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Supporting Information

Na-O_2 Batteries: An in-situ X-ray Absorption Spectroscopic Study

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Abstract: Developing high energy density batteries, such as metal-air systems, requires a good understanding of their underlying electrochemical principles. In-situ characterization methods provide valuable insight toward discharge/charge mechanism of Na-O_2 cells. However, previous application of soft X-ray absorption spectroscopy has been limited to ex-situ studies on the discharge products of the cell. Here we report the in-situ soft X-ray absorption spectroscopic characterization of Na-O_2 cells, in order to study the formation and de-composition of the discharge products during battery cy-cling. Taking advantage of the elemental selectivity and chemical sensitivity of soft X-ray absorption spectroscopy, we reveal the instability of discharge products in the Na-O_2 cell environment. Our results illustrate that in-situ soft X-ray absorption spectroscopy is an efficient probe to study the electrochemical mechanism of alkali metal-O_2 energy storage systems.

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Experimental Procedures

Na-O_2 Cell Development

The high vacuum compatible liquid cell developed at Canadian light source was used to prepare a Na-O_2 cell. The liquid cell was prepared by 3D printing using a SLA printer from Somos Next. The cells were thoroughly cleaned and dried in a vacuum oven at 80^{o}C.

Na metal (a disk of ~ 2mm in diameter) was used as the anode and Si_3N_4 window coated with 5nm Cr and 30nm Au acted as the cathode. 0.5 M sodium triflate ($NaSO_3CF_3$ 98%, Aldrich) dissolved in diethylene glycol diethyl ether (DEGDME, reagent grade ≥98%, Aldrich – 2ml) was used as the electrolyte. The Na-O_2 cell was assembled in an argon protected glove box and placed in a homemade test box. The testing box was purged with pure oxygen and kept at a positive oxygen pressure for 1 hour to saturate the electrolyte in the liquid cell. Subsequently, the inlets of the cell were sealed and transferred into the measurement chamber.

Electrochemical and Physical Characterization

Discharge/charge measurements of Na-O_2 in-situ liquid cell were carried out using a CompactStat portable potentiostat at room temperature (25^{o}C). Swagelok type cells composed of sodium foil, Celgard 3500 separator, gold coated carbon cloth and stainless-steel mesh as current collector were used to study the effect of gold on the behavior of Na-O_2 cells and morphology of discharge products. An Arbin BT-200 battery station was used for discharge/charge study of these cells. Morphological studies were performed by Hitachi S-4800 field emission scanning electron microscopy operated at 5 kV.

X-ray Absorption spectroscopy

XAS measurements were conducted at the Canadian Light Source (CLS) located on the campus of the University of Saskatchewan. The O K-edge XAS spectra were recorded at the high resolution spherical grating monochromator (SGM) beamline with an energy resolution of $E/\Delta E \geq 5000$. The spectra were recorded in X-ray fluorescence yield (FLY) mode using four silicon drift detectors (SDD) under 10^{-6} Torr with beam spot size of 25μm.

The partial fluorescence yield (PFY) signal (O Kα) of O K-edge XAS spectrum was collected every 8 minutes during the electrochemical cycling of the cell.

All XAS spectra were normalized to the incident photon flux. All O K-edge spectra were calibrated to the t_{2g} peak of the standard rutile TiO_2 (Sigma Aldrich) powder.

X-ray Fluorescence (XRF) maps were recorded at different incident beam energies in the range of O K-edge using O, C Kα emission line fluorescence signals via using four detectors positioned at two angles (~ 0^o and 45^o) with respect to the Si_3N_4 window. The beam was focused using K-B mirrors to 20μm × 20 μm. The maps were collected over the cathode Si_3N_4 window.

Results and Discussion

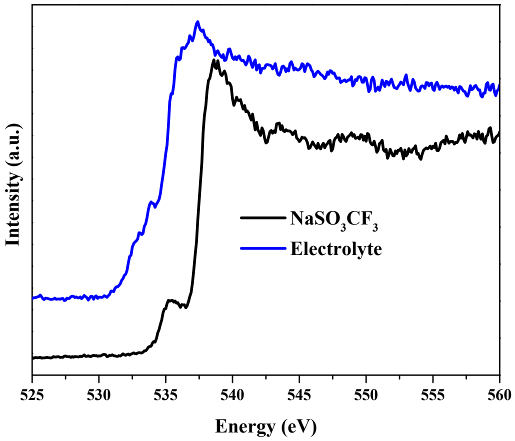

Figure S1. O k-edge XAS spectrum of Cell components. The O K-edge XAS spectra of the electrolyte and sodium salt as the main contributors of the O K-edge XAS spectrum, show a strong peak between 535eV and 540eV with small features between 533eVand 536eV.

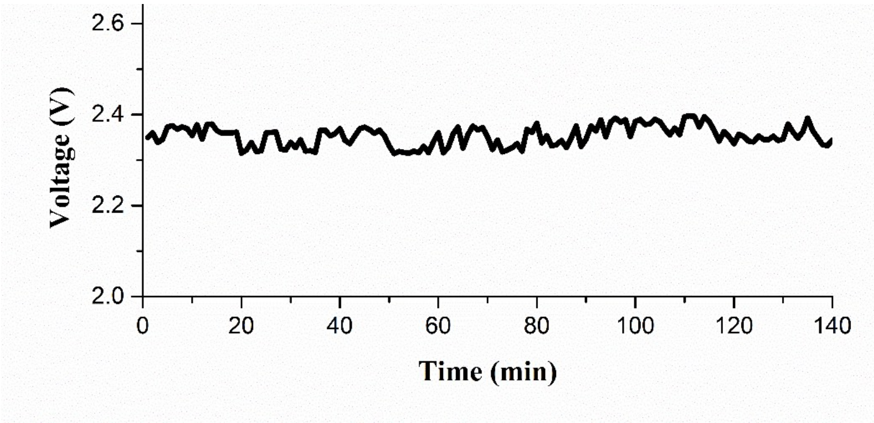

Figure S2. The open circuit voltage (OCV) of the liquid cell at different incident beam energies (500eV, 550eV and 600eV).

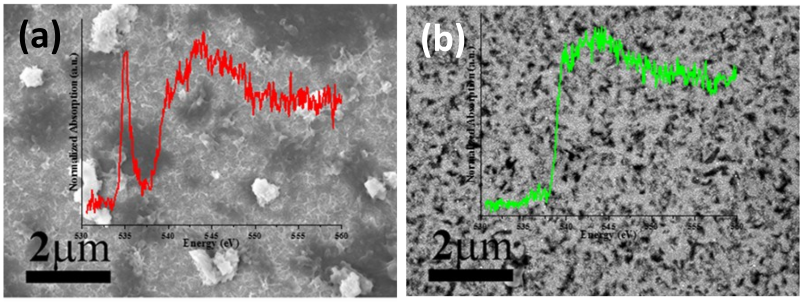

Figure S3. Scanning electron microscopy (SEM) and O K-edge XAS spectrum (inset) of the cathode electrode after (a) discharge process (b) charge process

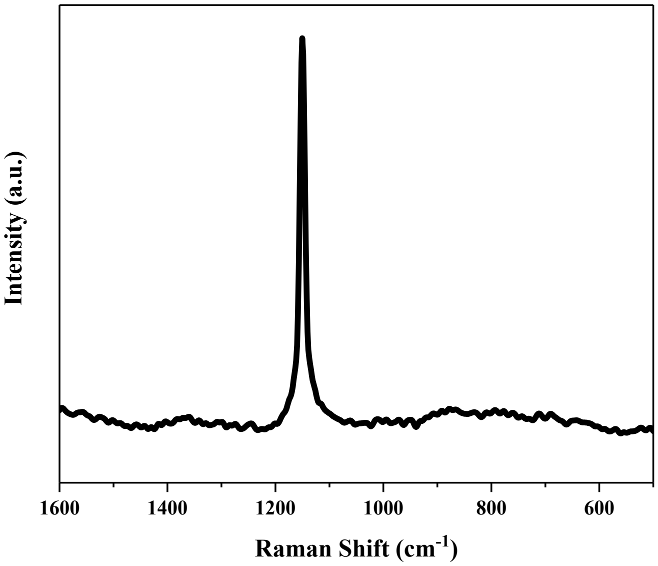

Figure S4. Raman spectrum of discharge products formed on the gold coated silicon nitride window after full discharge.

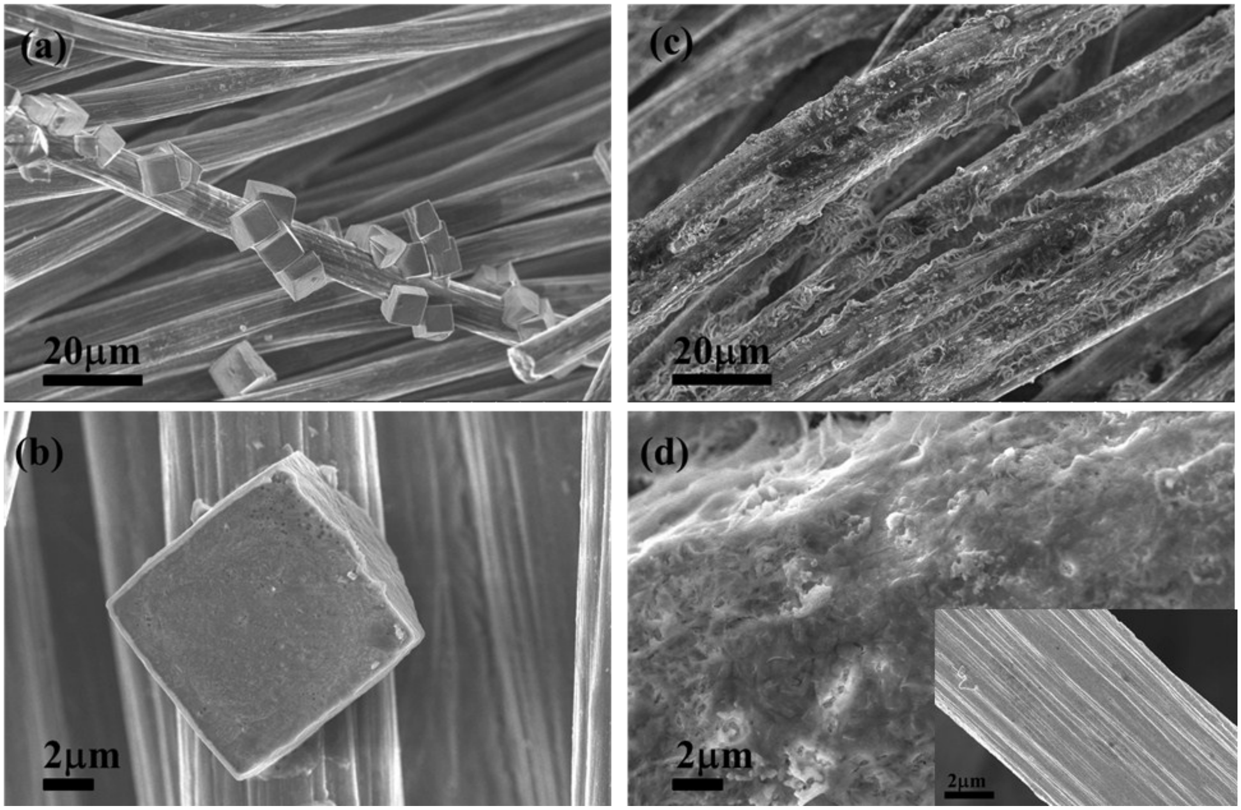

Figure S5. Discharge products on, (a, b) carbon cathode, (c, d) gold coated cathode after 1 hour discharge (inset: gold coated carbon fiber before discharge process).

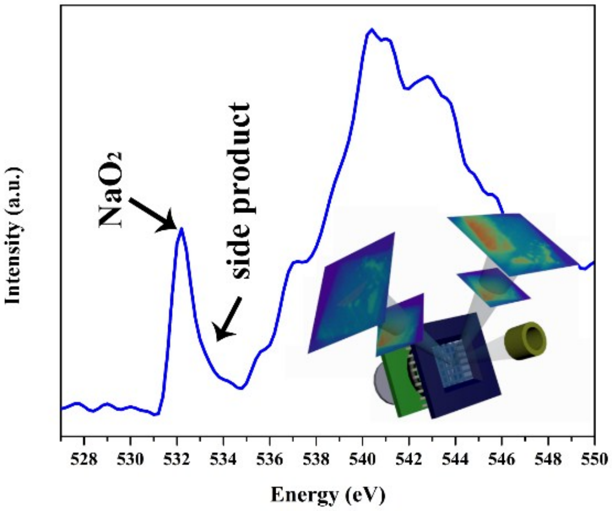

Figure S6. O K-edge XAS spectrum on cathode window, containing NaO_2 and side products formed after discharge and a 3 hours rest period.

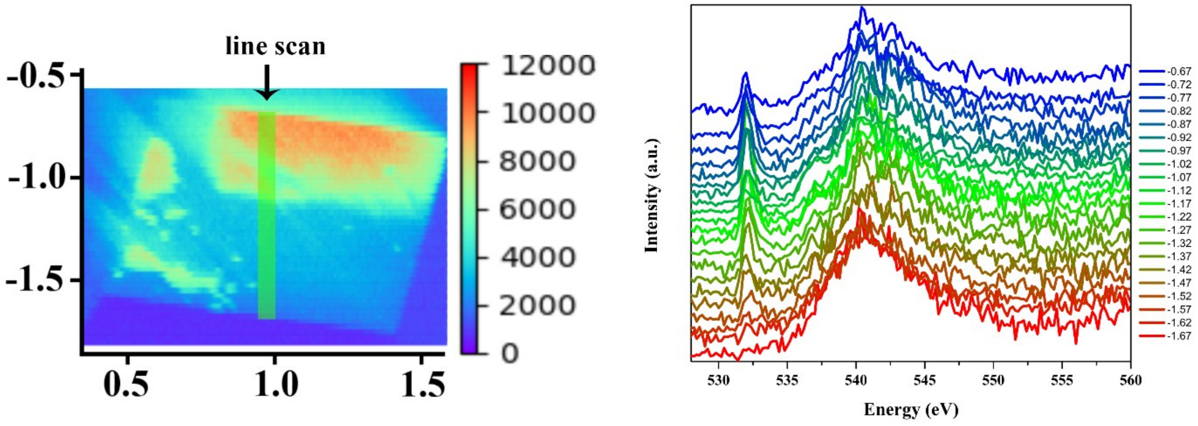

Figure S7. Line scan XAS spectra of O K-edge across the cathode window XRF oxygen emission map acquired at 600eV after discharge and a 3 hours rest period (the XAS spectra color corresponds to the color on the map).

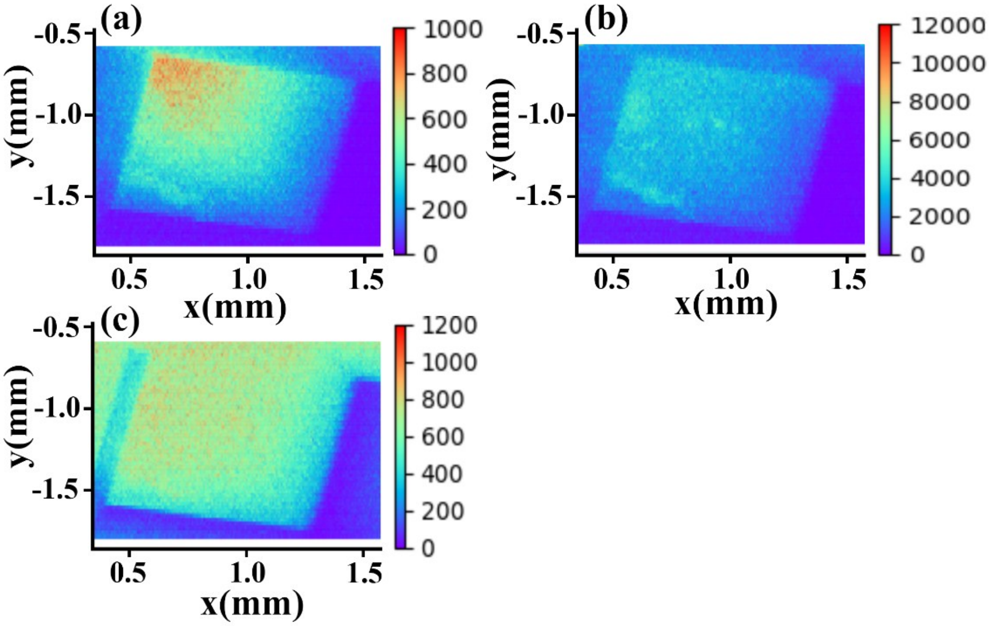

Figure S8. Oxygen emission line (Kα_2) XRF maps of the cathode window collected using 0^0 angle detector at incident energy of (a) 532eV [NaO_2 product], (b) 533.5 eV [side products]. (d) XRF map based on carbon emission line (Kα_2) of the cathode window at incident energy of 533.5eV

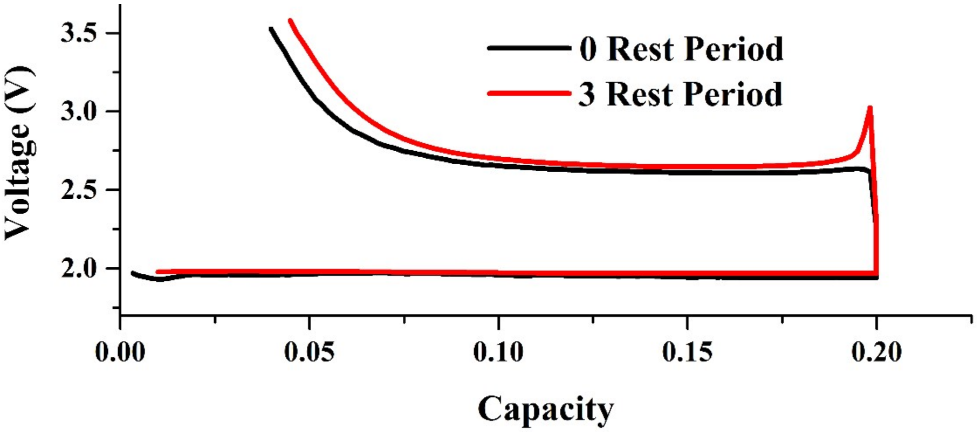

Figure S9. Restricted discharge/charge curves of Na-O_2 cell with and without 3 hours rest period.