Supporting Information

Tailoring Component and Morphology of Discharge Products towards Highly Rechargeable Li-CO/CO₂ Batteries

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Experimental Section

Chemicals and materials: Lithium sheets were purchased from China Energy Lithium Co., Ltd. (Tianjin, China). Multiwall carbon nanotubes were purchased from XianFeng nano materials technology co. LTD. Carbon cloth was bought from Dongguan carbon composite material co. LTD. Tretraethylene glycol dimethyl ether (TEGDME), N-methyl-2-pyrrolidinone (NMP), Polyvinylidene fluoride (PVDF) and lithium triflate (LiCF₃SO₃) were purchased from Aladdin Reagent.

Material characterization: The structure of the electrodes is characterized by X-ray diffraction (XRD). The crystal phases of the samples were recorded with X-ray diffractometer (PANalytical X' pert PRO, Netherlands). SEM images and EDS test were obtained using a Zeiss SIGMA 500 scanning electron microscope and TEM images were obtained using a JEM-2100 (HR) electron microscope. Cyclic voltammetry (CV) measurements were performed on an electrochemical workstation (Chi 660e) at a scan rate of 0.5 mV s⁻¹ within a potential range of 2.2~4.4 V. Gas chromatography test was obtained by using an Agilent 7820A GC system.

Preparation of air cathode: For preparation of the pure CNTs electrodes, CNT and PVDF binder in a weight ratio of 9:1 were dispersed uniformly in NMP solvent to prepare slurry. The resulting slurry was then cast onto carbon paper substrate and then dried at 60°C for 12 h under vacuum to remove residual solvent. The total loading density of CNT was 0.3~0.5 mg cm⁻².

Assembly of coin-type Li-CO/CO₂ cell: All the electrochemical cells were assembled in an Ar filled glove box (H₂O and O₂ < 0.1 ppm) as the following: Li metal anode, a glass fiber separator (GF/D, Whatman) pre-soaked in the electrolyte (1 M LiCF₃SO₃/TEGDME) and CNTs cathode. In this work, carbon cloth works as air diffusion layer. The galvanostatic discharge-charge tests were conducted on a LAND CT2001A battery testing system.



Fig. S1 Full discharge curves of batteries under CO and CO_2 atmosphere, with a current density of 100 mA g⁻¹.



Fig. S2 Nyquist plots of Li-CO₂ and Li-CO/CO₂ batteries before discharge



| Relationship between CO and the electron during discharge | | | | | | | |
|---|--------------------------------|---|-------------------------------------|--|-------|--|--|
| Discharge time (min) | Discharge capacity (mAh) | Amount of the passed electron (10 ⁻⁶ mol) | Consumed volume of CO (ΔV ml) | Consumed amount of CO (Δ10 ⁻⁶ mol) | CO/e- | | |
| 0 | 0 | 0 | 0 | 0 | | | |
| 35 | 0.059 | 2.19 | 0.0714 | 3.19 | 1.45 | | |
| 72 | 0.120 | 4.47 | 0.0728 | 3.26 | 1.44 | | |
| 107 | 0.179 | 6.62 | 0.0644 | 2.89 | 1.43 | | |
| 143 | 0.238 | 8.83 | 0.0651 | 2.92 | 1.43 | | |
| 176 | 0.294 | 10.6 | 0.0630 | 2.82 | 1.40 | | |
| Total | 0.294 | 10.6 | 0.3367 | 15.1 | 1.43 | | |

Fig. S3 (a) Schematic of isobaric gas consumption determination. Pure CO gas was bubbled into the cell from A constantly at a pressure of 1atm. for 10 mins, then some CO gas was pumped out from B by a syringe to make a certain amount of Si-oil get into the tubule through the rim C at 1 atm. During discharge, CO was consumed and the Si-oil will automatically move left to keep the pressure of CO constant because the rim C connects the air. At different stages of discharge, the volume of CO consumed can be worked out by the moving distance of Si-oil and the sectional area of the tubule. (b) The relationship between CO consumed and the amount of electron passed.

| Compound | Δ _f G _m (298K) /KJ⋅mol ⁻¹ | | |
|-------------------------------------|--|--|--|
| CO(g) | -137.2 | | |
| Li ₂ CO ₃ (s) | -1132.1 | | |
| C(s, graphite) | 0 | | |
| Li(s) | 0 | | |

Table. S1 The thermodynamic data at a temperature of 298 K.

According to the Gibbs free energy of the reaction: $2\text{Li} + 3\text{CO} = \text{Li}_2\text{CO}_3 + 2\text{C}$ can be calculated as follows: $\Delta G(298\text{K}) = -1132.1-3 \times (-137.2) = -720.5 \text{ KJ} \cdot \text{mol}^{-1}$. Therefore, the reaction is a spontaneous process in thermodynamic at room temperature. But it doesn't means that the reaction of $2\text{Li} + 3\text{CO} = \text{Li}_2\text{CO}_3 + 2\text{C}$ can happen in normal conditions at room temperature since the dynamics is also an important factor to be considered. In fact, the reaction of $2\text{Li} + 3\text{CO} = \text{Li}_2\text{CO}_3 + 2\text{C}$ is the total battery reaction. The real electrochemical reactions contain two steps as follows:

| Anode: | $Li \rightarrow Li^+ + e^-$ | (1) |
|----------|---|-----|
| Cathode: | $2Li^+ + 2e^- + CO \rightarrow Li_2CO_3 + 2C$ | (2) |

The calculation method and the thermodynamic data refer to some literatures and the CRC handbook. ^[1, 2] Furthermore, according to the isothermal relation of Gibbs free energy and electromotive force: $\Delta G = -nFE_0$. Where E_0 is the equilibrium potential which also stands for the electromotive force of the reaction, *n* is the number of electrons transferred, and F is the Faraday constant (96485.33C·mol⁻¹). The thermodynamic potential of $2Li^+ + 2e^- + 3CO = Li_2CO_3 + 2C$ can be calculated as: $E_0 = -\Delta G(298K)/96485.33 \times 2 = -(-720500 \div 96485.33 \div 2) = 3.73$ V, which is close to the relaxing potential (3.2V) of the Li-CO cell in this work, suggesting that there is a electrochemical driving force of the electrochemical reaction: $2Li^+ + 2e^- + 3CO = Li_2CO_3 + 2C$.





Two electrochemical tests have been carried out by using a pure CO atmosphere but without Li⁺ in the electrolyte and replacing the pure CO atmosphere with Ar atmosphere, Li⁺ respectively. The battery without under CO atmosphere can exhibit an equilibrium potential (about 3.2V) before discharge, which means that there may be an electromotive force between Li and CO. And it can be seen that without CO gas, battery exhibits a very low discharge capacity (80 mAh g⁻¹), which can hardly generate discharge products. Based on these results, it can be supposed that both CO and Li⁺ are the necessary reactants in the discharged process. Therefore the reaction of $2Li + 3CO = Li_2CO_3 + 2C$ can hardly happen in normal conditions at room temperature, but it can happen in this battery system in an electrochemical form: $2Li^+ + 2e^- + 3CO = Li_2CO_3 + 2C$.



Fig. S5 SEM image of CNTs cathode after the first discharge in Li-CO₂ battery system.



Fig. S6 XRD patterns of the cathode after full discharge in Li-CO/CO₂ battery system.



Fig. S7 Raman spectra of pristine carbon paper and discharged cathodes.



Fig. S8 Cycling stability of Li-CO/CO₂ (1: 1 in volume ratio) battery.



Fig. S9 First discharge-charge curves of Li-CO/CO₂ (1 : 1 in volume ratio) battery.



Fig. S10 Yield of gas in (a) Li-CO/CO₂ (1:0) battery and (b) Li-CO/CO₂ (1:1) battery charged in Ar atmosphere. (c) Gas in Li-CO/CO₂ (1:1) in volume ratio) battery after 146 cycles.



Fig. S11 The first discharge-charge curves of Li-CO/CO_2 batteries with different initial content of CO at a current density of 100 mA g⁻¹ with a capacity limitation of 500 mAh g⁻¹.



Fig. S12 Schematic diagram of the discharge process of Li-CO/CO₂ and Li-CO₂ batteries

- [1] Z. J. Liang and Y. C. Lu, J. Am. Chem. Soc. 2016, 138, 7574-7583.
- [2] Y. Qiao, J. Yi, S.C. Wu, Y. Liu, S. X. Yang, P. He and H. S. Zhou, Joule, 2017, 1, 359-370,