

**Supporting Information for**  
**Electrochemical Oxidation of Li<sub>2</sub>O<sub>2</sub> Surface-Doped with Li<sub>2</sub>CO<sub>3</sub>**

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## Experimental Method and Procedures

**Chemicals and Reagents:** Tetraethyleneglycol dimethyl ether (TEGDME, Aldrich, 99.9%) was distilled over Na metal under vacuum and dried for several days over freshly activated 4Å molecular sieves, leading to a final water content of <4 ppm (determined using a Mettler-Toledo Karl-Fischer titration apparatus). The molecular sieves were activated under vacuum at 300 °C for 24 h. Battery grade lithium bis(trifluoromethane)sulfonimide salt (LiTFSI, Aldrich, 99.99%) was dried at 160 °C under vacuum overnight prior to being used for preparing the electrolyte. Commercial Li<sub>2</sub>O<sub>2</sub> (Acros, 95%) was used after 30 min of grinding with a mortar and pestle in an Ar-filled glove box to generate abundant fresh surface of Li<sub>2</sub>O<sub>2</sub>. The Li<sub>2</sub>O<sub>2</sub> surface-doped with Li<sub>2</sub>CO<sub>3</sub> was achieved by purging CO<sub>2</sub> gas at 20 mL/min through a Li<sub>2</sub>O<sub>2</sub> column, and the amount of the dopants were controlled by the gas flowing time. After doping, the content of Li<sub>2</sub>O<sub>2</sub> in the samples was determined by iodometric titration.<sup>[1,2]</sup> High purity Li<sub>2</sub>CO<sub>3</sub> (Aldrich, 99%), and Li<sub>2</sub><sup>13</sup>CO<sub>3</sub> (Aldrich, 99 atom %) powders were dried under vacuum for 24 h at 120 °C prior to use.

**Preparation of Electrode:** The cathode was prepared by first making a slurry of pristine or doped Li<sub>2</sub>O<sub>2</sub>, Super P carbon, and Kynar2810 (mass ratios of 10:80:10), using 1-methyl-2-pyrrolidinone (NMP, spectrophotometric grade, 99%) as dispersion medium. The slurry was then coated onto a stainless steel mesh and dried in a vacuum oven for 12 h at 80 °C. All operations were performed in an Ar-filled glove box. The total mass applied onto the stainless steel mesh was ~3.3 mg. Similar procedure has been applied to the Li<sub>2</sub><sup>13</sup>CO<sub>3</sub> or Li<sup>18</sup>OH-loaded cathode.

**In Situ Differential Electrochemical Mass Spectrometry:** The *in situ* differential electrochemical mass spectrometer (DEMS) system was built in-house. In brief, it is based on a commercial magnetic sector mass spectrometer (Thermo Fischer) with turbo-molecular pump (Pfeiffer Vacuum) that is backed by a dry scroll pump (Edwards) and leak inlet which samples from the purge gas stream. The DEMS cell is based on a customized Swagelok™ design with polished stainless steel current collectors and double PTFE ferrules to ensure tightness. The cell was assembled in an Ar-filled glove box with a newly polished lithium metal anode, a glass fiber separator (Whatman) and the as-prepared cathode. A 0.1 M

LiTFSI-TEGDME was used as the electrolyte. The current collector of cathode is integrated with two embedded PEEK capillary tubes as purge gas inlet and outlet. The headspace above the cathode is ca. 100  $\mu$ L. Ultrapure Ar was used as carrier gas. Electrochemical control over the DEMS cell was carried out with a BioLogic VMP3 electrochemical workstation.

**Sample Characterization.** Powder X-ray diffraction (PXRD) was carried out using a Bruker D-8 Focus employing Cu-K $\alpha$  radiation ( $\lambda=1.5406$  Å). The air sensitive XRD sample holder was home-made and assembled in an Ar filled glove box. Samples were mounted on a polyimide stage having a low-background X-ray scattering, and sealed by polyimide film through which an X-ray beam passed. The FTIR spectra of the samples were carried out on a Bruker Optics Vertex 70 spectrometer. Raman spectroscopy (LabRAM HR800) was measured with an excitation wavelength of 633 nm. AC impedance was performed on VMP3 workstation (Biologic) with 100 m Hz to 100 KHz, and the electrodes were prepared with samples and super P carbon, and the mass ratio is 1:1.

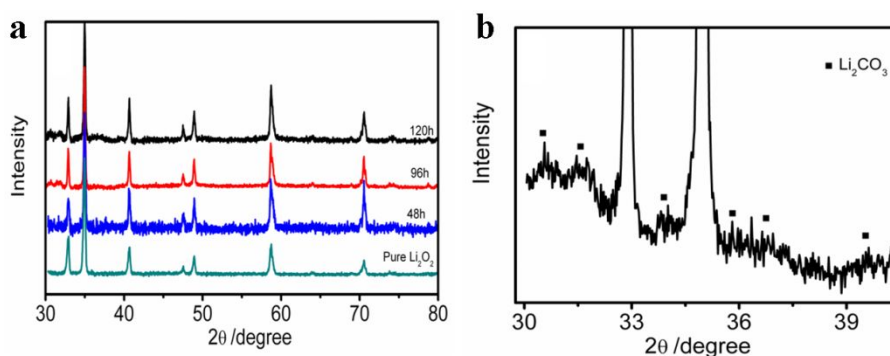
**Electron and Ion Transport:** A thin film of Li<sub>2</sub>O<sub>2</sub> was firstly deposited on 3 mm diameter glassy carbon electrode in O<sub>2</sub>-saturated 0.1 M LiTFSI-TEGDME by galvanostatic method at 5  $\mu$ A cm<sup>-2</sup>. It was then washed with MeCN and put into a vacuum to remove any residual solvent. The film thickness was estimated to be 30 Å according to the following calculation:  $d=QM/(2AFp)$ , where Q is the charge passed, F is the Faraday's constant, A is the geometric area of the GC electrode. M is the molar mass of Li<sub>2</sub>O<sub>2</sub>, and  $p$  is the bulk density of Li<sub>2</sub>O<sub>2</sub>. Li<sub>2</sub>CO<sub>3</sub> was obtained by expose the as-electrodeposited Li<sub>2</sub>O<sub>2</sub> to CO<sub>2</sub> gas for ~10 min.

Ionic blocking electrodes with configuration of GC|Li<sub>2</sub>O<sub>2</sub>|Hg were used to measure the electrical properties of the Li<sub>2</sub>O<sub>2</sub> according a published procedure.<sup>[3]</sup> The impedance spectra were recorded over the frequency range of 1 MHz to 10 Hz with voltage amplitude of 5 mV at open circuit potential. Measured impedance data were fitted according to an equivalent circuit with the program of ZView (Version 3.0a). The equivalent circuit consists two RQ circuits (Fig. S2a and Fig. S3a), where R is the resistance and Q is the constant phase element (CPE).<sup>[3]</sup> The subscripts g and gb denote the grain and the grain boundary, respectively. The total resistance was given as:  $R_{tot}=R_b+R_{gb}$ . The total conductivity ( $\sigma_{tot}$ ) was then calculated using the equations:  $\sigma_{tot}=l/(AR_{tot})$ , where  $l$  is the Li<sub>2</sub>O<sub>2</sub> film thickness and A is the electrode

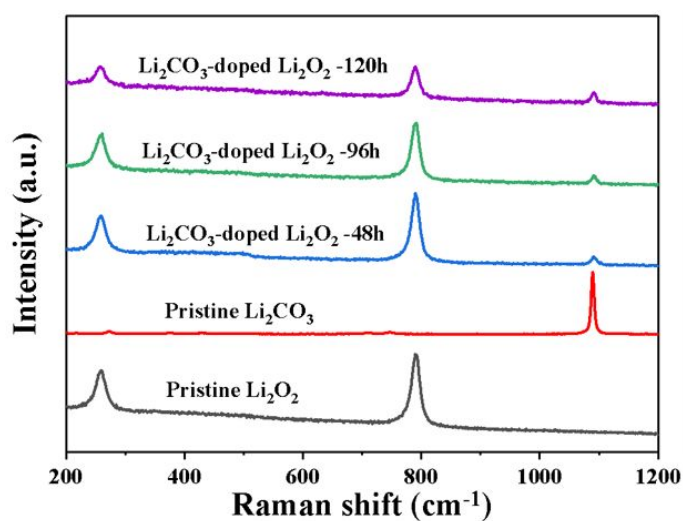
area. A bias voltage of 0.02 V( $U_{\text{bia}}$ ) was applied for the dc polarization experiments. The (quasi) stationary state current ( $I_{\text{sta}}$ ) was then reached at long polarization time (Fig. S2b and Fig. S3b). The electronic resistance could be obtained from  $R_{\text{ele}}=U_{\text{bia}}/I_{\text{sta}}$  and the electron conductivity was then evaluated using the equation:  $\sigma_{\text{ele}}=1/(AR_{\text{ele}})$ . The ionic conductivity was then defined as  $\sigma_{\text{ion}}=\sigma_{\text{tot}}-\sigma_{\text{ele}}$ .

**Table S1.** The content of  $\text{Li}_2\text{O}_2$  in the doped samples determined by iodometric titration.

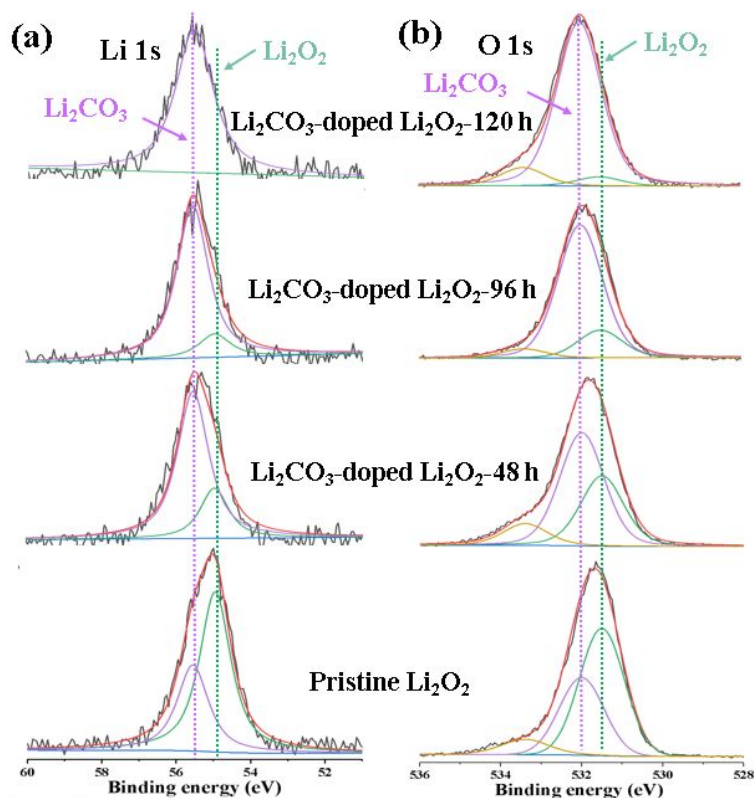
Sample	48 h	96 h	120 h
$\text{Li}_2\text{CO}_3$ -doped $\text{Li}_2\text{O}_2$	81.18%	68.83%	56.71%



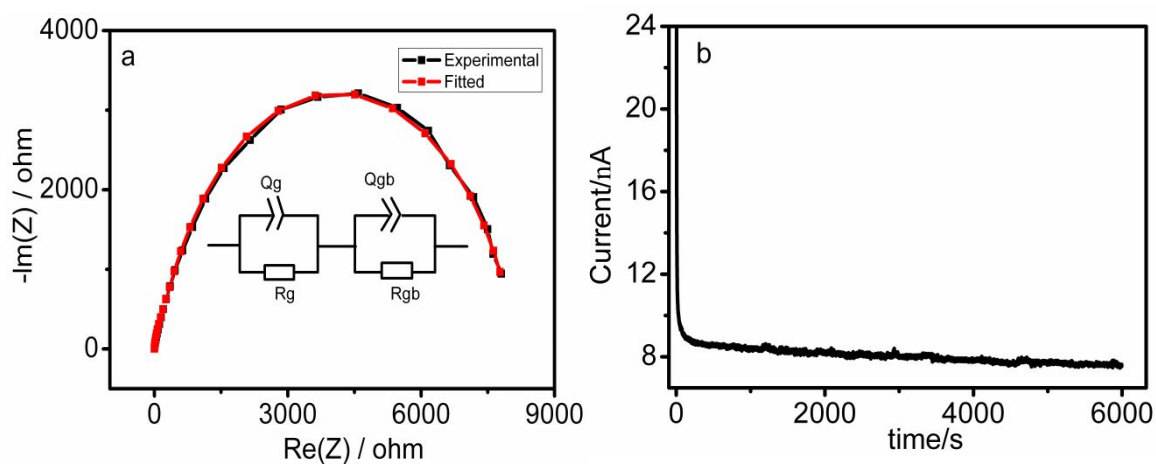
**Figure S1.** PXRD pattern of (a) carbonated  $\text{Li}_2\text{O}_2$ ; partial enlargement of the PXRD pattern of (b) carbonate  $\text{Li}_2\text{O}_2$  after a reaction time of 48h.



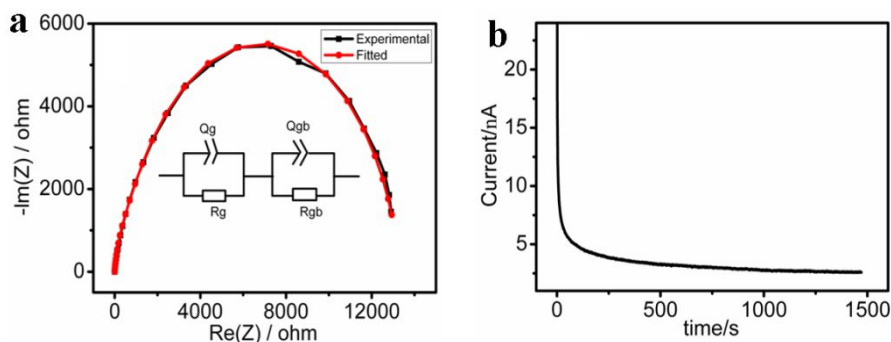
**Figure S2.** Raman spectra of pristine samples ( $\text{Li}_2\text{CO}_3$ ,  $\text{Li}_2\text{O}_2$ ) and carbonated  $\text{Li}_2\text{O}_2$ .



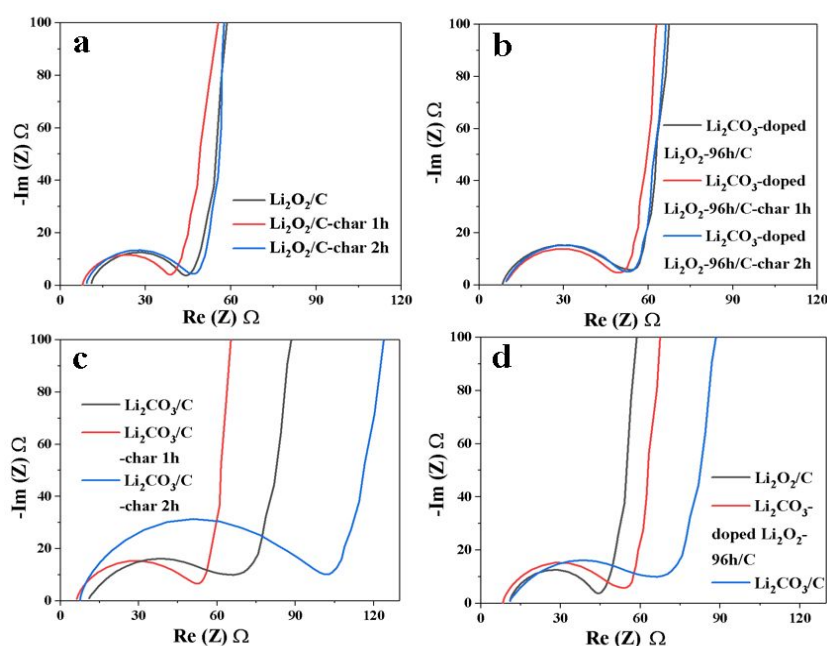
**Figure S3.** XPS spectra of pristine samples ( $\text{Li}_2\text{CO}_3$ ,  $\text{Li}_2\text{O}_2$ ) and carbonated  $\text{Li}_2\text{O}_2$ : (a) Li 1s spectra and (b) O 1s spectra. It should be noted that the samples are exposed to the air during the pretreatment for XPS measurement. Therefore, peak at 55.5 eV associated to  $\text{Li}_2\text{CO}_3$  can be clearly seen in Li 1s for pristine  $\text{Li}_2\text{O}_2$ , and one unclear peak centered at 533.4 eV appeared in O 1s for all samples.



**Figure S4.** Ac impedance spectra (a) and dc polarization curve (b) of  $\text{GC}|\text{Li}_2\text{O}_2|\text{Hg}$ ,  $I_{\text{steady}}=7.6 \text{ nA}$ , the inset in (a) is the equivalent circuit used to fit EIS.



**Figure S5.** Ac impedance spectra (a) and dc polarization curves (b) of GC|Li<sub>2</sub>CO<sub>3</sub>|Hg,  $I_{\text{steady}} = 2.6 \text{ nA}$ , the inset in (a) is the equivalent circuit used to fit EIS.



**Figure S6.** AC impedance of Li<sub>2</sub>O<sub>2</sub> (a), Li<sub>2</sub>CO<sub>3</sub>-doped Li<sub>2</sub>O<sub>2</sub>-96 h (b) and Li<sub>2</sub>CO<sub>3</sub> electrode (c). (d) The comparison of AC impedance curves of the three electrodes before charging. The electrode is prepared with samples and super P carbon, and the mass ratio is 1:1.

## References

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