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## Effective oxygen reduction on A-site substituted LaCuO<sub>3-δ</sub>: Toward air electrodes for SOFCs based on perovskite-type copper oxides

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## **Supplementary Information**



Fig. S1. Visualization of crystal structure for La<sub>4</sub>BaCu<sub>5</sub>O<sub>13</sub>. Please notice different coordination of copper cations.

## Iodometric titration

The oxygen content in the samples at RT was measured by using iodometric titration method, as described previously in the [62] reference (reference numbers as in the main paper). Just before the measurements, each material (in a form of powder) was annealed in air at 200 °C, and then was cooled to RT with 5 °C min<sup>-1</sup> rate in order to remove adsorbed at the surface water and CO<sub>2</sub>. The procedure consisted of two separate routes, which were carried out for each composition (SS as well as SG samples). The first part included the following steps:  $m_1$  (30-40) mg) of the oxide was put in a laboratory flask under inert conditions (Ar atmosphere), with 1 g of powdered KI was added as well. Then, 10 ml of 18 wt.% HCl solution was added dropwise, which resulted in dissolution of the sample. In the next step, 40 ml of deionized, oxygen-free H<sub>2</sub>O was added and the flask and was cooled to ca. 0 °C. Then, 10 ml of NH<sub>4</sub>OH solution (6N) was instilled, during which the solution changed color to yellow-green. Later, 2 ml of H<sub>3</sub>PO<sub>4</sub> (85 wt.%) was also added and mixed. Later the flask was slowly heated to RT, and the solution was titrated with  $V_1$  (ml) of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (~0,01 M) to the starch end point. In the second part of the procedure,  $m_2$  (mg) of the sample was dissolved in 10 ml HCl solution (18 wt.%), which was diluted to 50 ml with deionized  $H_2O$ . The obtained mixture was then heated on steam bath for approx. 10 min. While the solution was hot, the  $NH_4OH$  solution (6N) was slowly instilled (mixture changed color to light blue) and 2 ml of H<sub>3</sub>PO<sub>4</sub> (85%) was also added. Then, the flask was cooled down to RT under Ar atmosphere, and then, 1 g of KI powder was also added. After dissolution of KI, the prepared mixture was titrated with  $V_2$  (ml) of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (~0,01 M) to the starch end point.

The described above titration procedure is based on a fact that copper ions with different charge react differently with KI in acidic solutions. For  $Cu^{3+}$  and  $Cu^{2+}$  cations the following reactions take place [63,64]:

$$Cu_{(aq)}^{3+} + 3I_{(aq)}^{-} \to CuI_{(s)} + I_{2(aq)} \quad (S1)$$
$$Cu_{(aq)}^{2+} + 2I_{(aq)}^{-} \to CuI_{(s)} + \frac{1}{2}I_{2(aq)} \quad (S2)$$

In the reactions, both types of cations are reduced, in two- and one-electron process, respectively, with free  $I_2$  being also produced. While  $Cu^+$  can also react, it is not a redox process, and free  $I_2$  is not created. The liberated in reactions S1 and S2  $I_2$  can be titrated with solution of sodium thiosulphate, with one mole of sodium thiosulfate being equivalent to one mole of the oxidant in the tested sample [63,64]:

$$2S_2 O_{3(aq)}^{2-} + I_{2(aq)} \to S_4 O_{6(aq)}^{2-} + 2I_{(aq)}^{-}$$
(S3)

The average state of copper ions (*p*) may be calculated with formula [62]:

$$p = \frac{V_1}{m_1} \cdot \frac{m_2}{V_2} - 1 \qquad (S4)$$

As presented in the original paper [62], such complex methodology is justified by a fact that without reference value of the total concentration of all forms of copper (given by the second route), the results of simple titrations are often accompanied by substantial errors (as also observed by authors of this paper in some initial experiments). For each SS as well as SG compounds at least three attempts of titrations were performed, based on which average copper oxidation state and oxygen content were calculated with estimated error values.

For the SG samples oxygen contents with error values are evaluated as follows: 12.98(13) for LBCu, 9.80(12) for LSCu and 9.86(6) for LSBCu. The observed differences between SS and SG series (lower oxygen content for respective materials in the SG series and larger error values) can be caused by the difference in the preparation route. Contrary to the powders obtained by SS

method, which synthesis included several high temperature sintering steps with crushing and regrinding of the samples, the SG samples were obtained with the single high temperature step. Some residual carbon is expected to remain in such the preparation route, which then behaves as a reducing agent, lowering oxygen content and average copper oxidation state in the tested samples. The other possibility of lower oxygen content in SG samples may be due higher oxidation activity versus e.g. CO or NO<sub>x</sub> oxidation, as reported for LaCuO<sub>3- $\delta$ </sub> oxides, which stems from smaller grain size and consequently, larger active area of SG samples [38].



Fig. S2. XRD data with Rietveld refinement for: a)  $La_3SrCu_4O_{10\pm\delta}$  and b)  $La_3Sr_{0.6}Ba_{0.4}Cu_4O_{10\pm\delta}$  obtained by solid state reaction (SS) and by sol-gel method (SG). Data shown for the 2 $\theta$  range of 10-90 deg in order to present obtained diffractograms in more transparent way.

b)



Fig. S3. Visualization of crystal structure for  $La_3Sr_{0.6}Ba_{0.4}Cu_4O_{10}$ . Please notice different coordination of copper cations.



c)

e)

b) d)

Fig. S4. TEM images of LBCu material: a) SS, b) SG in bright field; c) SS, d) SG higher resolution data; and e) exemplary HR-TEM with FFT structural analysis (from marked region) for SS.



c)

b)

Fig. S5. XPS spectra of in the Cu  $2p_{3/2}$  region for La<sub>1-x</sub>(Sr,Ba)<sub>x</sub>CuO<sub>3- $\delta$ </sub> powders obtained by the solid state reaction. Curve-fitting confirms presence of both Cu<sup>2+</sup> and Cu<sup>3+</sup> oxidation states. Refined surface average oxidation state of copper is 2.31, 2.31 and 2.27 for LBCu, LSCu and LSBCu, respectively.



Fig. S6. X-ray diffractograms measured at 900 °C in air atmosphere for La<sub>1-x</sub>(Sr,Ba)<sub>x</sub>CuO<sub>3-δ.</sub>



Fig. S7. Relative weight changes of  $La_{1-x}(Sr,Ba)_xCuO_{3-\delta}$  recorded in inert (Ar) atmosphere as a function of temperature.



Fig. S8. X-ray diffractograms at different temperatures measured in inert atmosphere (Ar) of the A-site substituted LaCuO<sub>3- $\delta$ </sub>: a) LBCu, b) LSCu and c) LSBCu. Additional identified phases:  $\star$  La<sub>4</sub>BaCu<sub>5</sub>O<sub>11</sub>,  $\star$  La<sub>2-x</sub>(Sr,Ba)<sub>x</sub>CuO<sub>4- $\delta$ </sub>-type structure,  $\bullet$  La<sub>2</sub>Cu<sub>2</sub>O<sub>5</sub>-type oxide,  $\nabla$  Cu<sub>2</sub>O.



Fig. S9. TG curve recorded in 5 vol.%  $H_2$  in Ar for LBCu during 1<sup>st</sup> heating. Marks indicate points associated with release of the following oxygens [51].



Fig. S10. XRD diffractograms of the A-site substituted  $LaCuO_{3-\delta}$  powders annealed for 100 h at 900 °C in air.



Fig. S11. Temperature dependence of the linearized relative unit cell volume changes of the considered materials, allowing to evaluate average (linear) TECs.



Fig. S12. Temperature dependence of Seebeck coefficient of La<sub>1-x</sub>(Sr,Ba)<sub>x</sub>CuO<sub>3- $\delta$ </sub> series. Absolute error value is estimated as  $\pm 3 \ \mu V/K$ .



Fig. S13. Initial frame of the video showing mechanism of oxygen ion transport through vacancy mechanism in La<sub>8</sub>Ba<sub>2</sub>Cu<sub>10</sub>O<sub>25</sub> (oxygen nonstoichiometry  $\delta = 0.5$  rescpectively to the basic La<sub>4</sub>BaCu<sub>5</sub>O<sub>13</sub>). Please obtain video from the respective web page.



Fig. S14. SEM micrographs of La<sub>1-x</sub>(Sr,Ba)<sub>x</sub>CuO<sub>3-δ</sub> powders obtained by solid state reaction (a, c, e) and sol-gel method (b, d, f), respectively. LBCu: (a, b), LSCu: (c, d) and LSBCu: (e, f).



Fig. S15. XRD patterns of mixtures (1:1 wt. ratio with LSGM electrolyte powder) of: a) LSCu and b) LSBCu after annealing at different temperatures and times with LSGM.



Fig. S16. XRD patterns of mixtures (1:1 wt. ratio with LDC buffer powder) of: a) LSCu and b) LSBCu after annealing at different temperatures and times with annealed LDC.

chemical composition used polarization reference electrolyte resistance  $[\Omega \text{ cm}^2]$ SDC 54  $La_{0.7}Sr_{0.3}CuO_{3\text{-}\delta}$ 0.62 La<sub>0.7</sub>Sr<sub>0.3</sub>CuO<sub>3-δ</sub>-SDC SDC 0.29 55 (in ratio 3:1) SDC 0.094 56 graded  $La_{0.7}Sr_{0.3}CuO_{3-\delta}$ -SDC 95  $La_{1.7}Sr_{0.3}CuO_{4-\delta}$ CGO 0.16  $La_{1.5}Sr_{0.5}CuO_{4-\delta}$ LSGM 0.31 25  $Pr_{1.95}Ce_{0.05}CuO_{4\pm\delta}$ CGO 0.23 26  $PrBa_{0.5}Sr_{0.5}Cu_2O_{5+\delta}$ LSGM 0.043 57  $NdBa_{0.5}Sr_{0.5}Cu_2O_{5+\delta}$ LSGM 0.057 57 SmBa<sub>0.5</sub>Sr<sub>0.5</sub>CuFeO<sub>5+δ</sub> SDC 0.171 94  $SmBa_{0.5}Sr_{0.5}Cu_2O_{5+\delta}$ SDC 0.085 94 La<sub>4</sub>BaCu<sub>4</sub>CoO<sub>13+δ</sub> LSGM 0.34 72 0.13 La<sub>4</sub>BaCu<sub>5</sub>O<sub>12.98</sub> LSGM this work  $La_3SrCu_4O_{9.80}$ LSGM 0.14 this work La<sub>3</sub>Sr<sub>0.6</sub>Ba<sub>0.4</sub>Cu<sub>4</sub>O<sub>9.84</sub> LSGM 0.16 this work

Tab. S1. Comparison of electrode polarization resistance values measured at 800 °C for different proposed Cu-based oxide cathodes. \*Value reported at 700 °C; ^value reported at 750 °C.



Fig. S17. SEM micrograph of cross-section of Ni-CGO/LDC/LSGM/LDC/LBCu full cell (anode at the bottom side of the image). Thickness of the electrolyte is ca. 350 μm.



Fig. S18. Voltage and power density of button-type LSGM-based SOFC cells with LSCu (a) and LSBCu (b) cathode materials as a function of current density.



Fig. S19. Maximum of the power density of the constructed LSGM-based button-type cells as a function of temperature with reference data [11,90,96].



Fig. S20. Evaluation of the cathodic polarization dependence as a function of time for the LBCubased air electrode prepared at 1000 °C. Measurements done in the LSGM-based symmetrical cell at 800 °C in synthetic air flow. The evaluated degradation rate is 0.187% from the beginning and 0.113% h<sup>-1</sup> from 10<sup>th</sup> hour onward.



Fig. S21. SEM micrographs with EDS mapping of cation distribution for LSGM-based symmetrical cells with LBCu electrode: a) as prepared, and b) after 100 h annealing at 800 °C.

Description of colors corresponding to signals from particular elements in Fig. S21 above: (top row from the left) La – red, Ce – dark yellow, Sr – gray; (bottom row from the left) Ba – blue, Ga – green, Cu – dark red, Mg – brighter green. Some inhomogeneity in the Mg distribution is visible in the LSGM electrolyte, but it is not changed after 100 h annealing at 800 °C, not affecting chemical stability between the electrolyte, buffer layer and LBCu electrode. Inhomogeneous distribution of Mg seems as the intrinsic property of the used commercial LSGM powder.