

Supporting Information

A Core–Shell-Structured TiO₂ (B)@RuO₂ as a Carbon-Free Cathode Catalyst for High Performance Li–O₂ Battery

Ziyang Guo, Chao Li, Jingyuan Liu, Xiuli Su, Yonggang Wang and Yongyao Xia*

Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Institute of New Energy, Fudan University, Shanghai 200433, China.

* Corresponding author. Tel & Fax: 0086-21-51630318

E-mail address: ygwang@fudan.edu.cn

1. Material Preparation

Synthesis of TiO₂ (B) nanofibers The TiO₂ (B) nanofibers were synthesized at a concentrated alkaline condition via a hydrothermal route. Briefly, the TiO₂-B material was synthesized by adding 6g of anatase to 28 ml of a 15 M solution of NaOH in distilled water. The mixture was transferred to a 45ml Teflon-lined stainless steel autoclave, sealed and maintained at 150°C for 72 h in an electric oven. The white product of the hydrothermal reaction was directly dispersed in 200 mL acid solution (1 M HCl) under stirring condition. Then, the resulting solution was kept at rest for 24 hours. Next, the white product was washed and filtrated with a large amount of distilled water, dried in air and then heated to 400°C for 5 h.

Synthesis of RuO₂ nanoparticles RuO₂ nanoparticles were prepared following a similar sol-gel process for preparation of TiO₂ (B)@ RuO₂-75. Specifically, a 0.3 M NaHCO₃ aqueous solution was added slowly to 0.1 M RuCl₃ in the absence of TiO₂ (B) until the pH of the solution reached 7. After stirring, the sediments were washed with distilled water, and then dried in air flow at room temperature. The black powder was also annealed at 150 °C for 19 h in air.

2. Detection of Li₂O₂ via XPS

Firstly, a Li-O₂ battery with TiO₂ (B)@ RuO₂-75 cathode was discharged at a current density of 0.25 mA cm⁻² with a fixed capacity of 500 mAh g⁻¹. After that, the cell was disassembled in a glove box filled with Ar to obtain the discharged electrode. Then, the discharged electrode was washed with DMC and was dried under vacuum at room temperature for 3 hours. Next, the discharged electrode was detected by XPS. The O₂

catalytic electrode before discharge (or after recharge) was detected with the same method.

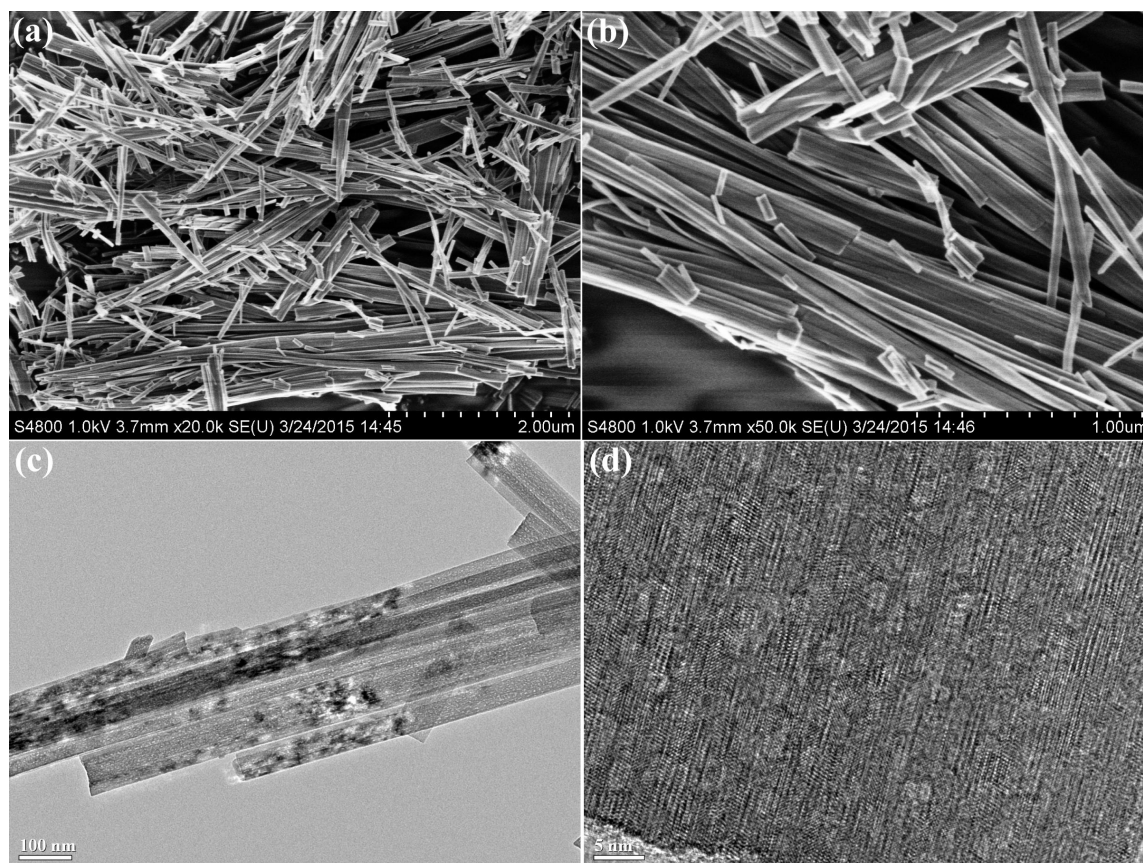


Fig. S1 Characteristic of the as-prepared TiO₂(B) nanofibers: (a, b) SEM images, and (c, d) TEM images with different magnifications.

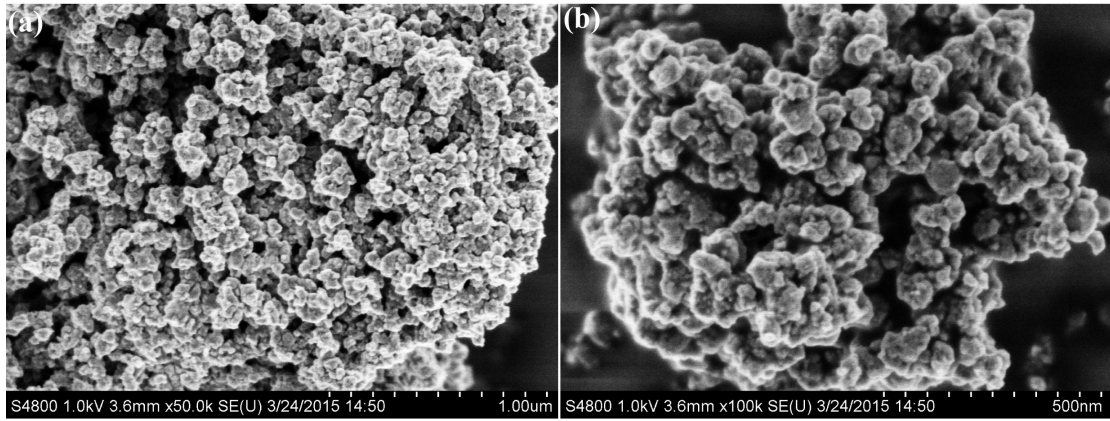


Fig. S2 SEM images of the as-prepared RuO₂ nanoparticles with different magnifications.

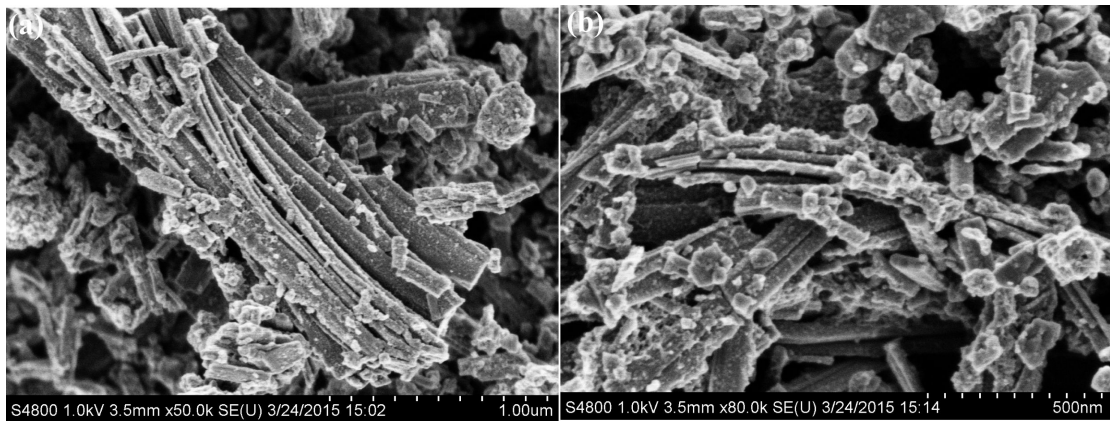


Fig. S3 SEM images of the as-prepared TiO₂ (B)@ RuO₂-50 with different magnifications.

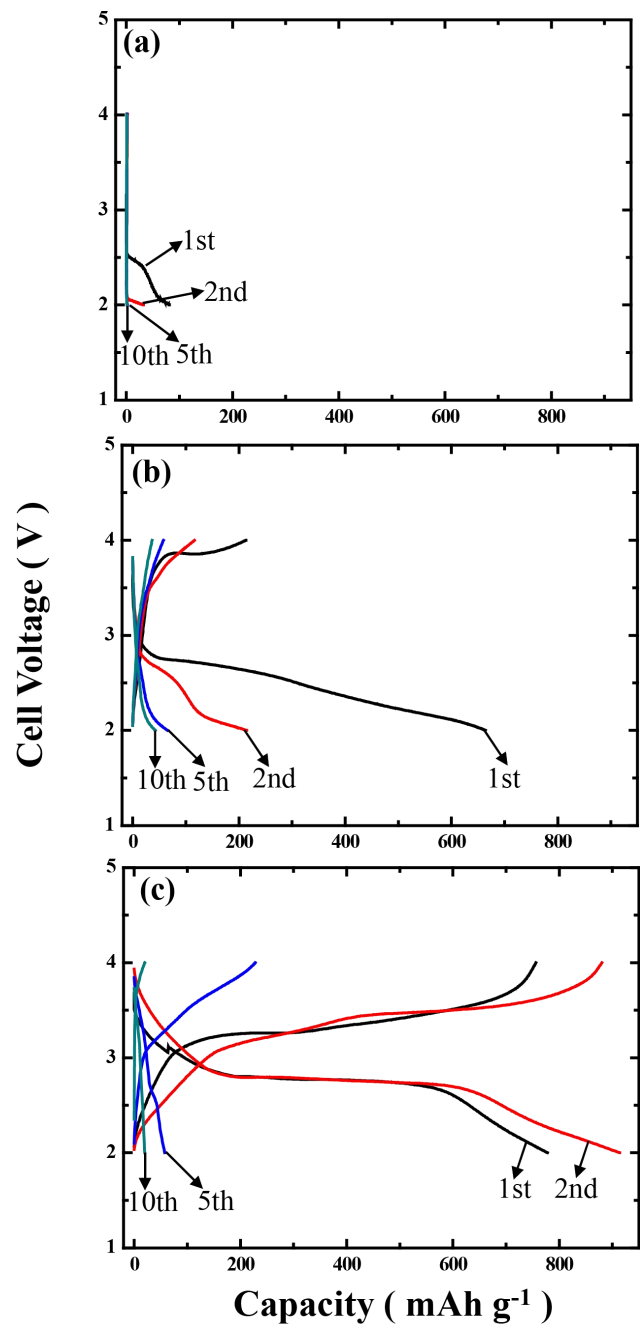


Fig. S4 Discharge/charge curves of Li-O₂ cells using different cathodes for initial 10 cycles at a current density of 0.125 mA cm⁻²: (a) TiO₂ (B) nanofibers cathode, (b) TiO₂ (B)@ RuO₂-50 cathode and (c) RuO₂ nanoparticles cathode. As shown in **Fig. S4**, the TiO₂ (B) nanofibers cathode, TiO₂ (B)@ RuO₂-50 cathode and RuO₂ nanoparticles cathode display poor cycle performance, compared with TiO₂ (B)@ RuO₂-75 cathode.

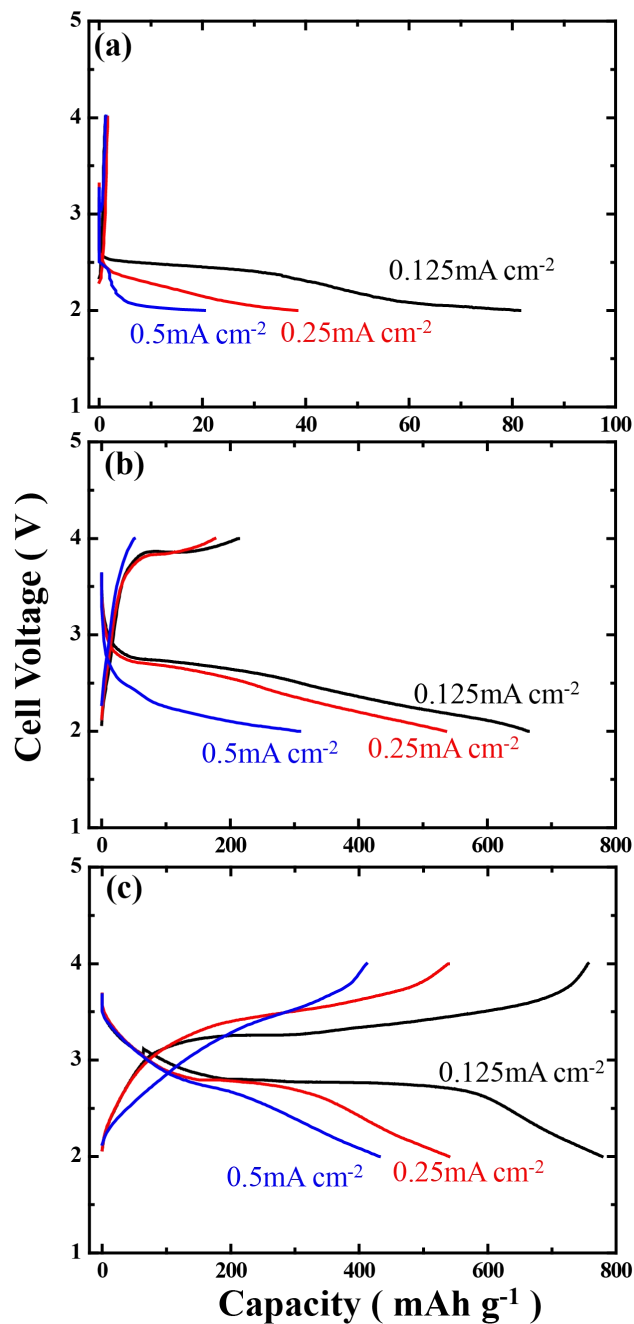


Fig. S5 The discharge/charge curves of Li-O₂ batteries using different cathodes at different applied current densities: (a) TiO₂ (B) nanofibers cathodes, (b) TiO₂ (B)@ RuO₂-50 cathodes and (c) RuO₂ nanoparticles cathodes. As shown in **Fig. S5**, the TiO₂ (B) nanofibers cathodes, TiO₂ (B)@ RuO₂-50 cathodes and RuO₂ nanoparticles cathodes display inferior rate performance, compared with TiO₂ (B)@ RuO₂-75.

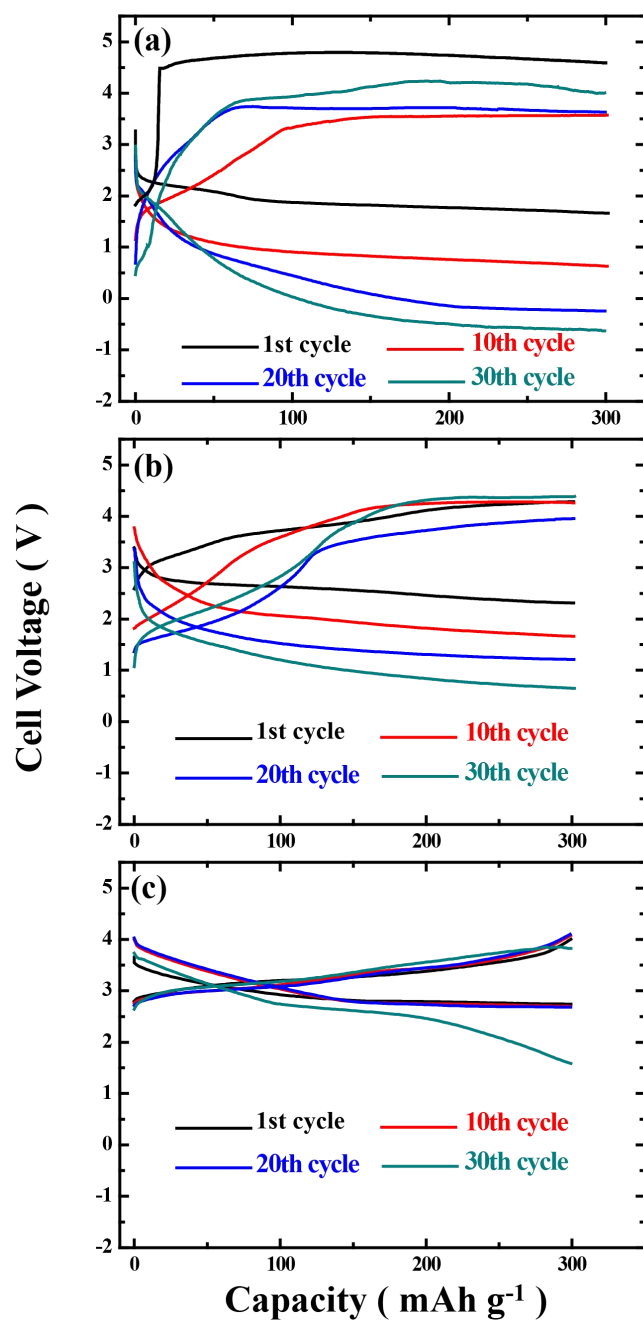


Fig. S6 Discharge/charge curves of Li–O₂ cells using different cathodes at a current density of 0.25 mA cm⁻² with a fixed capacity of 300 mAh g⁻¹: (a) TiO₂ (B) nanofibers cathode, (b) TiO₂ (B)@ RuO₂-50 cathode and (c) RuO₂ nanoparticles cathode. As shown in **Fig. S6**, the cycle performance of the TiO₂ (B) nanofibers cathode, TiO₂ (B)@ RuO₂-50 cathode and RuO₂ nanoparticles cathode with limited discharge/charge depth is still inferior to that of TiO₂ (B)@ RuO₂-75 cathode.

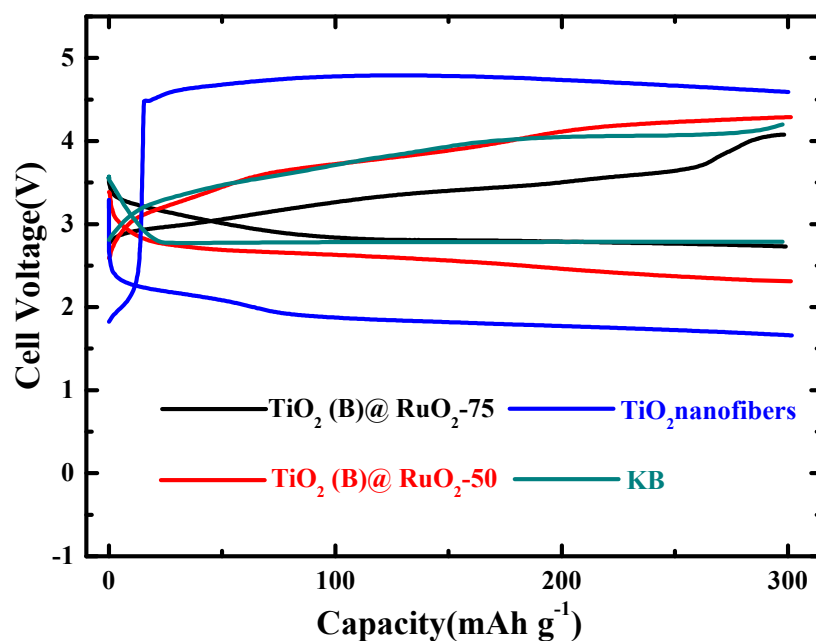


Fig. S7 Comparison of discharge/charge curves of Li–O₂ batteries using TiO₂ (B)@ RuO₂-75 cathode, TiO₂ (B)@ RuO₂-50, TiO₂ (B) nanofibers cathode and KB cathode. These cells were tested with a fixed capacity of 300 mAh g⁻¹ at current density of 0.25 mA cm⁻². As shown in **Fig. S7**, the round-trip efficiency (the ratio of discharge to charge voltage) of the TiO₂ (B)@ RuO₂-75 cathode is much higher than these of the TiO₂ (B) nanofibers cathode, TiO₂ (B)@ RuO₂-50 cathode and KB cathode, indicating that the discharge and charge voltage of the Li–O₂ cell can be significantly improved with the help of the uniform RuO₂ coating layer.

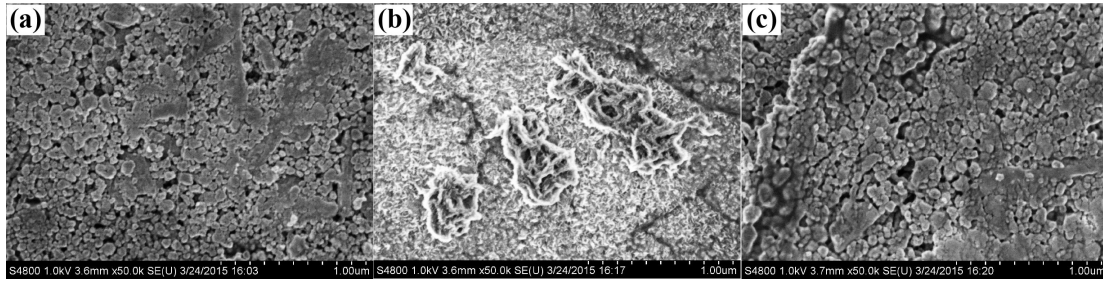


Fig. S8 SEM images of TiO_2 (B)@ RuO_2 -75 cathodes at different states: (a) before discharge, (b) after discharge and (c) after recharge. At the end of discharge, the surface of the TiO_2 (B)@ RuO_2 -75 cathode is almost fully covered by the Li_2O_2 nanosheets; and even some flower structure of discharge product is also formed, which consists of Li_2O_2 nanosheets (**Fig. S8b**). During the subsequent recharge process, all of the discharge products have been decomposed (**Fig. S8b**), indicating the reversible conversion from Li_2O_2 to O_2 .

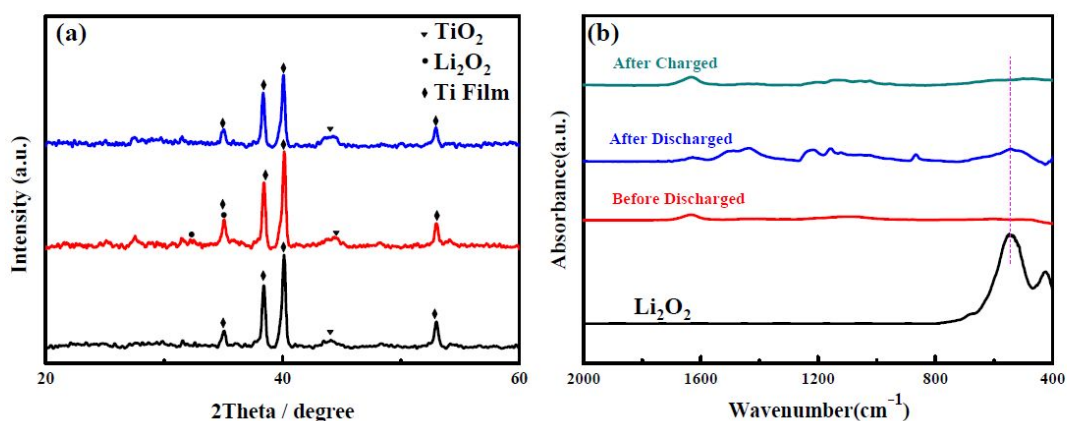


Fig. S9 The analyses for TiO₂ (B)@ RuO₂-75 cathodes: (a) ex-situ XRD patterns at different discharge-charge stages: before discharge, after discharge and after recharge; (b) ex-situ FTIR spectra before discharge, after discharge and at the end of charge at 1st cycle. As compared with the XRD pattern of the fresh electrode, new diffraction peaks were observed for the discharged electrode. Although these peaks were very weak, they can be reasonably assigned as the diffraction peaks of Li₂O₂ (as highlighted in **Fig. S9a**). Furthermore, the diffraction peaks of Li₂O₂ disappeared when the battery was completely recharged, which suggests that the discharge product Li₂O₂ is decomposed at the end of the charging process. This was further confirmed by the FT-IR spectra data in **Fig. S9b**, where the weak characteristic peak for Li₂O₂, observed at the end of discharge, is absent from the spectrum at the end of charge. These results also demonstrate the reversibility of the O₂/Li₂O₂ conversion over the cycles for the Li–O₂ batteries.



Fig. S10 Picture of a cell for the DEMS analysis. The DEMS system was built in-house and guided by the requirement to detect the gases evolved during the charge. A quadrupole mass spectrometer (NETZSCH QMS 403 C) with leak inlet is connected to a customized Swagelok cell assembly (**Fig. S10**). The cathode current collector is integrated with two tubes as purge gas inlet and outlet (**Fig. S10**). Each tested cell was discharged with a fixed capacitance of 500 mAh g^{-1} in the sealed assembly, and then online gas analysis was performed during the recharge process with a purge Ar stream at a current density of 0.25 mA cm^{-2} . Before the charge test and online gas analysis, the system was purged with pure Ar stream for 12 hours, and the background for O_2 and CO_2 was calibrated. Purge gas flows were typically 10 mL/min .