

## Supporting Information

### **The Role of the A-Site Cation on the Bifunctional Electrocatalytic Activities of $\text{Ln}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ (Ln=La, Pr and Sm) for Rechargeable Zinc–Air Batteries**

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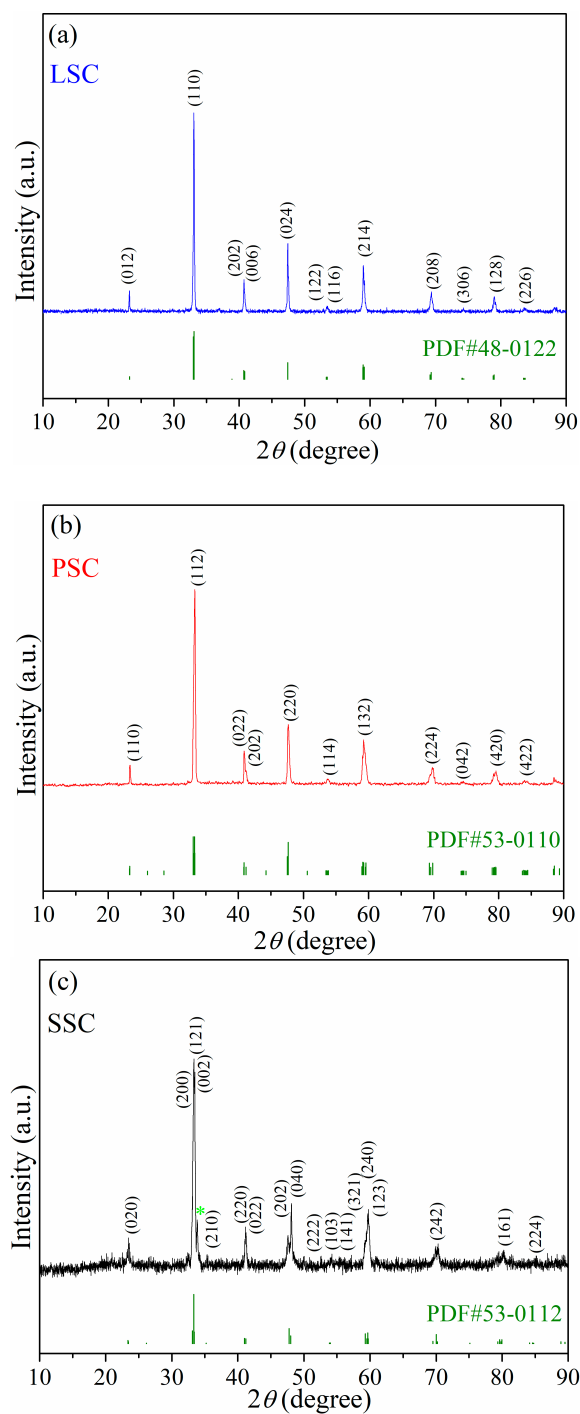
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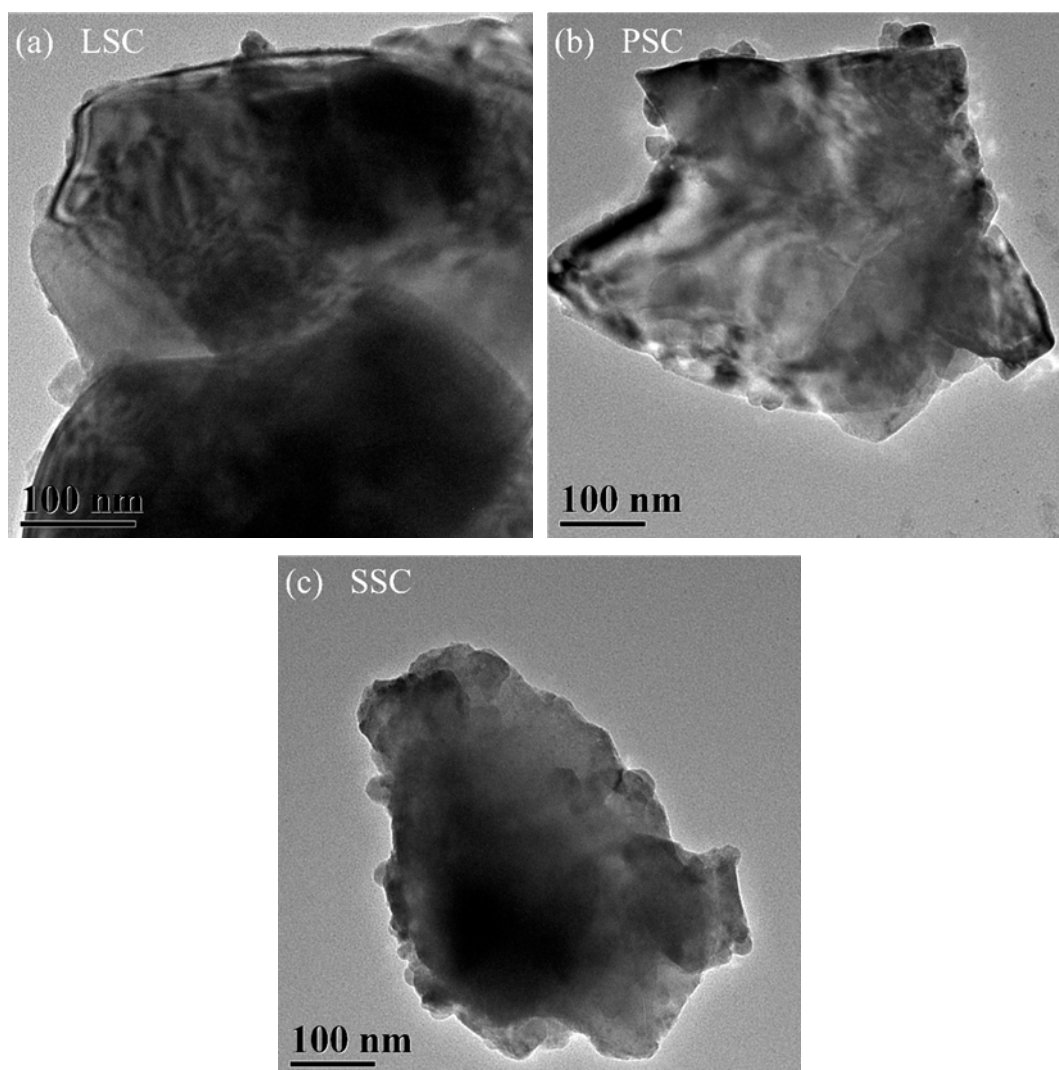
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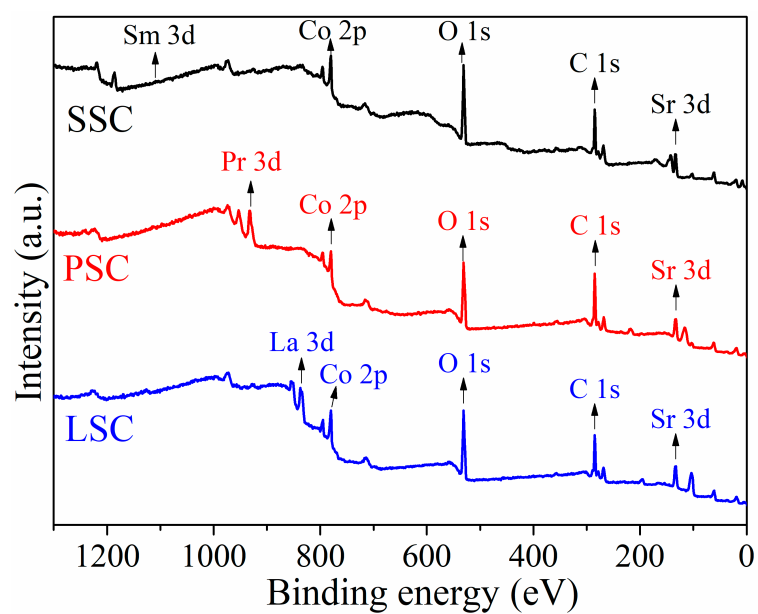
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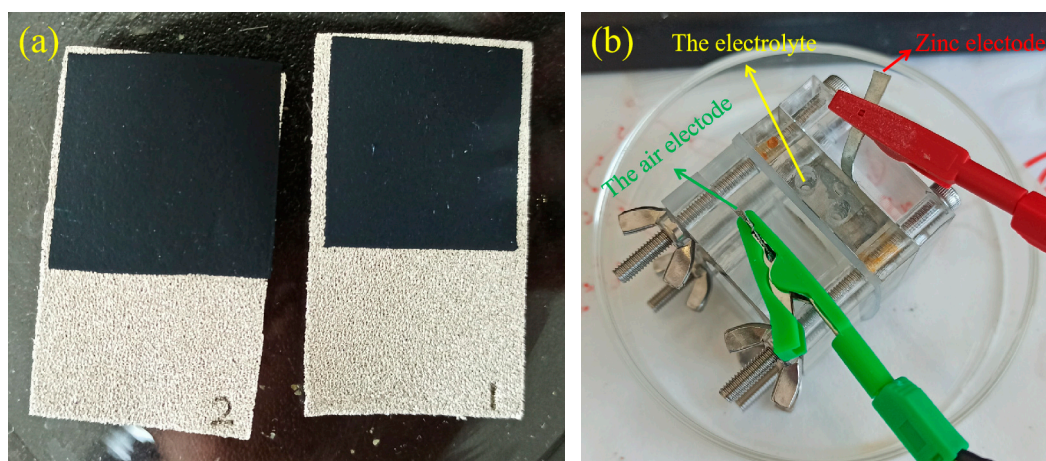
**Figure S1.** X-ray diffraction patterns of (a) LSC ( $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ ), (b) PSC ( $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ ) and (c) SSC ( $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ ) powders. The peak labeled with an asterisk corresponds to the phase of  $\text{SmCoO}_3$  (PDF#25-1071).



**Figure S2.** TEM images of (a) LSC ( $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ ), (b) PSC ( $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ ) and (c) SSC ( $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ ) powders.



**Figure S3.** XPS survey spectrum of LSC ( $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ ), PSC ( $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ ) and SSC ( $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ ).



**Figure S4.** (a) Digital photos of home-made air electrodes and (b) the zinc-air battery assembled with the home-made air electrode.

**Table S1.** The  $\text{Co}^{3+}/\text{Co}^{2+}$  ratio of LSC, PSC and SSC powders in XPS test.

| Sample | Peak       | Valence | B.E. (eV) | Area     |
|--------|------------|---------|-----------|----------|
| SSC    | $2p_{3/2}$ | 3+      | 780.01    | 13302.15 |
|        |            | 2+      | 781.17    | 13632.59 |
| LSC    | $2p_{3/2}$ | 3+      | 779.62    | 12743.58 |
|        |            | 2+      | 780.81    | 12465.55 |
| PSC    | $2p_{3/2}$ | 3+      | 779.50    | 13462.21 |
|        |            | 2+      | 780.69    | 9896.78  |
| SSC    | $2p_{1/2}$ | 3+      | 795.12    | 6651.07  |
|        |            | 2+      | 796.46    | 6816.29  |
| LSC    | $2p_{1/2}$ | 3+      | 794.75    | 6371.79  |
|        |            | 2+      | 796.27    | 6232.78  |
| PSC    | $2p_{1/2}$ | 3+      | 794.53    | 6731.10  |
|        |            | 2+      | 795.76    | 4948.39  |

$\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$  (LSC);  $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$  (SSC);  $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$  (PSC)

**Table S2.** The values of the equivalent circuit elements resulting from fitting the electrochemical impedance spectroscopy data of LSC, PSC, and SSC electrodes in the primary zinc-air batteries.

| Element            | LSC   | SSC   | PSC   |
|--------------------|-------|-------|-------|
| $R_{ohm} (\Omega)$ | 1.70  | 1.64  | 1.46  |
| $R_{int} (\Omega)$ | 0.515 | 0.390 | 0.411 |
| $R_{ct} (\Omega)$  | 1.06  | 1.06  | 0.929 |

$La_{0.5}Sr_{0.5}CoO_{3-\delta}$  (LSC);  $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$  (SSC);  $Pr_{0.5}Sr_{0.5}CoO_{3-\delta}$  (PSC)