Electronic Supplementary Information (ESI)

Size Effect of Lithium Peroxide on Charging Performance of Li-O_2 Batteries

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Experimental Details

Synthesis. Lithium peroxide samples with three different sizes were synthetized as follows. SL-600 was fabricated by discharging the Li-oxygen cell (based on Super P carbon electrode) at current density of 50 mA g^{-1}_{carbon}. By adjusting the cut-off discharge capacity, the nominal weight proportion of Li_2O_2:C was controlled at 1:1. SL-300 was prepared by mechanical mixing the commercial Li_2O_2 with Super P for 60 min under argon atmosphere. SL-160 was fabricated by ball-milling the commercial Li_2O_2 and Super P for 100 min under argon atmosphere. The weight ratio of Li_2O_2:C was fixed at 1:1 in SL-160 and SL-300.

Materials characterization. Power X-ray diffraction (XRD) analysis was performed on a MiniFlex600 X-ray generator with a Cu source in transmission mode. Fourier Transform Infrared (FTIR) spectroscopies were obtained by a FTIR-650 spectrometer (Tianjin Gangdong) at a resolution of 2 cm^{-1}. Scanning electron microscopy (SEM) images were collected on a JEOL JSM-7500F microscope.

Cell assembly. The CR2032-type and the Swagelok-type cells were used in this study. For the cathode: the slurry was consisted of Super P, Li_2O_2 and poly(vinylidene fluoride) (PVDF) with weight ratio of 45:45:10 using N-methyl-2-pyrrolidinone(NMP) as a dispersing agent. The slurry was smeared onto circular nickel foam with diameter of ~12

mm, which was dried overnight at 110 ^{o}C in a vacuum oven for 6 h. The separator was a glass fiber. Lithium foil was used as the anode. The electrolyte was 1 M Lithium bis-(trifluoromethanesulfonyl)-imide (LiTFSI) in tretraethylene glycol dimethyl ether (TEGDME) dried by molecular sieve. The cell assembly was carried out in a glove box under Ar atmosphere. After that, the cell was transferred to a sealed glass box filled with high-purity oxygen.

Electrochemical Measurements. The cells were kept in oxygen for 5 h at the open-circuit state (voltage is ~3.0 V vs. Li). Electrochemical tests were conducted by a LAND-CT2001A battery-testing instrument. All the three samples were charged at 50 mA g^{-1}_{carbon} to an end-up voltage of the 4.5 V. Cyclic voltammograms (CVs) were carried out with a Parstat 263A electrochemical workstation (AMETEK) at scanning rate of 0.1 mV s^{-1}. The electrochemical impedance spectroscopy (EIS) was conducted using Parstat 2273 potentiostat/galvanostat workstation (AMETEK) within the frequency range of 100 kHz–100 mHz at different controlled temperatures.

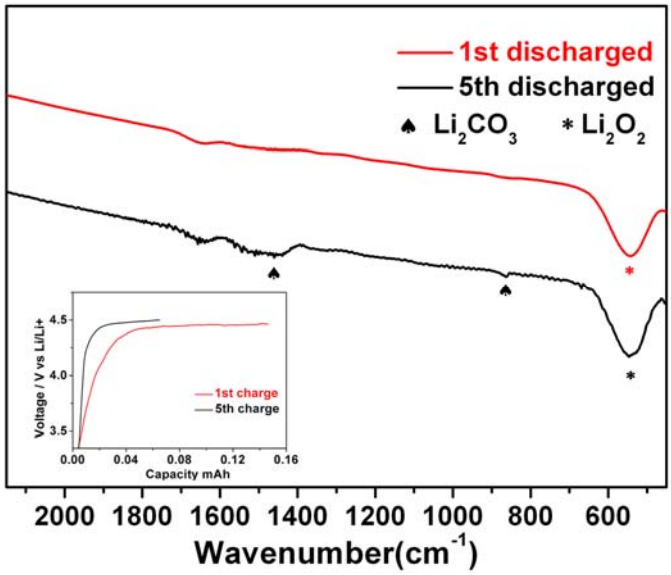

Fig. S1 FTIR spectra of SL-600 (red line) and the discharged product at the 5th cycle. The inset compares the charging plateaus at 1st and 5th cycle.

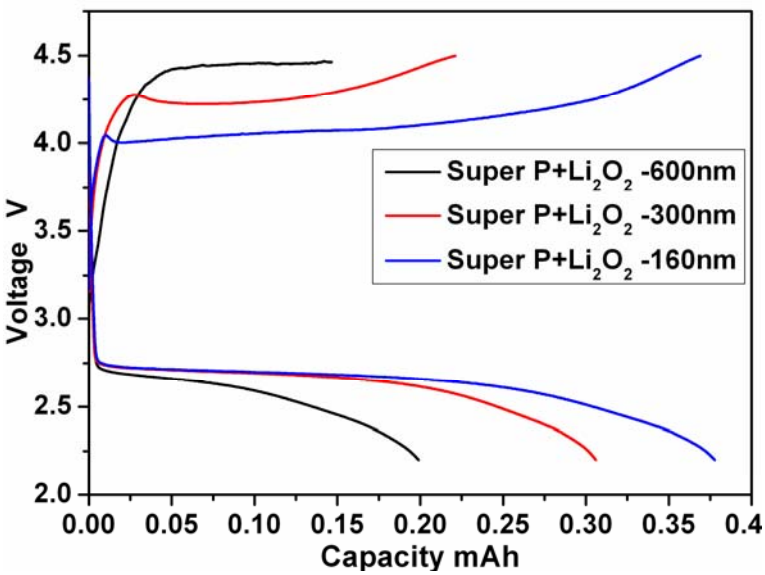

Fig. S2 Typical charge-discharge curves of SL-600, SL-300 and SL-160 at a current density of 50 mA g^{-1}_{carbon}.

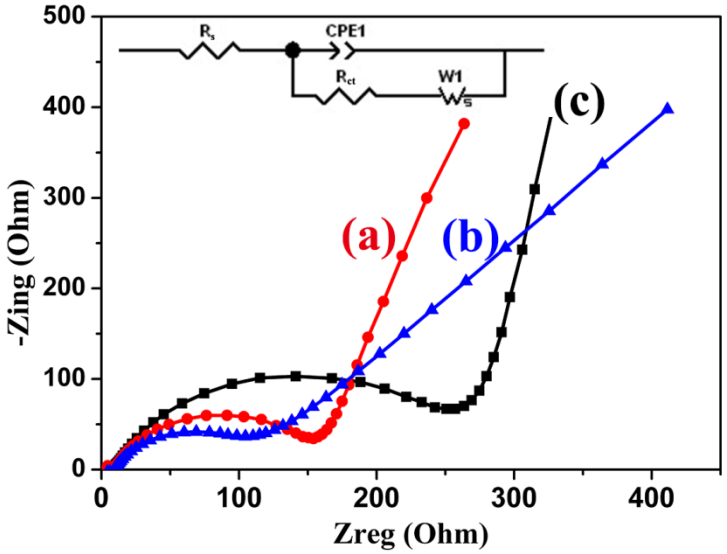

Fig. S3 EIS of the cells tested at midpoint charging plateau (at current density of 50 mA g^{-1}_{carbon}) and 298 K: (a) SL-600, (b) SL-300, and (c) SL-160. The inset shows the equivalent circuit to fit the EIS data.

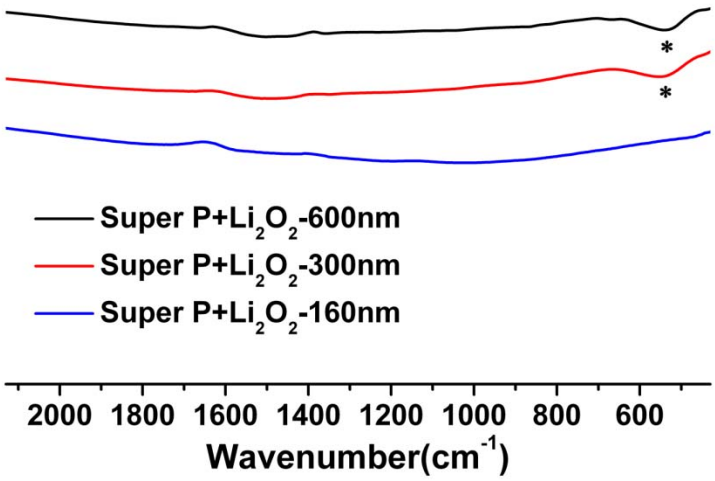

Fig. S4 FTIR spectra of SL-600 (black), SL-300 (red) and SL-160 (blue) electrodes after charging.