Supporting Information:

A dual pore carbon aerogel based air cathode for a highly rechargeable lithium-air battery

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This Supporting Information contains Experimental methods, results and discussion of 16 supplementary figures comprising 57 panels in total with brief legends and 6 supplementary tables.

1. Experimental methods

1.1 Synthesis and characterization of carbon aerogel

Synthesis of carbon aerogel

Carbon aerogel has been traditionally synthesized through various processes including sol-gel reaction, acetic acid treatment, solvent exchange, supercritical drying and carbonization under inert atmosphere. In this article, resorcinol (R) and formaldehyde (F) were chosen as reaction precursor. Sodium carbonate (C) and deionized water were used as catalyst and solvent, respectively. The molar ratio of R/C and R/F were controlled to 1000:1–2000:1, 1:2 respectively. The reactant mass fraction was 40% (or 30%). The mixture was first stirred vigorously into a homogeneous solution, and then cured at 353K for three days in a sealed container, followed by one day trifluoroacetic acid treatment to further strengthen the gel configuration net. After that, fresh acetone was utilized to immerse the

wet gels three times (one time a day) to replace water in the holes which was helpful to avoid net structure collapse. By this step, RF aerogel (ie, RF1500-40) was obtained. Finally, the wet gels were pyrolyzed in a tubular furnace under Ar atmosphere at 1323 K for 4 hours, yielding carbon aerogel (CRF1500-40). Other carbon aerogels, such as CRF1000-30 et al., were obtained simultaneously.

Materials characterization

The morphology and particle size of the RF aerogels and carbon aerogels were characterized by FE-SEM using the Hitachi SU-70 Thermal Field Emission Scanning Electron Microscope by operating at 2.0 KV and TEM using the PHILIPS TECNAI-10 with an accelerating voltage ranging of 40–120 KV. The TG-DTA test was employed to determine the carbonization temperature and following degas temperature using a STA409PC Sync thermal analyzer (Germany Netzsch Instruments Manufacturing Co., Ltd.), which was performed using 10 mg RF aerogel and a heating rate of 10 K min⁻¹, from ambient temperature to 1673 K under N₂ atmosphere. The BET surface area, porosity and pore size distribution of the sample were inspected by the analysis of static low temperature nitrogen adsorption-desorption measurement with a NOVA1200e adsorption analyzer (Micromeritics) at 77 K. The carbon aerogel powder was degassed at 573 K for 4 h prior to analysis.

1.2 Preparation and characterization of carbon cathode

Preparation of carbon cathode

A mixture of carbon aerogel and pVdF powder (with a weigh ratio of 9:1) was grinded for half an hour using mortar/pestle and was gathered in a weighing bottle. Several drops of NMP solution were added into the above mixture, stirring for 6h more in order to get appropriate viscosity slurry. The asprepared suspension was used to coat carbon fiber paper substrate (HCP120 fuel cell carbon fiber paper; size: 100 mm×70 mm×0.21 mm; purchased from Shanghai hesen Electric Co., Ltd.) with the coating thickness of 100 μ m. After drying in vacuum at 80 °C for another 6h, the above coated substrate was punched into round shape pellet (size: Φ 15 mm×(0.21±0.15 mm)). At last, various carbon cathode electrodes, with carbon loading varying from 0.1 mg to 0.6 mg unequally, were obtained. The aerogel loading also can be shown in the unit of mg cm⁻², that is in the range of 0.057 mg cm⁻² – 0.340 mg cm⁻².

Cathode characterization

The electrical conductivity of the air electrode and carbon aerogel was measured using the standard electrical four-probe method by a RTS-9 twin four-probe electrical measuring instrument (purchased from Guangzhou four probe tech. Co., Ltd.).

1.3 Cell assembling and testing

Assembling the cell

In this article, the coin cell (CR2032; all the related kits and assembling tools were purchased from MTI Shenzhen Corp.) was assembled in an argon-filled glove box (MBraun) with moisture and oxygen concentration lower than 0.5 ppm. The lithium air battery, in fact a laminated configuration like a sandwich (Li anode/separator/cathode, see Fig. S1.), was fabricated as below. The stainless steel spring was put at the bottom of the cell (Anode cap) first, on top of which was the gasket (stainless steel spacer). Then a lithium disk (Size: Φ 15 mm×0.5 mm; Bought from China Energy Lithium Co., Ltd.), the separator (whatman GF/D glass microfiber filter paper; Size: $\Phi 17 \text{ mm} \times 1 \text{ mm}$; Bought from Beijing Jingkehongda Biotechnology Co., Ltd) dipped in the 1 M LiTFSI/sulfolane electrolyte (Battery grade; purchased from Shenzhen Capchem technology Co., Ltd.) and the carbon electrode fabricated previously (with the coating side facing to the separator) were placed successively on the gasket. Since the carbon fiber paper had high conductivity of 150 S/cm and perfect hydrophobility on the opposite side of the coating, the collector and hydrophobic gas permeable membrane were saved. Finally, the positive electrode cap, containing a number of holes (Φ =1 mm) which were convenient for oxygen traveling, was covered the cell bottom and sealed under 40 MPa. Then, it aged for more than 12 h in the glove box.



Fig. S1. The schematic diagram of the lithium-air battery model (CR2032).

Cell testing and discharge/charge product characterization

The cell was then exposed to O_2 atmosphere (1 atm) for a minimum of 30 min prior to the electrochemical tests. Here, a minimum of 30 minutes exposing to the oxygen had been verified best by our previous experimental which contained series of exposure time. Among all the exposing time of 5 min, 15 min, 30 min, 45 min, 60 min, 2 h, 3 h and 4 h, cells exposed to oxygen with 30 min to 1 h exhibit the best cycling performance. When the exposure time is more than 1 h, no significant improvement of cycling performance has been achieved. Therefore, we choose an exposing time of more than 30 min as our experimental boundaries as well as for a short testing period. Galvanostatic charge-discharge test was performed in an oxygen-filled dry container (1 atm) by adopting a CT2001A battery tester (Wuhan blue Power Electronics Co., Ltd.) at room temperature (26 °C). Herein, we mainly focused on exploring carbon loading, discharge rates, discharge depth and air's effect on the

cycling performance. Lastly, the morphology and composition changes of the discharged or charged products were studied. After disassembling the cell and scraping the cathode surface to remove residual separator glassy fiber, the DME soaked discharged or charged products were vacuum dried for 12 h and quickly transferred to a gas-tight device to be analyzed by the FE-SEM and XRD measurement (D8 X-ray diffraction Analyzer). A.C. impedance and CV curves were carried out by a CHI660D electrochemical workstation (Shanghai Chenhua Device Company) simultaneously.

2. Results and discussion

Ca	Carbon	Resorcin	Reacti	\mathbf{S}_{BET}	Pore	Pore	Avera	Electri
se	aerogel	ol/	on	$[m^2/g]$	diamet	volum	ge	cal
		Sodium	mass		er[nm]	e[cc/g	pore	conduc
		carbonat	ratio		BJH]	diamet	tivity[
		e [n/n]	[w%]		method		er[nm]	S/cm]
1	CRF1000-30	1000		680.22	16.00	1.06	8.46	0.502
2	CRF1500-30	1500	30	786.87	3.15	0.68	4.87	0.323
3	CRF2000-30	2000		644.47	3.13	0.37	3.29	0.336
4	CRF1000-40	1000		769.54	18.57	1.22	8.66	1.340
5	CRF1500-40	1500	40	669.17	17.95	1.02	8.28	1.218
6	CRF2000-40	2000		646.55	13.39	0.73	5.78	1.253

Table S1. Pore size, pore volume, specific capacity and conductivity data for various carbon aerogels.

Carbon aerogels (see Fig. S2, Fig. S3) with different pore structure were synthesized by using the sol-gel method. As is shown in the Fig. S2 and Fig. S3, all the synthesized aerogels exhibit type-IV isotherms following the IUPAC classification. Especially, there exist hysteresis loops at the high relative pressure above 0.8, indicating the presence of a great number of meso-pores. All the above six aerogels coating cathodes were used to construct lithium-air batteries, generating several hundred stable cycles (highest for CRF1500-40, 525 cycles; others, no more than 375 cycles) in the galvanostatic charge/discharge cycling. This difference can be attributed to their special nano-porous structure and electrical conductivity.

Here, two kinds of carbon aerogels, CRF1000-30 and CRF1500-40, with characteristic single and dual pore size distribution, especially possessing extremely similar average mesopore diameter around 8.0 nm, were investigated in detail. At a current density of 0.05 mA cm⁻² and a fixed capacity of 0.1 mAh, the battery with dual pore and single pore aerogel coating obtains 525 and 332 cycles, respectively. At higher current densities of 0.3, 0.5 and 1.0 mA cm⁻², cathodes with dual pore structure show 64, 33 and 18 cycles comparing to 28, 20 and 8 cycles for that of single pore, highlighting the superiority for mass transfer. In addition, the discharge voltage is higher and the charge voltage is lower in the first cycle for the dual pore CRF 1500-40 cathode in all cases, which is apparently shown in the Fig. 4, Fig. S11and Fig. S15. Such sufficient preponderance has a direct relation with CRF1500-40's higher electrical conductivity and better mass accessibility (dual pore).

And we postulate that the mass accessibility may be the key factor to determine the electrochemical performance of the lithium-air batteries, originating from the basic results that aerogel CRF 1000-40 owns very similar (even superior) pore parameter and electrical conductivity with (to) CRF 1500-40 but exhibits poor cycling capability (Electrochemical performance data for CRF1000-40 are not shown here.). It is worthwhile to note that the electrical conductivity of the six aerogel cathodes is very close and almost in the same level (1 S/cm), which can meet the basic use of the active coating materials. Thus, all these demonstrate that dual pore far exceeds single pore for mass transfer. However, among the meso-pores, it needs further study to investigate whether the smaller pore (3.85 nm) or larger pore (17.95 nm) contributes more to the capacity. It is exactly right that these smaller pores may allow better conversion of discharge products during charge, however it initiates pore blockage and inefficient utilization of pore volume (see Fig. 4(d)). The smaller pores are apt to absorb and be filled with electrolyte due to capillarity, thus causing mass migrating obstacles. Conversely, the larger meso-pores would be feasible for oxygen and lithium ions transfer. As for the problem of thick layer discharge products (cathode passiviation), one can adjust it by limiting the discharge capacity. At

last, we conclude that the dual pore improves the mass transfer and enhances the high discharge rate capability.



Fig. S2. N₂ adsorption-desorption isotherms of carbon aerogel with different reactant/catalyst molar ratio ranging from 1000 to 2000 at a low temperature of 77K.



Fig. S3. BJH pore size distribution graph of carbon aerogels with different reactant/catalyst molar ratio varying from 1000 to 2000.



Fig. S4. XRD patterns and SEM test of the pristine and discharged/charged cathode (CRF1000-30) with a carbon loading of 0.4 mg after 10th cycle. The current density is 0.10 mA cm^{-2} .

Table S2. The variation of cycling performance with different carbon loadings when CRF1500-40 is

 used as cathode active material in the oxygen environment.

Cathode	Electrolyt	Carbon	Current	Specific	Capacity/	Cycling
	e	loading/m	density/m	capacity	mAh	number
		g	A cm^{-2}	/mAh		
				g^{-1}		
Carbon		0.1			0.1	363
paper	_					
	1 M	0.1			0.1	525
	LiTFSI/	0.2	0.05	1000	0.2	230
CRF1500-	sulfolane	0.3			0.3	150
40+pVdF=		0.4			0.4	100
9:1		0.5			0.5	90
		0.6			0.6	78



Fig. S5. Discharge-charge curves of the lithium-air batteries with a CRF1500-40 carbon cathode of various loadings at different cycles. 1M LiTFSI/sulfolane is used as electrolyte; The current density is 0.05 mA cm⁻² and specific capacity is 1000 mAh g⁻¹. The carbon loading in Fig. S5.(a-f) is ranging from 0.1 mg to 0.6 mg.

Herein, the specific energy and energy efficiency of the carbon aerogel (CRF1500-40) carbon

cathode composed lithium-air batteries were also investigated during the discharge and charge process. As is shown in Fig. S6, for most cases, the discharge specific energy was above 2750 Wh Kg⁻¹ while the charge specific energy was in the range of 3620 Wh Kg⁻¹ to 4792 Wh Kg⁻¹, resulting in a relative high energy efficiency varying from 57.38% to 78.32 % even though on the condition of encountering unstable disturbance (open the dry testing container to take out batteries for discharged or charged products analysis) or long term test above 400 cycles. Such high discharge specific energy and energy efficiency compared well with that (65 % or 62.5%) previous reported. [9, 12]

The final and median voltages in the discharge and charge process at various cycles were analyzed synchronously. Final voltage (FV) refers to charge or discharge voltage at the end of a charge or discharge process. MV can reflect the average value of voltages (MV is not the average voltage, but relatively close to the average voltage). FV can reflect the lowest discharge voltage and the highest charge voltage during a cycle. [35] Fig. S7 revealed that the final discharge voltage was above 2.5 V, which was similar to the median discharge voltage. The median charge voltage was below 4.75 V for all the cases in the initial 78 (Fig. S7 (e, f)) or 100 cycles (Fig. S7 (a-d)) before the final charge voltage reached 5.0 V (cut off voltage). The flat high discharge voltage plateau demonstrated stable electrochemical reaction in the lithium-air batteries and relative low polarization of cathode structure. However, the superior performance didn't maintain for a long time before the charge voltage soared to 5.0 V, which might have a direct relation with the pore blockage, cathode passivation and side reactions during discharge and charge process. The following impedance test and XRD test rendered the concrete proof (see Fig. S8, Fig. S9, Fig. S10 and Fig. S14).



Fig. S6. Specific energy and energy efficiency of lithium-air batteries that contain 1 M LiTFSI/sulfolane based electrolyte after discharge and charge. All the CRF1500-40 carbon aerogel carbon cathodes have different carbon loadings, varying from 0.1 mg to 0.6 mg (see **Fig. S6 (a-f)**).



Fig. S7. Median and final voltages of lithium-air batteries that contain 1 M LiTFSI/sulfolane based electrolyte after discharge and charge. All the CRF1500-40 (carbon aerogel) carbon cathodes have different carbon loading, varying from 0.1 mg to 0.6 mg (**Fig. S7 (a-f)**).



Fig. S8. Impedance spectra of the lithium-air batteries with different carbon loadings composed CRF1500-40 air cathode after 10th discharge/charge.

After various galvanostatic discharge/charge cycling, electrolyte ohmic resistance, interfacial resistance, charge transfer resistance all incline to increase during the discharge process and drop in the subsequent charge process except the case of aerogel loading of 0.4 mg and 0.6 mg. That may be ascribed to: 1) the manual assembly processes of different batteries are hardly to be completely identical; 2) the process of taking battery out of the sealed and dried testing box for electrochemical impedance test, SEM and XRD test may penetrate water and carbon dioxide, resulting in a fluctuating environment. If this just happens at a discharge state (for 0.4 mg, 0.6 mg), then great impedance changes may occur. It's highlighted that charge transfer resistance occupies the main part of the three resistance distribution, which has direct connection with the accumulation of low electrical conductivity discharged products of Li₂O₂ in the cathode. For the abnormal interfacial resistance increase during the charge process, it has somethings to do with the unimitate contact with the current collector due to cathode expansion in the previous discharging process.

Table S3. Dependence of equivalent-circuit parameters upon the porosity of CRF1500-40 cathode with a carbon loading ranging from 0.1 mg to 0.6 mg after 10th discharg/charge cycles. All the meanings of the subscripts for the resistance can be seen the **Table S4** below.

Carbon		Re(Ω	C int (F	$cm^{-2})$	$R_{int} (\Omega $ $C_m (F cm^{-2})$			n^{-2} R _{ct} (Ω		$W_{O}\left(\Omega\;cm^{-2}\right)$		
(mg	g)	cm^{-2})	C int-T	C int-P	cm^{-2})	C _{m-T}	C _{m-P}	cm^{-2})	Wo-	Wo-	Wo-	
			6.647	542.		2.98	958.		1 (1	30.3	460.	
	0.1	61.23	9	$62 \times$	49.77	$2 \times$	$3 \times$	121.4	1.61	$3 \times$	$84 \times$	
			×10 ⁻⁴	10^{-3}		10^{-5}	10^{-3}		4	10^{-3}	10^{-3}	
			19.70	713.		2.34	957.	102.2	36.9	671.	444.	
	0.2	63.5	$7 \times$	$58 \times$	18.05	$35 \times$	$24 \times$			$06 \times$	96×	
			10^{-5}	10^{-3}		10^{-5}	10^{-3}		4	10^{-3}	10^{-3}	
			19.48	745.		2.23	950.	100.4	25.2	650.	456.	
After	0.3	71.23	6×	$94 \times$	14.64	93×	$17 \times$		25.5	$28 \times$	$44 \times$	
10th			10^{-5}	10^{-3}		10^{-5}	10^{-3}		0	10^{-3}	10^{-3}	
disch	0.4 40.77		49.11	583.		5.82	920.	146.3	6.35	56.9	393.	
arge		40.77	$7 \times$	19×	30.71	$62 \times$	94×			$15 \times$	$12 \times$	
			10^{-5}	10^{-3}		10^{-5}	10^{-3}			10^{-3}	10^{-3}	
		22.56	650.		3.43	946.		4 26	23.5	366.		
	0.5	75.81	$2 \times$	97×	22.88	$04 \times$	$22\times$	147.2	ч.20 1	$14 \times$	$84 \times$	
			10^{-5}	10^{-3}		10^{-5}	10^{-3}		I	10^{-3}	10^{-3}	
			28.38	665.	23.01	4.69	968.	115.1	129 0	60.9	687.	
	0.6	80.45	5×	39×		59×	1×			9	34×	
			10-5	10^{-3}		10-5	10^{-3}			,	10^{-3}	
	0.1 40.81	24.06	719.		3.01	977.		29.8	750.	463		
		40.81	×10 ⁻⁵	89×	14.96	48×	53×	85.1	7	61×	×	
				10^{-3}		10-5	10^{-3}			10^{-3}	10-3	
			24.06	719.		3.01	977.		29.8	750.	463	
	0.2	40.81	4×	89×	14.96	48×	$53\times$	85.1	7	61×	×	
			10-5	10-3		10-5	10-3			10-3	10-3	
			62.48	575.		2.71	<i>9</i> 58.		1.11	14.7	450.	
	0.3	65.65	/×	I×	38.13	13×	/×	82.83	8	6×	$3\times$	
After			10 ⁻³	10-3		10-3	10-3		0	$\frac{10^{-3}}{10^{-3}}$	$\frac{10^{-3}}{10^{-3}}$	
10th	0.4	40.02	169.5	421.	42.22	5.97	942.	160 5	7.23	68.1	436.	
charg	0.4	40.83	8×	48×10^{-3}	43.23	61×10^{-5}	95×	168.5	6	10-3	13×10^{-3}	
e			$\frac{10^{-5}}{70.01}$	<u>10 ³</u>		10 5	$\frac{10^{-5}}{07}$			10 5	$\frac{10^{-5}}{112}$	
	0.5	57.02	/8.01	528. 967	5((0)	5.79 20v	9/6.	06.00	F (0)	41.9	413.	
	0.5	57.83	9× 10-5	80× 10-3	30.09	29×	10× 10-3	96.83	5.69	54×	88×	
			10 -	<u>10 ³</u>		<u>10 °</u>	10 5			$\frac{10^{-5}}{52^{-4}}$	$\frac{10^{-5}}{417}$	
	0.6	00.40	/0.00	322. 6	25 10	5.28 61 y	931. 224	1257	10.0	33.4	41/.	
	0.6	89.49	0× 10 ⁻⁵	0^{\times}	35.19	01× 10 ⁻⁵	52×10^{-3}	135./	3	10× 10-3	$\delta 2 \times 10^{-3}$	
			10 5	10 5		10 5	10 5			10 5	10 5	



Fig. S9. The variation of the resistance distribution with the increase of cathode carbon loading in the lithium-air batteries after 10th discharge/charge. Re, Rint and Rct are on behalf of the electrolyte ohmic resistance, interfacial resistance, charge transfer resistance, respectively.



Fig. S10. Impedance spectra of lithium-air batteries at various cyclings after discharge/charge. All the cases were based on the CRF1500-40 air cathode with a carbon loading of 0.4 mg, a limited specific

capacity of 1000 mAh g⁻¹ and the current density of 0.05 mA cm⁻². **Fig. S10 (a-d)** corresponded to 1st, 30th, 70th, 150th cycle after discharge/charge, respectively. 10th and 100th cycle after discharge/ charge were shown in **Fig. S8** and **Fig. 5 (d)** separately.

Carbon	$\operatorname{Re}(\Omega)$	C int (F	cm^{-2})	$R_{int}(\Omega)$	C _m (F	$cm^{-2})$	$R_{ct}(\Omega)$	Wo	(Ωcn)	n^{-2})
(0.4 mg)	cm 2)			cm 2)			cm ²)			
		$C_{\text{int-T}}$	C int-P		C_{m-T}	C m-P		Wo-	Wo-	Wo-
								R	Т	Р
CRF150	13.60	32.96	664.	45.88	877.	675.	31.18	133.	285.	493.
0-40		$\times 10^{-3}$	66×		$05 \times$	$18 \times$		$85 \times$	29×	$73 \times$
			10^{-3}		10^{-4}	10^{-3}		10^{-3}	10^{-5}	10^{-3}
1 st	25.69	2.604	821.	14.34	1.87	983.	45.41	47.3	779.	449.
		$\times 10^{-5}$	$76 \times$		$28 \times$	$37 \times$		9	$5 \times$	$92 \times$
			10^{-3}		10^{-5}	10^{-3}			10^{-3}	10^{-3}
10th	40.77	49.11	583.	30.71	5.82	920.	146.3	6.34	56.9	393.
		$7 \times$	$19 \times$		$62 \times$	94×		8	$15 \times$	$12 \times$
		10^{-5}	10^{-3}		10^{-5}	10^{-3}			10^{-3}	10^{-3}
30th	134.2	17.13	836.	174.9	8.06	697.	156.5	3.19	661.	308.
		$2 \times$	$58 \times$		56×	$87 \times$		$43 \times$	$04 \times$	$86 \times$
		10^{-3}	10^{-3}		10^{-5}	10^{-3}		10^{-6}	10^{-3}	10^{-3}
70th	610.5	6.054	87.7	848.6	2.30	845.	799.7	17.1	23.0	327.
		$2 \times$	$65 \times$		$47 \times$	$21 \times$		8	$44 \times$	$44 \times$
		10^{-5}	10^{-3}		10^{-5}	10^{-3}			10^{-3}	10^{-3}
100th	521.6	4.901	746.	876.5	5.11	835.	970.4	208.	34.5	518.
		$4 \times$	$49 \times$		$78 \times$	$89 \times$		49	6	$8 \times$
		10^{-7}	10^{-3}		10^{-6}	10^{-3}				10^{-3}
150th	938.7	8.561	630.	1400	5.45	805.	914.6	156.	38.4	333.
		6×	16×		$08 \times$	$31 \times$		5	3	62×
		10^{-7}	10^{-3}		10^{-6}	10^{-3}				10^{-3}

Table S4. Dependence of equivalent-circuit parameters upon the porosity of CRF1500-40 cathode with a carbon loading of 0.4 mg at the initial state and discharged state for various cycles.

Note: Re, R_{int} , R_{ct} are electrolyte ohmic resistance, interfacial resistance, charge transfer resistance, respectively. CPE is constant phase element, and C_{int} is typical of surface films formed on the electrode. C_m is double-layer capacitance distributed between the ohmic and faradaic processes. W_o is finite length Warburg resistance (open-circuit terminus), on behalf of kinetic resistance for oxygen and Li⁺. The subscripts of R, P, and T stand for the corresponding state and phase parameters.

Table S5. The relationship between cycling performance and current density as well as discharge depth with a CRF1500-40 cathode in the oxygen environment.

Cathode	Electrolyt e	Carbo n loadin/	Current density/m A cm ²	Specific capacity/ mAh g ⁻¹	Capacity / mAh	Cycling number
		mg		8		
			0.05	1000	0.4	100
			0.1	1000	0.4	112
			0.1	1500	0.6	44
CDE1500	1 M		0.1	2000	0.8	34
CRF1500- 40+nVdE=	I MI I itesi/	0.4	0.2	2000/1000	0.8/0.4	24/94
40 ° p v ur − 9·1	sulfolane	0.4	0.3	3000/1000	1.2/0.4	10/64
5.1			0.4	4000/1000	1.6/0.4	3/56
			0.5	5000/1000	2.0/0.4	1/33
			1.0	10000/1000	4.0/0.4	1/18



Fig. S11. Discharge-charge curves of the lithium-air batteries with a CRF1500-40 carbon cathode at various current densities and discharge depth of different cycles. 1 M LiTFSI/sulfolane is used as electrolyte and the carbon loading is 0.4 mg. Current density and specific capacity are noted as below:

(a) 0.10 mA cm⁻², 1000 mAh g⁻¹; (b) 0.10 mA cm⁻², 1500 mAh g⁻¹; (c) 0.10 mA cm⁻², 2000 mAh g⁻¹; (d) 0.20 mA cm⁻², 1000 mAh g⁻¹; (e) 0.30 mA cm⁻², 1000 mAh g⁻¹; (f) 0.40 mA cm⁻², 1000 mAh g⁻¹; (g) 0.50 mA cm⁻², 1000 mAh g⁻¹; (h) 1.00 mA cm⁻², 1000 mAh g⁻¹.

It is worth mentioning that each carbon paper cathode had a mass of 26.4 ± 2 mg, which was about 250 times higher than 0.1 mg of the carbon loading described below. Therefore, it actually contributed less than 4 mAh g⁻¹ specific capacity to the whole lithium air battery. In addition, more coating would lead to cathode pore blockage and deterioration of cycling performance, which was inconsistent with the experimental results. This strongly suggested that carbon aerogel was an effective electro-active material.

To construct a practical applied lithium-air battery, all the galvanostatic charge-discharge tests were simultaneously conducted in a long period of time (≥ 2.3 h). Particularly, for a perspicuous comparison, the testing time was fixed to 2.3 hours when the current density increased to 0.20 mA cm⁻² or above. This discharge time comes from the case of a current density of 0.1 mA cm⁻² and specific capacity of 1000 mAh g⁻¹ (see I in the below). Therefore, the discharge specific capacity differed from each other, ranging from 1000 to 5000 mAh g⁻¹ unequally (see Table S5, Fig. 4(b), Fig. S11 and Fig. S12). All the cycling number was recorded under the cut off voltage of 5.0 V (for charge) or 2.0 V (for discharge). As is shown in Fig. S12, it revealed fast cycling performance deterioration at the same current density compared to that of a relative low specific capacity of 1000 mAh g⁻¹. This further demonstrated deep discharge was detrimental for the realization of highly rechargeable lithium-air batteries, consistent with the lithium-ion batteries. Meanwhile, high discharge rates also cause sharp recession of cycling performance.

Discharge time = $0.4 / (0.1 \times 3.14 \times 1.5 \times 0.25) = 2.3 h$ (I)

Note: Aerogel loading: 0.4 mg; Current density: 0.10 mA cm⁻²; Cathode diameter (d): 1.5cm; $S=1/4 \pi d^2$



Fig. S12. Discharge-charge curves of the lithium-air batteries with CRF1500-40 carbon cathode at various current densities of different cycles. 1 M LiTFSI/sulfolane was used as electrolyte; the current density and specific capacity were described as below: (a) 0.20 mA cm⁻², 2000 mAh g⁻¹; (b) 0.30 mA cm⁻², 3000 mAh g⁻¹; (c) 0.40 mA cm⁻², 4000 mAh g⁻¹; (d) 0.50 mA cm⁻², 5000 mAh g⁻¹.



Fig. S13. Discharge curves of the lithium-air batteries with CRF1500-40 carbon cathode at various current densities in the first cycle.



Fig. S14. XRD patterns of the discharged cathode (CRF1500-40) with a carbon loading of 0.4 mg after 1st cycle. The current density varied from 0.02 mA cm⁻² to 0.20 mA cm⁻², corresponding to discharge state of **Fig. S13**, respectively. The discharged products agree well with the PDF 74-115 of the crystalline lithium peroxide, and PDF76-1074, PDF85-0736 and PDF83-1454 of the parasitic reaction products for LiOH H₂O, LiOH and Li₂CO₃, respectively, most of which disappear after the corresponding charging process.



Fig. S15. Discharge-charge curves of lithium-air batteries with CRF1000-30 air cathode at various current densities of different cycles. 1 M LiTFSI/sulfolane is used as electrolyte. The current density and specific capacity are described as below: (a) 0.30 mA cm⁻², 1000 mAh g⁻¹; (b) 0.50 mA cm⁻², 1000 mAh g⁻¹; (c) 1.00 mA cm⁻², 1000 mAh g⁻¹.

Table S6. The relationsh	ip between cyclin	g performance and	d current density with	n a CRF1500-40
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Cathode	Electrolyt e	Carbon loading/ mg	Current density/ mA cm ⁻²	Specific capacity / mAh g ⁻¹	Capacity / mAh	Cycling number
			0.05	1000	0.4	40
CRF1500- 40+pVdF= 9:1	1 M LiTFSI/ Sulfolane	0.4	0.1 0.2	1000 2000	0.4 0.8	48 8

cathode in the air environment.



Fig. S16. Discharge-charge curves of the lithium-air batteries with CRF1500-40 air cathode at various current densities of different cycles in the air environment (a, b, c) and oxygen environment (d). 1 M LiTFSI/sulfolane is used as electrolyte. The current density and specific capacity are described as below: (a) 0.05 mA cm⁻², 1000 mAh g⁻¹; (b,d) 0.10 mA cm⁻², 1000 mAh g⁻¹; (c) 0.20 mA cm⁻², 2000 mAh g⁻¹.