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Materials and Methods

Materials.

Agate mortar, precision disc cutter, compact tape casting film coater with dryer, electric precision 4" width rolling press with dual micrometer, argon-filled glove box and argon tank, lithium tablets, electrolytes, micropipette, button battery box set, battery separator, compact hydraulic crimping machine, disassembling machine, etc (Figure S1). Electrolyte solvents are gamma-butyrolactone, dimethylsulfoxide (DMSO) and sulfolane. Electrolyte salt is 1 M $LiPF_6$. The composition of the carbon cathodes are Ketjen black (KB) carbon:polytetrafluoroethylene (PTFE):Cu 8:1:1 (m/m) or KB carbon:PTFE 9:1 (m/m) in this work.

Methods.

Carbon electrode preparation. Ketjen black (KB) carbon EC600JD (Akzo Nobel Corp ~1400 m^2/g) was dried at 80 ℃ for 0.5 h then a certain amount of KB, Teflon PTFE and conductive Cu powder (as conductive agent). fluoropolymer resin aqueous dispersion (60% solid) and NMP were blended with a pestle and mortar (Figure S1). The slurry was cast onto carbon paper to make carbon electrode sheet. Then the sheet was heated at 80 ℃ for 3 h to remove NMP. Electric precision 4" width rolling press with dual micrometer (purchased from MTI Shenzhen Corp.) was used to planish carbon electrode sheet (Figure S1). The composition of the carbon cathode is Ketjen black (KB) carbon:polytetrafluoroethylene (PTFE):Cu 8:1:1 (m/m). In the 110 cycles test, Cu is not used so the the composition of the carbon cathode is Ketjen black (KB) carbon:polytetrafluoroethylene (PTFE) 9:1 (m/m).

Constructing and testing. Li-O_2 cells were constructed in an argon-filled glove box (MBraun) in which the oxygen and moisture concentration were both less than 5 ppm (Figure S1). Type 2032 coin cell kits (purchased from MTI Shenzhen Corp.) with a diameter of 20 mm and a thickness of 3.2 mm were used to assemble our batteries. The positive pans of the coin cells were scattered by apertures with a diameter of 1 mm, these holes can allow oxygen to pass through. A lithium disk (15 mm in diameter and 1 mm thick) was used as the anode. The salt and solvent used in the electrolyte were all battery-grade materials purchased from Shenzhen Capchem technology Co.Ltd.. In order to absorb more electrolyte for our Li-O_2 batteries, a Whatman GF/D glass microfiber filter paper (19 mm in diameter) was chosen as the separator. The schematic structure of assembled coin cells is shown in Figure S2. In order to avoid any negative effects of humidity and CO_2, the coin cells were tested in a closed box filled with oxygen (99.999% in purity). Discharge performance tests were carried out using a CT2001A battery tester (Figure S3).

Figure S1. Main devices, materials, and battery assembly methods. (**A**) Agate mortar is used to triturate carbon electrode materials, an precision disc cutter is used to shape carbon electrode sheet. (**B**) Compact tape casting film coater with dryer is applied to coat carbon electrode materials onto carbon paper to make carbon electrode sheet. (**C**) Electric precision 4" width rolling press with dual micrometer is used to planish carbon electrode sheet. (**D**) Argon-filled glove box and argon tank. (**E**) Lithium tablets are stored in the glove box. (**F**) Lithium tablets, electrolytes, micropipette, button battery box set, battery separator, compact hydraulic crimping machine, disassembling machine, etc.

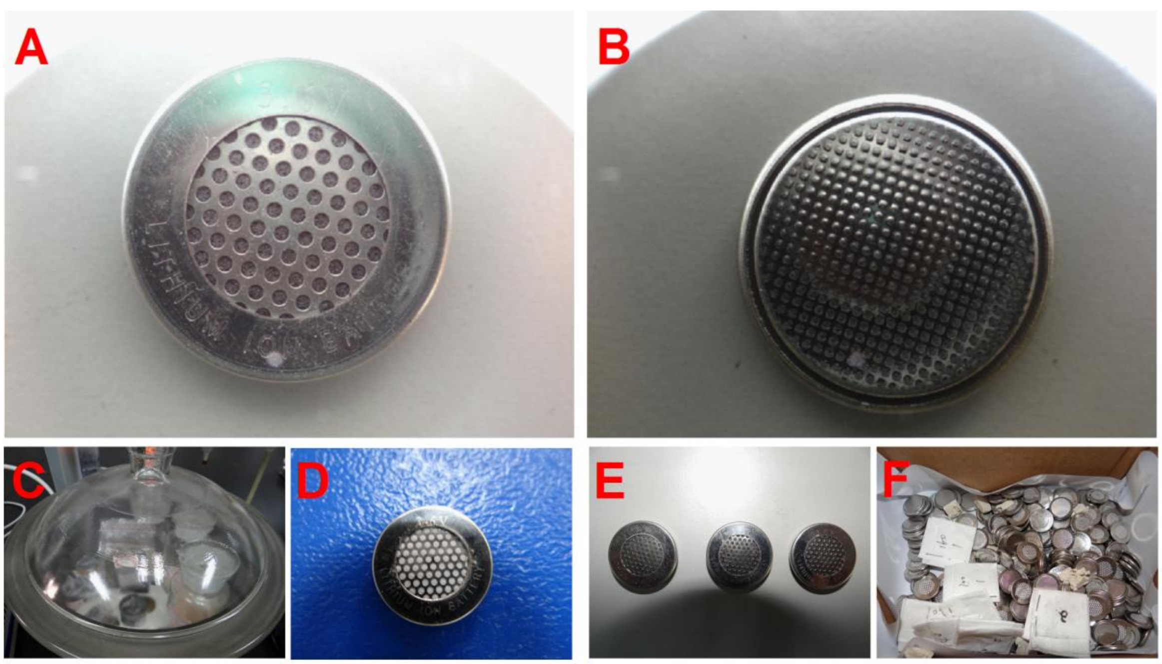

Figure S2. Constructed Li-air batteries. (**A**) Positive electrode. (**B**) Negative electrode. (**C**) Carbon electrode materials. (**D**)~(**F**) Li-air battery samples.

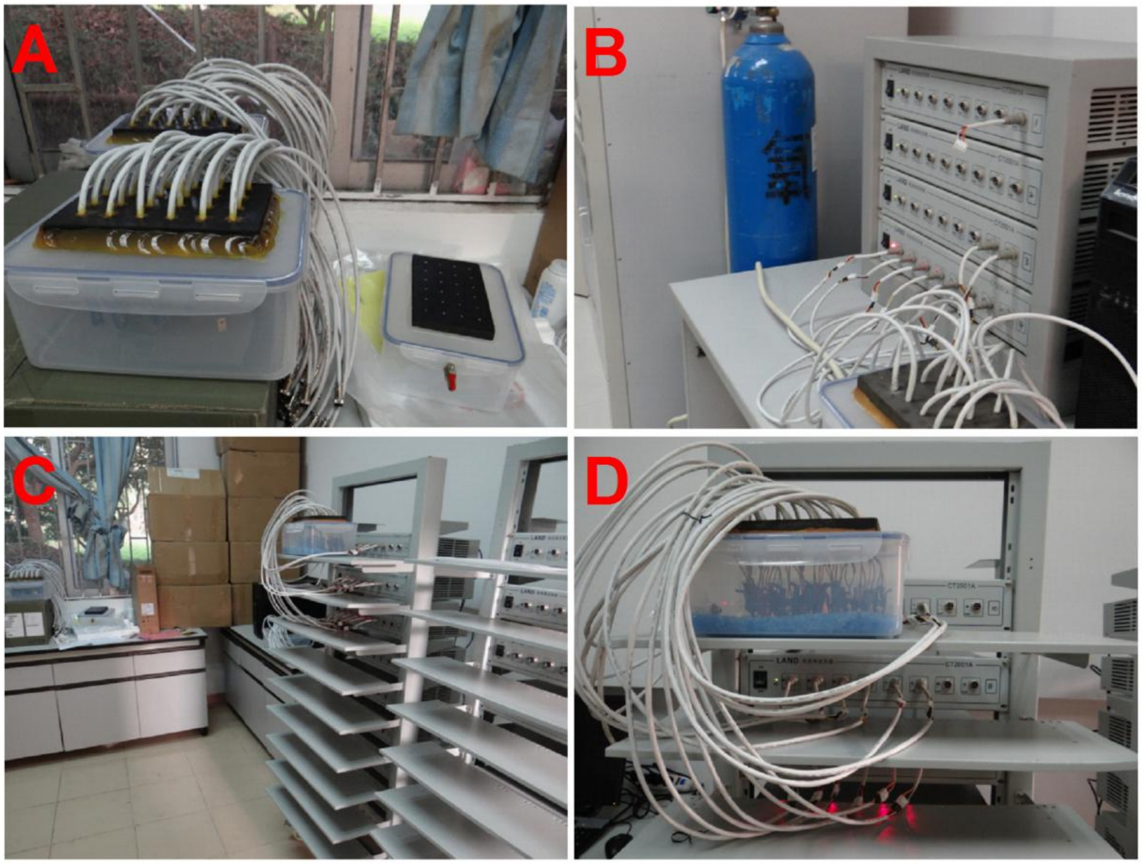

Figure S3. Testing of Li-air batteries. (**A**) Testing boxes of Li-air batteries. (**B**) Li-air batteries tested in oxygen-filled box. (**C**) Testing environment: dry air (left) and ambient air (right). (**D**) Battery testing process.

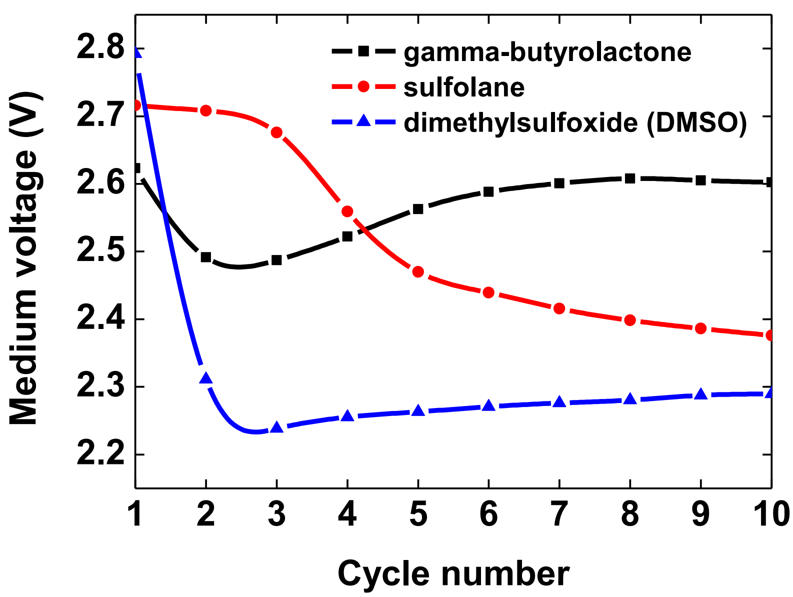

Figure S4. Medium voltage comparison of cells composed of three different electrolyte solvent. (A) gamma-butyrolactone , (B) sulfolane , (C) dimethylsulfoxide (DMSO). The current densities and carbon cathode composition here are identical with that of Fig. 1.

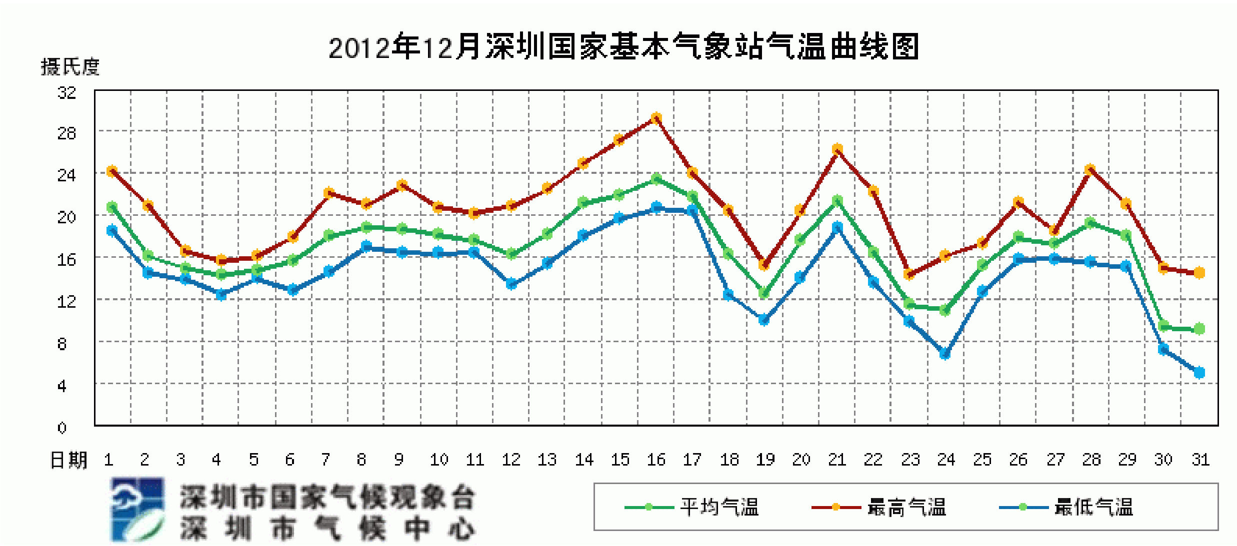

Figure S5. Temperature data. Horizontal and vertical ordinates represent date and Celsius degree respectively. Green, red and blue represent the average, highest and lowest air temperature respectively. [Courtesy of Meteorological Bureau of Shenzhen Municipality.]

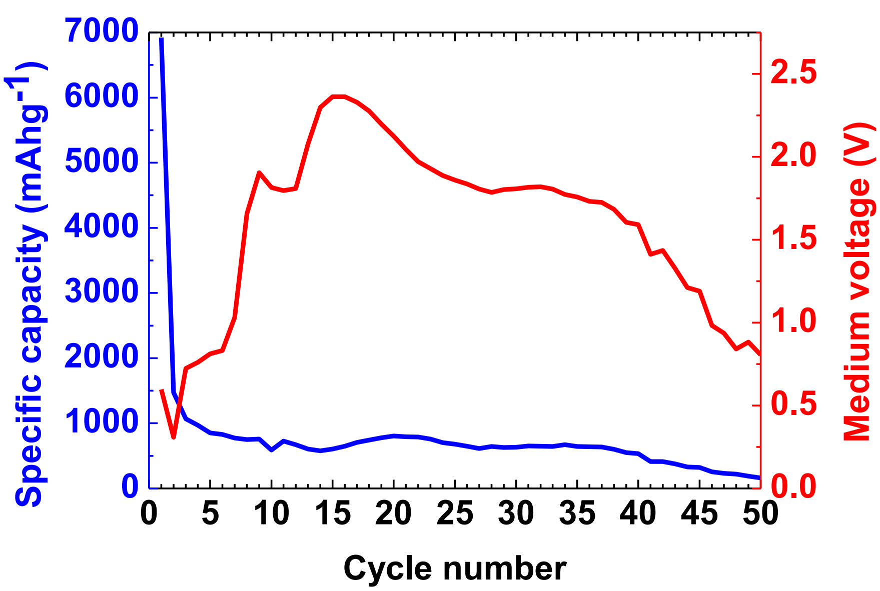

Figure S6. Testing result of sulfolane based Li-O_2 cell which was in dry air (5 ℃~25 ℃) at ~200 mAg^{-1}. Capacity-cycle curv (blue) and voltage-cycle curve (red). The bottom of the testing box was carpeted with desiccant to make dry condition. Different from the aforementioned, the specific capacity here is normalized by the mass of Li_2O_2.

The main reactions in the Sulfolane based Li-air batteries can be illustrated as follows:

$$\text{Negative electrode reaction}: 2\text{Li} \leftrightarrow 2\text{Li}^{+} + 2e^{-} \quad (1)$$

$$\text{Positive electrode reaction}: 2\text{Li}^{+} + \text{O}_2 + 2e^{-} \leftrightarrow \text{Li}_2\text{O}_2 \quad (2)$$

$$\text{Cell reaction}: 2\text{Li} + \text{O}_2 \leftrightarrow \text{Li}_2\text{O}_2 \quad (3)$$

"$\rightarrow$" represents discharge reaction, "$\leftarrow$" represents charge reaction.

Table S1 Testing result of sulfolane based Li-O_2 cell which was in dry air.
The bottom of the testing box was carpeted with desiccant to make dry condition. Specific capacity is normalized by the mass of Li_2O_2.

Cycle number	Charge specific capacity ($mAhg^{-1}$)	Discharge specific capacity ($mAhg^{-1}$)	Efficiency (%)	Discharge medium voltage (V)
1	-	6921.8	-	0.5965
2	1263.1	1473.9	116.7	0.3086
3	999.6	1068.8	106.9	0.724
4	999.7	970.4	97.1	0.7612
5	999.6	852.7	85.3	0.8122
6	999.7	829.4	83	0.8315
7	999.5	772.4	77.3	1.0313
8	999.5	749.1	75	1.6573
9	999.5	759.7	76	1.9044
10	999.5	589.2	58.9	1.8155
11	999.6	727.5	72.8	1.7956
12	999.7	671.9	67.2	1.808
13	999.7	606.3	60.6	2.0771
14	999.6	579.2	57.9	2.2972
15	999.7	603.2	60.3	2.3626
16	999.7	648.5	64.9	2.363
17	999.6	706.9	70.7	2.3284
18	999.5	742.9	74.3	2.2767
19	999.5	779.3	78	2.1981
20	999.6	807	80.7	2.1252
21	999.5	792.8	79.3	2.0454
22	999.6	790.2	79	1.9709
23	999.5	757.2	75.8	1.9293
24	999.5	703.5	70.4	1.888
25	997.8	679.2	68.1	1.8591
26	995	647.3	65.1	1.8366
27	986.3	613.7	62.2	1.8059
28	989.5	644	65.1	1.7862
29	995.4	630.2	63.3	1.8028

30	997.2	631.1	63.3	1.8069
31	999.6	651.8	65.2	1.8163
32	999.6	646.7	64.7	1.8196
33	999.5	643.3	64.4	1.8049
34	999.5	673.3	67.4	1.7728
35	999.6	643.5	64.4	1.757
36	999.5	641.2	64.1	1.7318
37	999.5	638.3	63.9	1.7256
38	998.1	602.3	60.3	1.6841
39	988.8	550.7	55.7	1.6044
40	982.9	533.2	54.2	1.5914
41	997.4	413.3	41.4	1.4122
42	966.4	413.4	42.8	1.4358
43	952.6	378.5	39.7	1.327
44	955.7	331.8	34.7	1.2108
45	647.7	323.6	50	1.1891
46	957.1	255.7	26.7	0.9837
47	878.3	233.5	26.6	0.9371
48	716.4	219	30.6	0.8408
49	609	190.1	31.2	0.883
50	688.7	159.6	23.2	0.8055

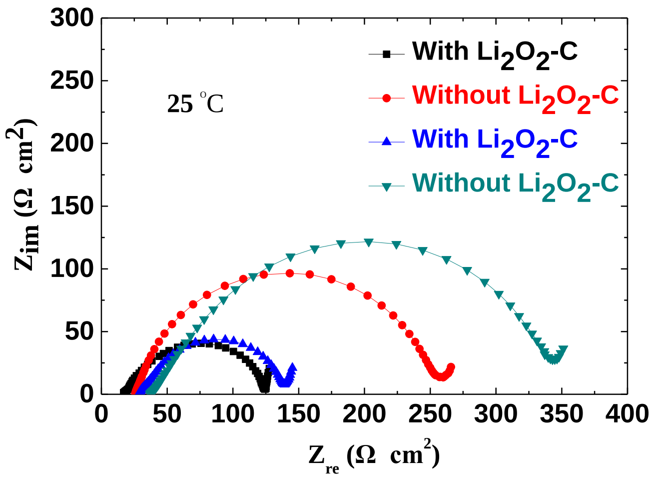

Figure S7. A.C. Impedance comparison. The open circuit potential of the batteries with Li_2O_2-C (lithium peroxide and KB carbon) is about 2.9 V and the real part of A.C. Impedance is about 135 Ω cm^2 before the first discharge. The open circuit potential of the batteries without Li_2O_2-C is about 2.7 V and the real part of A.C. Impedance is about 300 Ω cm^2 before the first discharge.

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