Supporting Information

A High Power Li-air Battery Enabled by a Fluorocarbon Additive

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Experimental Details

Cell assembly

3-[2-(Perfluorohexyl)ethoxy]-1,2-epoxypropane from J&K chemicals was added to a slurry of ketjenblack (KB) and polytetrafluoroethylene (PTFE) (KB:PTFE=85:15, w/w) with various amounts, then the mixture was cast onto a piece of nickel foam and dried in vacuum at 120°C for 12 h, then die cut into a circular chip with a diameter of 14mm. The carbon loading was controlled at ~0.10 mg cm^{-2}. The CR2032 cells were assembled in a glove box filled with Ar. A piece of lithium foil (200 μm thick) was used as the anode, and a Whatman GF/D glass fiber filter as the separator. 140 μL of the 0.1 mol L^{-1} $LiClO_4$/DMSO was used as the electrolyte. After 12 h of resting, the cells were relaxed for 12 h.

Electrochemical Measurements

The assembled cell was placed into a home-made air-tight canister with gas inlet (connected to Ar and O_2 bombs) and outlet, to conduct electrochemical tests with a Solatron 1470E electrochemical workstation. The atmosphere switching potentiostatic polarization tests were carried out at 2.0 V vs. Li/Li^+; the galvanostatic tests were conducted under designated current densities with cut-off voltage of 2.0-4.55 V; and electrochemical impedance spectroscopy tests were performed in the range of 100000–0.1 Hz with a bias voltage of 5 mV at open circuit.

Physical characterizations

Scanning electron microscopy (SEM, FEI Quanta FEG 250) was used to observe the morphology of the discharge products, and Raman spectra were recorded using a Renishaw inVia Reflex spectrosmeter with 532 nm laser.

The electrolytes were bubbled with O_2 for 15 min before measuring their O_2 solubility using a polarography based Model 8403 dissolved oxygen meter from AZ instrument. It employs a semi-permeable membrane to separate the measured solution from the intrument's own electrolyte, and let O_2 through to reduce on the Pt electrode. And the O_2 solubility was automatically calculated according to the equation $i_\infty=nFA(P_m/L)C_s$, where i_∞ refers to the steady-state current of oxygen reduction, n to the number of electron transfer, F to the Faraday constant, P_m to the membrane's osmotic coefficient, L to the membrane's thickness, and C_s to the concentration of dissolved oxygen. After each measurement, the probe was thouroughly rinsed with aqueous KCl solution to avoid crossover of DMSO.

Supplementary Figures and Tables

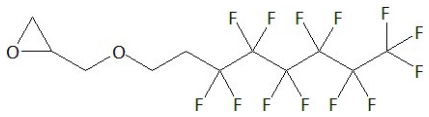

Figure S1 The structure of 3-[2-(Perfluorohexyl)ethoxy]-1,2-epoxypropane.

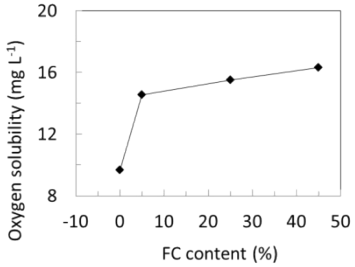

Figure S2 The O_2 solubility of electrolytes with various FC contents.

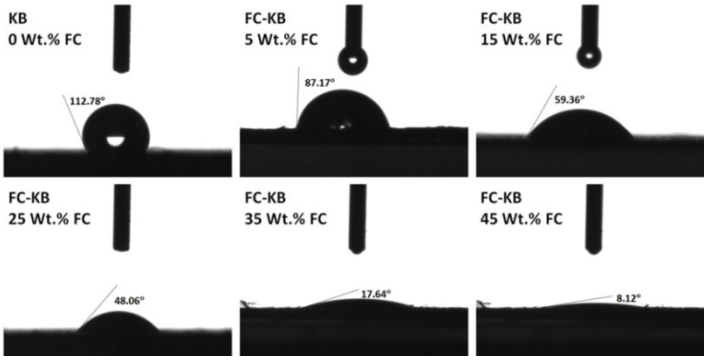

Figure S3 The contact angle tests of air cathodes with various FC contents.

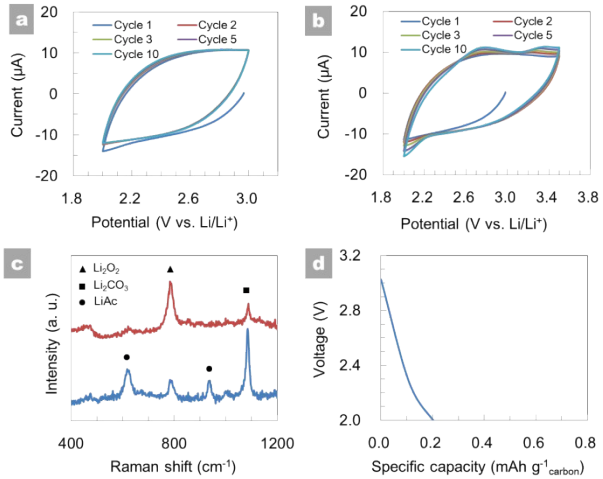

Fig. S4 Cyclic voltammograms of the cathode with 35% FC between (a) 2.0-3.0 V and (b) 2.0-3.5 V *vs.* Li/Li^+ in Ar, scan rate 1 mV s^{-1}; (c) the Raman spectra of the discharged cathodes with and without 35% FC in N_2-O_2 (78:22, v/v); (d) the discharge curve of the cell with 35% FC in Ar, current density 100 mA g^{-1}_{carbon}.

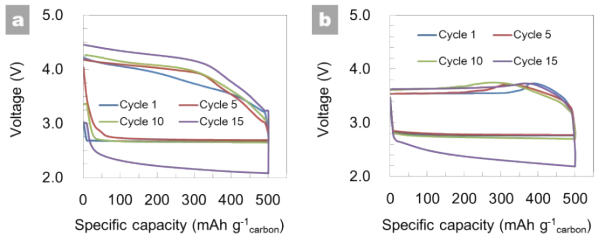

Fig. S5 Cycling performances of the cells (a) without FC or (b) with 35% FC at current density of 100 mA g^{-1}_{carbon} and fixed capacity of 500 mAh g^{-1}_{carbon}, The cut-off voltages are 2.00-4.55 V.

Table S1 The parameters of the equavalent circuit used for fitting the impedance spectra of the cell with various FC contents as prepared

FC content	0	5	15	25	35	45
R_{el} (Ω)	780.9	23.8	21.6	13.8	37.4	31.9
R_{HF} (Ω)	2709	264.7	158.1	133.4	279.7	230.3
CPE-T_{HF} ($\times10^{-6}$ Ω^{-1} s^{-n})	22.027	20.814	6.915	9.326	8.294	24.23
CPE-P_{HF}	0..655	0.757	0.926	0.885	0.845	0.756
R_{MF} (Ω)	465.8	32.4	31.6	22.6	43.2	80.5
CPE-T_{MF} ($\times10^{-6}$ Ω^{-1} s^{-n})	0.874	6.815	3.089	2.587	3.241	7.141
CPE-P_{MF}	0.888	0.901	0.965	0.986	0.955	0.845
W_O-R (Ω)	7029	2722	534.4	371.8	233.2	93.7
W_O-T (Ω^{-1} s^{-n})	57.8	4.823	0.485	0.289	0.328	0.174
W_O-P	0.486	0.518	0.369	0.359	0.395	0.332

Table S2 The parameters of the equavalent circuit used for fitting the impedance spectra of the cell without FC at various states of discharge

Data point	1	2	3	4	5	6	7	8	9	10
R_{el} (Ω)	780.9	794	844.9	950.8	973.3	975.5	986.5	1018	1039	1066
R_{HF} (Ω)	2709	481	615	836	804	833	810	919	1006	1071
CPE-T_{HF} ($\times10^{-6}$ Ω^{-1} s^{-n})	22.027	0.845	0.796	0.897	0.825	0.998	0.951	1.197	1.506	1.812
CPE-P_{HF}	0..655	0.888	0.870	0.837	0.845	0.821	0.822	0.789	0.765	0.748
R_{MF} (Ω)	465.8	3077	4719	7574	9329	11336	14864	20283	24709	34833
CPE-T_{MF} ($\times10^{-6}$ Ω^{-1} s^{-n})	0.874	21.893	17.633	13.502	10.010	9.543	9.606	9.788	11.287	14.388
CPE-P_{MF}	0.888	0.652	0.671	0.702	0.711	0.708	0.690	0.686	0.608	0.634
W_O-R (Ω)	7029	3620	4260	3978	5579	10023	5059	4919	10402	57291
W_O-T (Ω^{-1} s^{-n})	57.800	13.170	10.370	6.898	8.965	13.350	5.156	3.618	7.791	86.140
W_O-P	0.486	0.490	0.526	0.611	0.559	0.560	0.715	0.740	0.676	0.892

Table S3 The parameters of the equavalent circuit used for fitting the impedance spectra of the cell with 35% FC at various states of discharge

Data point	1	2	3	4	5	6	7	8	9	10
R_{el} (Ω)	37.44	38.90	39.01	44.41	52.97	57.30	59.06	61.68	65.14	70.13
R_{HF} (Ω)	279.7	311.3	260.3	228.7	323.4	413.5	442.9	474.8	454.4	435.5

CPE-T_{HF} ($\times 10^{-6}$ Ω^{-1} s^{-n})	8.294	10.647	8.265	6.296	6.631	8.186	8.566	9.551	7.278	7.614
CPE-P_{HF}	0.845	0.798	0.848	0.858	0.797	0.733	0.721	0.700	0.735	0.752
R_{MF} (Ω)	43.25	40.54	51.33	49.77	55.56	24.79	22.29	17.60	43.01	97.98
CPE-T_{MF} ($\times 10^{-6}$ Ω^{-1} s^{-n})	3.241	4.766	4.444	3.206	5.262	5.333	5.278	5.419	8.438	9.282
CPE-P_{MF}	0.955	0.922	0.904	0.915	0.843	0.900	0.910	0.929	0.794	0.726
W_O-R (Ω)	233.2	1990	1642	1923	2087	2590	2664	2756	3477	2342
W_O-T (Ω^{-1} s^{-n})	0.328	8.307	13.56	21.94	16.62	14.29	12.7	12.44	19.83	12.2
W_O-P	0.395	0.645	0.498	0.441	0.488	0.565	0.595	0.605	0.608	0.536

Table S4 The discharge capacities of the cells with various FC contents and current densities

FC content	0	5	15	25	35	45
Capacity under 100 mA g^{-1}_{carbon} (mAh g^{-1}_{carbon})	814	1849	7434	11577	16495	2381
Capacity under 500 mA g^{-1}_{carbon} (mAh g^{-1}_{carbon})	0.28	195	1624	9091	16368	94