Supporting Information

Mesoporous La_{0.6}Ca_{0.4}CoO₃ Perovskite with Large Surface Area as Stable Air Electrode for Zn-air Rechargeable Battery

Tatsumi Ishihara,^{1,2*} Limin Guo,¹ Takayoshi Miyano,² Yuiko Inoishi,² Kenji Kaneko,³ and Shintaro Ida^{1,2}

¹⁾International Institute for Carbon-Neutral Energy Research (WPI-I²CNER), Kyushu University, Motooka 744, Nishi-ku, Fukuoka 819-0395, Japan
²⁾Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Motooka 744, Nishi-ku, Fukuoka 819-0395, Japan
³⁾ Department of Materials, Faculty of Engineering, Kyushu University, Motooka 744, Nishi-ku, Fukuoka 819-0395, Japan

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Experimental details

1. Preparation of bulk and mesoporous LCC perovskite

Bulk LCC was prepared by the conventional solid state reaction method. The precursor solution was prepared according to the molar ratio of $La_{0.6}Ca_{0.4}CoO_3$ using corresponding metal nitrates and proper amount of citric acid was also added as chelating agent. The experimental details for LCC precursor solution are as follows. 12 mmol La(NO₃)₃·6H₂O, 8 mmol Ca(NO₃)₂·4H₂O, 20 mmol Co(NO₃)₂·6H₂O, and 40 mmol citric acid were dissolved into the solution of 50 mL water and 50 mL ethanol. The LCC precursor was dried and caclined at 973K.

The mesoporous LCC was prepared by so-called "hard template method" and the mesoporous silica KIT-6 was used as hard template. [1,2] Firstly, KIT-6 was prepared according to the reported method.[3.4] Typically, 6 g of surfactant P123 and 6 g of n-butanol were dissolved in a HCl solution, which was prepared by mixing 11.8 g of HCl (37%) in 217g distilled water. After the solution became clear, 12.9 g of tetraethylorthosilicate (TEOS) was added into above prepared solution and stirred at 313 K for 24h. Then, the mixture was heated at 373 K for 24h. Thus obtained precursor powder was collected by filtration and dried in the oven at 358 K. After calcination at 823 K for 4 h, KIT-6 with single phase (BET surface area 535.3 m2/g, average pore size 3.1 nm) was obtained and further use for hard template.

10 mL LCC precursor solution was added into 0.5 g KIT-6. Then, the mixture was stirred to evaporate the solvent for 6 h at room temperature. Hereafter, the mixture was totally dried in the oven at 353K. The obtained KIT-6 impregnated with LCC precursor powder was calcined at 973K for 4 h. Then, the silica template KIT-6 was removed by 2 M NaOH at room temperature and dried after thoroughly washing by water. The obtained mesoporous LCC was analyzed with N2 gas adsorption method, TEM (JEOL 2010) and XRD (Cu K α line used, Rigaku Rinto type 2500).

2. Air electrode performance

Oxygen air electrode performance of the obtained LCC was measured with gas diffusion electrode (GDE). LaCoO₃, graphitic carbon, and PTFE powder was mixed at 42.5:42.5:15 and pressed onto gas diffusion carbon plate. 4M KOH aqueous solution and Hg/HgO standard electrode were used for electrolyte and reference electrode. Oxygen was flowed for air electrode at 100ml/min and constant current was applied by Potentiostat/Galvanostat (Hokuto HA301) and potential was measured with digital multimeter (Advantest 5406).

Zn-air battery was fabricated by using the mixture of $La_{0.6}Ca_{0.4}CoO_3$;graphitic carbon (Denka Black); PTFE=52.5:42.5;15, which was pressed onto stainless steel mesh. Zn plate was used for anode and 4MKOH solution was used for electrolyte. Handmade cell was used and the fabricated cell was set into air atmosphere. Two probe method was used for charge and discharge performance. Battery test equipment was used for measurement of electrochemical performance in the potential windows from 0 to 2V. Current density at 8, 10, 50, and 100 was applied for discharge and that at 4 mA/cm² was applied for charge.

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Figure S1. Schematic image of the mesoporous LCC preparation process.[1,2]



Figure S2 TEM image of the prepared mesoporous LCC.

TEM image shows the sample is highly porous and consisted of nanorodes and plate like particles.



Figure S3. (a) ORR and (b) OER curves on bulk and mesoporous LCC. Measurement was performed at rotating electrode at 2000 rpm in O_2 bubbling condition. Obviously, reasonably high on-set potential for ORR (ca.0.75V) and OER (1.35V) was observed. For ORR current, bulk LCC shows higher current density than mesoporous LCC, however, for OER, mesoporous LCC shows much larger reduction current.



Figure S4. Comparison of discharge and charge curves of Zn-air battery using Pt/C, mesoporous and bulk LCC64 for air electrode. When Pt/C was used for air electrode, discharge potential is high at low current density, however, discharge can not be performed at high current density and the observed discharge capacity was only 300 mAh/g_{-Zn}. In contrast, the cell using LCC, much larger discharge capacity was achieved.



Figure S5 I-V characteristics for Zn-air batteries with (a) bulk LCC and (c) mesoporous LCC electrodes. 4M KOH electrolyte was used. Discharge period at 8,10,20 and 30 mA cm⁻² was 30 min each and other current density was 1 min. Obviously, the cell using mesoporous LCC shows superior rate property and the current up to 250 mA/cm² was achieved. The cell using mesoporous LCC shows higher terminal potential at each current density resulting in the higher power density.