

Supporting Information

Chemically Synthesized Lithium Peroxide Composite Cathode for Closed System Li-O₂ Batteries

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Materials and Methods

Materials

Graphitized carbon nanofiber (CNF) (D × L 100 nm × 20-200 μm, Sigma-Aldrich), lithium hydroxide monohydrate (LiOH.H₂O, 98+%, Acros Organics), hydrogen peroxide solution (H₂O₂, 50 wt. % in H₂O, Sigma-Aldrich), methanol (CH₃OH, low water, Fisher Chemical), lithium trifluoromethanesulfonate (LiCF₃SO₃, 98%, Acros Organics), lithium nitrate (LiNO₃, 99+%, Acros Organics), and 1,2-dimethoxyethane (DME, anhydrous, 99.5%, Sigma-Aldrich) were purchased and used as received.

Methods

Cathode preparation

Lithium hydroxide monohydrate was dissolved in 100 mL methanol to prepare 0.1 M LiOH solution. 100 mg of CNF was first vigorously stirred into the lithium hydroxide solution to

disperse it. This mixture was then ultrasonicated using a vibracell VC505 sonicator for 15 minutes causing the CNF to interweave. 15 mol % excess (with respect to $\text{LiOH}\cdot\text{H}_2\text{O}$) of 50% hydrogen peroxide solution was added dropwise into the dispersion under vigorous stirring at 35°C to form the composite consisting of $\text{Li}_2\text{O}_2\cdot\text{H}_2\text{O}_2\cdot 3\text{H}_2\text{O}\cdot 8\text{CH}_3\text{OH}$ in CNF. The products were vacuum filtered on to a 7 cm filter paper and washed repeatedly with methanol and ethanol. The cathodes thus formed were free-standing, flexible films of approximately 350 micron thickness and 7 cm in diameter. The cathode was dried under vacuum at $100\text{-}110^\circ\text{C}$ for 24 h to obtain the Li_2O_2 -CNF composite cathode that was quickly transferred into the glovebox with minimal exposure to air for further handling and testing.

Materials characterization

The Li_2O_2 content in the cathode was determined by thermogravimetric analysis (TGA) performed on a TA instruments SDT Q600 analyzer under argon gas flow at 50 mL min^{-1} while heating from 25°C to 500°C at $10^\circ\text{C min}^{-1}$. For comparison, TGA was also performed on mechanically ground Li_2O_2 powder and CNF mixed in appropriate ratios. TGA samples were transferred in alumina crucibles in sealed, argon filled vials. X-Ray Diffraction (XRD) was performed on a Bruker D8 Discover diffractometer with $\text{Cu K}\alpha$ radiation source for 2θ between 20° and 80° at a scan rate of $1.25^\circ\text{ min}^{-1}$. The XRD samples were prepared in the glovebox by washing the cathode several times with pure DME, dried in the glovebox and covered with a Kapton[®] film to prevent any exposure to air. Scanning electron microscopy (SEM) was performed with a JEOL JSM-7800F field emission scanning electron microscope equipped with energy-dispersive X-ray spectroscopy (EDS). SEM samples were mounted inside the glovebox after washing and drying and the samples were transferred to the microscope in an argon filled

sealed container. The cells used for *ex-situ* characterizations were appropriately cycled at $C/10$ rate before opening them to extract the cathode.

Cell assembly

The Li_2O_2 -CNF samples were cut into 7/16 inch cathode disks without additional current collectors. Electrodes were weighed before cell assembly to determine the mass of Li_2O_2 present. The electrodes weighed between 3 mg to 4.5 mg. The weight percent of Li_2O_2 in the sample obtained from TGA analysis was used to determine the active material loading in the cathode. An electrolyte consisting of 0.5 M LiCF_3SO_3 and 0.5 M LiNO_3 in DME was prepared. CR2032 coin cells were assembled with the binder-free, current collector-free, free standing flexible composite film as the cathode. 50 μL of the electrolyte was added to this cathode and a Celgard® 2400 separator was placed on it. An additional 30 μL of electrolyte was added before placing the Li-foil anode with a nickel foam current collector to complete the cell for crimping. The handling of the cathode and cell assembly were performed in an M-Braun glovebox with O_2 and H_2O content less than 0.1 ppm.

Electrochemical testing

The coin cells were galvanostatically cycled on an Arbin battery cycler at the appropriate C -rate calculated based on the active material loading on the cathode. A C -rate of 1C corresponds to 1,168 mA g^{-1} . The cells were charged to 4.3 V and discharged to 2 V. The cell was rested for 5 minutes between each step. Capacity controlled charging was done by limiting the charge capacity to 50% of the theoretical charge capacity of the cathode while cycling the

cell at the appropriate *C*-rate. These cells also had charge cutoff at 4.3 V and discharge cutoff to 2 V. Electrochemical impedance spectroscopy (EIS) data was collected using a Bio-Logic VSP impedance analyzer in the frequency range of 500 kHz – 100 mHz with Li metal foil as both counter and reference electrodes. The cells were cycled at *C*/10 in between these tests. Cyclic voltammetry (CV) was performed on a Bio-Logic VSP potentiostat between 4.3 and 2 V at a scanning rate of 0.1 mV s⁻¹.

Supporting Data

Thermogravimetric analysis

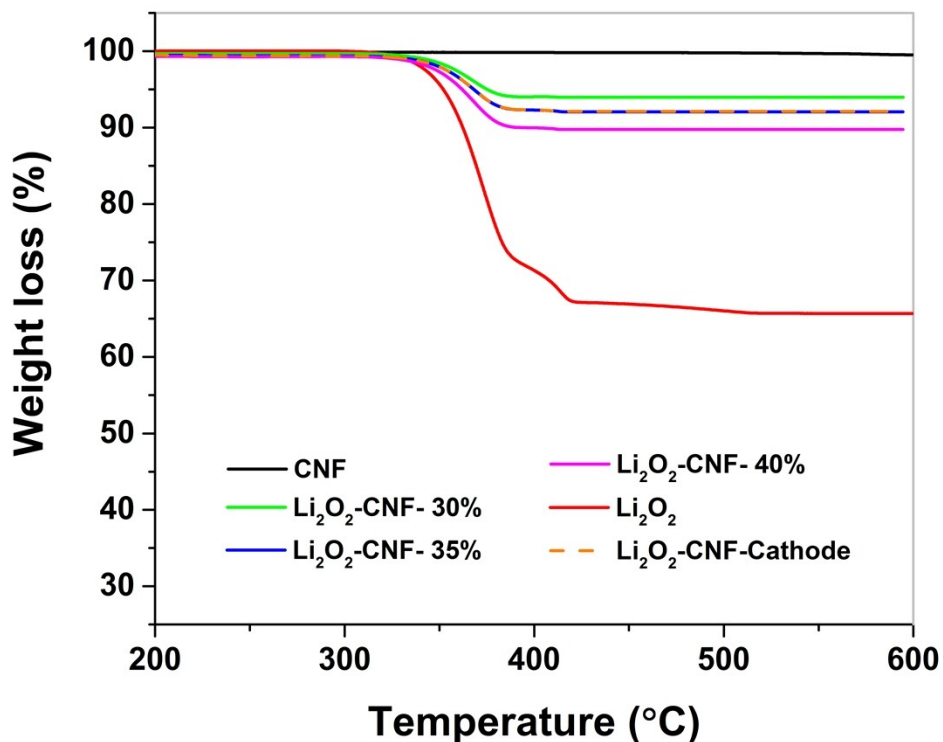


Figure S1. Thermogravimetric analysis of CNT, premixed Li₂O₂-CNF composites, pure Li₂O₂, and the Li₂O₂-CNF cathode sample.

High magnification SEM image

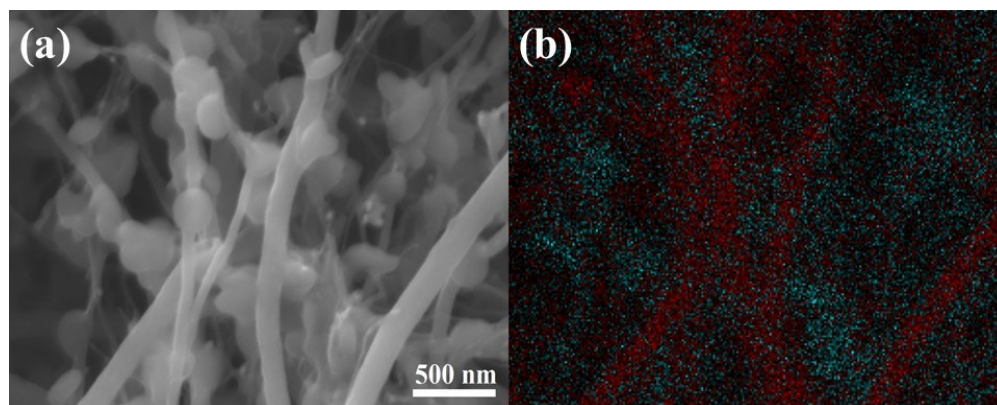


Figure S2. High magnification SEM showing (a) the Li₂O₂ platelets formed during discharge with (b) EDX mapping of the same. Blue represents oxygen and red represents carbon in the EDX map.

Voltage profile-capacity controlled cycling at *C*/10

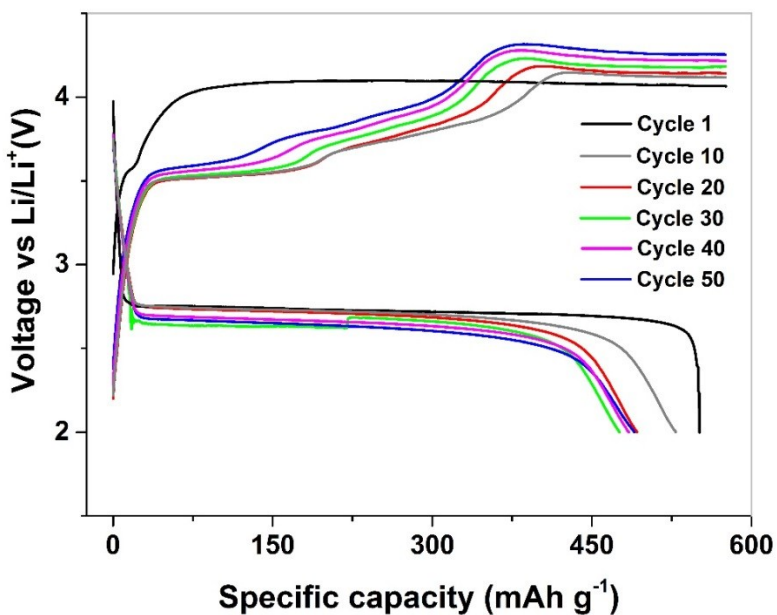


Figure S3. Voltage profile of charge capacity limited cell cycled at *C*/10 showing increased charge voltage and reduced discharge voltage as cell is cycled to 50 cycles. Charge capacity was limited to 50% of theoretical charge capacity of the cathode ($1 C = 1,168 \text{ mA g}^{-1}$).

Voltage profile-capacity controlled cycling at higher rates

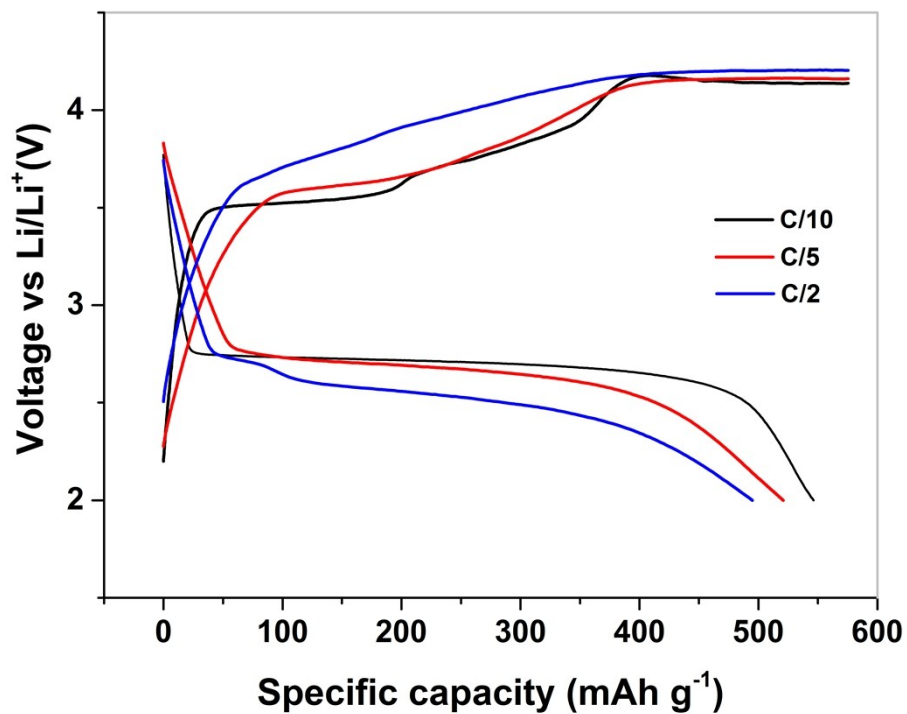


Figure S4. Representative voltage profiles of 5th cycle for cells cycled at different C-rates under capacity controlled regime with capacity limited to 50% of theoretical charge capacity of the cathode. ($1C = 1,168 \text{ mA g}^{-1}$).