

Supplementary Information

Promoting Li_2O_2 oxidation by $\text{La}_{1.7}\text{Ca}_{0.3}\text{Ni}_{0.75}\text{Cu}_{0.25}\text{O}_4$ layered perovskite in lithium-oxygen batteries

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1. Materials preparation

For preparation of an $\text{La}_{1.7}\text{Ca}_{0.3}\text{Ni}_{0.75}\text{Cu}_{0.25}\text{O}_4$ (LCNC) material, desired amounts of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99%, Aldrich), $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (> 99.0 %, Aldrich), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.999 %, Aldrich) and $\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (99.999 %, Aldrich) were dissolved in a mixture of deionized water and ethylene glycol (EG, $\text{HOCH}_2\text{CH}_2\text{OH}$, 99.8%, Aldrich). Citric acid ($\text{HOC}(\text{COOH})(\text{CH}_2\text{COOH})_2$, $\geq 99.5\%$, Aldrich) was added to the solution under stirring conditions and then heated to 70°C. The molar ratios of citric acid to metal were maintained at 3:1. The resulting solution was heated to 150°C to form a viscous gel. The gel was dried at 250°C and then calcined at 900°C for 5 h to remove any remaining organic materials. The sample was finally pulverized by grinding into fine powders.

2. Materials characterization

(a) X-ray diffraction (XRD) analysis

XRD patterns were recorded with an automated Rigaku diffractometer (2500 D/MAX, Rigaku) using Cu K_α radiation. The measurements were conducted over the scanning angle range of 20 – 80° using a step width of 0.025° and a holding time of 5 s.

(b) Neutron powder diffraction (NPD) analysis

NPD data were collected at room temperature for all the compounds using the high-resolution powder diffractometer (HRPD) at Hanaro Center of the Korea Atomic Energy Research Institute. NPD data were collected over scattering angles ranging from 0° to 160° using 1.8348 Å neutron. 3 g of each sample was contained in a vanadium can. The collection

time was 4 h per pattern. Diffraction data were analyzed by the Rietveld method, using the General Structure Analysis System (GSAS), with the use of its internal tables for scattering lengths. The line shape of the diffraction peaks was generated by a pseudo-Voigt function and the background refined to a 1st degree polynomial. In the final run the following parameters were refined: background coefficients, zero point, half width, pseudo-Voigt and asymmetry parameters for the peak shape, scale factor and unit-cell parameters.

(c) Surface area and FTIR measurements

Brunauer-Emmett-Teller (BET) surface area was determined from N₂ sorption isotherms by using a BEL-SORP mini system. FTIR measurements were carried out on a Nicolet 6700 spectrometer (ThermoFisher Scientific) in transmission mode with a KBr pellet.

3. Electrochemical experiments

(a) Charging experiments with Li₂O₂-packed electrodes

Electrochemical cells were constructed based on a Swagelok design and composed of a Li metal anode, an electrolyte (1 M LiTFSI in TEGDME) impregnated into a glass fiber separator and a porous cathode. Cathodes artificially packed with Li₂O₂ were prepared by casting a mixture of Ketjen black (KB), catalyst, ground Li₂O₂ (Alfa Aesar) and PVdF-co-HFP (Kynar 2801) in N-Methyl pyrrolidinone (NMP) onto Ni mesh current collector, followed by vacuum drying at 70°C for 24 h. The composite electrode consisted of 50 wt.% KB, 15 wt.% catalyst, 15 wt.% Li₂O₂ and 20 wt.% binder. Galvanostatic charging tests were performed at a current density of 67 mA g⁻¹ (based on the mass of Li₂O₂) using a Maccor Series 4000, and potentiostatic current transient measurements were conducted by jumping the potential from an open circuit potential to 4.1 V vs. Li/Li⁺.

(b) Evaluation of Li-O₂ battery performances

Li-O₂ batteries and cathodes were prepared under the same conditions as described above, except no Li₂O₂ was initially included in the cathode. Galvanostatic discharge-charge profiles were measured at a current density of 40 mA g⁻¹ (based on the mass of carbon). For cycling experiments, batteries were discharged and charged at 80 mA g⁻¹.

4. NPD refinement results

Table S1 Refined structural parameters for $\text{La}_{1.7}\text{Ca}_{0.3}\text{Ni}_{0.75}\text{Cu}_{0.25}\text{O}_4$ obtained from the Rietveld refinement using NPD data at room temperature. Here, g and U_{iso} represent the occupation and isotropic thermal parameters, respectively. The numbers in parentheses are the estimated standard deviations of the last significant figure.

atom	site	x	y	z	g	$100*U_{\text{iso}}/\text{\AA}^2$
La	4e	0	0	0.3621(2)	0.85 ^{a)}	0.49(2) ^{b)}
Ca	4e	0	0	0.3621(2)	0.15	0.49(2)
Ni	2a	0	0	0	0.75 ^{a)}	0.58(2) ^{b)}
Cu	2a	0	0	0	0.25	0.58(2)
O1	4c	0	1/2	0	1.0	0.85(1)
O2	4e	0	0	0.1764(2)	1.0	1.73(2)

space group: $I4/m\ m\ m$ (No. 139) and $Z = 2$

$a = b = 3.8173(6)\ \text{\AA}$, $c = 12.7752(2)$, $\alpha = \beta = \gamma = 90^\circ$

$R_{\text{wp}} = 7.39\%$, $R_{\text{p}} = 5.30\%$, $S (= R_{\text{wp}}/R_{\text{e}}) = 2.82$

a) Constraints on isotropic thermal factors: $U_{\text{iso}}(\text{La}) = U_{\text{iso}}(\text{Ca})$, $U_{\text{iso}}(\text{Ni}) = U_{\text{iso}}(\text{Cu})$.

b) Constraints on occupation factors: $g(\text{La}) + g(\text{Ca}) = 1$, $g(\text{Ni}) + g(\text{Cu}) = 1$.