Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.
This journal is © The Royal Society of Chemistry 2019

Supplementary Information

Highly Nanocrystalline Interconnected $La_{0.5}Ca_{0.5}CoO_{3-\delta}$ as an Efficient Bi-functional Electrocatalyst for Zinc-Air Battery with Structural and Morphological Evidence for ZnO Mitigation

Inthumathi Kanagaraj[a,b], Prabu Moni[a,b],A. S. Prakash[‡ a,b]

[a]CSIR-Central Electrochemical Research Institute-Chennai Unit, CSIR Madras Complex, Taramani, Chennai 600113, India.

[b]Academy of Scientific and Innovative Research (AcSIR), Ghaziabad- 201002, India.

[‡]Corresponding author Email: prakash.as@gmail.com

Electronic supplementary Information (ESI) available: XRD, EDX, FE-SEM images of LCCO.

Synthesis of $La_{0.5}Ca_{0.5}CoO_{3-\delta}$ by solid state method (Bulk LCCO)

All chemicals La_2O_3, $CaCO_3$, and $Co(CH_3COO)_2.4H_2O$ were procured from ACROS Organics and used without further purification. In a typical synthesis, 0.4147 g of La_2O_3, 0.2548 g of $CaCO_3$ and 1.2681 g of $Co(CH_3COO)_2.4H_2O$ were manually ground for 20 minutes using agate mortar and pestle. The ground mixture was pretreated at 400 ℃ for 2h then obtained powders were pressed into a pellet by applying hydraulic pressure (2 ton). The pellets were annealed at 1000 ℃ for 24 h in a box furnace at the heating rate of 5 ℃ min^{-1}. Finally, the sintered pellet was reground and used for further studies.

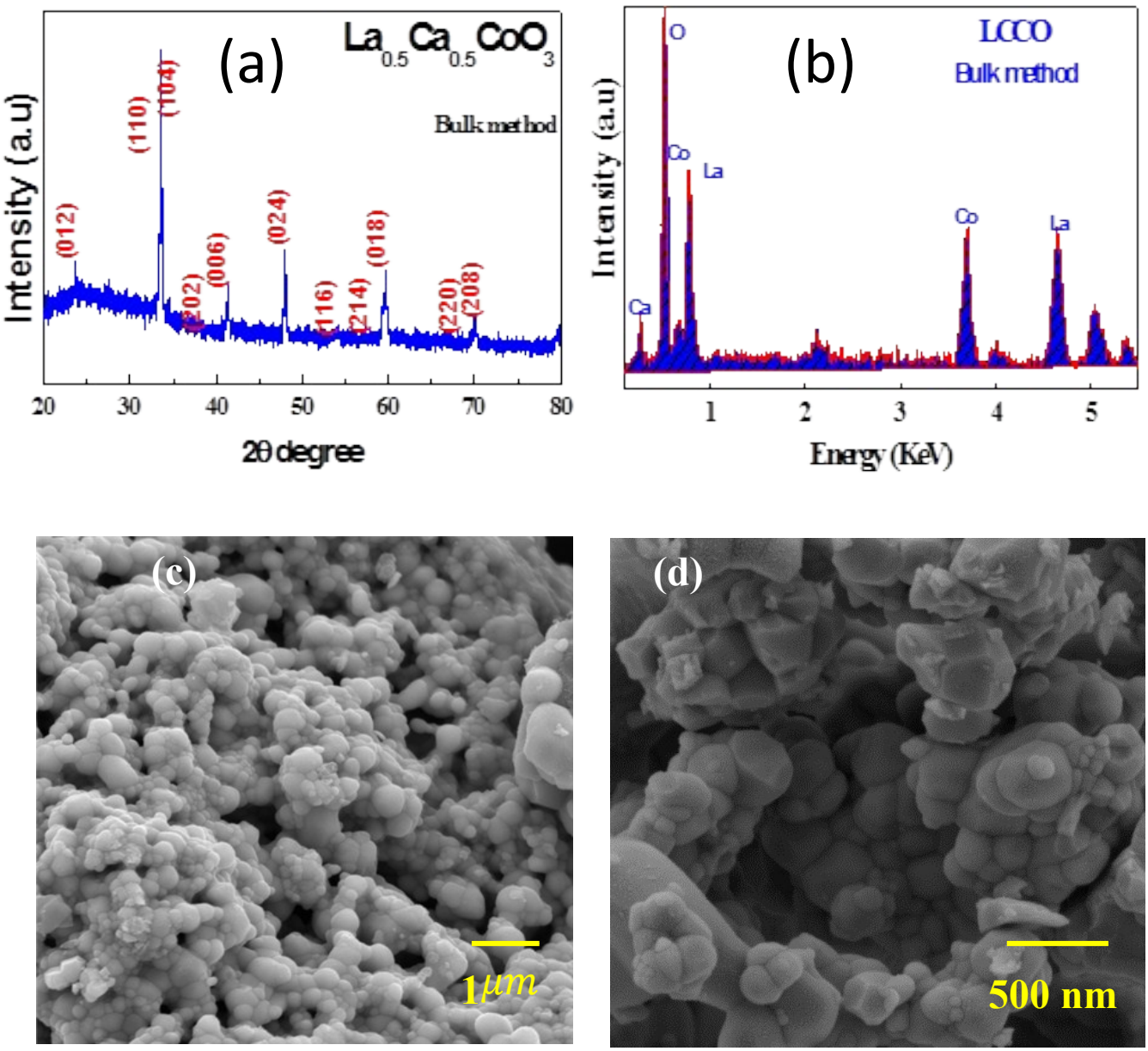

Fig. S1 *(a) XRD pattern, (b) EDX profile (c-d) FE-SEM images of bulk LCCO*

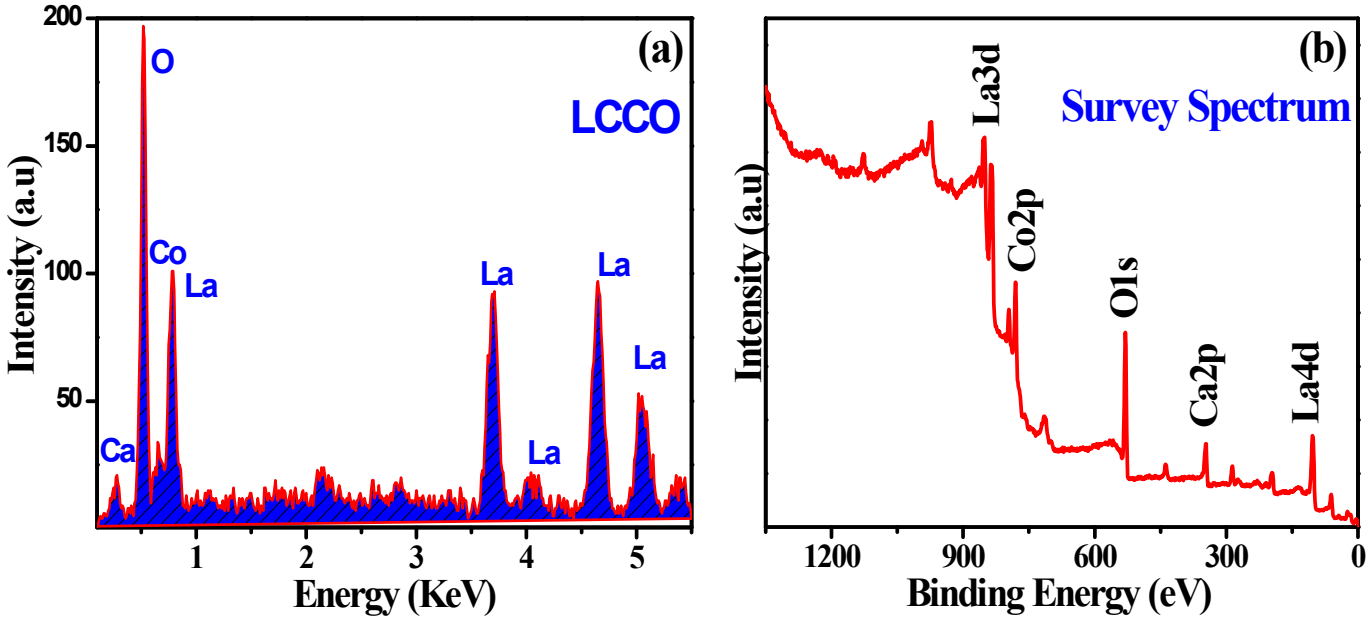

Fig. S2 *(a) EDX profile and (b) XPS survey spectrum of the nano LCCO*

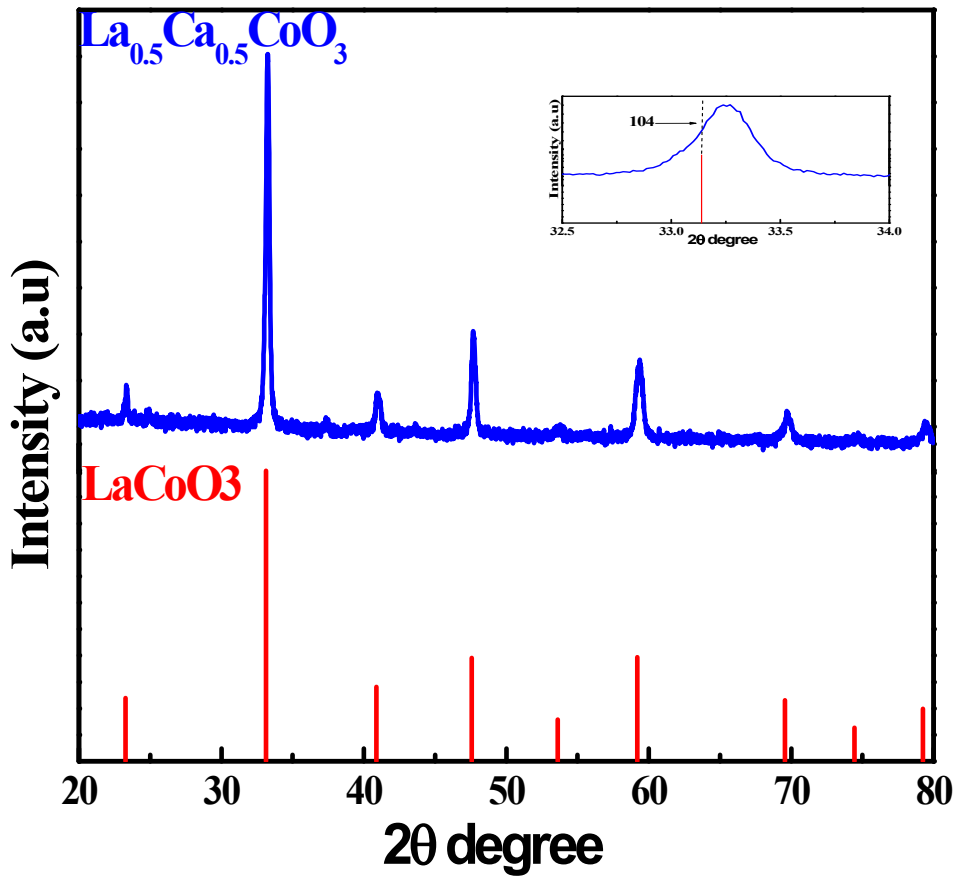

Fig. S3 *Comparison of $La_{0.5}Ca_{0.5}CoO_3$ X-ray diffraction pattern with parent $LaCoO_3$*

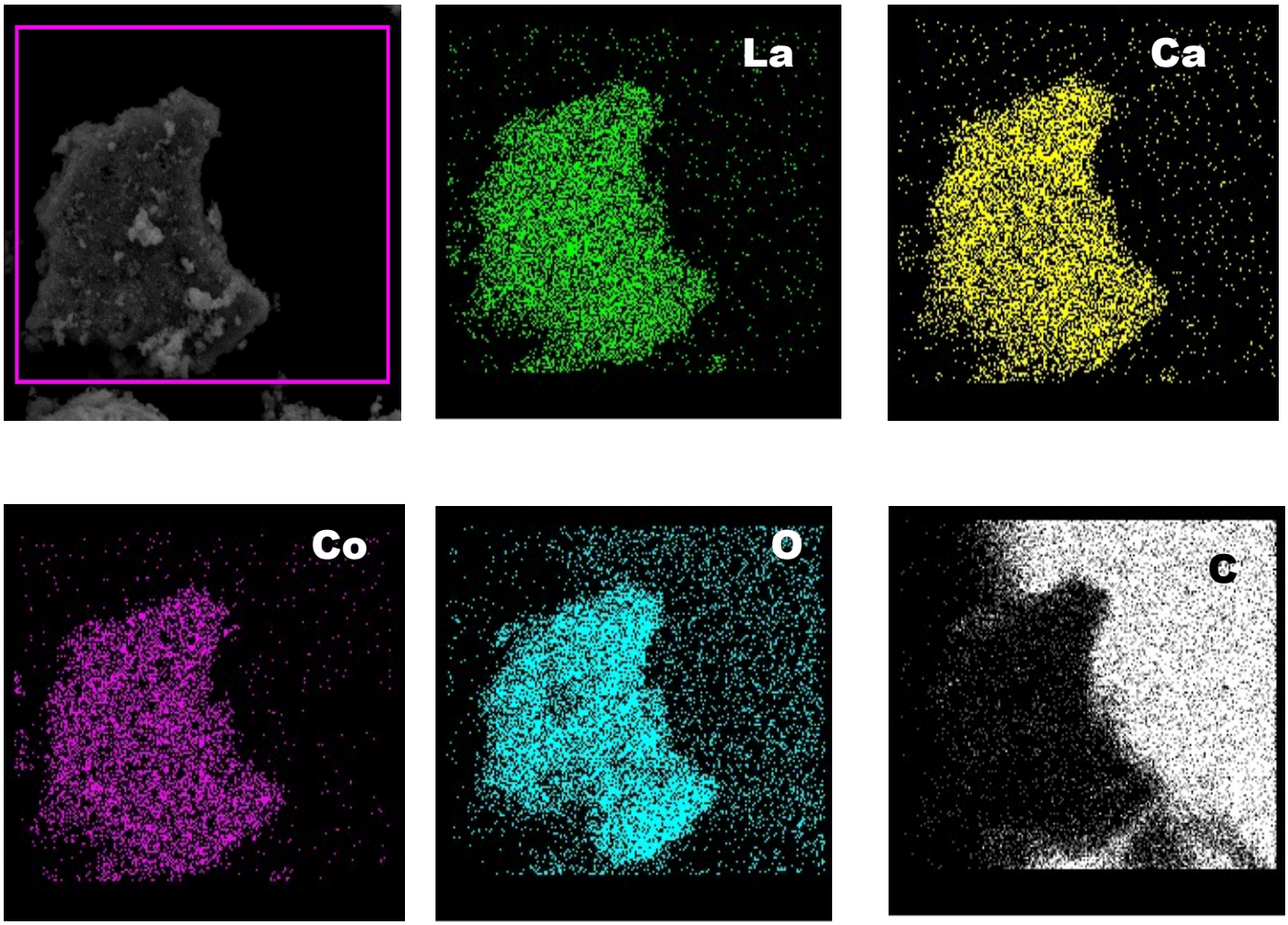

Fig. S4 *Elemental mapping of nano LCCO*

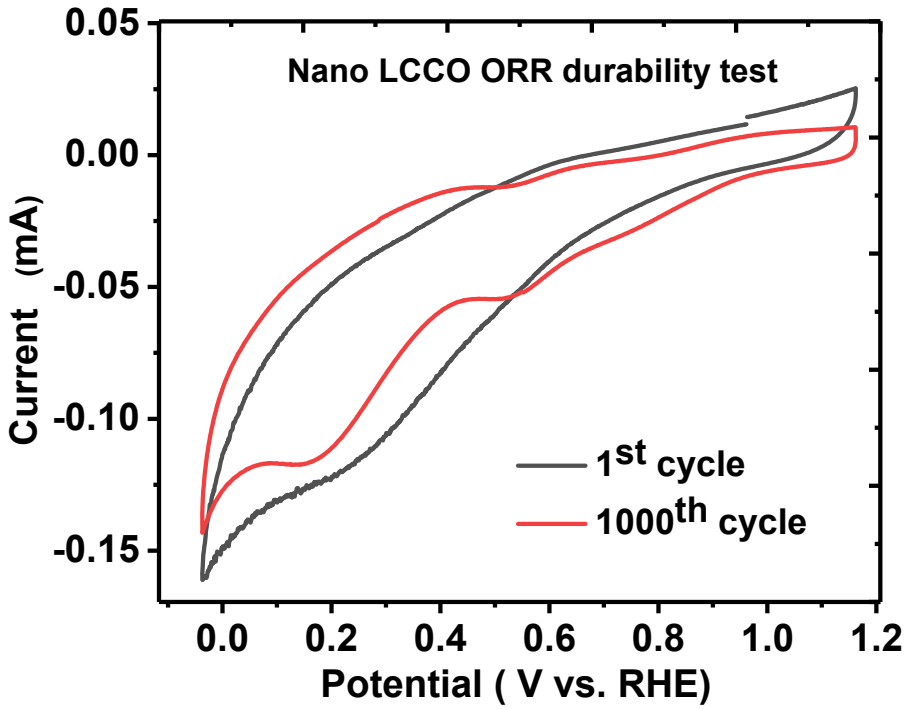

Fig. S5 *CV curves over time of stability testing (0.0–1.2 Vvs. RHE, O_2-saturated 0.1 M KOH solution) for nano LCCO*

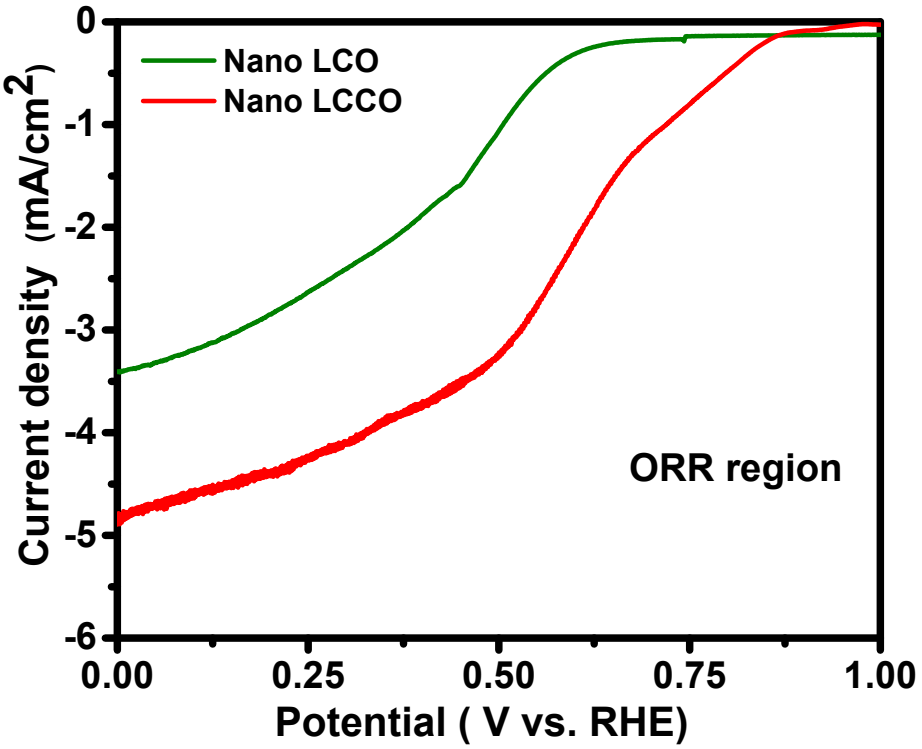

Fig. S6 *ORR activity comparison of nano LCO vs nano LCCO*

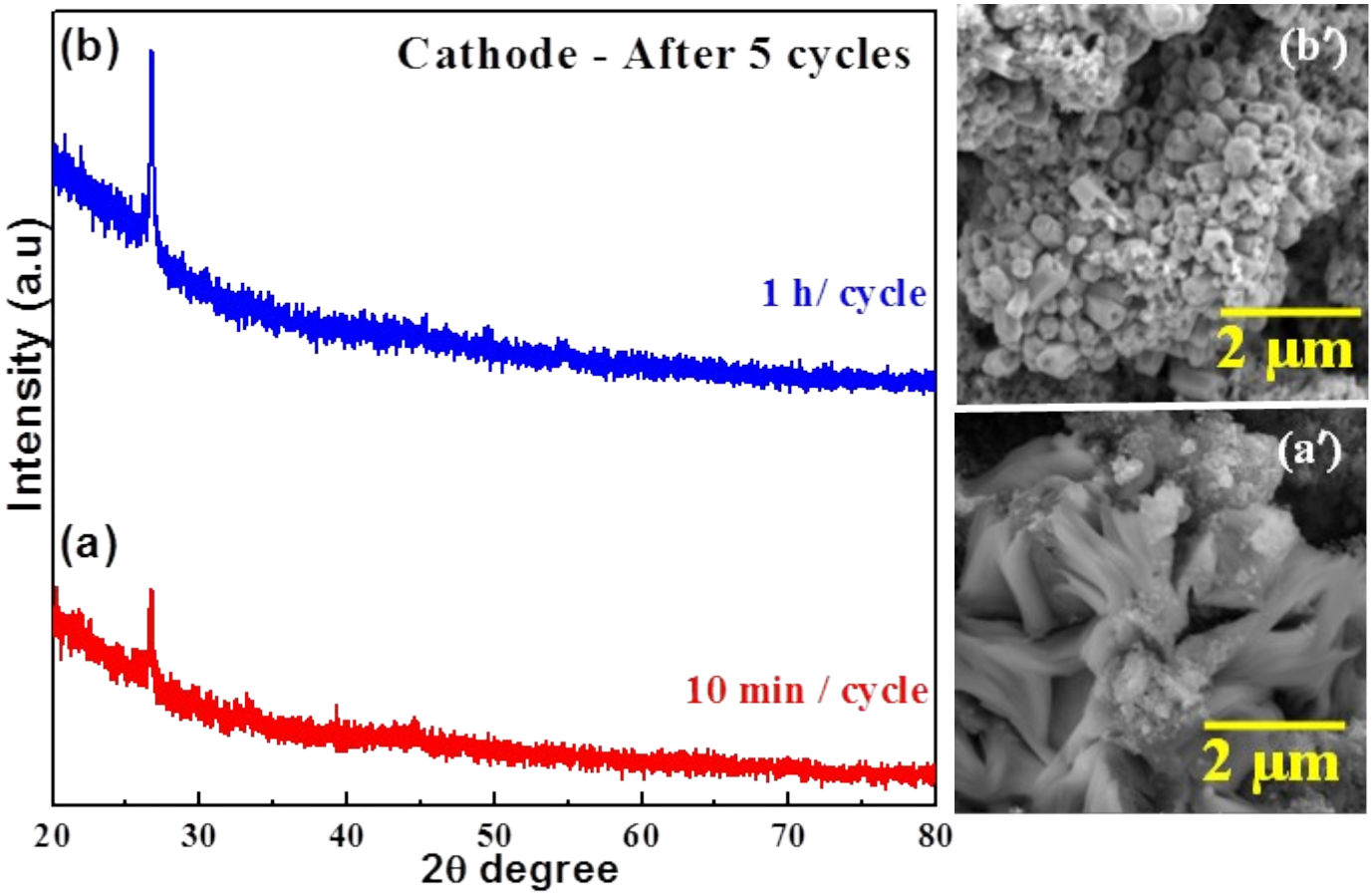

Fig. S7 *XRD pattern and FE-SEM images of cathode at different time duration: 10 minutes / cycle (a,a') and 1 hour / cycle (b,b') respectively*

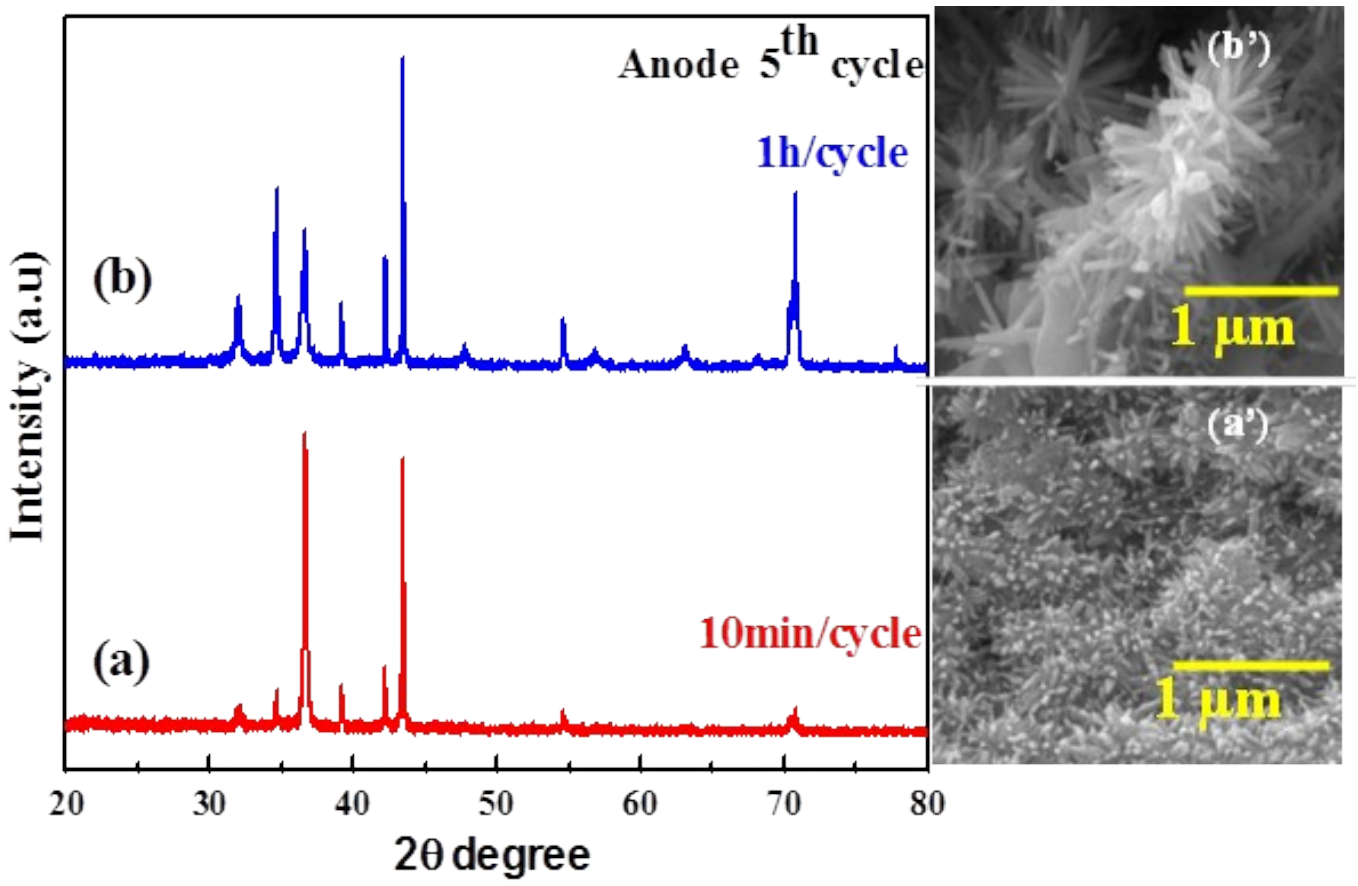

Fig.S8 *XRD pattern and FESEM images of anode at different time duration:(i) 10 minutes / cycle (a,a') and 1 hour / cycle (b,b') respectively*

Table S1 *Impedance parameters derived from experimental Nyquist plots of bulk, nano, and 5wt% conductive carbon mixed LCCO as cathode catalyst in a zinc-air battery setup*

Material	**R_1 (Ohm)**	**R_2 (Ohm)**	**R_3(Ohm)**
Nano LCCO + 5 wt% C	1.0233	2658	4823.30
Nano LCCO	1.3649	2760	5568.73
Bulk LCCO	1.7665	3108	7417.92

Determination of Oxygen vacancy:

Quantitative evaluation of oxygen stoichiometry in the $La_{0.5}Ca_{0.5}CoO_3$composition was performed similarly to the earlier reports using iodometric titration.[1] In a typical procedure, 10mg of the compound was dissolved in 6N HCl (5 ml) followed by addition of 5ml of 10% KI. Thus obtained green color solution was titrated against standardized 0.01 M $Na_2S_2O_3$. When the solution appeared as pale yellow in color, 3 drops of starch (1%) were added and the titration was continued till the disappearance of dark blue color. The volume of $Na_2S_2O_3$ consumed was recorded and the experiment was repeated to obtain concordant values. The amount of oxygen was calculated using the below-mentioned formula.[1]

$$\delta = \frac{(4 - Y)m - Mn}{2m - 16n}$$ **; where n = C × ΔV**

Hence we found that the δ = 0.29 in $La_{0.5}Ca_{0.5}CoO_{3-\delta}$

Reference:

1. Shen, Q.; Li, S.; Yang, G.; Sunden, B.; Yuan, J. Effect of A-/B-site Doping on Oxygen Non-Stoichiometry, Structure characteristics, and O_2 Releasing Behavior of $La_{1-x}Ca_xCo_{1-y}Fe_yO_{3-\delta}$ Perovskites. *Energies* **2019**, *12*, 410.