Real Time Monitoring of Generation and Decomposition of Degradation Products in Lithium Oxygen Battery during Discharge/Charge Cycles by Online Cold Trap Pre-concentrator–Gas Chromatography/Mass Spectroscopy System

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CTPC-GC/MS analysis of the LOB prepared using TEGDME (HP) during the discharge/charge cycle

Figure S1(a) shows time dependencies of voltage and current (left panel) and GCs of head space gas of the LOB, sampled during 4 cycles of OCP (2h), constant current (0.4 mA) discharge (10 h or 2V cut off), OCP (2h), constant current (0.4 mA) charge (10h or 4.5 V cut off). Time dependencies of voltage (bottom panels) and the peak intensities of all 37 peaks during 4 cycles are shown in **Figure S1(b)**. The full capacity (10 h) discharge was possible in the first 2 discharge but the 3rd and 4th discharge were terminated by cut off at 2 V (7.4 and 2.7 h, respectively). On the other hand, charge was terminated by cut off at 4.5 V even from the 1st charge (9.4 h) and charge duration (capacity) decreased as cycle number increased (2nd: 4.2 h, 3rd: 3.0 h, and 4th: 1.3 h).



Figure S1. (a) GCs of head space gas of the LOB, which was prepared by using TEGDME (HP), sampled during 4 cycles of OCP, discharge, OCP, and charge. Left panel: voltage and current as a function of time. Blue, pink/red, green, and grey/black lines are for the 1st, 2nd, 3rd and 4th cycle, respectively. Lines of lighter colour are of OCP and discharge, and of darker colour are of OCP and charge. (b) Voltage (bottom panels) and intensities of the peaks 1 - 37 during 4 cycles of OCP (+), discharge (•), OCP (\Box), and charge (Δ) as a function of time. Blue, red, green, and black lines/symbols are for the 1st, 2nd, 3rd and 4th cycle, respectively. Note 5 different scales are used for y-axis: 1x10⁸ (blue), 5x10⁷ (green), 2x10⁷ (pink), 1x10⁷ (yellow), and 5x10⁶ (white).



Figure S2. Voltage (a) and intensities of peak 1 (b), 19 (c), 7 (d), and 25 (e) as a function of time during OCP (+) and discharge (•) (broken lines), and OCP (\Box) and charge (Δ) (solid lines) in the 1st (blue), 2nd (red), 3rd (green), and 4th (black) cycle.