Supporting Information

**Exploring the Electrochemical Reaction Mechanism of Carbonate Oxidation in Li-Air/CO_2 Battery through Tracing Missing Oxygen**

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**Content:**

Experiment Details

Thermodynamic Calculations

Figure S1. Charge profile of Li_2CO_3 with ^12C or ^13C carbon as conductive additive. Gas evolution for Fragment-58 and Fragment-88 in the Li_2CO_3-^12C cell and the Li_2CO_3-^13C cell.

Figure S2. Potential setting of the multi-potential steps measurement with a potential range of 4.7 V~ 5.2 V and gas generation of the cell with or without superoxide and dissolved oxygen in the electrolyte.

Figure S3. Potential setting of the multi-potential steps measurement with a potential range of 2.6 V~ 1.5 V and gas generation of the cell with superoxide and dissolved oxygen in the electrolyte.

Table S1. The percentage of ^12CO_2 and ^13CO_2 in the total gas generation.

Table S2. Mass spectra (GC-MS) of the vaporized tetruglyme electrolyte and charge product using tetruglyme as electrolyte and Li_2CO_3@C as electrode.

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-$^{12}$C$_6$(AR, Nanjing Chemical Reagent Co., Ltd., P.R. China) and D-Glucose-$^{13}$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$_2$CO$_3$ (AR, Nanjing Chemical Reagent Co., Ltd., P.R. China), 20 wt% carbon and 10 wt% polytetrafluoroethene(PTFE) binder. The as-prepared carbon, Li$_2$CO$_3$, PTFE binder was mixed and rolled into a film with a mass loading of ~3mg 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$_3$SO$_3$ 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 spectroscope (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$_3$SO$_3$ in tetraglyme (1:2 molar ratio) (3ml) was added in to form a solution with a 2:1 molar ratio of LiCF$_3$SO$_3$ and KO$_2$. The resulting solution was used as electrolyte.

**Thermodynamic Calculation:**

Path I: Li$_2$CO$_3$ $\rightarrow$ CO$_2$ + 1/2O$_2$ + 2Li$^+$ + 2e$^-$

Path II: Li$_2$CO$_3$ + 1/2C $\rightarrow$ 2Li$^+$ + 1/2 CO$_2$ + 2e$^-$

$\Delta G^0$(CO$_2$) = -394.4kJ / mol, $\Delta G^0$(Li$_2$CO$_3$) = -1132.12kJ / mol

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

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

(2): $\Delta G(2) = \Delta G^0$(CO$_2$)×3/2 - $\Delta G^0$(Li$_2$CO$_3$) = 540.52kJ/mol $\quad E = 2.80$V
Figure S1. Charge profile of Li$_2$CO$_3$ with $^{12}$C (a) or $^{13}$C(e) carbon as conductive additive at 36 mA g$_{Li2CO3}^{-1}$ under helium atmosphere with Li metal as anode. LiCF$_3$SO$_3$ in tetraglyme (molar ratio of 1: 4) was used as the electrolyte. Gas evolution for Fragment-58 and Fragment-88 in the Li$_2$CO$_3$-$^{12}$C cell (b) and the Li$_2$CO$_3$-$^{13}$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$_3$SO$_3$ 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(e), 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 LiCF$_3$SO$_3$ in tetraglyme (1:4 mole ratio) as electrolyte. Superoxide radicals are added into the electrolyte using the method described in supporting information—experimental details.
Table S1. The percentage of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ in the total gas generation

<table>
<thead>
<tr>
<th>Conductor</th>
<th>Reaction</th>
<th>$^{12}\text{CO}_2$</th>
<th>$^{13}\text{CO}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{12}\text{CO}_2$</td>
<td>$2\text{Li}_2\text{CO}_3 + ^{12}\text{C} \rightarrow 4\text{Li}^+ + 3^{12}\text{CO}_2(g)$</td>
<td>100%</td>
<td>0%</td>
</tr>
<tr>
<td>$^{13}\text{CO}_2$</td>
<td>$2\text{Li}_2\text{CO}_3 + ^{13}\text{C} \rightarrow 4\text{Li}^+ + 2^{12}\text{CO}_2(g) + ^{13}\text{CO}_2(g)$</td>
<td>66%</td>
<td>33%</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Major Fragment / (m/z)</th>
<th>Tetraglyme</th>
<th>Charge Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>45, 58, 59</td>
<td>40$^a$, 44$^b$, 45, 58, 88</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Fragment with m/z of 40 stands for the background Ar atmosphere. $^b$ Fragment with m/z of 44 stands for CO$_2$. 

S5
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.