

Supporting Information for

The Carbon Electrode in Non-aqueous Li-O₂ Cells

Muhammed. M. Ottakam Thotiyl, Stefan A. Freunberger[†], Zhangquan Peng, Peter G. Bruce*

*School of Chemistry, University of St-Andrews, North Haugh, St-Andrews, Fife KY16 9ST, U.K.

[†]Present address: Institute for Chemistry and Technology of Materials, Graz University of Technology, Stremayrgasse 9, 8010 Graz, Austria

Experimental Section

Chemicals and reagents. HPLC grade dimethyl sulfoxide (DMSO) and tetraethyleneglycol dimethyl ether (Tetraglyme) were first pre-dried over activated type 4Å molecular sieves for several days before distilling. The solvents were distilled over a packed bed column under vacuum and transferred into an Ar filled glove box without any exposure to air. DMSO was distilled with added sodium amide. The distilled solvents were stored over activated type 4Å molecular sieves in an Ar- filled glove box. All solvents had 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 LiClO₄ (Aldrich 99.99%) and electrochemical grade LiPF₆ (Stella 99.99%) salts were used for preparing the electrolytes. Prior to use LiClO₄ and LiPF₆ salts were dried under vacuum for 24 h at 160 and 120 °C, respectively. Isotopically labeled carbon (99 atom % ¹³C, BET surface area 150 m²/g) was purchased from Sigma Aldrich. Highly pure Li₂O₂ was required for this study and was synthesized as follows. All operations were performed in an Ar filled glove box. Freshly cut Li metal was dissolved in 5-fold excess of ultra-pure water (Millipore, 18.2 MΩ) that was degassed by an Ar flow. The excess water was removed under vacuum and LiOH was obtained by further drying at 120°C under vacuum. Its purity was confirmed by the carbonate/carboxylate analysis method (see below). The LiOH was converted into Li₂O₂ by 1.85-fold excess of 30 % H₂O₂, after stirring for half an hour the water was removed and the Li₂O₂ was dried at 120°C for 12 h under vacuum. Identity and purity was confirmed by XRD, FTIR, and the carbonate/carboxylate analysis method.

Hydrophilic and hydrophobic carbons. As received ¹³C carbon was converted into hydrophilic and hydrophobic carbon using previously reported procedures. To make ¹³C hydrophilic, the as-received carbon was treated with 5 M HNO₃ under refluxing conditions for 24 hours.¹ The resulting material was filtered and washed with copious amounts of distilled water until the pH of the water was 7. These powders were then dried at 60°C under vacuum for several hours and then transferred to an Ar filled glove box without exposure to air. To prepare the hydrophobic carbon, ¹³C carbon was heated under an Ar:H₂ (95:5 v/v) atmosphere at 900°C for three hours,² and transferred to an Ar filled glove box without exposure to air.

Preparation of electrodes and cell design. The electrochemical cells used to investigate cycling were based on a Swagelok design. Carbon cathodes were fabricated by first making a

slurry of carbon with PTFE binder in the ratio 8:2 (m/m) using isopropanol. The slurry was then coated onto a stainless steel mesh current collector. The electrodes were vacuum dried at 200°C for 24 hours and then transferred to an Ar filled glove box without exposure to air. The electrolyte (0.5 M LiPF₆ in tetraglyme or 0.5M LiClO₄ in DMSO) was impregnated into glass fiber separator (Whatman). The glass fiber separators were washed with ethanol and dried overnight at 200 °C under vacuum prior to use. The cell was gas tight except for the stainless steel window that exposed the cathode to the O₂ atmosphere. The cell was operated in 1 atm of O₂. A LiFePO₄ anode was employed because DMSO is not stable in contact with Li metal.³ The LiFePO₄ anode was constructed by mixing partially charged active material with Super P (TIMCAL) and PTFE in the ratio 8:1:1(m/m). The electrodes were vacuum dried at 200°C for 24 hours. The counter electrode had three fold the expected capacity of the positive electrode.

Methods and Techniques. A Thermo Nicolet 6700 FTIR spectrometer housed in a N₂ filled glove box was used for FTIR measurements. It was equipped with a CsI window to extend the analysis to sufficiently lower wavenumber region such that the peaks for Li₂O₂ could be observed. Measurements were carried out either in transmission mode by making a pellet with CsI powder or by ATR unit using a diamond crystal. Electrochemical measurements were carried out at room temperature using a BioLogic VMP3 electrochemical workstation. The differential electrochemical mass spectrometer (DEMS) was built in-house. The details may be found elsewhere.³ Briefly it is based on a commercial quadrupole mass spectrometer (Thermo Fischer) with turbomolecular pump (Pfeiffer Vacuum) that is backed by a dry scroll pump (Edwards) and leak inlet which samples from the purge gas stream. The cell is based on a customized Swagelok design with polished stainless steel current collectors and double PTFE ferrules to ensure tightness.

Calibration of the DEMS. To capture nonlinearity and cross-sensitivity the setup was calibrated for different gases Ar, O₂, CO₂, H₂, N₂ and H₂O using calibration mixtures in steps over the anticipated concentration ranges. The details may be found elsewhere.³

Carbonate/Carboxylate analysis method. The carbon cathodes at different states of discharge and charge were removed and washed in acetonitrile in an Ar filled glove box and then dried under vacuum. The carbon composites were carefully removed from the current collector and transferred to a small glass vial (1mL volume) with a magnetic stirrer bar. A rubber septum integrated with two inserted PEEK capillary tubes as purge gas inlet and outlet for Ar was fixed onto the glass vial containing the carbon composites. The purge gas system

consists of a gas cylinder, a digital mass flow controller (Bronkhorst), PEEK or stainless steel capillary tubing, a high pressure 2-position 6-port GC valve that allows for transfer out of the glove box without air exposure (all Valco), a T-piece where the MS is sampled and an outlet check valve (Swagelok) with an additional capillary to avoid back diffusion. Tightness was checked by Helium leak testing by means of the MS. For the detection of all gases evolved, Ar carrier gas was used. Purge gas flows were typically 2.5 mL/min.

The method consists of injecting 0.3 mL of 2M H₃PO₄ into the glass vial containing the sample under stirring. This decomposes all Li₂CO₃ to CO₂ present in the sample. At the very acidic pH-value the CO₃²⁻ ↔ HCO₃⁻ ↔ CO₂ equilibrium is fully to the right hand side and CO₂ is poorly soluble under these conditions. Li₂O₂ present is converted into H₂O₂. After any CO₂ evolution has ceased 0.3 mL of 2M H₃PO₄ containing 0.5M FeSO₄ and 20μL of 30% H₂O₂ (Fenton's reagent) were injected. This decomposes all organic species (lithium carboxylates) present in the system into CO₂, due to formation of the very reactive OH• radical according to Fe²⁺ + H₂O₂ → Fe³⁺ + OH• + OH⁻. The head space was again purged until CO₂ evolution has ceased. The concept is shown in Figure S6 for a mixture of 20% Li₂CO₃ and 15% Li formate in Li₂O₂. The point 'A' corresponds to injection of acid and point 'F' corresponds to injection of Fenton's reagent. The number of moles of CO₂ evolved was extracted by integrating the appropriate regions in the plot. The accuracy of the method is presented in Figure S7 for different amounts of Li₂CO₃ in Li₂O₂. As shown in Figure S7b, the amounts observed and predicted agree well, demonstrating that acid can efficiently decompose all the Li₂CO₃ in the sample. Similarly the accuracy of the method for lithium carboxylates is shown in Figure S8 for different amounts of lithium formate in Li₂O₂. Injection of acid (point A) does not produce any CO₂ evolution whereas the injection of Fenton's reagent efficiently evolves CO₂, demonstrating decomposition of lithium carboxylates. Again observed quantities agree well with those predicted as shown in Figure S8b, demonstrating that Fenton's reagent can efficiently oxidize all the lithium carboxylates in the system. It is important to note that acid alone does not decompose any lithium carboxylates and therefore the advantage of the method lies in the efficient and quantitative separation of Li₂CO₃ from the lithium carboxylates present in the system. We also demonstrate that a ¹³C carbon/PTFE composite electrode alone does not produce any CO₂ (Figure S9), i.e. the CO₂ evolved in the case of the cathode removed from the cells arise only from the products formed.

REFERENCES

1. Azzi Rios, R. R. V.; Alves, D. E.; Dalmázio, I.; Vargas Bento, S. F.; Donnici, C. L.; Lago, R. M. *Materials Research* **2003**, 6 (2), 129.
2. Considine, R.; Denoyel, R.; Pendleton, P.; Schumann, R.; Wong, S.-H. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2001**, 179, 271.
3. Peng, Z.; Freunberger, S. A.; Chen, Y.; Bruce, P. G. *Science* **2012**, 337, 563

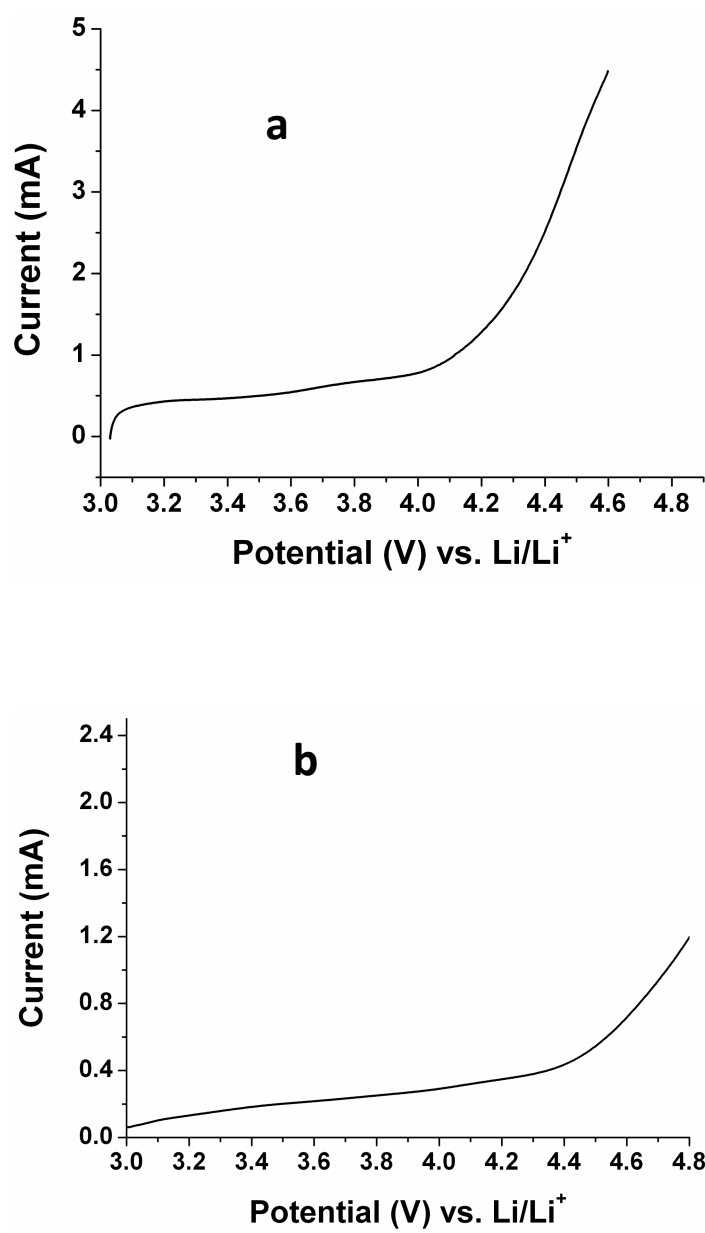


Figure S1. Anodic stability of (a) 0.5 M LiClO₄ in DMSO and (b) 0.5 M LiPF₆ in tetraglyme at 1mV/s in O₂ atmosphere (1 atm).

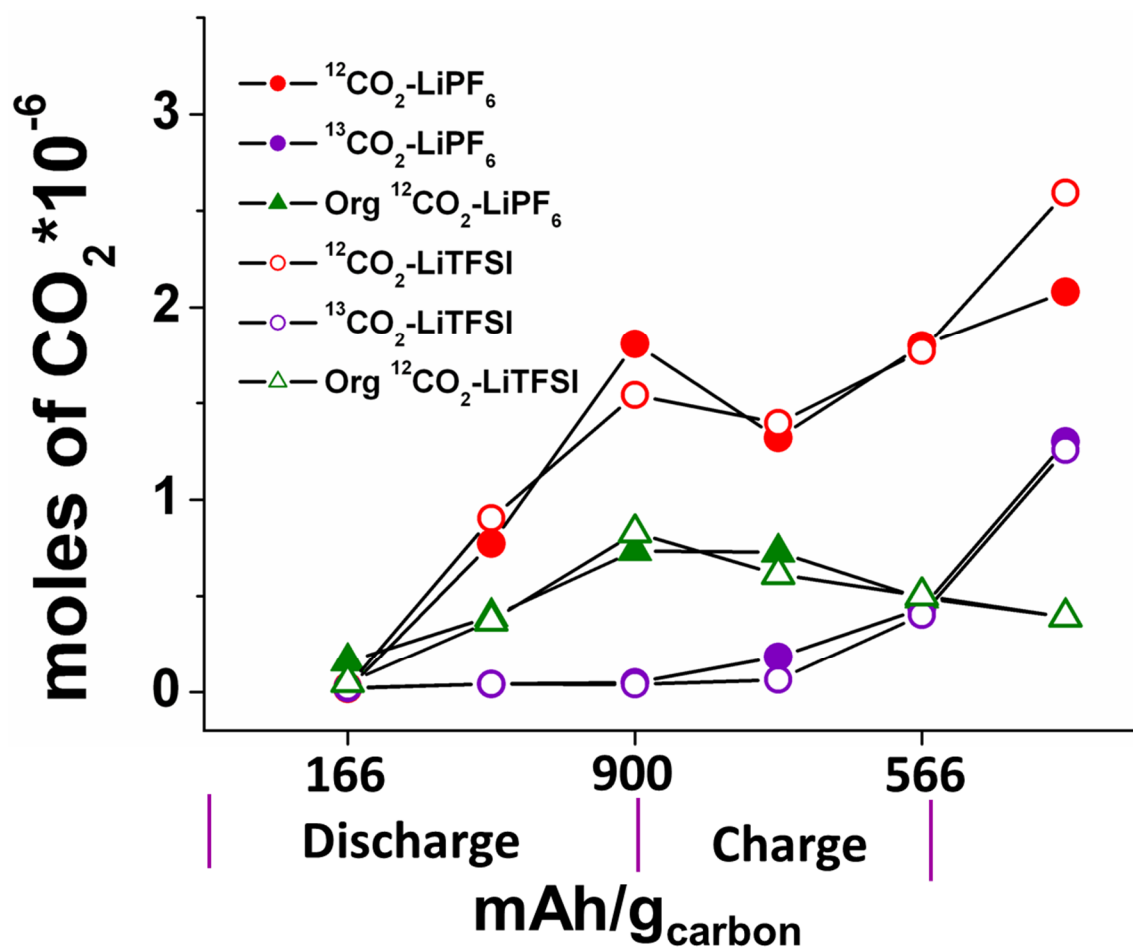


Figure S2. Direct comparison of the CO_2 evolution from decomposition of $\text{Li}_2^{12}\text{CO}_3$, lithium carboxylates and $\text{Li}_2^{13}\text{CO}_3$ when a carbon cathode is cycled in 0.5 M LiPF_6 in tetraglyme and 0.5 M LiTFSI in tetraglyme.

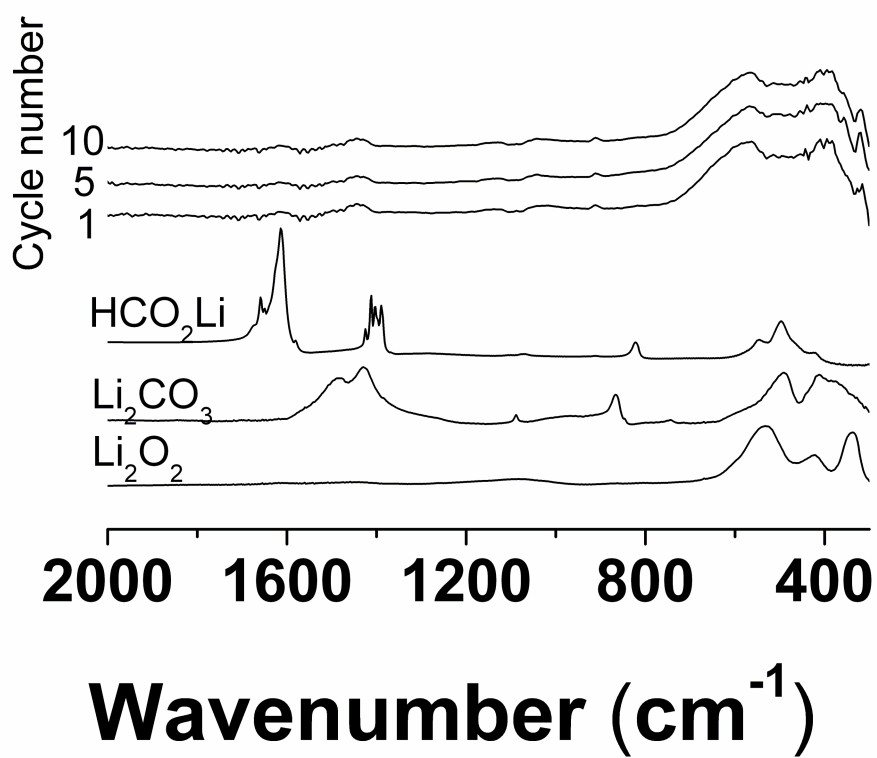


Figure S3. FTIR spectra collected at the end of discharge on a nanoporous Au electrode when cycled in 0.1 M LiClO_4 in DMSO.

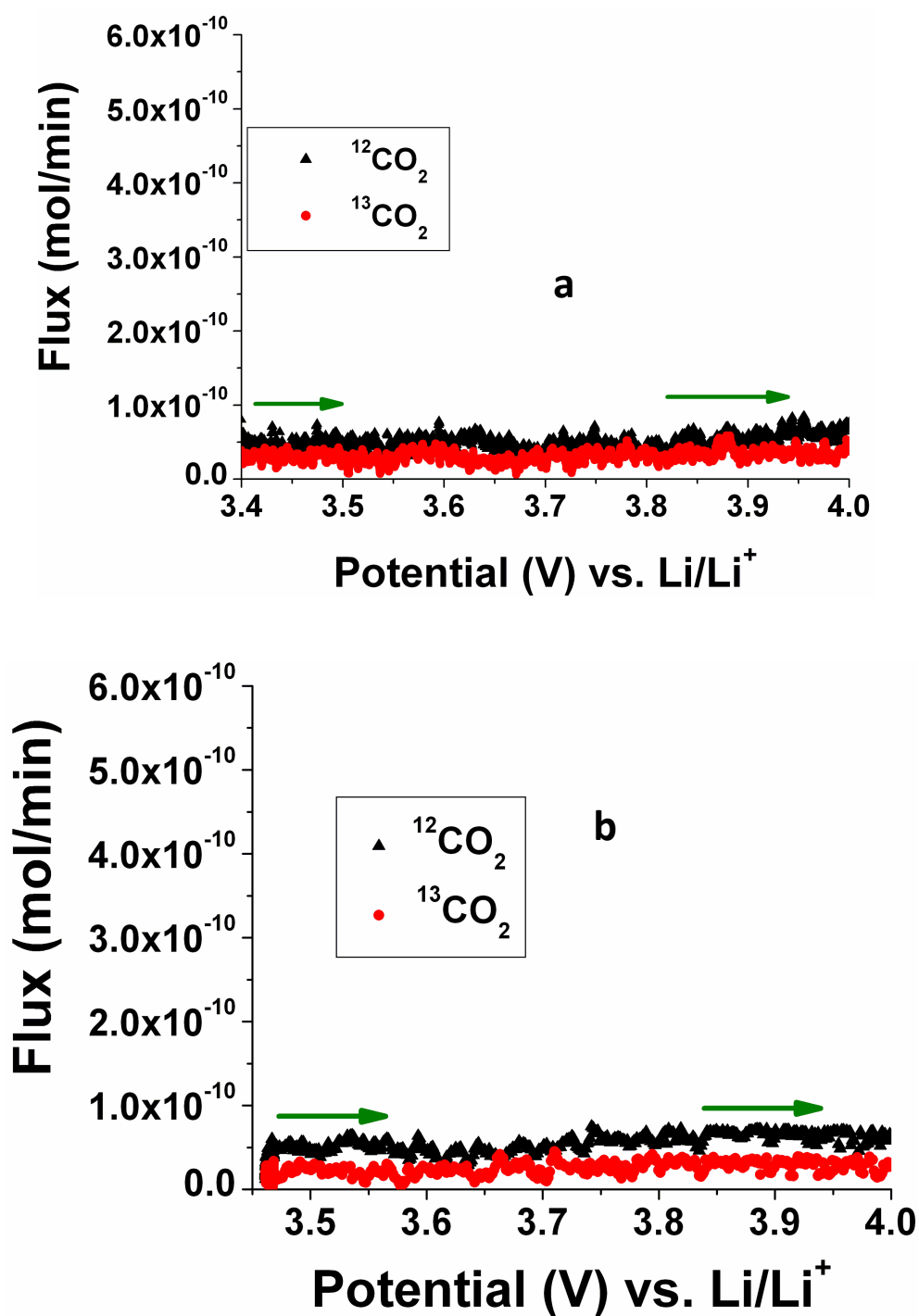


Figure S4. In-situ DEMS data for $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ fluxes during the charge carried out without prior discharge in an Ar: O_2 gas mixture (5:95 v/v). (a) 0.5 M LiClO_4 in DMSO and (b) 0.5 M LiPF_6 in tetraglyme.

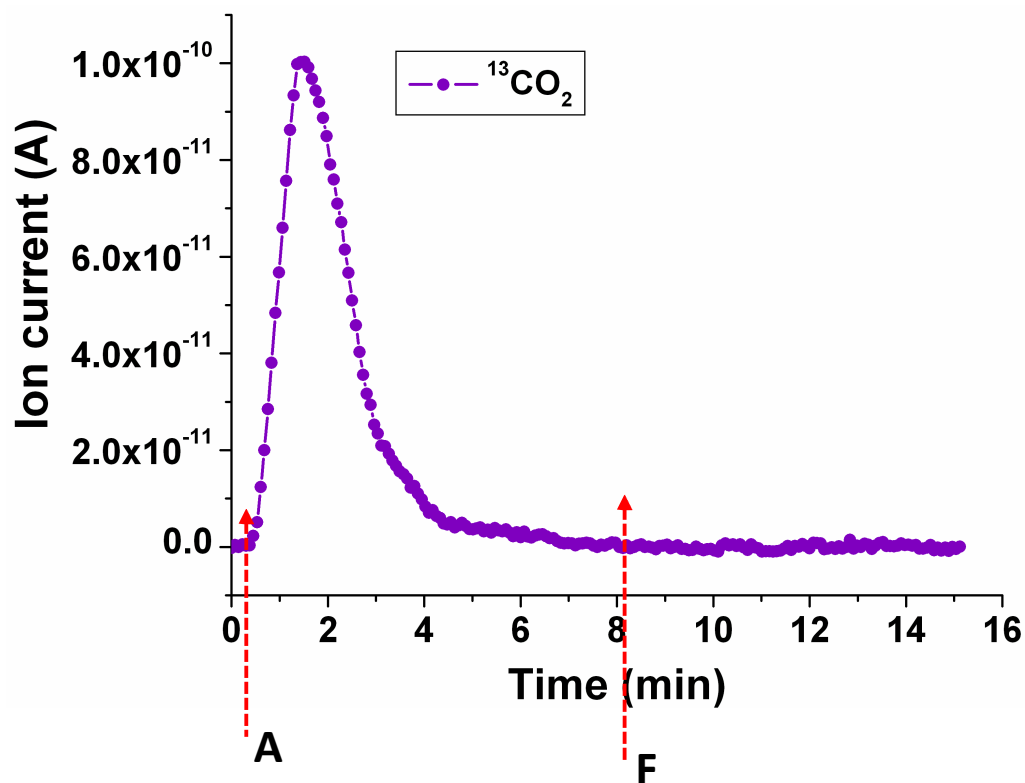


Figure S5. Mass spec. ion current corresponding to $^{13}\text{CO}_2$ evolution from a mechanical mixture of ^{13}C carbon and Li_2O_2 . Point (A) corresponds to injection of 2M H_3PO_4 to decompose the Li_2CO_3 and point (F) corresponds to injection of Fenton's reagent. The amount of $\text{Li}_2^{13}\text{CO}_3$ formed by reaction between the carbon and Li_2O_2 corresponds to $\sim 0.1\%$ (9 nanomoles of $^{13}\text{CO}_2$) of a monolayer on the carbon surface

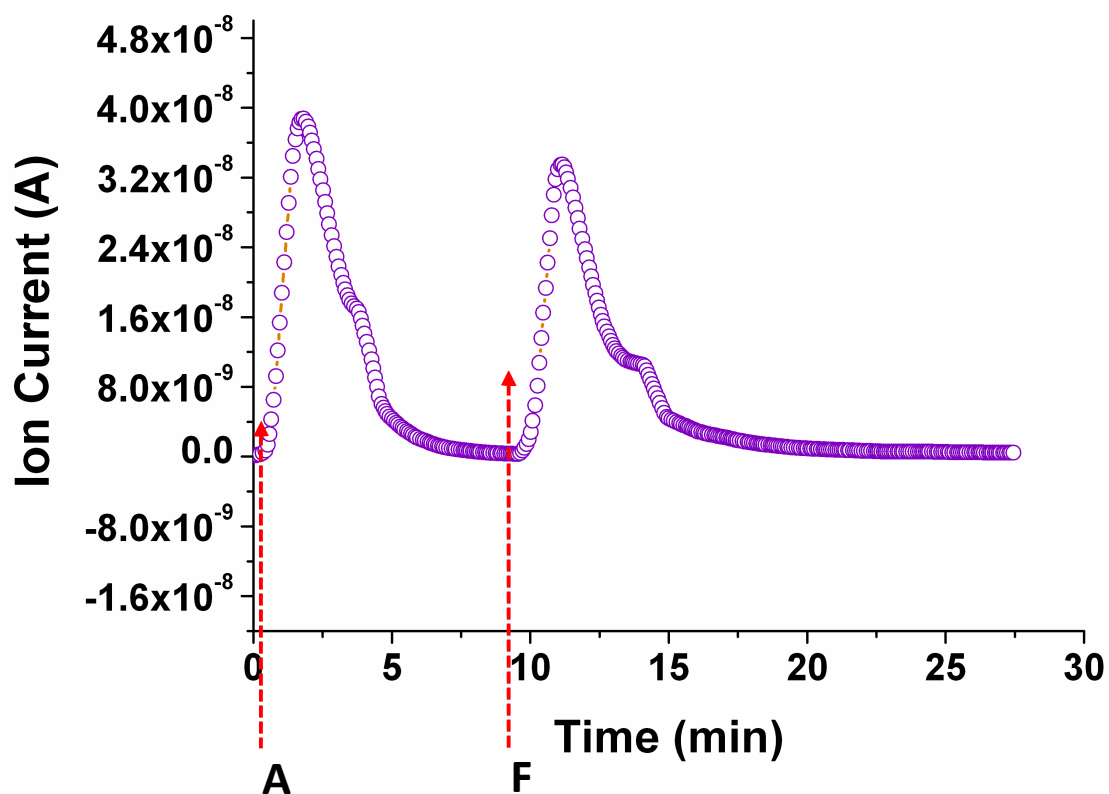


Figure S6. Mass spec. ion current corresponding to $^{12}\text{CO}_2$ evolution from a mechanical mixture of 20% Li_2CO_3 and 15% Li formate in Li_2O_2 . Point (A) corresponds to injection of 2M H_3PO_4 to decompose the Li_2CO_3 and point (F) corresponds to injection of Fenton's reagent to decompose the lithium formate.

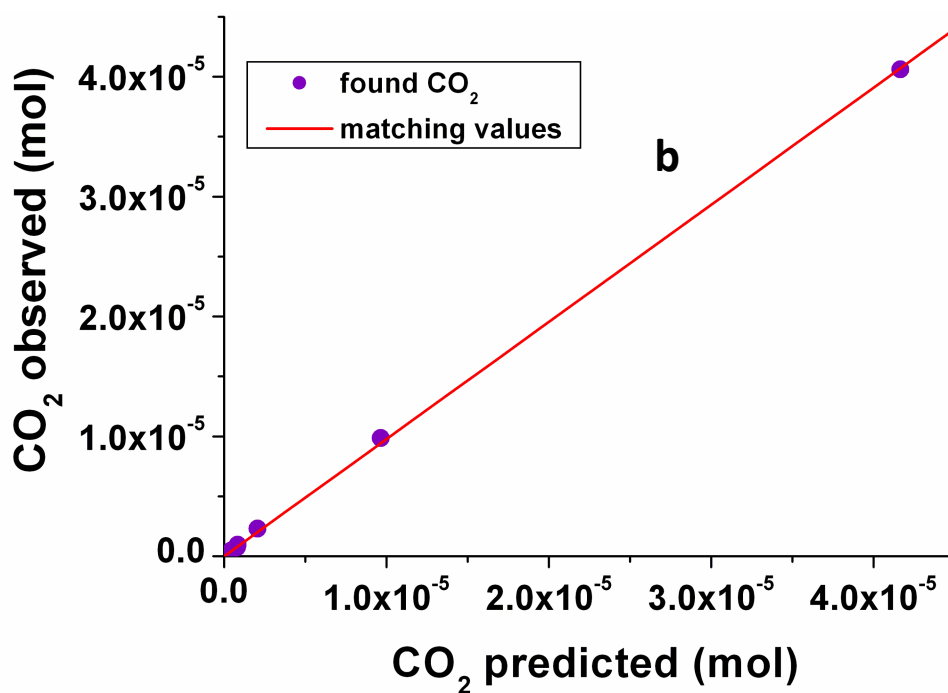
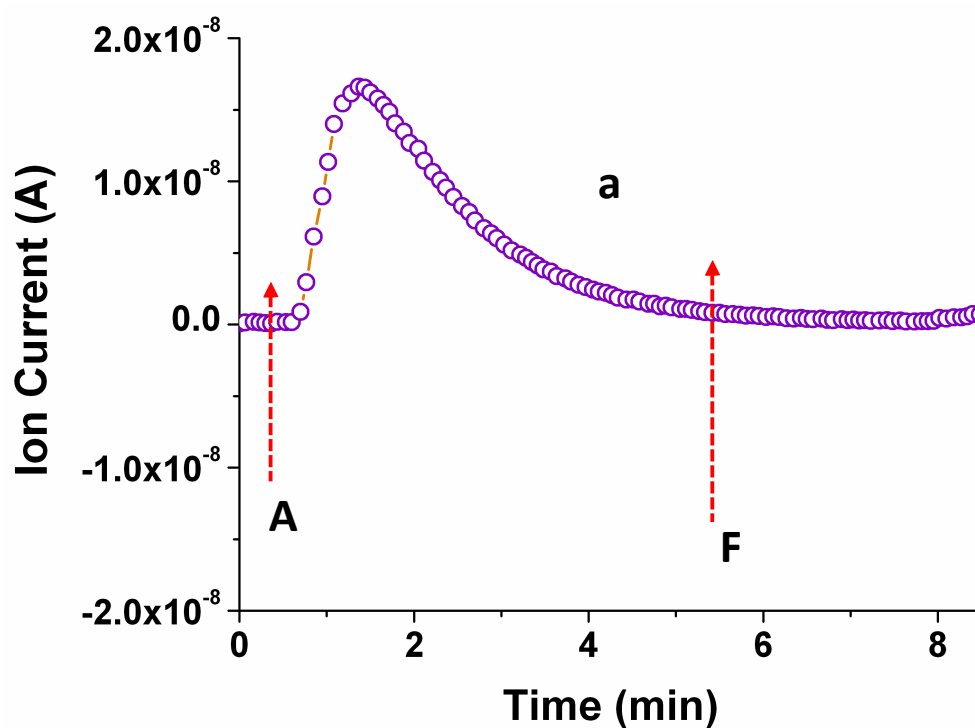


Figure S7. (a) Mass spec. ion current corresponding to $^{12}\text{CO}_2$ evolution from a mechanical mixture of 5% Li_2CO_3 in Li_2O_2 . Point (A) corresponds to injection of 2M H_3PO_4 to decompose the Li_2CO_3 and point (F) corresponds to injection of Fenton's reagent. (b) demonstrates the accuracy of the method.

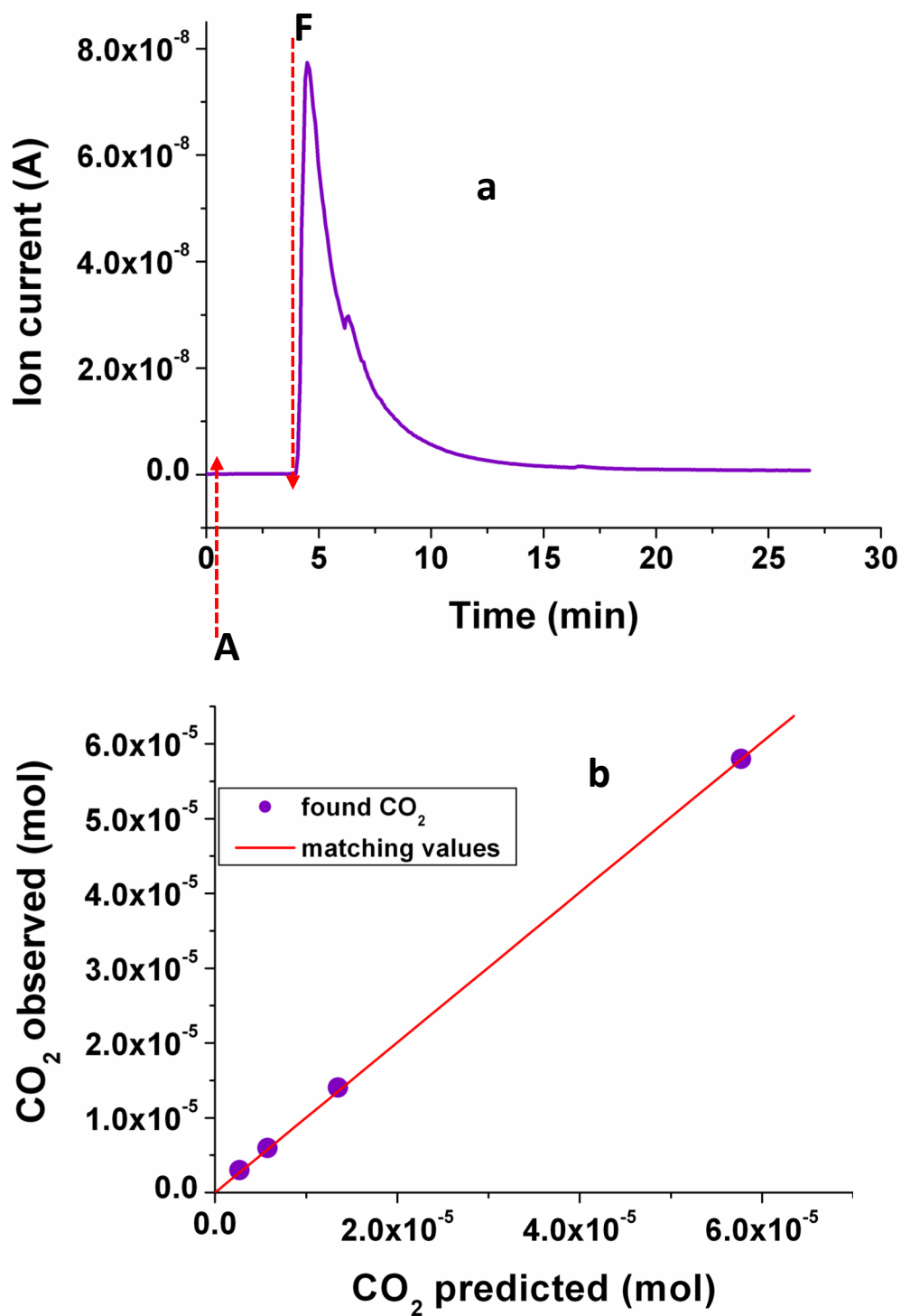


Figure S8. (a) Mass spec. ion current corresponding to $^{12}\text{CO}_2$ evolution from Li formate. Point (A) corresponds to injection of 2M H_3PO_4 and point (F) corresponds to injection of Fenton's reagent. (b) demonstrates the accuracy of the method.

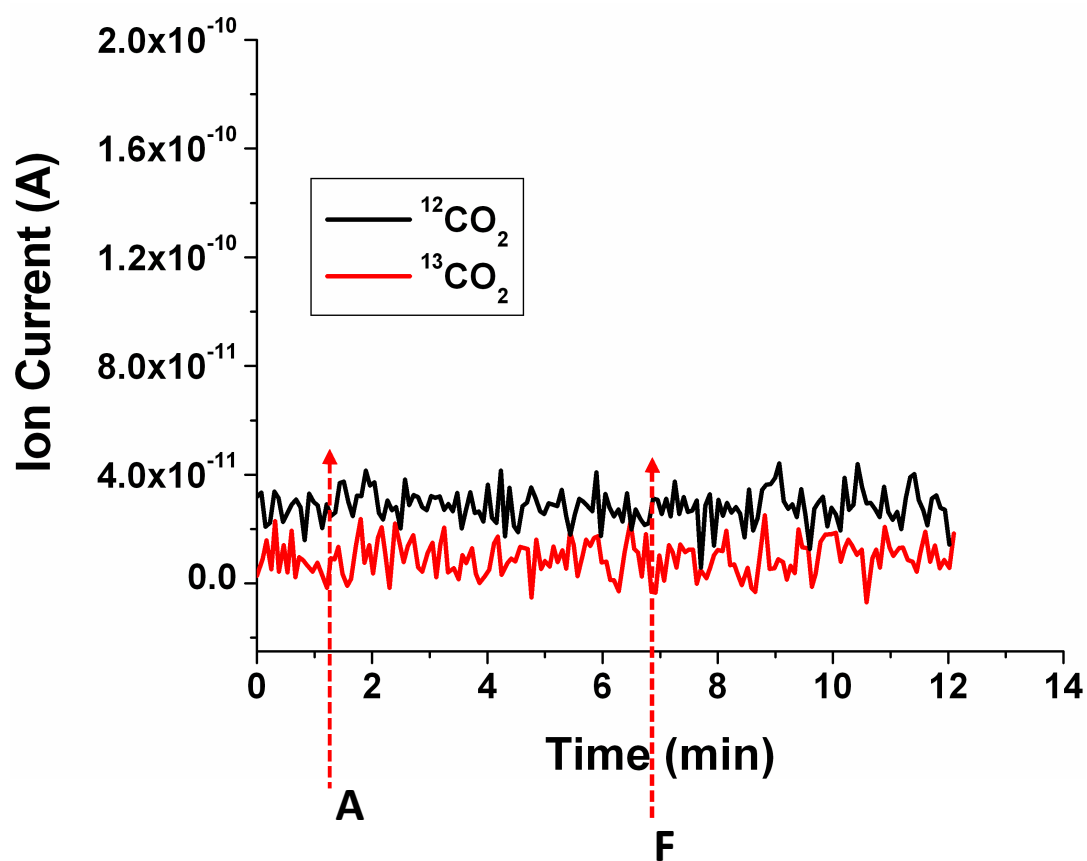


Figure S9. Mass spec. ion current corresponding to $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ evolution from a ^{13}C carbon/ PTFE composite electrode. Point (A) corresponds to injection of 2M H_3PO_4 and point (F) corresponds to injection of Fenton's reagent.