Electronic Supplementary Information Molybdenum Nitride based hybrid Cathode for Rechargeable Lithium-O₂ Batteries

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S1 Preparation and Characterization of MoN/GNS

1.0 g of molybdic acid (Alfa Aesar) and 0.34 g graphite oxide (self-made according to previous literature¹) was mixed with 50 mL water through stirring and sonicating for 2 hrs at room temperature. Then 10 mL dodecanethiol (Alfa Aesar) was added to the above solution as a reducing agent under stirring for 10 min. The mixture was sealed in an autoclave and kept at 200 °C for 16 hrs. After synthesis, the autoclave was cooled down to room temperature. The resultant dark precipitate was obtained by centrifugation, followed by washing with water and for 3 times and subsequently dried at 50 °C for further usage. Finally, the dark powder was calcined in a tubular furnace at 800 °C for 5 hrs under ammonia atmosphere to obtain MoN/GNS hybrid materials. For a fair comparison, bare GNS was also obtained by the same procedure without molybdic acid.

X-ray diffraction (XRD) of MoN/GNS hybrid materials were recorded in a Bruker-AXS Micro-diffractometer (D8 ADVANCE) from 10 to 85°. X-ray photoelectron spectroscopy (XPS) data was obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using Al Ka radiation. Elemental analysis was performed using a Flash EA 1112 CHNS/O elemental analyzer from Thermo Scientific. The morphology of the MoN/GNS were attained from field emission scanning electron microscopy (FESEM, HITACHI S-4800), high-resolution transmission electron microscopy (TEM, JEOL 2010F).

The electrode samples were cut into plates of 0.5 cm \times 0.5 cm and pasted on a stainless steel current-collector (with the thickness of 150 µm) under a pressure of 15 MPa. Galvanostatical discharge-charge experiments were carried out with a LAND battery testing system and the cyclic voltametry (CV) of the electrodes were carried out on an electrochemical workstation (ZAHNER ZENNIUM). The CV was carried out in the potential range from 2.7 to 4.2 V at a scanning rate of 1 mV s⁻¹.

Figure S1. The digital camera image of Swagelok cell



S2 XPS study

Figure S2 displays the presence of the principal C 1s, Mo 3d, N 1s, and O 1s levels (Fig S2 a).A Mo3d peak at about 229.2 eV (Fig S2 b) and a binding energy about 397.3 eV for the N1s signal (Fig S2 c) suggest the formation of Mo–N bond.² As shown in Fig S2 c, the deconvoluted bands of N 1s center at 398.8, 400.3, 401.3, representing pyridinic, pyrrolic and graphitic type, which confirmed the presence of doped N atoms in the graphene structure.^{1, 3} It is worth noting that the shoulder peak at 395.0 eV can be attributed to the binding energy of Mo $3p_{3/2}$.^{2, 4} The O 1s peak mainly arises from the thermal stable group of GO such as quinine besides some oxygen or water absorbed on the surface of the GNS.⁵ Considering the overlap of the Mo3p_{3/2} spectra with the N1s spectra and the possible aerial surface oxidation of the hybrid materials, only qualitative analysis was done.^{2, 4}





level for hybrid materials.

S3 SEM characterization of bulk MoN particles



Figure S3. SEM image of bulk MoN particles

S4 Reversibility study

The reversibility of the Li-O₂ air was investigated by charging/discharging the cell with a constant cutoff voltage. As shown in figure S4 a, the hybrid material based Li-O₂ cell was discharged to 2.6 V and then charged to 4.15 V with a current density of 0.2 mA cm⁻². However, the specific capacity dropped dramatically during the second charging process. (The result was even worse when the cell was operated at a lower current density) This result could be due to the partial irreversible accumulation of the discharge products. According to recent reports by Bruce et al.,⁵ Li₂CO₃, as a main discharge product, may not be decomposed completely during the charge process. Therefore, the accumulated Li₂CO₃ aggravated the polarization leading to

higher charge potential to decompose the discharge products. Therefore, in this study, the constant capacity approach of cycling was introduced. As shown in the Figure S4 b, by charging the cell to a higher voltage, even at a lower current density of 0.04 mA $\rm cm^{-2}$, the Li-O₂ battery still maintained an acceptable reversibility.

Figure S4. the cycling performance of MoN/NGS cathode based Li-O₂ batteries (a) with a constant potential approach at the current density of 0.2 mA cm⁻² and (b) a constant capacity approach at the current density of 0.04 mA cm⁻².



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