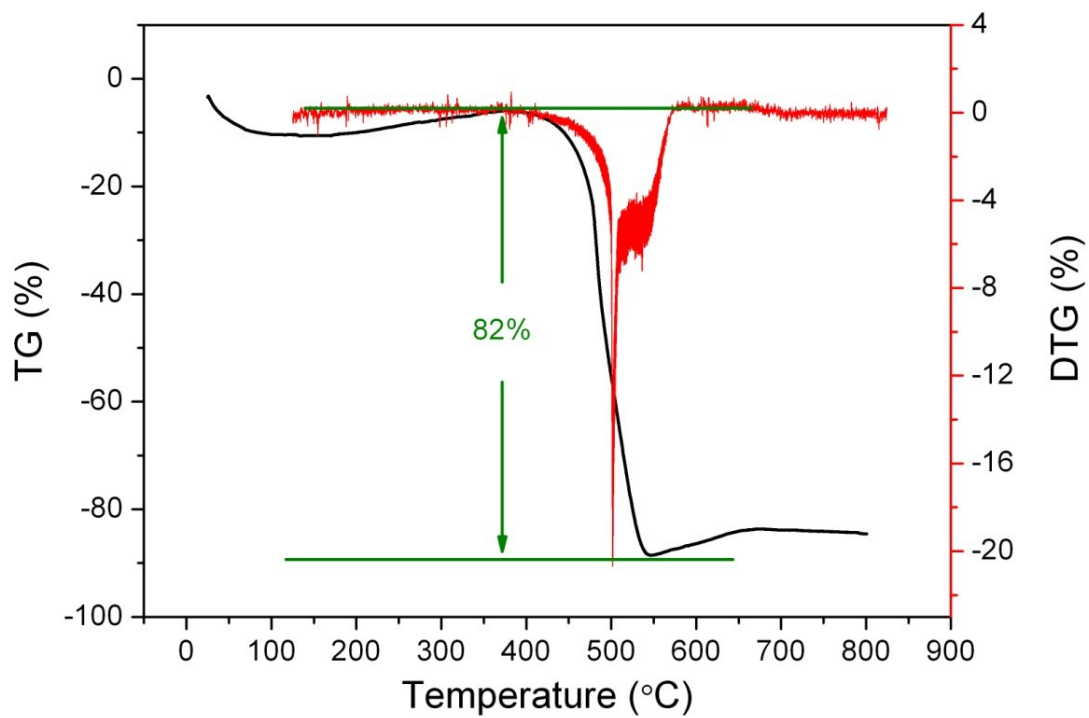


Figure S2. TG and DTG curves of the sample from 1:2 rate carried out in air atmosphere.

The most serious weight lost around 500 °C is from graphitic sheets, thus the mass percentage of graphitic content is about 82%.

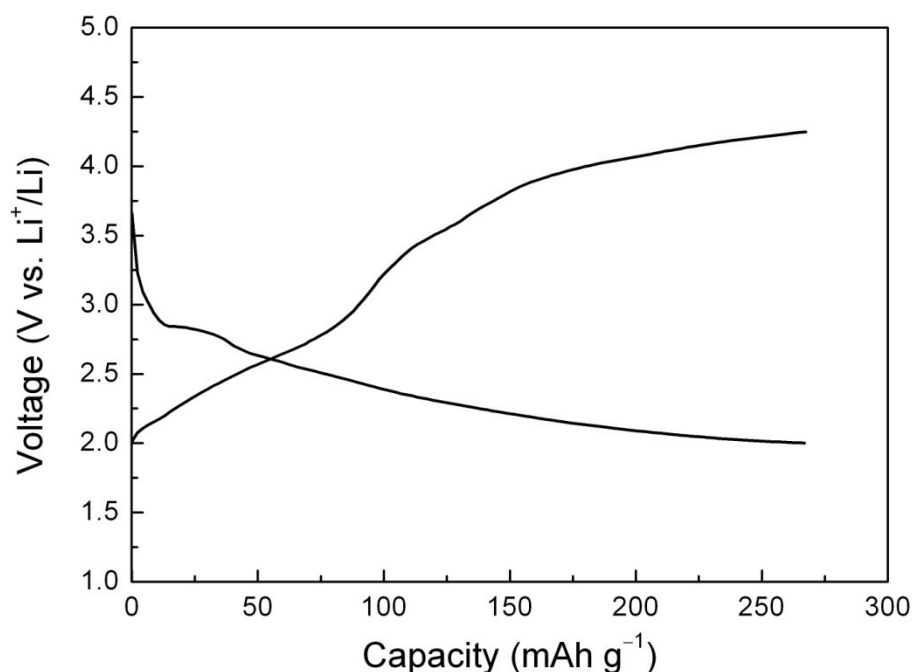


Figure S3. Discharge/charge curves of the LOB based on pure MoO₂.

The pure MoO₂ was prepared by a hydrothermal method referring to the literature (J. Rajeswari, P. S. Kishore, B. Viswanathan and T. K. Varadarajan, *Electrochem. Comm.*, 2009, **11**, 572–575). The MoO₂ cathode was prepared following a conventional process of mixing MoO₂ (around 20 mg) with PVDF binder and casting the paste into Ni foam current collectors (15 mm diameter). Apparently, MoO₂ almost has no catalytic activity to the ORR/OER in LOBs, since the much lower capacity (260 mAh g⁻¹) compared with graphitic foam from various rates even pure graphitic foam with no MoO₂ (2000 mAh g⁻¹).

Table S1. Surface areas of the graphitic foam obtained from various rates of charge.

Rates of charge ((NH ₄) ₂ Mo ₂ O ₁₁ :GO in weight)	(NH ₄) ₂ Mo ₂ O ₁₁ free	1:9	1:2	1:1	5:1
BET surface area (m ² g ⁻¹)	231	265	286	238	118

The graphitic foam obtained from 1:2 rate has the largest surface area, resulting in the most abundant active sites for electrochemical reactions. The through-hole structure is responsible for the largest surface area.

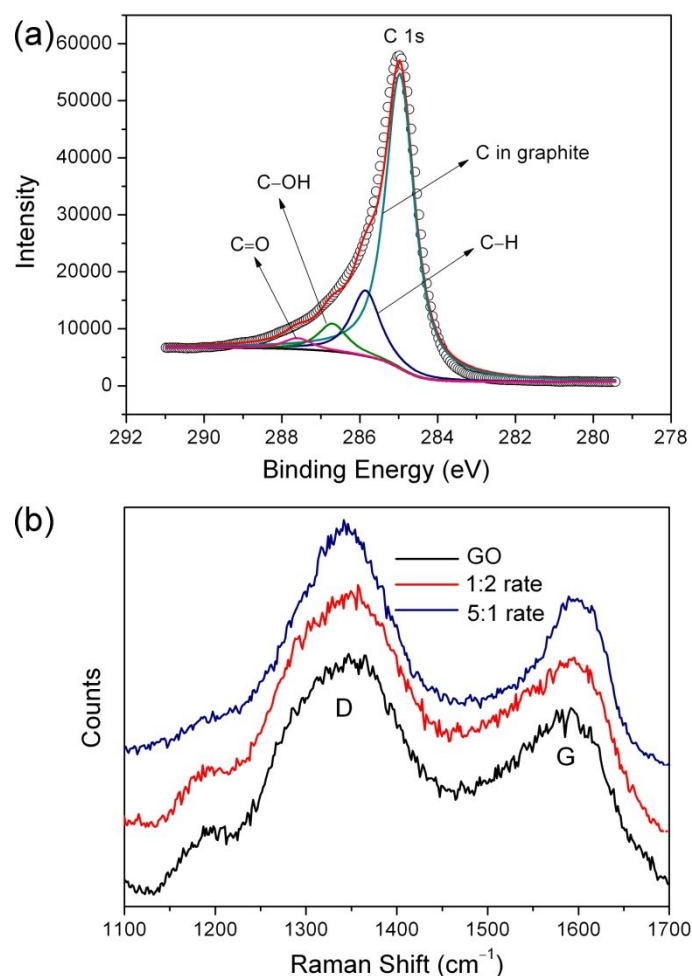


Figure S4. XPS (a) and Raman (b) patterns of the sample from 1:2 rate.

The XPS results of the as-prepared foam indicates abundant functional groups on the graphitic surface, which is favorable to the formation and decomposition of Li_2O_2 (Nano Lett., 2011, 11, 5071–5078) and act as active sites of the foam. The hydrothermal treatment tailors the graphene oxide sheets to smaller fragments, which can be verified by the SEM images in Fig. 2 and Raman analysis. The Raman spectra of the samples ($(\text{NH}_4)_2\text{Mo}_2\text{O}_{11}$ free, 1:2 and 5:1) exhibit a typical graphene-like pattern with a characteristic strong G band attributed to the vibration of sp^2 -bonded carbon atoms in a two-dimensional hexagonal lattice, as well as a D band caused by edges of imperfections. The I_D/I_G ratio showed an increase from $(\text{NH}_4)_2\text{Mo}_2\text{O}_{11}$ free sample to the foam form 1:2 and 5:1 rates (1.10, 1.15 and 1.38 respectively). The decrease in graphitic sheet size and in-plane pore foaming results in a higher concentration of edge sites at the periphery of the sheets, causing the I_D/I_G ratio rising.

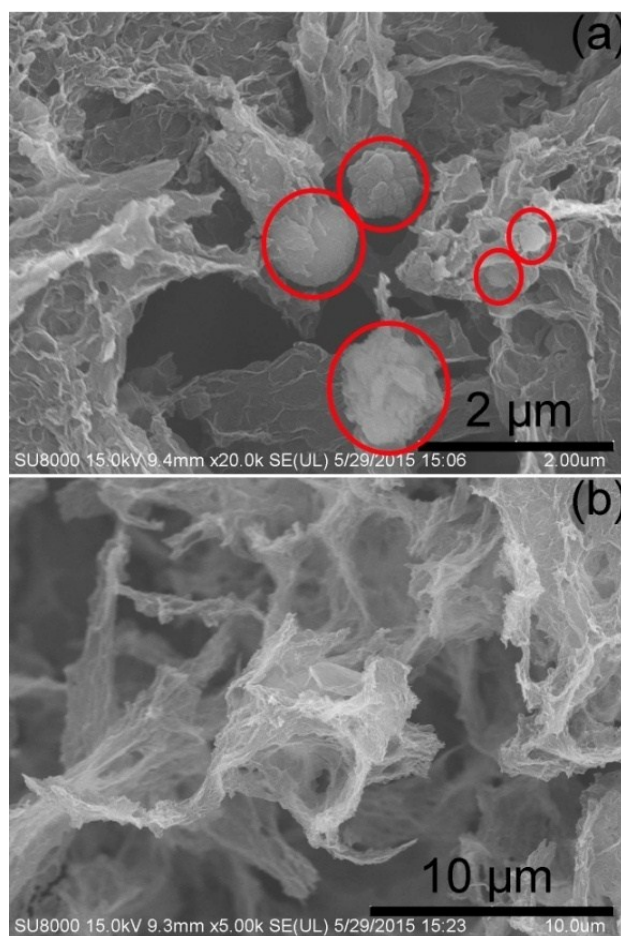


Figure S5. SEM images of the graphitic foam after the 1st discharge (a) and charge (b).

The sphere aggregation in Figure S5a can be ascribed to discharge product, while the product has been decomposed after charge process, as shown in Figure S5b.

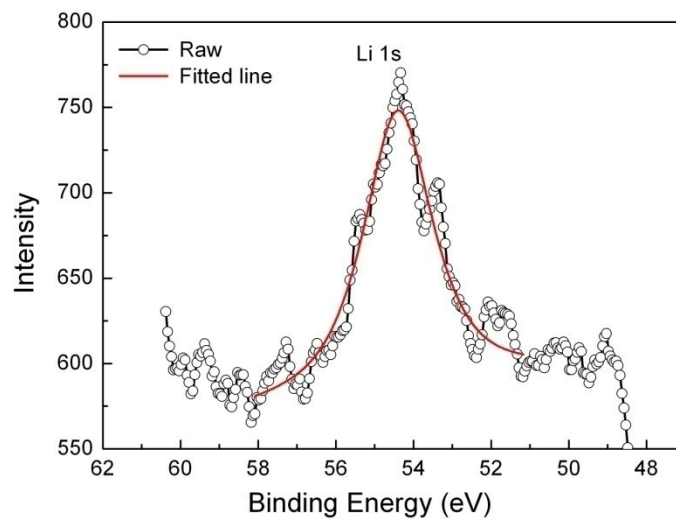


Figure S6. Li 1s of the graphitic foam after the 1st discharge in a Li–O₂ battery.

Li1s XPS on the graphitic foam after the 1st discharge reveals the generation of Li₂O₂ (54.3 eV), based on the previous result on the discharged sample using the same electrolyte.

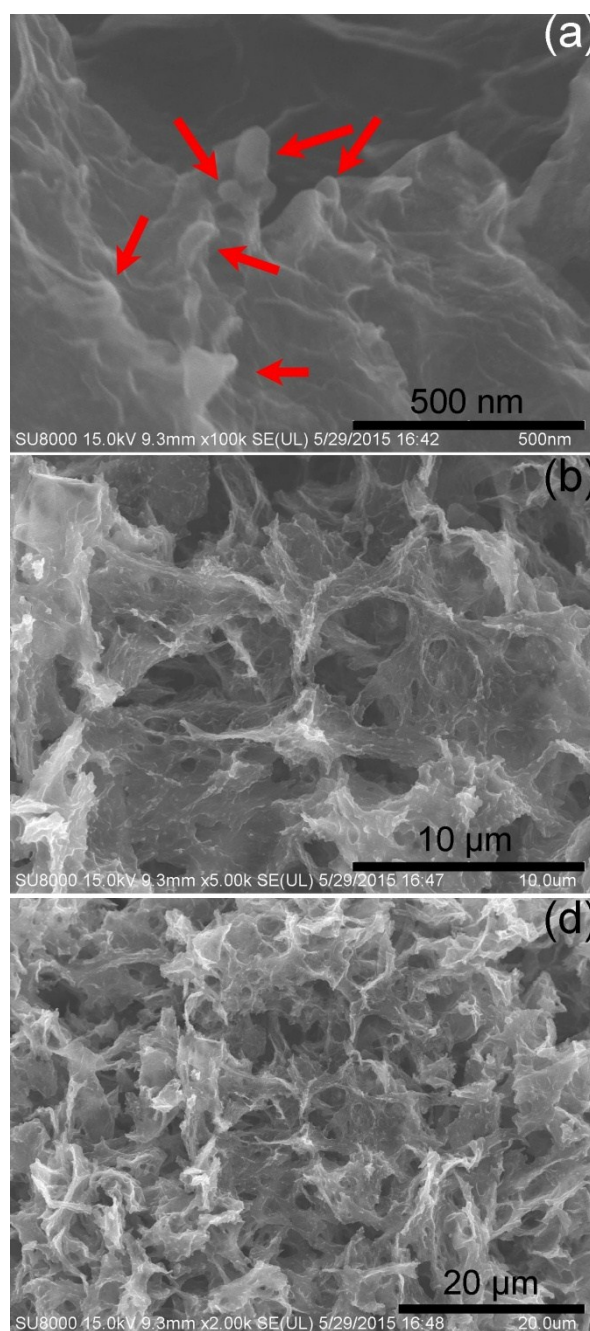


Figure S7. SEM images of the graphitic foam after cycle test.

A layer of undecomposed discharge product coats on graphitic nanosheets visibly, and the precipitate layer is homogeneous with no obvious aggregation. The size of Li₂O₂ (red arrows) is decades of nm, and the Li₂O₂ distributes on the graphitic sheets homogeneously. The pore structure remains in the foam due to the homogenous aggregation of discharge product, which is favorable to maintain the through-hole structure.

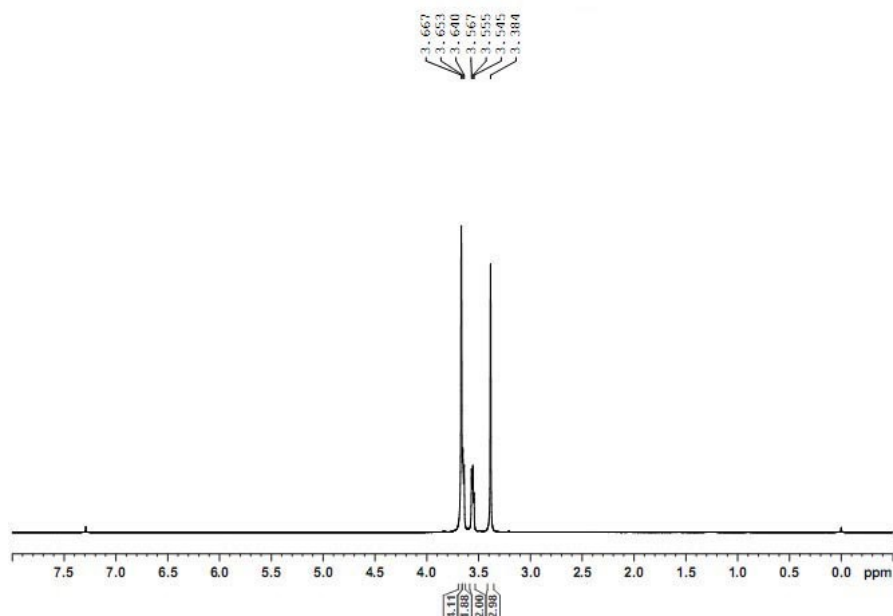


Figure S8. ^1H NMR of TEGDME electrolyte after cycle test.

The electrolyte is investigated after cycle test, and there is no evidence of TEGDME electrolyte decomposition, as confirmed by ^1H NMR analysis in Fig. S8. The major structure of the TEGDME molecule shows no decomposition, as verified by the integral area ratio (4:2:2:3) of the four ^1H peaks, that can be ascribed to four species hydrogen in TEGDME molecule.

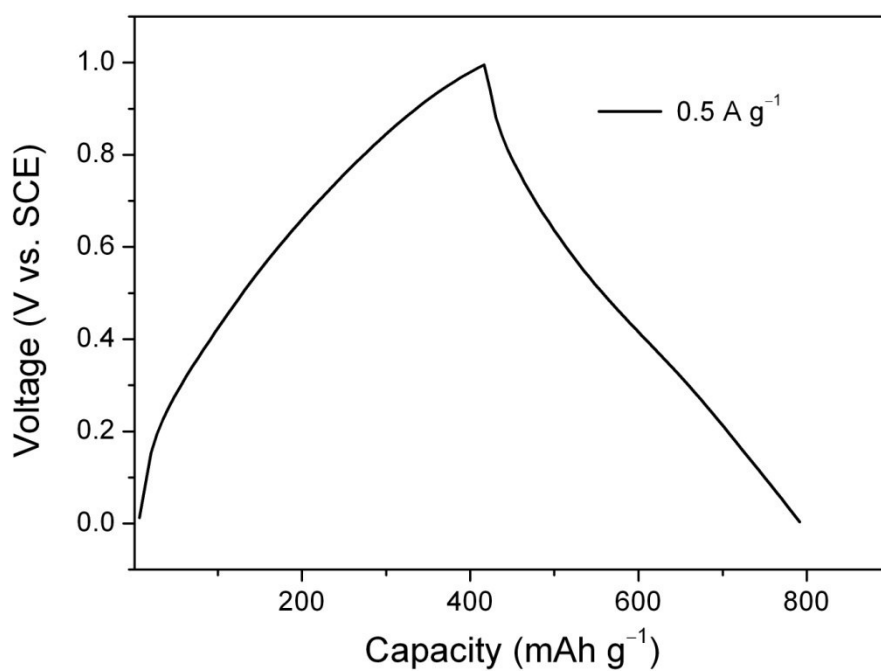


Figure S9. Galvanostatic charge/discharge curves of pure graphitic foam in Na_2SO_4

aqueous solution (1.0 M).

For investigating the capacitance of pure graphitic foam, the foam obtained from $(\text{NH}_4)_2\text{Mo}_2\text{O}_{11}$ free is tested in Na_2SO_4 aqueous solution (1.0 M) with the graphitic foam as working electrode, a Pt plane as the counter electrode and a SCE as the reference electrode. The measurement in aqueous solution without Li^+ can prevent the capacity from Li^+ insertion/deinsertion into/out of graphitic layers, and help us obtaining the capacitance from double layer capacitance and pseudocapacitance. The discharge/charge curves of the pure foam are shown in Fig. S9, and the calculated capacity is 417 mAh g^{-1} .