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Electronic Supplementary Information

for

Porous Mn₂O₃ cathode for highly durable Li–CO₂ batteries

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Fig. S1 Schematic illustration of a $Li-CO_2$ battery with a porous-structured Mn_2O_3 (P- Mn_2O_3) as cathode.



Fig. S2 XRD pattern of the Mn-based organometallic precursor.



Fig. S3 Raman spectrum of the $P-Mn_2O_3$.



Fig. S4 XPS spectra of the KB-free P-Mn₂O₃ electrodes at (i) pristine, (ii) discharged and (iii) charged states: (a) the survey spectra and (b) high-resolution spectra of Mn 2p. The C 1s XPS peaks in Fig. 3a had been normalized to the Mn 2p XPS peaks.



Fig. S5 SEM images of $P-Mn_2O_3$ with different magnifications.



Fig. S6 (a) Nitrogen adsorption/desorption isotherms and (b) BJH pore size distribution curves of the P-Mn₂O₃ and commercial Mn₂O₃ particles (335 meshes, Alfa Aesar). The specific surface area of the P-Mn₂O₃ and commercial Mn₂O₃ particles were comparatively measured to be 31.09 and 5.94 m² g⁻¹, respectively. For Mn₂O₃ particles, there's almost no pore exists in the range of 10 – 200 nm. Whereas, a very different pore size distribution curve can be observed on P-Mn₂O₃. These results are consistent well with the SEM (Fig. 1c and S5) and TEM (Fig. 1d and 1e) observations and further revealed the porous feature of the as-synthesized P-Mn₂O₃.



Fig. S7 SAED pattern of the $P-Mn_2O_3$.



Fig. S8 (a) SEM image and (b,c) the corresponding O and Mn elemental mapping of the P-Mn₂O₃.



Fig. S9 (a) SEM image and (b-d) the corresponding C, Mn and O elemental mapping of the P-Mn₂O₃/KB electrode. Both the signals of Mn and O can be clearly detected although there is no obvious P-Mn₂O₃ particle on the corresponding SEM image. It should be noted that, a small port of P-Mn₂O₃ is partially exposed on the surface of the electrodes (highlighted with white dashed circles as a guide for the eye).



Fig. S10 Discharge–Charge profile of the Li–CO₂ battery with KB-free P-Mn₂O₃ electrode at a current density of 50 mA g⁻¹ within the voltage window from 2.0 to 4.5 V. Without sufficient conductivity and porous for mass transportation, the corresponding Li–CO₂ battery performance is unsatisfactory. A high charge overpotential is observed and the charge capacity is lower than the discharged one. That is, the KB-free P-Mn₂O₃ Li–CO₂ battery can be hardly completely recharged.



Fig. S11 Gas analysis results with (a) MS and (b) GC during the discharge and charge of a $Li-CO_2$ battery with a P-Mn₂O₃/KB electrode.

For MS test, the battery was firstly discharged in a Swagelok type cell filled with pure CO₂ for 10 h at 50 mA g⁻¹, from which a gas sample was collected and marked as Sample 1. Then, the gas in the Swagelok type cell was completely purged by pure Ar. After this, the battery was charged in Ar for 10 h at 50 mA g⁻¹, after which we collected a gas sample from the cell and marked as Sample 2. The pure CO₂, pure O₂, pure Ar and samples 1 and 2 were analyzed by MS. These results indicate that the pure Ar sample gave signals of m/z = 20 and 40, while pure O₂ sample gave signals of m/z = 16 and 32. Pure CO₂ gave signals of m/z = 12, 16, 28, 32 and 44, which correspond to the fragments of $[C]^+$, $[O]^+$, $[CO]^+$, $[O_2]^+$ and $[CO_2]^+$, respectively. Sample 1 gave signals of CO_2 only, while both CO_2 and Ar signals exist in the MS result of Sample 2, indicating that CO₂ molecules were released during the charge process. Therefore, the P-Mn₂O₃/KB electrode is worked for Li₂CO₃ oxidation reactions in our batteries. For GC test, Ar was used as the carrier gas. Calibration of the GC was conducted using a custom-designed gas mixture with known concentrations. The battery was firstly discharged for 10h. Then, the battery was charged at 50 mA g⁻¹ for each pulse for 2h and following relaxation for 20 min for gas identification. Most of the gas evolved upon the charging process is CO₂, and the difference between the theoretical and experimental values of the amount of charge is indeed low. Thus, the CO₂ reversible utilization has been further demonstrated.



Fig. S12 Full discharge–charge curves of the Li–CO₂ batteries with P-Mn₂O₃/KB and KB electrodes at a current density of 50 mA g⁻¹. The full discharge specific capacities of the Li–CO₂ batteries with P-Mn₂O₃/KB and KB electrodes are 9434 and 7741 mAh g⁻¹, respectively. This result demonstrates that the discharge products accommodation ability is mainly inherits from KB. And the main role of P-Mn₂O₃ here is the catalyst for CO₂ reduction and evolution reactions. The discharge/charge voltage gap of the electrodes with (P-Mn₂O₃/KB) and without P-Mn₂O₃ (KB) thus show an obvious difference (Figure 4a-c and S11). Furthermore, the porous structure and interconnected channels of the P-Mn₂O₃ can further enhance the mass transportation and discharge products accommodation ability of the whole P-Mn₂O₃/KB electrode to some extent.



Fig. S13 The initial discharge–charge curves of the Li–CO₂ batteries with P-Mn₂O₃/KB and KB electrodes at a current density of 50 mA g⁻¹.



Fig. S14 The evolutions of the middle discharge/charge potentials and voltage gap of the P-Mn₂O₃/KB Li–CO₂ battery at a current density of 50 mA g^{-1} with a cutoff capacity of 1000 mAh g^{-1} . Here, the voltage gap is the difference between the middle voltage values of the charge/discharge plateaus.



Fig. S15 Discharge/charge profiles of the $P-Mn_2O_3/KB$ cathodes in lithium ion batteries at a current density of 50 mA g⁻¹ (potential window: 2.0–4.5 V) at 25 °C.



Fig. S16 The (a) Raman spectra and (b) XRD patterns of the as-retrieved $P-Mn_2O_3/KB$ electrodes after the (i) 40th charging and (ii) 50th discharging.

Carbon material	$(I_D:I_G)_{Discharged}/(I_D:I_G)_{Pristine}$	Ref.	
Super P	>1	12	
Ketjen Black	≈1	15	
Multi-wall carbon nanotube	≈1	2 1	
Carbon nanotube	≈1	2 6	
Ketjen Black	<1	This work	

Table S1 Comparisons of the graphitization evolution of the carbon species in the Li–CO₂ batteries cathodes.

Cathode catalyst	Current density (mA g ⁻¹)	Battery operation time (h)	Cycling number	Discharge –charge voltage	Ref.
Ketjen Black	30	466.7	7	~1.6	1
B,N-codoped holey graphene	1000	436	200	~1.75	6
Carbon nanotube	50	1160	29	~1.6	9
Graphene	50	800	20	~1.5	11
Ru nanoparticles decorated Super P	100	1400	70	~1.5	12
Carbon nanotube	100	1200	60	~1.65	13
Ni nanoparticles decorated N-doped graphene	100	2020	101	~1.75	14
N-doped worm-like carbon					
with embedded MoFeNi and MoC nanoparticles	100	1800	90	~1.0	18
Porous Mn-based metal– organic frameworks	200	500	50	~1.55	19
Molybdenum carbide/	~5	400	40	~0.7	28
carbon nanotube	5	400	40	0.7	20
NiO decorated carbon nanotube	50	1680	42	~1.55	32
Porous structured Mn ₂ O ₃ /	50	2000	50	~1.4	This
Ketjen Black	-		-		work

Table S2 Comparison of the cycle performance and discharge–charge voltage gap for the $Li-CO_2$ batteries.