

Supporting Information

Exploring the Electrochemical Reaction Mechanism of Carbonate Oxidation in Li-Air/CO₂ Battery through Tracing Missing Oxygen

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Scheme S1. Schematic of the homemade cell which was applied to conduct in situ GC-MS measurement.

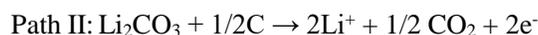
Experiment Details:

Materials preparation. The ^{12}C carbon and ^{13}C carbon was achieved by carbonizing D-Glucose- $^{12}\text{C}_6$ (AR, Nanjing Chemical Reagent Co., Ltd., P.R. China) and D-Glucose- $^{13}\text{C}_6$ (Shanghai Engineering Research Center of Stable Isotope, P.R. China) at 900 °C for 6 hr under N_2 atmosphere in a tubular furnace.

Cell assembly. The pre-filled electrode material consisted of 70 wt% Li_2CO_3 (AR, Nanjing Chemical Reagent Co., Ltd., P.R. China), 20 wt% carbon and 10 wt% polytetrafluoroethene (PTFE) binder. The as-prepared carbon, Li_2CO_3 , PTFE binder was mixed and rolled into a film with a mass loading of $\sim 3\text{mg cm}^{-1}$. The electrode film was pressed onto an Al mesh to work as a cathode. Li metal was used as the anode of the cell. Tetraglyme mixed with LiCF_3SO_3 in a molar ratio of 4:1 (G4) was used as the electrolyte. The cell assembly in a homemade cell (shown in Scheme S1) was conducted in an Ar-filled glove box.

Characterization and measurements. In situ gas chromatography-mass spectrometry (GC-MS) measurements were carried out with a homemade cell connected to the equipment from Perkin-Elmer (Clarus 680 and SQ 8S). The mass spectrometer absolute sensitivity is calibrated for CO_2 and O_2 , therefore, the evolution rate of these gases can be acquired. The evolution of other fragments can be only expressed by relative intensity (the evolution intensity of same kind of fragment from different cells is comparable) XRD was performed on a Bruker D8 Advanced diffractometer. Fourier transform infrared spectroscopy (FTIR) characterization was performed on a Nicolet Nexus 870 FT-IR Spectrometer. A CHI 660 electrochemical workstation was utilized for electrochemical performances tests. Superoxide radicals were generated and added into electrolyte following the steps below: KO_2 and 18-crown-6 (crown ether) (Aladdin Industrial Inc., P.R. China) were added (1:1 molar ratio) to 3ml of tetraglyme and stirred for 12 hr. Then a solution of LiCF_3SO_3 in tetraglyme (1:2 molar ratio) (3ml) was added in to form a solution with a 2:1 molar ratio of LiCF_3SO_3 and KO_2 . The resulting solution was used as electrolyte.

Thermodynamic Calculation:



$$\Delta_f G^0(\text{CO}_2) = -394.4\text{kJ/mol}, \Delta_f G^0(\text{Li}_2\text{CO}_3) = -1132.12\text{kJ/mol}$$

According to the isothermal relation of Gibbs free energy and electromotive force: $\Delta G = -nFE$

$$(1): \Delta G(1) = \Delta_f G^0(\text{CO}_2) - \Delta_f G^0(\text{Li}_2\text{CO}_3) = 738.02\text{kJ/mol} \quad E = 3.82\text{V}$$

$$(2): \Delta G(2) = \Delta_f G^0(\text{CO}_2) \times 3/2 - \Delta_f G^0(\text{Li}_2\text{CO}_3) = 540.52\text{kJ/mol} \quad E = 2.80\text{V}$$

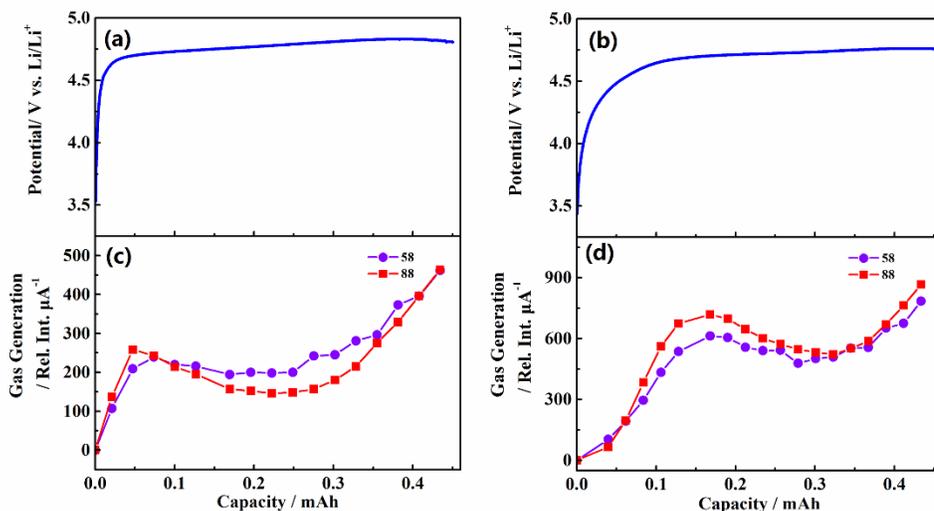


Figure S1. Charge profile of Li_2CO_3 with ^{12}C (a) or ^{13}C (c) carbon as conductive additive at $36 \text{ mA g}_{\text{Li}_2\text{CO}_3}^{-1}$ under helium atmosphere with Li metal as anode. LiCF_3SO_3 in tetraglyme (molar ratio of 1: 4) was used as the electrolyte. Gas evolution for Fragment-58 and Fragment-88 in the Li_2CO_3 - ^{12}C cell (b) and the Li_2CO_3 - ^{13}C (d)

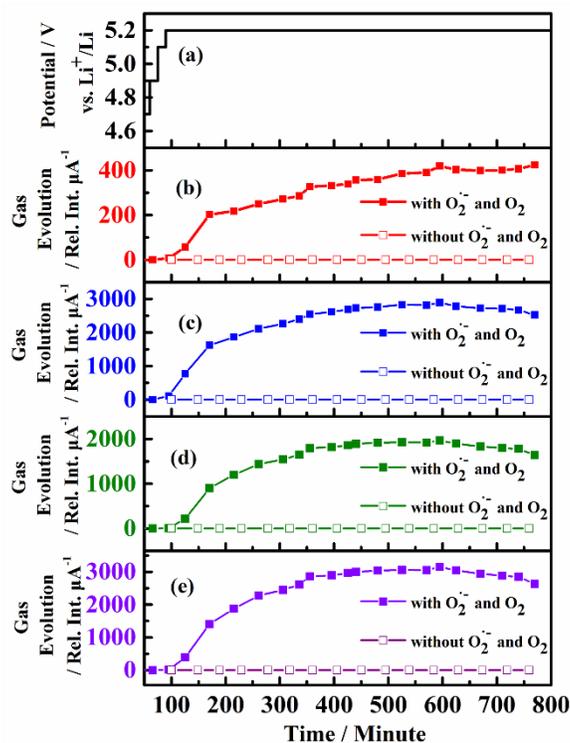


Figure S2. Potential setting of the multi-potential steps measurement with a potential range of 4.7 V~ 5.2 V (a) Gas generation of Fragment-15 (b), 45 (c), 58 (d), 88 (e) for the cell with or without superoxide and dissolved oxygen in the electrolyte. The cell use Al mesh as cathode, Li metal as anode and LiCF_3SO_3 in tetraglyme (1:4 mole ratio) as electrolyte. Superoxide radicals are added into the electrolyte using the method describe in supporting information---experimental details.

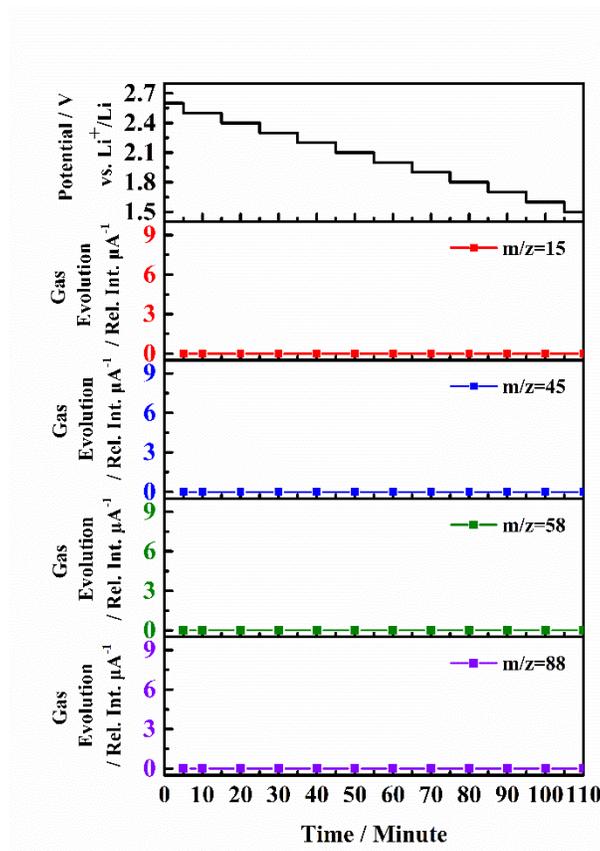
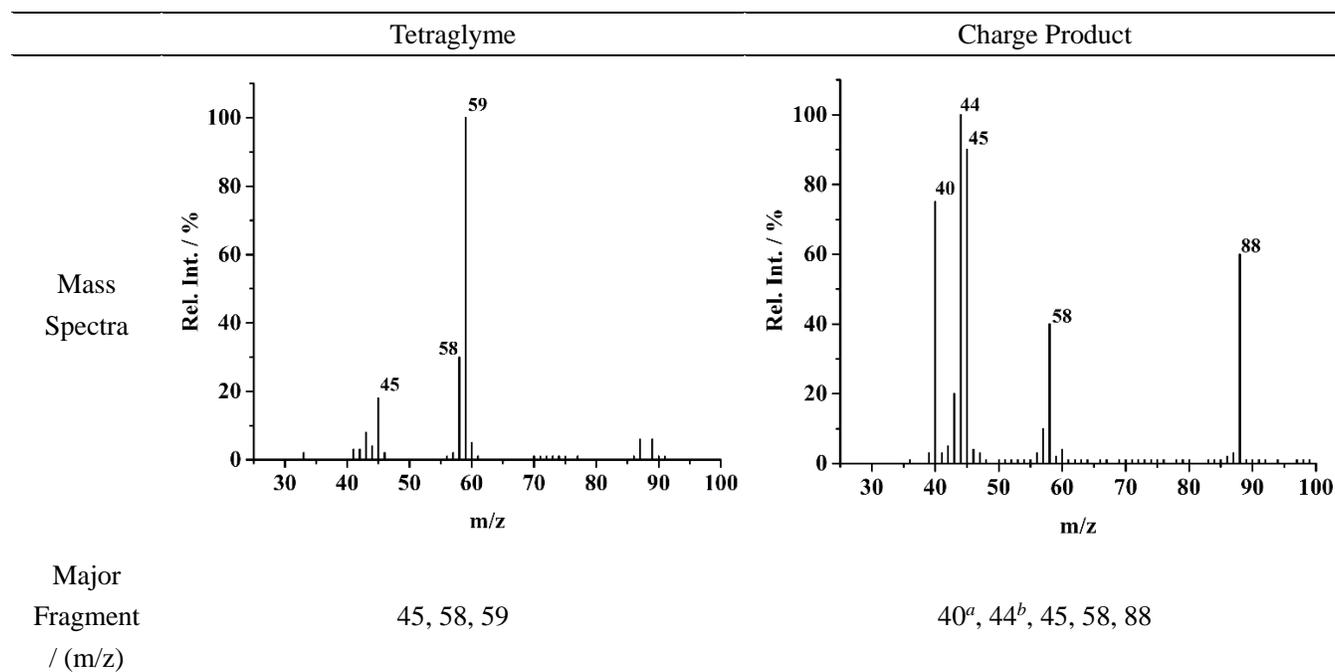


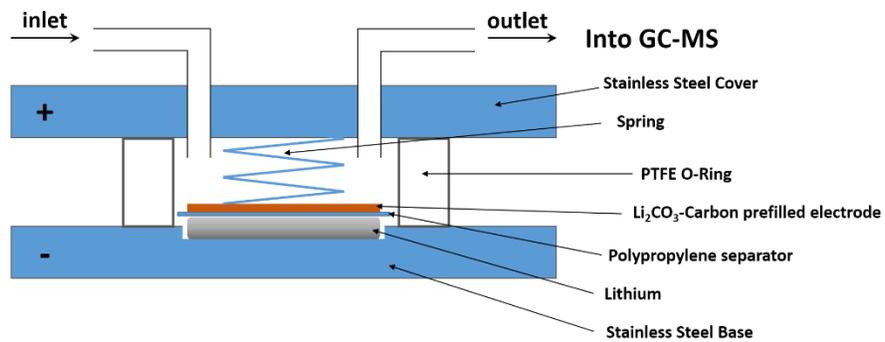
Figure S3. Potential setting of the multi-potential steps measurement with a potential range of 2.6 V~ 1.5 V(a) Gas generation of Fragment-15(b), 45(c), 58(d), 88(e) for the cell with superoxide and dissolved oxygen in the electrolyte. The cell use Al mesh as cathode, Li metal as anode and LiCF₃SO₃ in tetraglyme (1:4 mole ratio) as electrolyte. Superoxide radicals are added into the electrolyte using the method describe in supporting information---experimental details.

Table S1. The percentage of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ in the total gas generation

Conductor	Reaction	$^{12}\text{CO}_2$	$^{13}\text{CO}_2$
$^{12}\text{CO}_2$	$2\text{Li}_2\text{CO}_3 + ^{12}\text{C} \rightarrow 4\text{Li}^+ + 3^{12}\text{CO}_2(\text{g})$	100%	0%
$^{13}\text{CO}_2$	$2\text{Li}_2\text{CO}_3 + ^{13}\text{C} \rightarrow 4\text{Li}^+ + 2^{12}\text{CO}_2(\text{g}) + ^{13}\text{CO}_2(\text{g})$	66%	33%

Table S2. Mass spectra (GC-MS) of the vaporized tetraglyme electrolyte and charge product using tetraglyme as electrolyte and $\text{Li}_2\text{CO}_3@\text{C}$ as electrode.

a. Fragment with m/z of 40 stands for the background Ar atmosphere. *b.* Fragment with m/z of 44 stands for CO_2



Scheme S1. Schematic of in situ GC-MS electrochemical cell. We employed a spring to connect the cathode to the stainless steel cover. The PTFE O-ring was used to seal the cell and keep the cell from short circuit.