A New Strategy for Improving the Electrochemical Performance of Perovskite Cathode: Pre-calcining the Perovskite Oxide Precursor in Nitrogen Atmosphere

Jing Chen\textsuperscript{a}, Zhenxiang Zhao\textsuperscript{a}, Yu Feng\textsuperscript{a}, Xuzhuo Sun\textsuperscript{a}, Bo Li\textsuperscript{a}, Dongjin Wan\textsuperscript{a}, Yuan Tan\textsuperscript{b,*}

\textsuperscript{a}School of Chemistry and Chemical Engineering, Henan University of Technology, Zhengzhou 450001, China

\textsuperscript{b}The Key Laboratory of Optoelectronic Chemical Materials and Devices, School of Chemical and Environmental Engineering, Jianghan University, Wuhan 430056, China

Table S1 Structural parameters calculated by XRD Spectrum

| sample | SSC-400 | SSC-600 | SSC-800 | SSC-air |
|--------|---------|---------|---------|---------|
| a(Å)   | 5.406   | 5.413   | 5.408   | 5.407   |
| b(Å)   | 7.551   | 7.539   | 7.612   | 7.508   |
| c(Å)   | 5.324   | 5.348   | 5.342   | 5.364   |
| V(nm\textsuperscript{3}) | 216.48 | 217.96 | 219.96 | 217.80 |

Table S2 Oxygen non-stoichiometry of SSC powders at room temperature

| Atmosphere,T/°C | n\textsubscript{0} | δ\textsubscript{0} |
|-----------------|-----------------|-----------------|
| Untread         | 2.90            | 0.10            |
| N\textsubscript{2}, 400°C | 2.90 | 0.10 |
| N\textsubscript{2}, 600°C | 2.89 | 0.11 |
Table S3 The result parameters calculated by XPS fitting Spectrum of Co 2p

| Conditions | Co$^{3+}$ | Co$^{4+}$ | Oxygen nonstoichiometry |
|------------|-----------|-----------|-------------------------|
|            | B.E/eV    | Proportion% | B.E/eV    | Proportion% |                   |
| Untreated  | 780.1-795.1 | 83.56      | 782.3-797.1 | 16.44      | 2.8996             |
| N$_2$,400°C | 780.0-795.1 | 73.67      | 782.2-797.1 | 26.33      | 2.9006             |
| N$_2$,600°C | 780.0-795.1 | 62.88      | 781.75-797.1 | 37.12      | 2.8877             |
| N$_2$,800°C | 780.2-795.2 | 61.29      | 782.1-797.1 | 38.7       | 2.8747             |

Table S4 The result parameters calculated by XPS fitting Spectrum of O 1s

| Conditions | Lattice oxygen | Adsorbed oxygen |
|------------|----------------|-----------------|
|            | B.E/eV | Proportion% | B.E/eV | Proportion% |
| Untreated  | 528.4   | 35.71       | 530.9  | 64.29       |
| N$_2$,400°C | 528.4   | 33.36       | 530.9  | 66.64       |
| N$_2$,600°C | 528.4   | 33.16       | 530.9  | 66.84       |
| N$_2$,800°C | 528.8   | 33.05       | 531.1  | 66.95       |
Fig. S1 SEM images of SSC powders: (a) SSC-400; (b) SSC-600; (c) SSC-800; (d) SSC-air, untreated.
Fig. S2 Surface section SEM images of SSC cathodes prepared at 1050 °C, (a) SSC-400; (b) SSC-600; (c) SSC-800; (d) SSC-air.
Firstly, the precursors were pre-calcined at 600 °C in different concentration of hydrogen (0%, 5%, 10% H₂/N₂), and then the powders were recalcined in air for 2 h at 900 °C. Fig. S3a shows the XRD image of the SSC powders. There was no impurity phase formed, which proves that the reduction atmosphere pretreatment (5%, 10% H₂/N₂) will not have a significant effect on the crystal structure of the sample. Fig. S3b shows the experimental results of δ and thermogravimetry of SSC tested in air atmosphere. The δ values are 0.23, 0.26 and 0.27 for 0%, 10% and 5% H₂/N₂ at 800 °C, respectively. The oxygen vacancies of the samples pretreated with hydrogen (5%, 10% H₂/N₂) are slightly higher than those of the samples pretreated with pure nitrogen atmosphere which tested in air atmosphere. The sample in a hydrogen
atmosphere (5%, 10% H₂/N₂) treatment increased the oxygen vacancy of the sample. Because hydrogen is a reducing gas, it can also carbonize organic compounds in hydrogen atmosphere during the pre-sintering process. At the same time, hydrogen may reduce the metal ions, thus increasing the oxygen vacancies in the samples. Fig. S3c shows the Rₚ of the cathodes. The polarization resistance of 5% and 10% H₂/N₂ pretreated samples is slightly higher than that of nitrogen pretreated samples at 600-650 °C. At 700-750 °C, the polarization resistance of the three samples was almost the same. The results showed that the samples treated with 5% and 10% H₂/N₂ have similar oxygen vacancies and catalytic performance as those treated with pure N₂.