

## **Supporting information**

### **Reactivity of carbon in lithium-oxygen battery positive electrodes**

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#### **Cathode materials**

Aqueous suspension of graphite oxide was prepared by conventional Hummers method and then chemically reduced by ascorbic acid in order to obtain reduced graphene oxide (RGO). Pure graphite (99.99%, Aldrich) and ascorbic acid were used as starting chemicals. Thermally exfoliated graphite (TEG) was produced by Unichimtek company (Russia) and used as received.

#### **Cell assembly and electrochemical measurements**

RGO and TEG were deposited from aqueous suspensions onto the solid glass-ceramic lithium-conductive plate (Ohara inc.) and acted as a positive electrode. Total mass loading of carbon was about 0.1 mg. Nickel stripes were magnetron-sputtered on the solid electrolyte plate prior to carbon material deposition to collect the electric current from positive electrode and provide proper grounding of the positive electrode during photoemission studies. Low vapor pressure electrolyte comprising a solution of lithium bis(trifluoromethylsulfonyl)imide (Aldrich) in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquid (Aldrich) was used to wet a polymer separator that was located between negative electrode and solid electrolyte membrane to allow ionic transport to and from metallic lithium foil. Cells

were assembled inside Ar-filled glove box (M-Barun, humidity and oxygen concentration inside glove box were kept at 0.1 ppm levels), transported to the XPS spectrometer inside the transfer chamber without exposure to air and located inside analysis chamber (Figure S2); electrode connections to the potentiostat were made via electric feed-through ports. Biologic SAS SP-200 potentiostat was utilized for electrochemical measurements during experiments at synchrotron sources.

### **Materials characterization**

Field-emission SEM (Leo Supra 50 VP) was utilized to observe RGO and TEG film morphology. AFM images were obtained using NT-MDT N'Tegra Aura microscope with Mikromasch NSC15 cantilever in tapping mode. Carbon flakes were deposited onto silicon wafer for imaging. Estimations of specific surface area for TEG and RGO were done based on SEM and AFM image analysis. Raman scattering spectra of carbon materials were collected with Renishaw inVia microscope; Ar<sup>+</sup>-laser operating at 514 nm wavelength and focused on the sample with 50x objective served as an excitation source.

### **XPS analysis**

Photoemission spectra were collected at the ISIS beamline and station (A. Knop-Gericke *et al.* in *Advances in Catalysis* **52** Ch. 4, Elsevier, London, 2009) installed at BESSY II, Helmholtz Zentrum Berlin and equipped with a SPECS Phoibos 150 analyzer under oxygen pressures of 0.1 - 0.3 mbar. The Li 1s, C 1s and O 1s core level spectra were recorded at fixed kinetic energy of 190 eV with different pass energies of 5-20 eV to adjust the time resolution required. The Li 1s intensity maps with a lateral resolution of about 500 nm were obtained under *operando* conditions at Spectromicroscopy beamline (P. Dudin *et al.*, *Journal of Synchrotron Radiation* **17**,

445-450 (2010)) of ELETTRA Sincrotrone Trieste (Trieste, Italy) at local oxygen pressure of  $10^{-3}$  -  $10^{-4}$  mbar. All spectra were fitted by Gaussian/Lorentzian convolution functions. The background was modeled using a combination of Shirley and Tougaard backgrounds. Background parameters were optimized simultaneously with spectral parameters. The composition changes were calculated using photoemission cross-sections and calibrated photon flux values.

### **Fitting of the core-level spectra**

All spectra were fitted by Gaussian/Lorentzian convolution functions. The background was modeled using a combination of Shirley and Tougaard backgrounds. Background parameters were optimized simultaneously with spectral parameters.

We tried to keep the number of components in C 1s spectra as low as it was possible to maintain fitting quality. Initial parameter values were adopted from A. Ganguly et al., *J. Phys. Chem. C* 115 (2011), Md. Z. Hossain et al., *Nature Chem.* 4, 305-309 (2012) and R. Dedryvère et al., *J Electrochem. Soc.* 152, A689-A696 (2005). Binding energies were fixed relative to  $sp^2$  component position, the Gaussian widths were varied in reasonable limits. The line asymmetry of high resolution C 1s core level spectra was described with Doniach–Sünjić functions with the corresponding parameter of 0.1.

**Table S1.** Binding energies of C 1s components used in spectra deconvolution.

<b>Component</b>	<b>Binding energy, eV</b>
$sp^2$ (carbon in graphene lattice)	284.50
$sp^3$ (defects in graphene)	285.00
COH (hydroxyl groups)	285.85
COC (epoxy groups)	286.30

C=O (carbonyl groups)	287.55
COOH (carboxyl groups)	288.95
CO <sub>3</sub> (carbonate)	290.20

### Calculation of the surface concentrations

Surface concentrations of oxygen, carbon and lithium were calculated using the following formula:

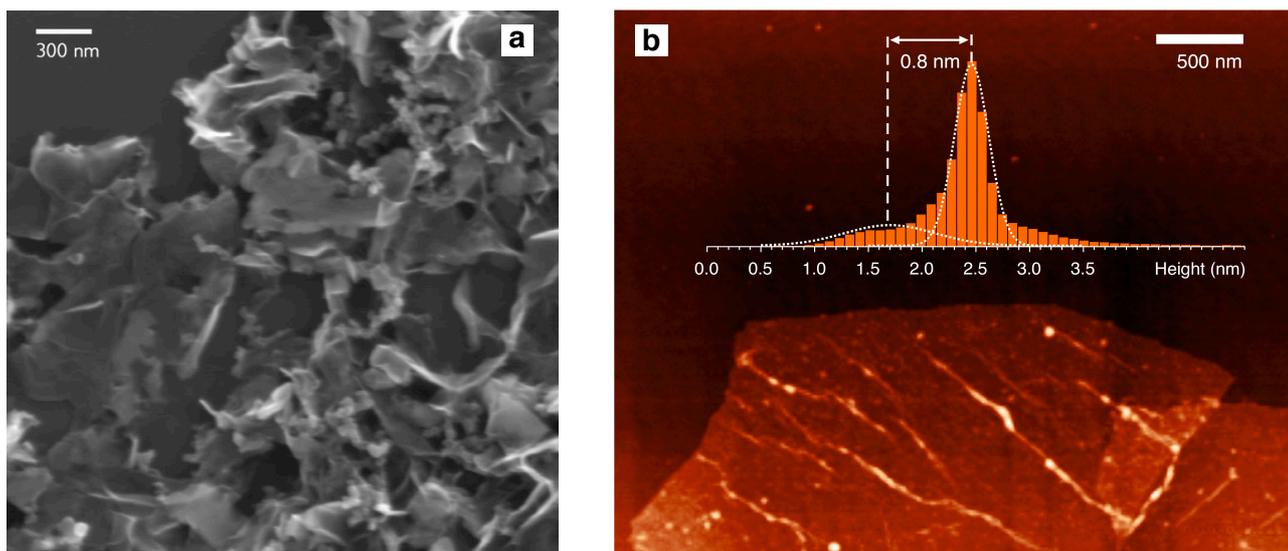
$$C = 10^6 \cdot I / k,$$

where C is a surface concentration, I - integral intensity of a spectral line, k - normalization constant. Values were multiplied by 10<sup>6</sup> for convenience.

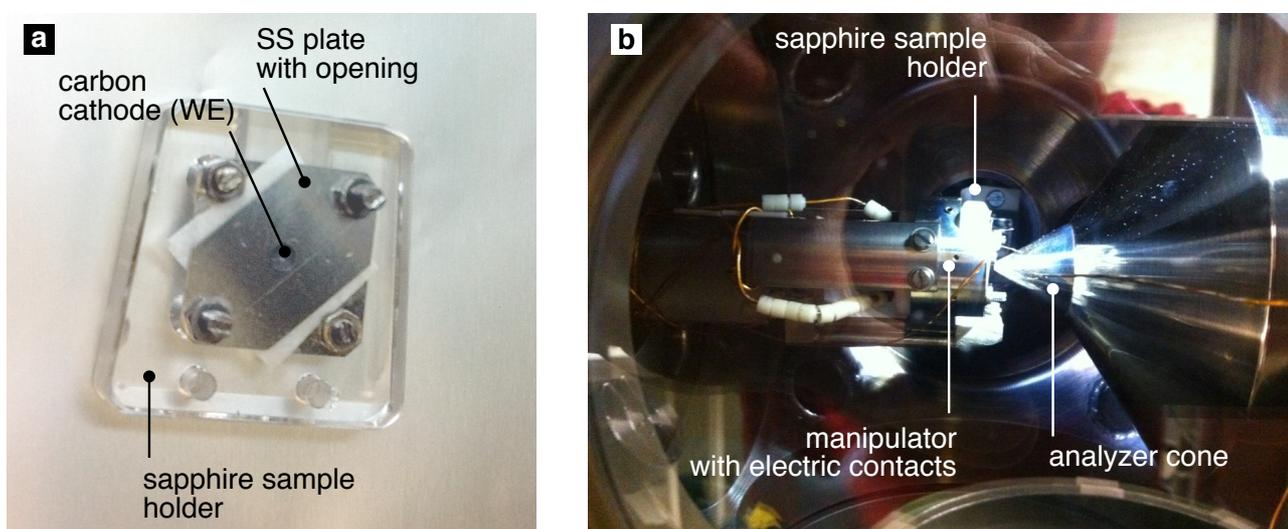
Normalization coefficients were calculated as a product of photon flux and photoionization cross-section for a given photon energy (see Table S2). Kinetics of carbonate formation was investigated while synchrotron operated in top-up regime with a constant ring current so no normalization for ring current was applied. Deep cell discharge was performed during decay mode so the normalization for ring current was applied.

**Table S2.** The normalization coefficients for composition calculations.

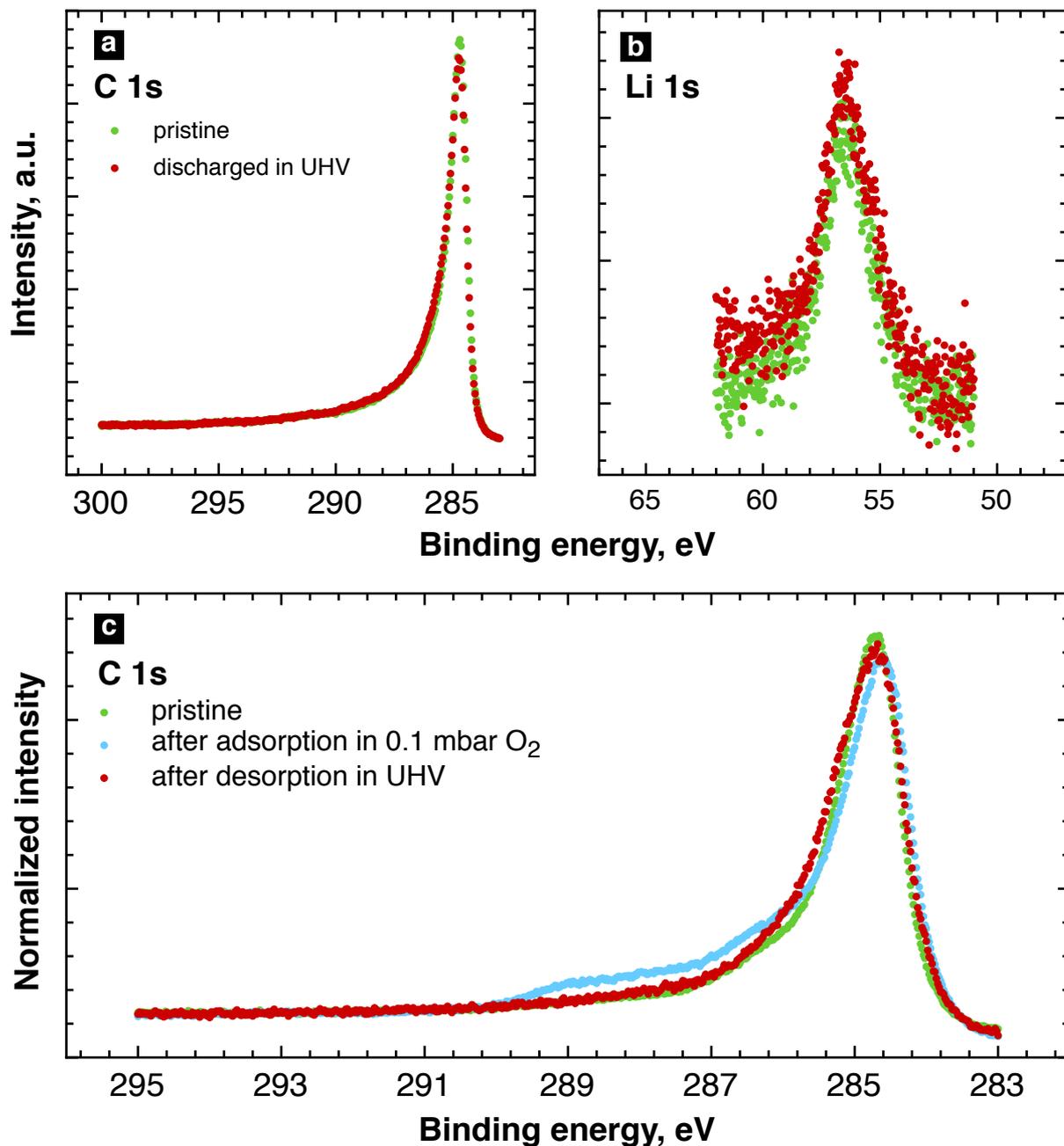
Line	Photon energy, eV	Flux, photons per 100 mA of ring current	Photoionization cross-section, Mbarn	k, a.u.
Li 1s	250	2.34E+10	0.1500	3.52E+09
C 1s	479	4.04E+10	0.2989	1.21E+10
O 1s	727	3.40E+09	0.2550	2.64E+10



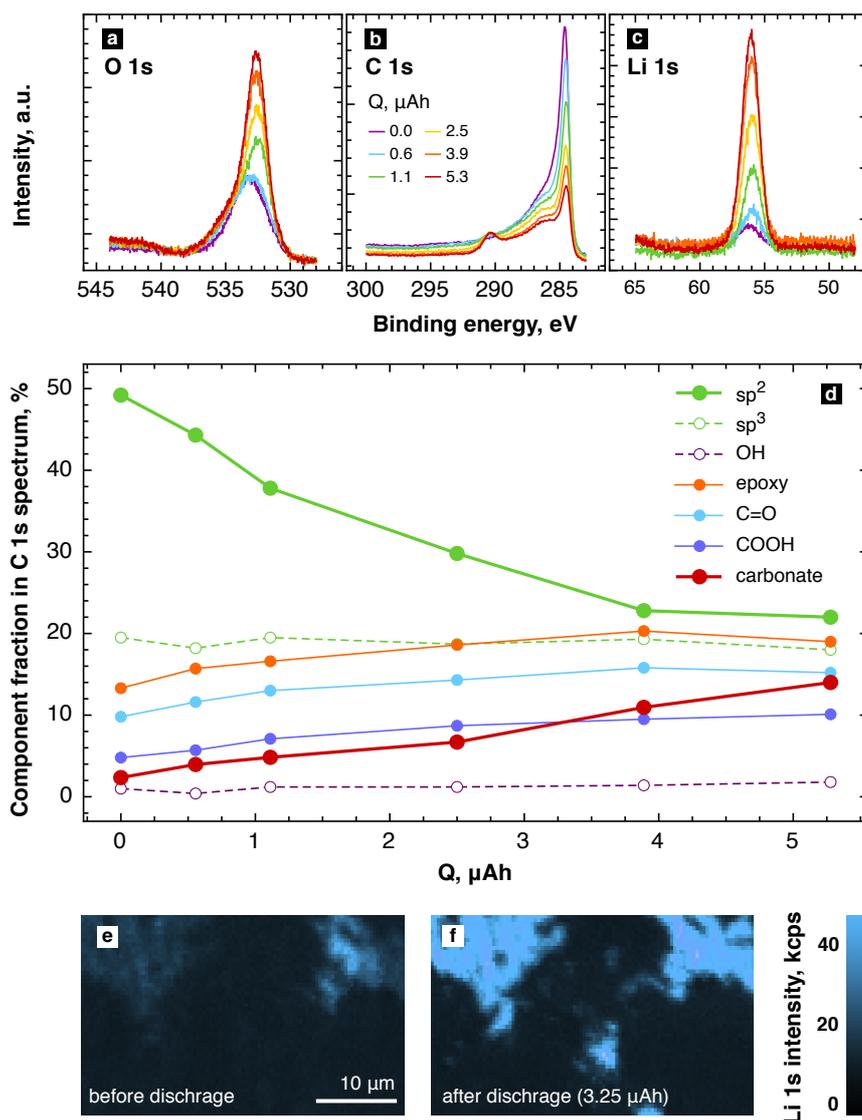
**Figure S1.** (a) SEM image of RGO flakes on silicon. (b) Tapping mode AFM image of an RGO flake. Histogram in the inset shows the height distribution for the image. Flake thickness is believed to be about 1 nm.



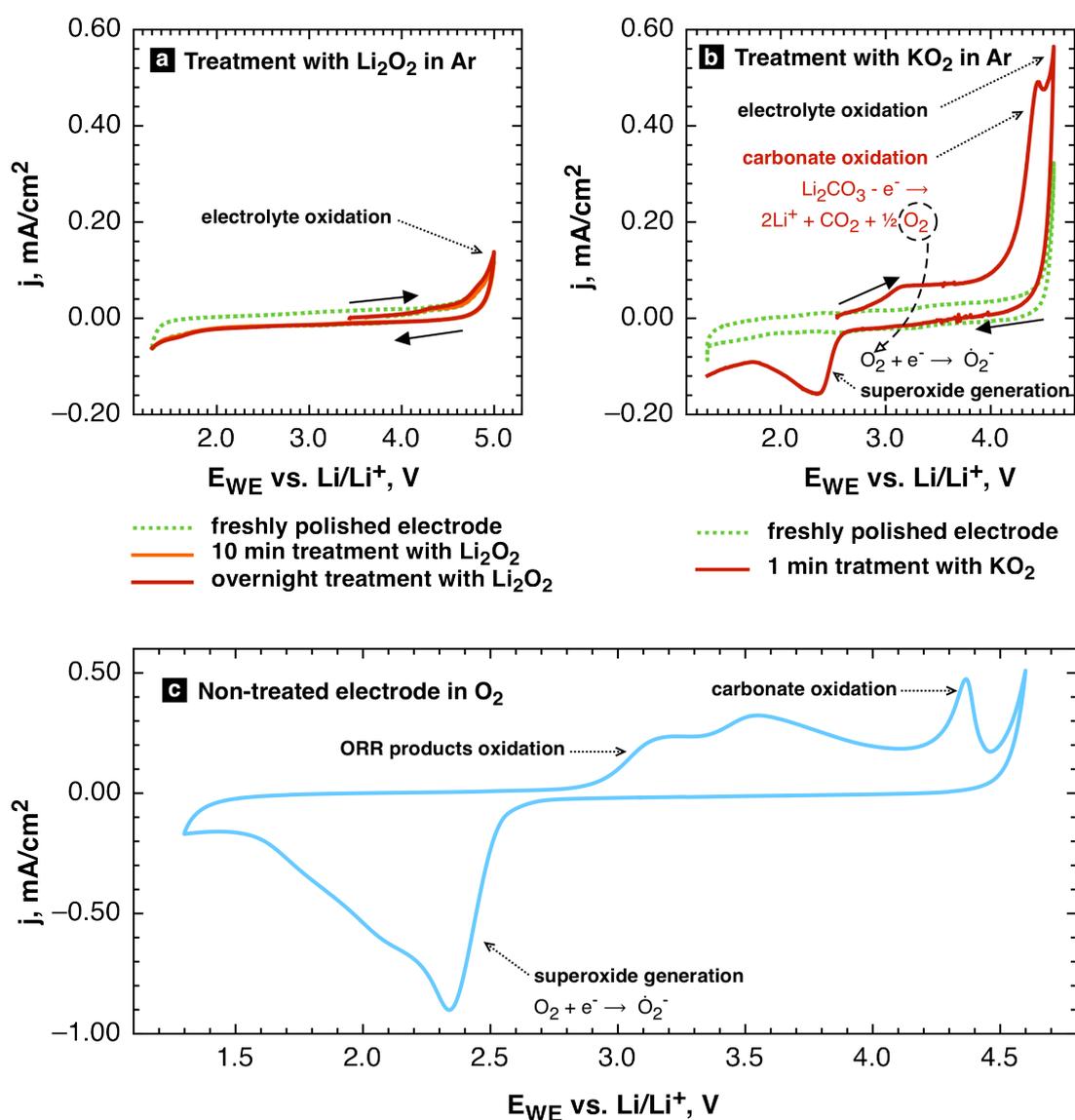
**Figure S2.** (a) Picture of the electrochemical cell for XPS studies in *operando* conditions mounted on the sapphire sample holder. (b) The same cell placed inside high-pressure XPS chamber of ISIS station at BESSY II.



**Figure S3.** Core-level C 1s (a) and Li 1s (b) spectra of a pristine RGO cathode and the same cathode after discharge current was applied. (c) C 1s spectra of the pristine RGO cathode, the same cathode after 1 hour exposure to 0.1 mbar oxygen and after oxygen desorption (1 hour in UHV). The shoulder in C 1s peak after exposure to oxygen is attributed to chemisorption of oxygen on carbon surface.



**Figure S4.** Core-level O 1s (a), C 1s (b) and Li 1s (c) spectra recorded at different states of the cell discharge (RGO was used as a cathode). Spectra of the pristine RGO cathode are marked as 0 mC (deep violet). (d) Component contributions to C 1s spectra recorded at different states of discharge. (e), (f) Maps of the Li 1s line intensity in initial and discharged states, respectively. Light-blue regions in the map of the RGO electrode discharged by 3.25  $\mu\text{Ah}$  correspond to high concentration of lithium-containing ORR products. Dark regions are non-conductive so no photoemission was registered. These non-conductive regions are not covered by conducting RGO film.



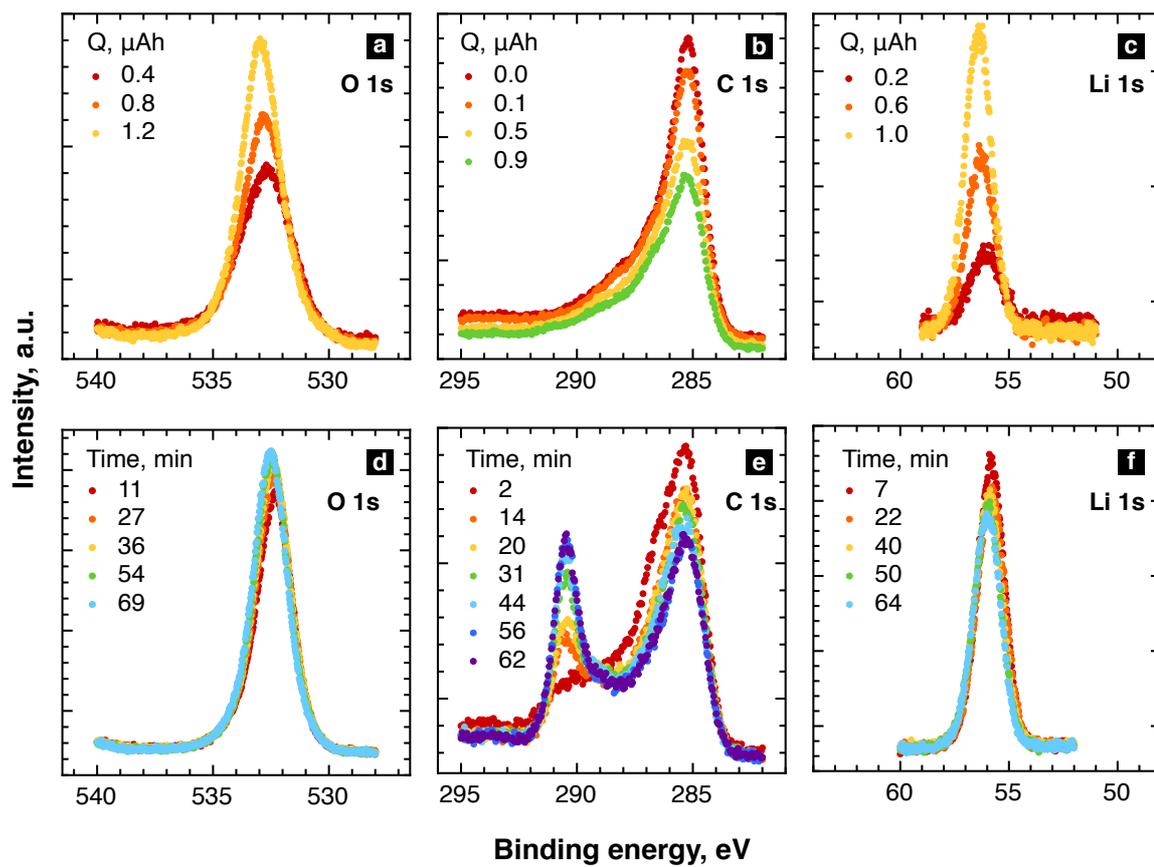
**Figure S5.** (a) Cyclic voltammograms (CVs) of clean freshly polished glassy carbon disk electrode (GCE) and the same electrode after treatment in lithium peroxide ( $\text{Li}_2\text{O}_2$ ) suspension in electrolyte. (b) CV of GCE treated with potassium superoxide ( $\text{KO}_2$ ). CVs after treatment with  $\text{Li}_2\text{O}_2$  and  $\text{KO}_2$  were recorded in Ar (inside the glovebox) starting from anodic scan. In contrast to  $\text{Li}_2\text{O}_2$ , treatment with  $\text{KO}_2$  resulted in the peak attributed to carbonate oxidation that occurred on first anodic scan. (c) CV of glassy carbon electrode recorded in oxygen-saturated electrolyte. Curves were recorded at 100 mV/s sweep rate.

Glassy carbon structure was investigated by Raman spectroscopy (see Figure S9) and found to be similar to RGO in terms of  $sp^2$ -to- $sp^3$  carbon ration (concentration of defects).

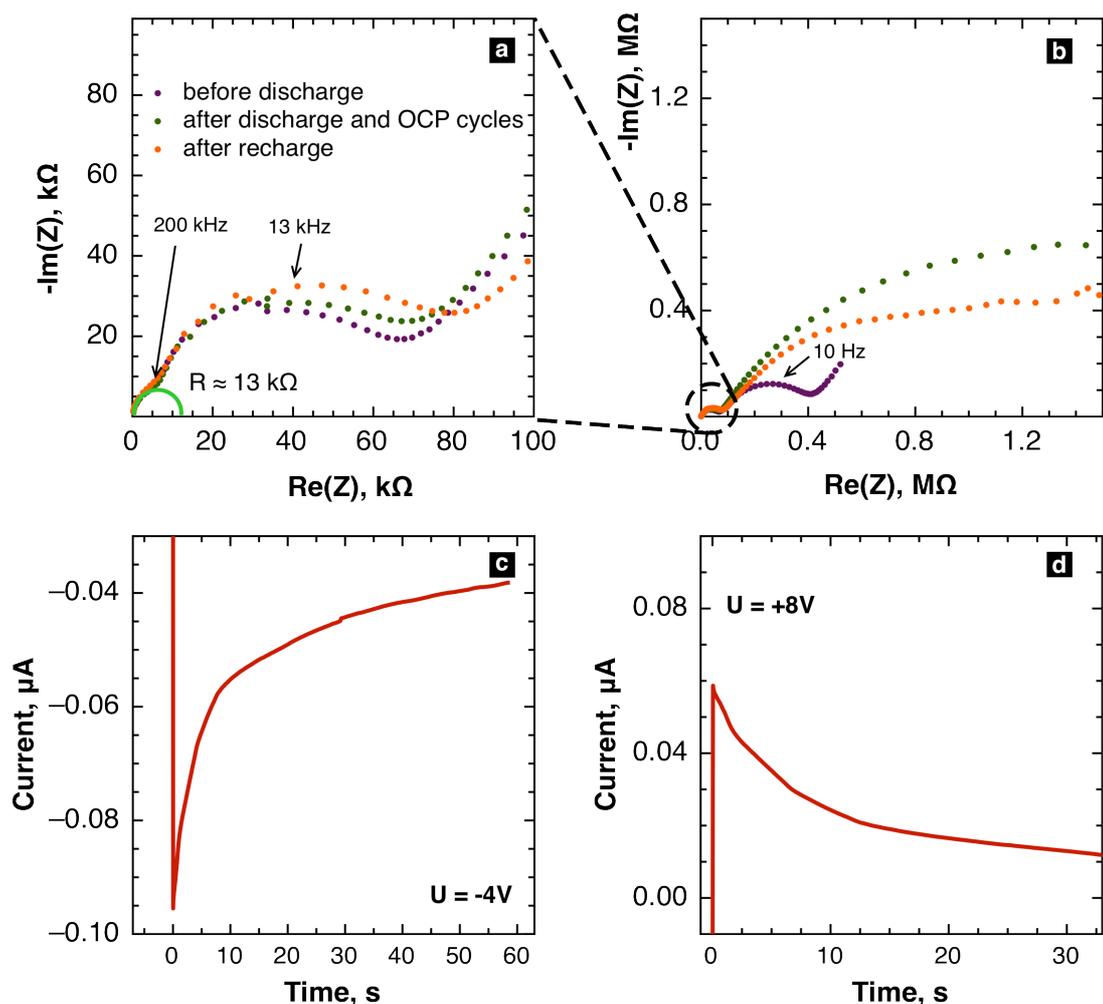
Cyclic voltammograms were recorded using Biologic SAS SP-300 potentiostat. Three-electrode glass cells (Dr.Bob's cell, Gamry instruments) with Pt counter electrode (CE) and lithium reference electrode (RE) were assembled inside Ar-filled glove box and filled with 0.1 M solution of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, Aldrich) in dimethylsulfoxide (anhydrous, Aldrich). Total water content in electrolyte was estimated to be about 90 ppm. Pt-wire CE was hermetically sealed inside a fritted tube. Lithium foil that served as RE was pressed onto Ni-grid, placed inside Vycor-isolated tube and sealed. RE tube was filled with 1M solution of  $LiClO_4$  (Aldrich, battery grade) in propylene carbonate 1,2-dimethoxyethane (7:3 by volume, both Aldrich, anhydrous). RE potential was checked versus ferrocene/ferrocenium redox couple. Oxygen purging was performed via gas bubbler tube.

Glassy carbon (Pine Research) treatment with  $Li_2O_2$  suspension was performed by immersion of the electrode into the slurry made of freshly prepared lithium peroxide and electrolyte inside the glove box. Lithium peroxide was prepared as described in Feher et al., *Chemische Berichte* 86, 1429-1437 (1953) using metallic lithium (China Energy Lithium Co.) and ethanol.  $Li_2O_2$  was dried over  $P_2O_5$  in vacuum ( $10^{-2}$  mbar) in the desiccator.

Treatment with  $KO_2$  was performed in the same way.  $KO_2$  (Aldrich) was used as received, suspension was prepared in pure dimethylsulfoxide (Aldrich, anhydrous).

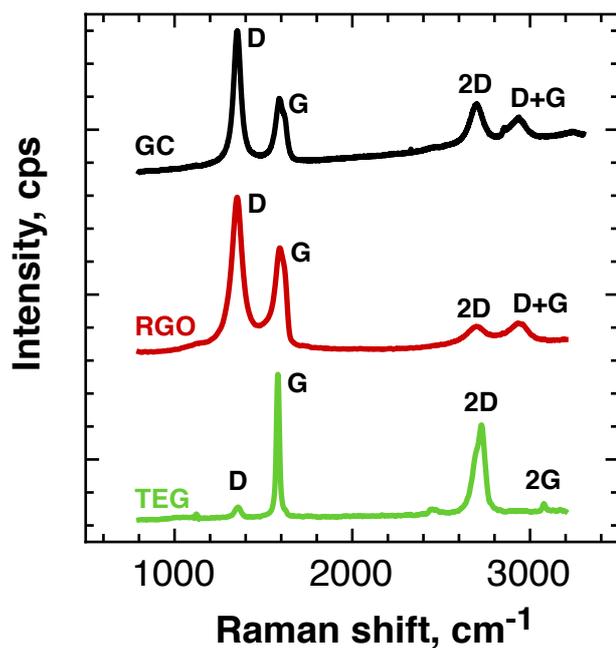


**Figure S6.** Oxygen, carbon and lithium 1s core level spectra recorded at 0.1 mbar  $\text{O}_2$  pressure during constant current discharge (a-c) and OCP cycle (d-f). Corresponding voltage profiles are reported in Figure 4a in the main text.

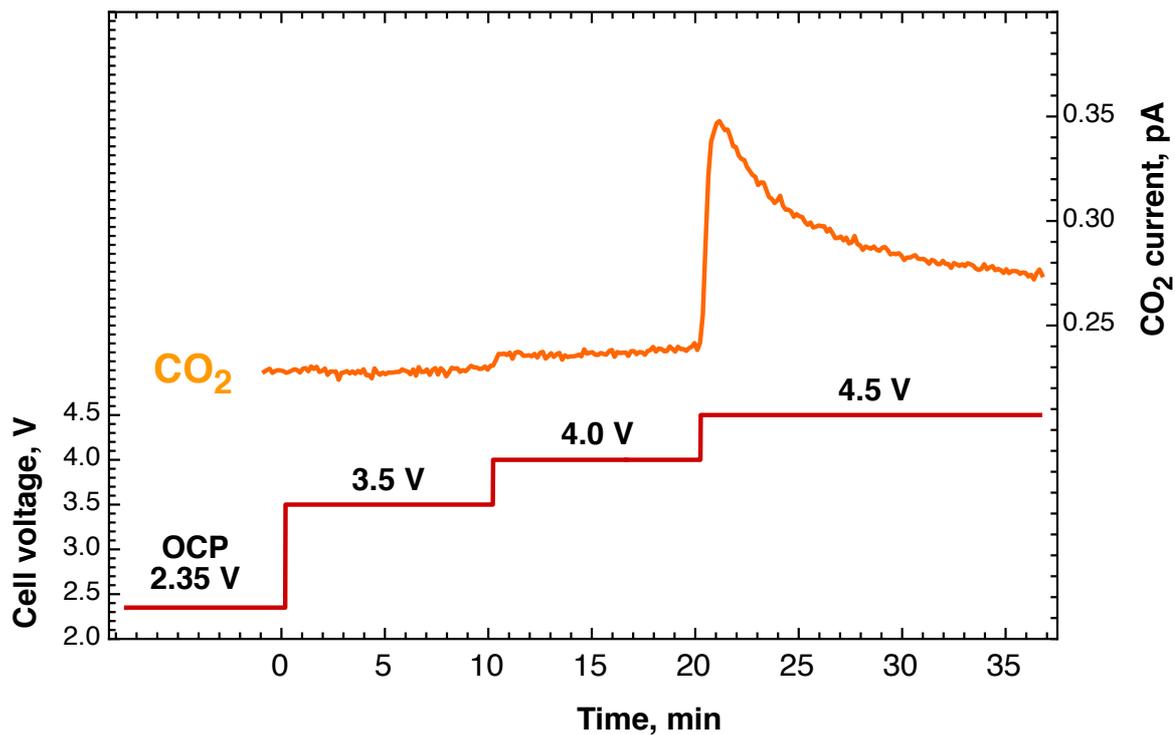


**Figure S7.** High-frequency part (a) and general view (b) of Nyquist plots of AC impedance spectra recorded for the cell with all-solid RGO cathode right after assembly and exposure to 0.1 mbar oxygen pressure, after OCP period, and after recharge (see Figure 4a in the main text). High-frequency semi-circle attributed to the ionic conductivity in the bulk of solid electrolyte is not altered after discharge and recharge. Working electrode was temporary ungrounded for recording of electrochemical impedance spectra (EIS). Spectra were registered at open circuit potential in the frequency range from 3.5 MHz to 30 mHz with 10 mV amplitude. (c, d) Cathodic and anodic currents recorded in Ar for the cell with ionic-blocking electrodes (20 nm Ni-film was sputtered onto the solid electrolyte surface instead of RGO deposition) after voltages -4V (c) and 8V (d) were applied. Recorded currents

(<0.1  $\mu\text{A}$ ) can be possibly attributed to solid electrolyte decomposition however they are much lower than those used in galvanostatic experiments (5  $\mu\text{A}$ ).



**Figure S8.** Raman spectra of glassy carbon (GC) electrode, used for cyclic voltammetry (see Figure S5), TEG and RGO. TEG is characterized by a much smaller amount of defects in contrast to RGO which are observed as a rise of the D band in the RGO Raman spectra, satisfying the fundamental selection rule for zone-boundary phonons. Moreover, TEG has more ordered stacking layers than RGO that is indicated by higher 2D peak intensity (Ferrari, A. C. *et al.*, *Phys. Rev. Lett.* 97, 187401 (2006)). GC has the D/G intensity ratio close to that of RGO.



**Figure S9.** CO<sub>2</sub> generation during cell recharge at constant voltage. Cell was preliminary discharged in constant current regime by about 1  $\mu$ Ah. Recharge was performed in UHV conditions.

The CO<sub>2</sub> ionic current was measured using Blazers Prisma QMS-200 quadrupole mass-spectrometer, installed in XPS chamber.