

Material Balance in the O₂ Electrode of Li-O₂ Cells with a Porous Carbon Electrode and TEGDME-Based Electrolytes

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We used a typical porous carbon electrode based on a Ketjenblack, which is a proprietary self-standing sheet consisting of a Ketjenblack and a carbon fiber (250 mm thick, 7 mgcm⁻²-carbon). This porous carbon electrode has large pore volume in mesopore region as shown in Fig. S1.

The cycle life of Li-O₂ cells was much lower than those expected from the electrolyte dry-up, which were simply calculated from average TEGDME consumption rates. The cause of the early failure is the by-product accumulation in the carbon electrode, which results in large potential polarization by pore clogging. This pore clogging was confirmed by a scanning electron microscope, Fourier transform infrared spectroscopy and impedance spectroscopy in Figs. S2, S3 and S4, respectively. The results were given for the Li-O₂ cell with 0.5 M LiTFSI + 0.5 M LiNO₃ + 0.2 M LiBr/TEGDME at 0.4 mAcm⁻².

Compared to the SEM images of a pristine porous carbon electrode in Fig. S2a, the surface of the electrode was completely covered by a product layer after cycling as shown in Fig. S2b. The porous structure was almost completely clogged by product deposits, which may include Li₂O₂ and LiOH.²³

FT-IR spectra in Fig. S3 demonstrated that Li₂O₂ was accompanied by many other peaks that confirm extensive electrolyte decomposition. Although it is difficult to identify the all products by FT-IR only, Fig. S3b revealed the presence of Li₂CO₃.²⁵

Electrochemical impedance spectra in Fig. S4 clearly reflected the increase of the impedance after cycling, which was observed continuously during cycling.²⁹

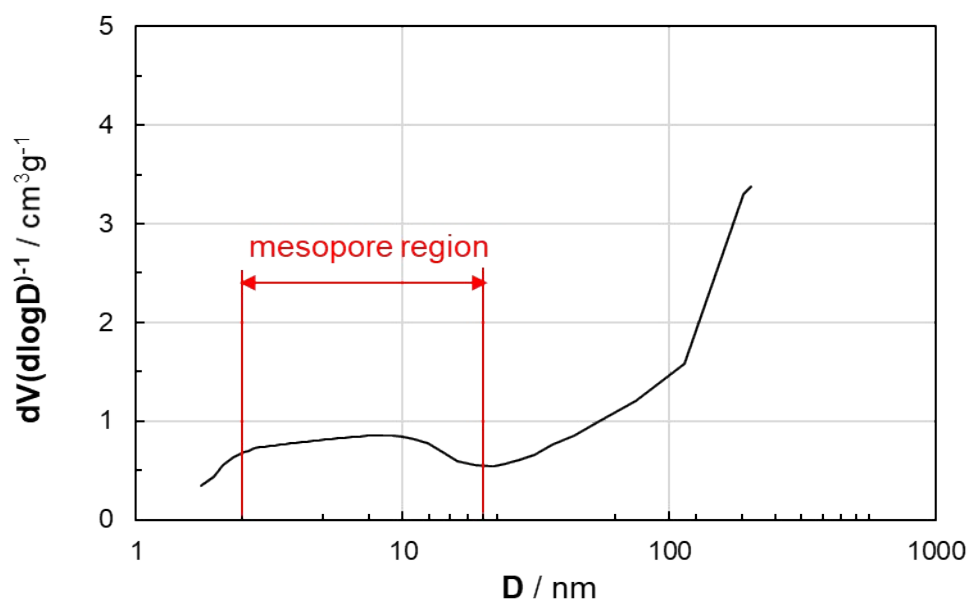


Fig. S1 Pore size distribution of the pristine porous carbon electrode consisting of a Ketjenblack and a carbon fiber (250 μm thick, 7 mgcm^{-2} -carbon). D ; pore diameter, $dV(d\log D)^{-1}$; pore volume.

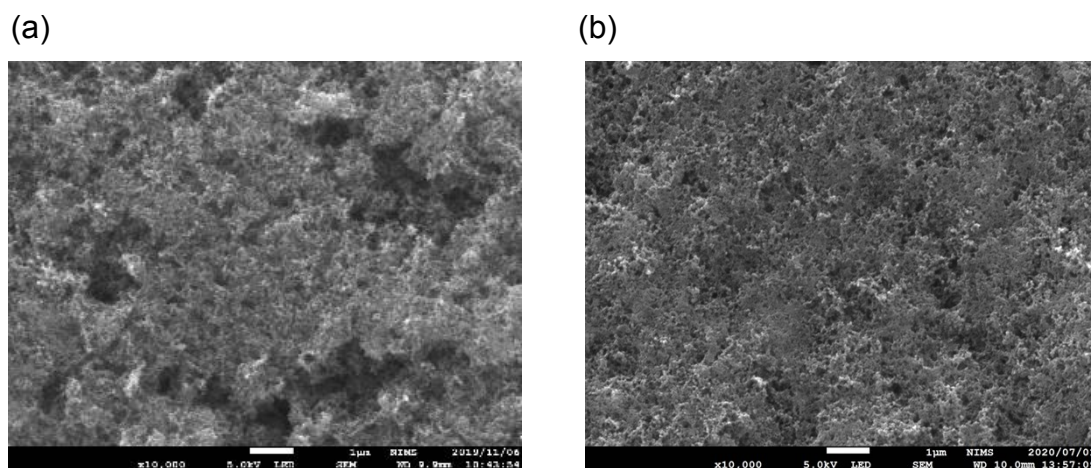


Fig. S2 SEM images of the porous carbon electrode (a) before and (b) after cycling.

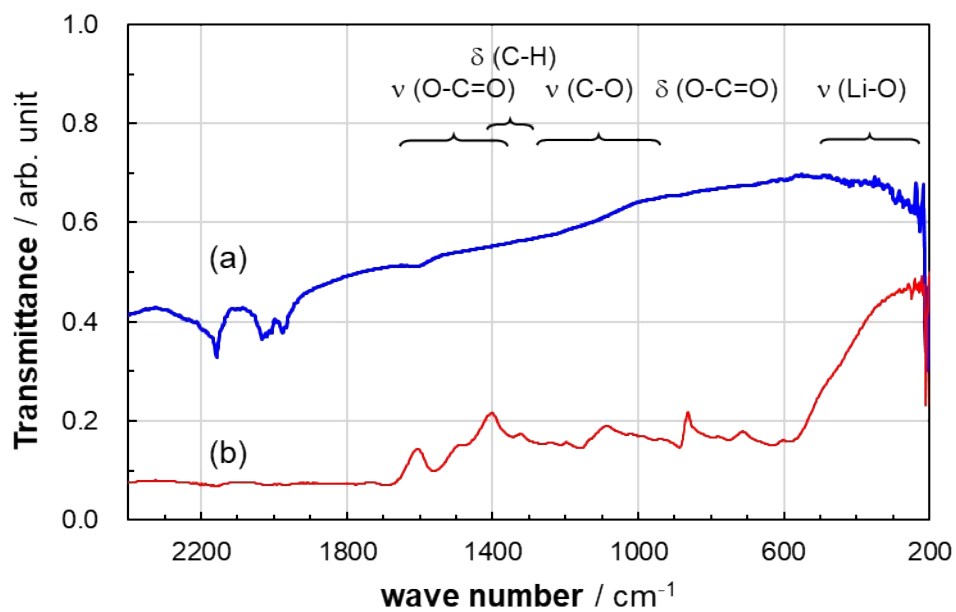


Fig. S3 FT-IR spectra of the porous carbon electrode (a) before and (b) after cycling.

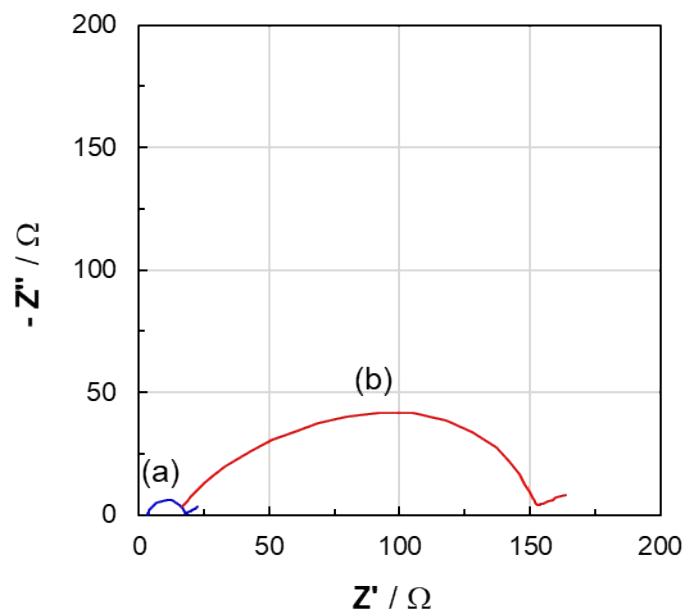


Fig. S4 Nyquist plots of the Li/O_2 cell (a) before and (b) after cycling.