Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

A New Type of cyclic silicone Additive for Improving Energy Density and Power Density of Li-O_2 Batteries

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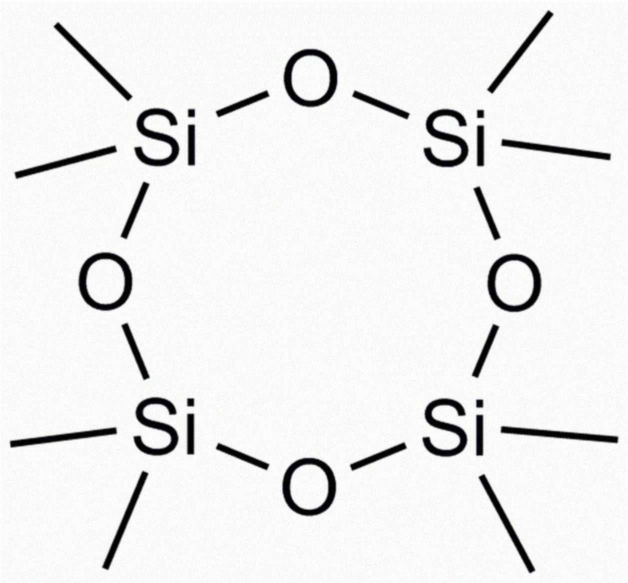

Fig. S1. The structure of octamethylcyclotetrasiloxane (OMTS).

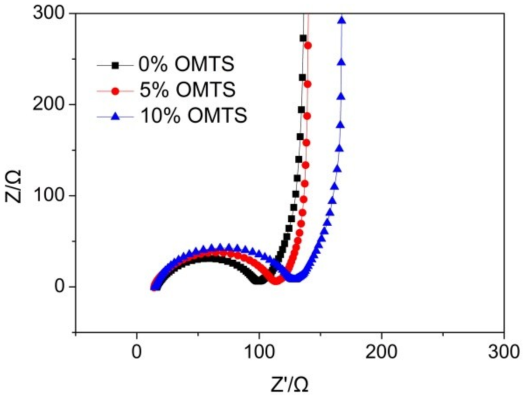

Fig. S2. EIS of Li-O_2 batteries at open-circuit potential with various amounts of OMTS content at a storage time of 2h under O_2 atmosphere.

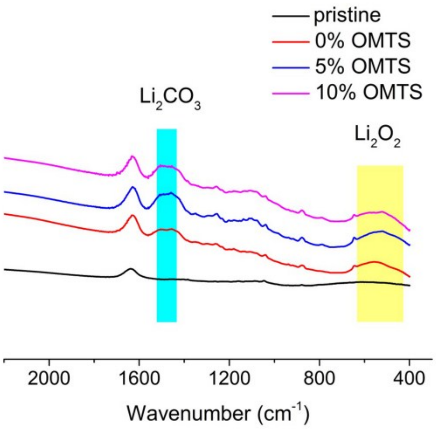

Fig. S3. FTIR measurements of the electrode at the end of first discharge with various amounts of OMTS content.

Explaination: It is obvious that the discharge products are mainly Li_2O_2 with a characteristic peak at 556 cm^{-1}. Some by-products occur inevitably in the process of discharge. The blue area corresponds to the peak of by-product Li_2CO_3 peak.

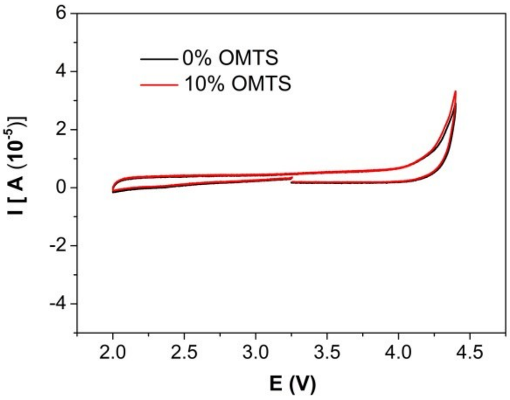

Fig. S4. CV curves under Ar atmosphere at a scan rate of 100 mV s^{-1} in three-electrode system.

Glassy carbon (GC), Ag/Ag^+ (CH_3CN, 0.01 M $AgNO_3$+0.1 M $TBAPF_6$) and platinum (Pt) sheet were employed as the working electrode, reference electrode and counter electrode, respectively.

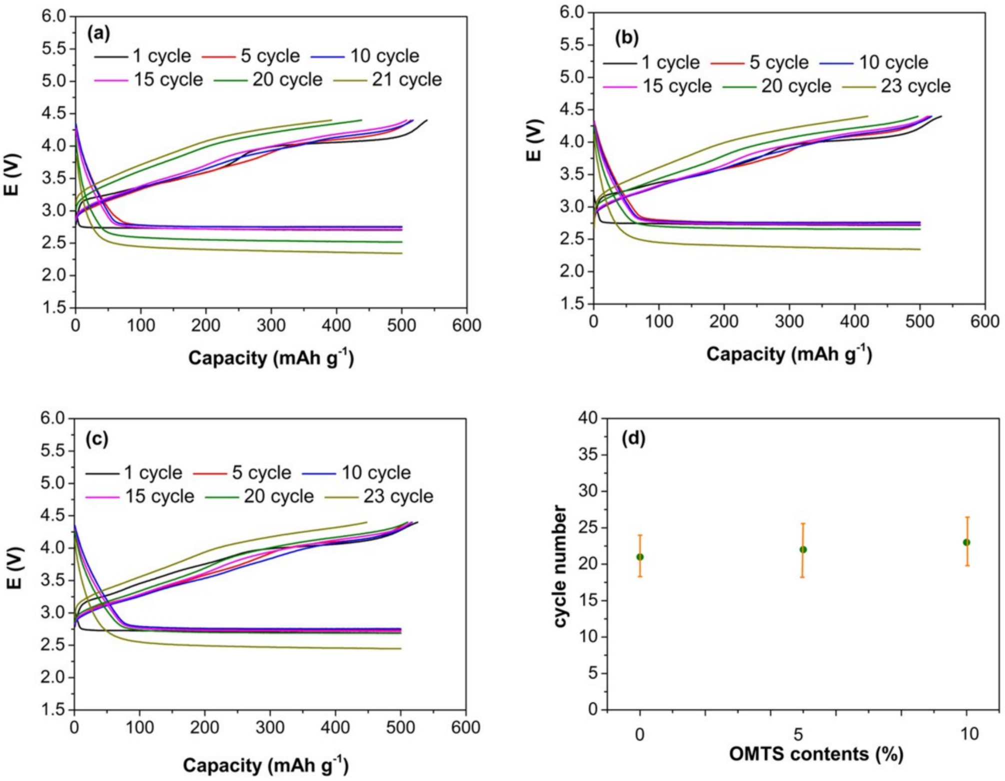

Fig. S5. Cyclic performance of Li-O_2 batteries in the electrolyte system with various amounts of OMTS content: (a) 0% OMTS, (b) 5% OMTS, and (c) 10% OMTS. (d) cycle number in different electrolytes.

Supplementary Methods

1. Measurement the oxygen solubility of diffusion coefficient

The oxygen solubility and diffusion coefficient of the electrolytes were carried out in 0.1 M TBAPF$_6$ salt by the potential-step chronoamperometry for ORR at a 25μm Pt microelectrode. The test condition was firstly holding a potential where no faradic process was evident and then stepping to a potential where diffusion-limited ORR took place. The current was measured for pulse width of 10 s and a sample interval of 1 ms. The values of oxygen solubility and diffusion coefficient were determined by fitting the potential-step chronoamperometric curve using a nonlinear curve fitting function using Shoup and Szabo's equation. [23, 24]

$$I = -4nFDrc_o f\,(\tau)$$

Where

$$f\,(\tau) = 0.7854 + 0.8862\tau^{-1/2} + 0.2146e^{-0.7823\tau^{-3/2}}$$

$$\tau = \frac{4Dt}{r^2}$$

Where r is the radius of microdisk electrode, c_o is the initial concentration and t is the time.

2. Measurement the yield of Li_2O_2 of discharge.

- **Calculate the yield of Li_2O_2 during discharge**

Li_2O_2 yields (Y_{Li2O2}) was calculated using the following equation:

$$Y_{Li2O2} = n_{Li2O2,t}/n_{Li2O2,e}$$

Where, $n_{Li2O2,t}$ is the amount of Li_2O_2 titrated after discharge. $n_{Li2O2,e}$ is the amount of Li_2O_2 expected given a 2 e^-/ Li_2O_2 process during discharge. All dates were tested at least three replicate trials.

- **Titration of Li_2O_2 after discharge**

Cathodes are extracted from discharged or charged cells in an Ar glove box and dried under vacuum. The electrode was placed in an unsealed conical flask and the conical flask is then sealed with a silicone septa lid and transferred out of the glove box. 10 mL of de-ionized water is injected into the sealed vial using a syringe. The flask was vigorously shaken (about 1 min) to promote the complete reaction of Li_2O_2 with H_2O. The alkaline solution was titrated with a standard 5 mmol L^{-1} of HCl, and the end point was indicated by 0.1 mL of phenolphthalein in isopropanol.

Involved reaction:

$Li_2O_{2(s)} + 2H_2O_{(l)} \rightarrow H_2O_{2(l)} + 2LiOH_{(aq)}$ (1)

1) After the alkaline titration was finished, three reagents were added into the existing solution in sequence: 2 mL of 2 wt% KI in H_2O, 0.4 mL of 60 wt% H_2SO_4, and 100 μL of a molybdate based catalyst solution. The catalyst solution was prepared by dissolving 1 g ammonium molybdate in 10 mL of 30 wt% ammonia aqueous solution, followed by adding 3 g of ammonium nitrate and

diluting the solution to 50 mL total using de-ionized water. The resultant solution turns yellow upon reagent addition due to I_2 formation, and the I_2 was immediately titrated to a pale yellow color using 2 mmol L^{-1} of $Na_2S_2O_3$ solution. At this point, 0.1 mL of 5 wt% starch indicator was added, which turned blue, and the titration was continued until the color disappeared.

Involved reactions:

$H_2O_2 + 2KI + H_2SO_4 \rightarrow I_2 + K_2SO_4 + 2H_2O$ (2) over molybdate-based catalyst

$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$ (3)