1 Supporting Information

2 Superior efficient rechargeable lithium-air battery via a

3 bifunctional biological enzyme catalyst

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1 Supplementary Materials

2 Chemicals used in this study.

3 Laccase from *Trametes versicolor* (15 U mg⁻¹), single-walled carbon nanotube 4 (SWCNT, purity \geq 85%, diameter: 1.8 nm, length: >5 µm), Pt/C (5 wt.%), calcein, 2,2'-5 azino-bis (3- ethyl benzothiazoline -6 –sulfonic acid) (ABTS), dithionite, 1-ethyl-3-(3-6 dimethyl-aminopropyl) carbodiimide hydrochloride (EDC), N-hydroxysuccinimide 7 (NHS) and Nafion (5 vol.% in a mixture of lower aliphatic alcohols and water) were all 8 purchased from Sigma Aldrich. Lithium perchlorate (LiClO₄, 99.99%), lithium acetate 9 (LiAc, >98%) and glutaraldehyde (24~26% in water) were from TCl, Japan.

10 Pretreatment of SWCNT

11 The SWCNT was pretreated with an acidic solution, containing H_2SO_4 and HNO_3 in a 12 volumetric ratio of 3:1, for purification and carboxylation. The process is simply 13 dispersing 10 mg SWCNT into 10 mL of the acid mixture solution under stirring for 24 14 h, followed by centrifugation and rinsing with deionized water. Finally, the resultant 15 carboxylated-SWCNT was dried at 60 °C in air.

16 Characterization of the electrocatalytic activity of the Lac-SWCNT via stationary CV,

17 LSV on RDE and RRDE.

18 **Preparation of the working electrode**

In all these measurements, a glassy carbon disk electrode (0.247 cm²) was used as the working electrode, onto which the analyst particles are to be immobilized as a thin film by drop-casting a 10 μ L suspension, containing the target catalyst and a small amount of Nafion as binder. Before each loading of the catalyst, the glassy
 carbon disk was manually polished with an alumina paste and rinsed with ethanol.

3 The suspensions of Pt/C and bare SWCNT were prepared by ultrasonically dispersing 4 5 wt% Pt/C (10 mg) or 10 mg carboxylated SWCNT (10 mg), respectively, into a 1 mL 5 Nafion aqueous solution (1 mL, 0.1 wt% Nafion). Each of 10 uL of the resultant 6 catalyst suspension was then, respectively, drop-casted onto the glassy carbon disk 7 electrode and air dried at room temperature.

8 The Lac-SWCNT electrode was prepared by ultrasonically dispersing 7 mg 9 carboxylated SWCNT and 3 mg laccase into 1 mL Nafion aqueous solution (1 mL, 0.1 10 wt% Nafion). After drop-casting 10 μL laccase-SWCNT suspension on the glassy 11 carbon electrode and being air-dried, the laccase-SWCNT layer on the electrode was 12 further incubated in an aqueous solution, containing 5% glutaraldehyde and 20% 13 ethanol, for 5 min to ensure the immobilization of laccase by glutaraldehyde 14 crosslinking. Finally, the surface of the electrode was rinsed by deionized water, and 15 ready for use.

16 CV measurement

17 Cyclic voltammograms were conducted in a three-electrode system with the 18 Solartron 1287/1260 electrochemical work-station using Pt wire as counter 19 electrode, saturated calomel as reference electrode, and glass carbon electrode 20 coated with Lac-SWCNT, 5 wt% Pt/C and SWCNT as the working electrode. The CV 21 curves at different scan rates were recorded from 0.0 V to 0.9 V vs SCE in 1 M LiAc-22 HAc buffered electrolyte (pH 6.0) saturated with O₂ or Ar.

1 LSV measurement

The LSV was performed using RRDE/RDE instrument (CHI760E) with Lac-SWCNT, Pt/C and SWCNT immobilized on glassy carbon electrode as working electrode. The LSV measurements were carried out in a week acidic electrolyte of 1 M LiAc-HAc buffer (pH 3.5) saturated with O_2 at 25 °C, using a three-electrode glass cell equipped with RDE/RRDE as working electrode, Pt wire as the counter electrode, and saturated calomel as the reference electrode. The measurements were performed by sweeping the potential from 1.0 - 0.0 V vs SCE at various rotation rates.

9 For obtaining the H_2O_2 yield, disk and ring current were recorded while sweeping the 10 disk potential from 0.0 V to 1.0 V, with the ring potential fixed at 1.0 V. The rotation 11 rate of the RRDE was set at 1600 r.p.m. The electrocatalytic activity of the catalysts 12 for OER were also studied by recording LSV from 0.8 V to 1.4 V on RDE with a 13 rotating rate of 1600 r.p.m. in the same electrochemical system, except for a 14 different pH (7.4) of the electrolyte (Figure S7).

15 The electrocatalytic activity of laccase/SWCNT in Li-Air battery

Preparation of the air electrodes: The air electrodes of Pt/C or bare SWCNT were made by pressing a catalyst paste layer (8 mm) onto a hydrophilic carbon paper. The homogenous catalyst paste was prepared by repeatedly folding and rolling out a mixture paste, which contains the catalyst (5 wt% Pt/C or bare carboxylated SWCNT) and polytetrafluoroethylene (PTFE) (in a 15% emulsion) in a weight percentage of 85% and 15%, respectively. The homogenous catalyst paste was rolled out into a thin

1 sheet, which can be cut into desired size and pressed onto carbon paper. The mass 2 loads of the SWCNT and Pt/C were same, $\sim 0.5 \text{ mg cm}^{-2}$. 3 The Lac-SWCNT air electrode was fabricated by loading and immobilizing LacTv onto the bare SWCNT air electrode via following steps: 4 5 (1) Activation of the carboxyl group on SWCNT by immersing the SWCNT air electrode in an aqueous solution of EDC/NHS (1 mg mL⁻¹) for 30 min. 6 7 (2) The activated SWCNT electrode was incubated with aqueous LavTv solution (50 mg mL⁻¹ of LacTv) for 12 h, thus binding the LacTv onto carboxylated SWCNT. 8 9 (3) The LacTv was immobilized on the SWCNT via glutaraldehyde crosslinking by 10 soaking the Lac-SWCNT electrode in a diluted glutaraldehyde aqueous solution 11 for 5 min and then rinsed with deionized water. Typically, the diluted 12 glutaraldehyde aqueous solution was prepared by adding 50 uL 24-26% glutaraldehyde and 200 uL 99.9% ethanol into 1 mL deionized water with 13 stirring. The mass ratio of LacTv and SWCNT was estimated to be 30:70 by 14 15 comparing weight of the SWCNT electrode before and after the LacTv loading. 16 (4) For labeling the LacTv on SWCNT electrode, we immersed the SWCNT electrode 17 and Lac-SWCNT electrode in a dye solution of calcein which can specifically 18 stain protein to produce green fluorescence signal in situ, and collected the 19 confocal images on a Leica SP5 resonant inverted confocal microscope (small 2017, 13, 1700399-1700408; Adv. Mater. 2017, 29, 1701086-1701096). 20 21 Specifically, the SWCNT electrode and LcacTv electrode were both incubated with 5 mg mL⁻¹ calcein solution at 25 $^{\circ}$ C for 6 h, followed by a thorough washing 22

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in deionized water to remove the unreacted calcein. The confocal images were obtained at laser wavelengths of 493 nm (excitation) and 540 nm (emission).

3 The assembly of the aqueous Li-Air battery with hybrid electrolyte

4 The rechargeable aqueous Li-Air battery is a home-made prototype battery with a
5 cell structure described as: Li metal | organic electrolyte | LATP | aqueous
6 electrolyte | Air electrode

7 The organic electrolyte 1 M LiClO₄ in EC/DME was used as anolyte, and 1 M LiAc-HAc 8 aqueous buffer solution with pH 3.5 was used as starting catholyte. The LATP, a 9 ceramic Li⁺ ion conductor, was used as a separator to selectively transfer Li⁺ ion 10 while separating the organic and aqueous electrolytes. Li-metal was pressed onto a 11 copper mesh as anode and was sealed in the anode compartment in an argon-filled 12 glovebox. The air electrode was immersed in the catholyte inside the cathode 13 compartment, which has direct contact to the open air.

14 The electrochemical performance of the aqueous Li-Air battery

15 The discharge and charge performances of the batteries with different air electrodes

16 were measured at a constant current density of either 100 or 500 mA g⁻¹ using a SM8

17 charge/discharge system (Hokutou Denkou Co.)

18 Calculation of the electron transfer number and the peroxide yield during ORR.

19 Calculation of the electron transfer number

20 Based on the RDE results, the electron transfer number per dioxygen in ORR was

21 calculated by Koutechy-Levich (K-L) formula:

$$\frac{1}{j^2} = \frac{1}{j_k} + \frac{1}{B\omega^{0.5}}$$
(1)

1 in which j_k and ω represent the kinetic current and rotating speed (r.p.m.),

2 respectively. B is determined according to the following equation:

$$B = 0.2NF(D_{0_2})^{2/3} v^{-1/6} C_{0_2}$$
(2)
4 in which N is attributed to electron transfer number, F is faraday constant, v is the
5 kinetic viscosity while D_{02} and C_{02} are, respectively, the diffusion coefficient and

6 concentration of dioxygen in electrolyte.

7 Calculation of the peroxide yield

8 In order to inspect the yield of peroxide in reduction of O2, RRDE measurements 9 were also performed at 1600 r.p.m. rotating speed. All ring electrodes were scanned 10 at a rate of 5 mV s⁻¹. In addition to the peroxide yield, the number of transferred 11 electron could also be calculated on basis of RRDE results according to the followed 12 formulas:

$$H_{2}O_{2}\% = 200 \frac{\frac{I_{r}}{N}}{I_{d} + \frac{I_{r}}{N}}$$
(3)
$$N = 4 \frac{I_{d}}{I_{d} + \frac{I_{r}}{n}}$$
(4)

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15~ where $I_r,\,I_d$ and n represent the ring current, disk current and the current collection 16 efficiency of Pt ring electrode, respectively.

(4)

17 The procedure and principle of the UV-vis measurements of LacTv:

18 The UV-vis absorption spectra were acquired on an Agilent 8453 diode array spectrophotometer, in the energy range from 250 to 800 nm in a sealed quartz cell. 19 20 In order to elucidate the intermediate state of the copper activity center of LacTv, 21 we have investigated the reversible redox behavior of the T1 Cu and the T2/T3 Cu 1 cluster during ORR/OER by observing the UV-vis spectra of LacTv under anaerobic
2 condition in presence of dithionite which can reduce the T1 Cu of LacTv. Before
3 testing, the LacTv (0.3 mM) solution was purged with a stream of nitrogen for 3 h to
4 completely remove the oxygen, followed by adding excess deoxygenated dithionite.
5 And then we recorded the UV-vis spectra at 0 min, 1 min, 3 min, 5 min, 10 min,
6 respectively. Finally, feeding oxygen to the quartz cell and recording the UV-vis
7 spectra after 10 min. Dithionite was chosen as the reducing substrate for the
8 following reasons: (1) it has no absorption in the 600 nm (the characteristic
9 absorption band of T1 Cu region) and has no absorption at ~330 nm (the
10 characteristic absorption band of T3 Cu); (2) the low potential (<-200 mV) ensures</p>
11 complete electron delivery to LacTv, reducing T1 Cu.

12 The catalytic activity of LacTv toward ORR at different pH was also investigated by
13 UV-vis analysis:

ABTS solutions (10 mM) with different pH were prepared by dissolving ABTS in
 phosphate buffer with pH of 3.5, 4.5, 5.5, 6.5, 7.4.

2) Introducing 10 mM ABTS with different pH into the quartz cell containing 0.3 mM LacTv in presence of oxygen, and monitoring the absorbance at 420 nm within 180 s. It is well known that LacTv can catalyze the oxidation of ABTS to generate ABTS⁺ employing oxygen as electron acceptor, and ABTS⁺ has characteristic UV-vis absorbance at 420 nm, therefore, the absorbance versus time curves can reflect the catalytic activity of LacTv toward ORR.

1 Supplementary Figures



Figure. S1. A schematic representation of the preparation of Lac-SWCNT electrode.
For purification and carboxylation of SWCNT, the pristine SWCNT was first treated
with acid mixture solution; EDC/NHS acted as an activating agent to activate carboxyl
on SWCNT to immobilize LacTv.

During the activation of SWCNT, the carboxyl groups on SWCNT firstly react with EDC to form $-C^{-NH-R_1}$ terminal groups. Afterwards, such $-C^{-NH-R_1}$ terminal groups react with NHS, producing amine-reactive ester groups. While, after the activated SWCNT being incubated with LacTv, fast amidation reactions take place between the amine-reactive ester groups on SWCNT and the terminal amino groups of LacTv, thus allowing the formation of covalent amide bond to immobilize the LacTv (Figure 2b). So, the FTIR results can preliminarily prove the successful linkage between SWCNT and LacTv.



Figure. S2. Laser Scanning Confocal analysis of the immobilization of LacTv. The
intense green fluorescence appeared on the Lac-SWCNT electrode while no
detectable green fluorescence was observed on SWCNT electrode. So, the successful
immobilization of LacTv on SWCNT was further confirmed by confocal results.



7 **Figure S3.** Impedance Nyquist plots of SWCNT (black plots) and Lac-SWCNT (red plots) 8 electrode in 10 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ aqueous solution with 1 mM KNO₃ as 9 supporting electrolyte, within a frequency range of 0.01 Hz to 100 KHz. As shown in 10 this figure, the resistance of Lac-SWCNT electrode dramatically increases comparing

with naked SWCNT electrode. This is because the protein-Laccase- produces steric
 hindrance on electrode, thus strongly indicating the successful immobilization of
 laccase on SWCNT.

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5 **Figure S4.** CV curves of three parallel Lac-SWCNT electrodes in 1 M LiAc-HAc 6 electrolyte (pH=6.0) saturated with O_2 at scanning rate of 5 mV s⁻¹.

7 The results clearly demonstrated that the cathodic peak potentials were slightly 8 different for the parallel Lac-SWCNT electrodes because of the systematic error. 9 Through calculating the mean cathodic peak potential and the standard deviation, 10 we finally get the precise cathodic peak potential of 0.78±0.02 V (for parallel 11 electrodes).

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Figure S5. Cyclic voltammograms (CVs) of LacTv (a) and Pt/C (b) in the range of no
Faradaic processes for measuring C_{dl}. The electrolyte is LiAc-HAc solution with pH of
7.4. (c) CV fitting curves of LacTv and Pt/C.

5 The electrochemically active surface area (ESCA) of catalyst is estimated from electrochemical double-layer capacitance (C_{dl}), which is obtained by measuring 6 double-layer charging from the cyclic voltammograms (CVs) at different scan rates in 7 non-Faradaic potential range in LiAc-HAc electrolyte with pH of 7.4. The linear slope 8 9 of charging current versus the scan rate represents C_{dl}. As shown in Figure S5, the slope of CV fitting curves of LacTv-SWCNT (0.057) is higher that of Pt/C (0.032), 10 suggesting that the C_{dl} of LacTv-SWCNT is higher, that is, the LacTv-SWCNT possesses 11 12 a larger ESCA. Therefore, LacTv-SWCNT can expose more active sites and promote 13 the adsorption and activation of ORR-relevant species.

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2 **Figure S6.** Linear scan voltammogram (LSV) curves of Pt/C (a) and SWCNT (b) in O_2 3 saturated 1 M LiAc-HAc buffer (pH=3.5) on rotating-disk electrode at different 4 rotating speeds. Scan rate (v): 5 mV s⁻¹.

7 Figure S7. Correlative K-L plots for Lac-SWCNT (a), Pt/C (b) and SWCNT (c) at various

⁸ potentials.

Figure S8. (a) RRDE tests of Pt/C electrode for ORR in dioxygen saturated 1M LiAc-HAc buffer (pH 3.5) at the rotating speed of 1600 r.p.m.. (b) The peroxide yield and the electron transfer number during whole ORR process based on the results of RRDE. As we can see, the Pt/C could catalyze ORR through four-electron transfer path with releasing lower yield of peroxide which was less than 15%, indicating the high activity for ORR.

9 Figure S9. (a) RRDE tests of SWCNT electrode for ORR in dioxygen saturated 1 M 10 LiAc-HAc buffer (pH 3.5) at the rotating speed of 1600 r.p.m.. (b) The peroxide yield 11 and the electron transfer number during whole ORR process based on the results of 12 RRDE. Instead of four-electron-transfer, the ORR on SWCNT electrode was a two-

electron-transfer reaction, therefore, the peroxide yield was markedly higher,
 suggesting the lower activity of SWCNT toward ORR.

4 Figure S10. The probing of OER activity of Lac-SWCNT (red) and Pt/C (blue) and
5 SWCNT (black) at the rotating speed of 1600 r.p.m. in 1 M LiAc-HAc buffer (pH=7.4)
6 and the calculated Tafel Slope of Lac-SWCNT (red) and Pt/C (blue).

7 To further assess catalytic kinetics of LacTv-SWCNT and Pt/C, we have estimated 8 the Tafel slope. As shown in Figure S10, compared with Pt/C, the Tafel slope for 9 LacTv-SWCNT is apparently lower, further confirming the better OER kinetics of 10 LacTv-SWCNT.

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Figure S11. (a) Black dots: the pH change of the typical electrolyte (1 M Li₂SO₄-H₂SO₄ with initial pH value of 3.5) during discharge/charge cycle at the current density of 500 mA g⁻¹; Red dots: the pH change of the electrolyte (1 M LiAc-HAc with initial pH value of 3.5) with strong buffer capacity during discharge/charge cycle; And the corresponding full discharge-charge cycle of the Li-air battery in Li₂SO₄-H₂SO₄ electrolyte (b) and in LiAc-HAc buffer (c) based on Pt/C (black curve) and Lac-SWCNT (red curve).

Generally, the pH of the electrolyte increases with increasing the discharge depth 9 due to the continuous consumption of proton, thus not only resulting in a liner 10 decreasing discharge voltage, but also hindering the long-term cycling durability of 11 battery. In this work, we overcome the problem by employing buffer solution with 12 high Li⁺ conductivity as electrolyte to avoid dramatic pH change during cycle. 13 Considering that, we investigated the pH change of the typical electrolyte (Li₂SO₄-14 15 H₂SO₄) and the LiAc-HAc electrolyte during discharge/charge cycles under high current density of 500 mA g⁻¹. As Figure S11 revealed, the pH of the two types of 16 electrolyte both exhibit synchronous increase with increasing discharge depth, 17 indicating the consumption of proton during discharge. The pH of the Li₂SO₄-H₂SO₄ 18

electrolyte linearly increases to ~7.4 from ~3.5 after discharging for ~8 h and linearly
returns to the initial value of ~3.5 with a short term 8 h charge. But, for the LiAc-HAc
electrolyte, the variation time of the pH in the range of ~3.5 to ~7.4 is as long as 30 h
(Figure S11). The above results clearly reveal that the LiAc-HAc electrolyte is a buffer
which is resistant to dramatic changes in pH, thus we can see a relatively flat pH
change in LiAc-HAc electrolyte, thereby, enabling relatively long-term stable
thermodynamic potential.

2 Figure S12. The photograph of the device for the *in situ* observation of the dissolved
3 oxygen level in electrolyte.

For testing dissolved oxygen level *in situ*, working electrode (Lac-SWCNT), reference electrode (saturated calomel), counter electrode, and the probe of dissolved oxygen meter are sealed in a four-neck flask, as shown in Figure S12. To rensure the oxygen in the system entirely originate from electrochemical oxidation of water at Lac-SWCNT electrode, a LiAc-HAc buffer electrolyte with initial pH value of 4.5 is prepared followed by purging with a stream of nitrogen for 2 h to completely remove the oxygen from air, hence, the initial dissolved oxygen is 0.03 mg L⁻¹. And to enable the cycle to proceed in a closed system, the flask is completely sealed.

- 2 Figure S13. The UV-vis spectra of LacTv obtained in pH 3.5 (black curve) and pH 7.4
- 3 (red curve) under air condition.

Figure S14. (a) The absorbance versus time curves of the ABTS solution with LacTv
obtained at different pH values and (b) the curves obtained after changing the pH
back to 5.5 from 7.4.

1 As revealed by Figure S14, the absorbance at 420 nm attributing to ABTS⁺, is able 2 to increase to a plateau within 180 s over the pH range of 3.5-6.5, clearly indicating 3 the vigorous catalytic activity of LacTv over a broad pH range. Thus, from the LacTv 4 catalytic discharge profiles in Figures 4a and 4b we observed a flat discharge voltage plateau in the pH range of 3.5 to 6.5 at 3.75 V vs Li⁺/Li that is well consistent with the 5 6 redox potential of the T1-Cu (0.79 vs NHE), which is not sensitive to the pH of 7 electrolyte. Conversely, only a small increase in the absorbance at 420 nm is 8 observed when increasing the pH to 7.4, clearly proving the inhibited activity of LacTv toward ORR (Figure S14). Hence, the discharge voltage dropped when the pH 9 10 of electrolyte increased to neutral upon continues discharge for about 130 h (Figure 11 4b). In addition, when we recover the pH back to 5.5 from 7.5, the LacTv exhibit the 12 same vigorous activity as that of the LacTv in pH 5.5 (Figure S14, b), proving that the 13 declined activity of LacTv can fully restored to its initial vigor in situ by purely 14 recovering the initial environment.

Table S1. Comparative analysis of the performance of the recently reported hybrid
lithium-air battery based on abiotic or precious metal catalysts.

Catalysts	Catholyte	Discharge voltage (stabilization time)	Round-trip overpotential	Cycle life (cycles, current density)	Ref
Graphene Nanosheet	1 M LiNO ₃ +0.5 M LiOH	~3.0 V (25 h)	~1.0 V	~200 h (50, 0.5 mA cm ⁻²)	ACS Nano. 2011, 4, 3020.
CNT arrays+ Ni	0.5 M LiNO₃+0.5 M LiOH	~2.9 V (~2 h)	~1.35 V-1.58 V	~60 h (20, 0.5 mA cm ⁻²)	Energy Environ. Sci., 2013 , 11, 3339

Pt/IrO ₂	0.01 M H ₂ SO ₄	~3.5 V (2.5 h)	~1.1 V	~100 h (20, 0.2 mA cm ⁻²)	Electrochimi. Acta 2013 , 103, 44.
ON-CNW+ NiCo₂O₄	1 M LiNO₃+0.5 M LiOH	~2.8 V (2 h)	~1.0 V	~60 h (30, 0.5 mA cm ⁻²)	Adv. Energy Mater. 2014 , <i>4,</i> 1301795.
N-MC+ NCONF@Ni	1 M LiNO ₃ +0.5 M LiOH	~2.8 V (2 h)	~1.1 V	~450 h (100, 0.5 mA cm ⁻²)	Energy Environ. Sci., 2014, 7, 2630.
40 wt.% Pt/C	6 M HCl + 6.06 M imidazole + 1 M LiCl	~3.0 V (100 h)	No cycle	No cycle	Electrochem. Comm. 2014, 47, 67.
Ordered Pd₃Fe	1 M LiNO ₃ +0.5 M LiOH	~2.8 V (2 h)	~0.9 V	~880 h (220, 0.5 mA cm ⁻²)	J. Am. Chem. Soc. 2015, 137, 7278.
Hierarchical macro/meso-NC- NH ₃ /COMT@Ni LaMn _{0.7} Co _{0.3} O _{3-x}	1 M LiNO₃+0.5 M LiOH	~3.0 V (2 h)	~0.8 V	~1200 h (300, 0.5 mA cm ⁻²)	Energy Environ. Sci., 2015, 11, 3274.
	0.5 M LiOH	~3.0 V (5 h)	~0.8 V	~660 h (161, 200 mA g ⁻¹)	J. Mater. Chem. A, 2018, 6, 16943.
Biological enzyme- Laccase	1 M LiAc- HAc (pH 3.5)	~3.75 V (165 h)	~0.24 V	~1120 h (56, 500 mA g ⁻¹ /~0.4 mA cm ⁻²)	This study

In this work, we realized the first biological enzyme enhanced Li-air battery, achieving the win-win combination of biology and secondary energy storage. As Table S1 shown, comparing with the recently reported hybrid Li-air battery based on abiotic catalysts, LacTv catalytic Li-air battery with buffer catholyte exhibits higher and more flat discharge voltage of ~3.75 V, and the battery possesses extraordinarily long cycle life of ~1120 h (56 cycles) with stable round-trip overpotential of ~0.24 V.