



This is an electronic reprint of the original article. This reprint may differ from the original in pagination and typographic detail.

Fan, Lijun; Rautama, Eeva Leena; Lindén, Johan; Sainio, Jani; Jiang, Hua; Sorsa, Olli; Han, Nana; Flox, Cristina; Zhao, Yicheng; Li, Yongdan; Kallio, Tanja

Two orders of magnitude enhancement in oxygen evolution reactivity of  $La_{0.7}Sr_{0.3}Fe_{1-x}Ni_xO_{3-\delta}$  by improving the electrical conductivity

Published in: Nano Energy

DOI: 10.1016/j.nanoen.2021.106794

Published: 01/03/2022

Document Version Publisher's PDF, also known as Version of record

Published under the following license: CC BY

*Please cite the original version:* Fan, L., Rautama, E. L., Lindén, J., Sainio, J., Jiang, H., Sorsa, O., Han, N., Flox, C., Zhao, Y., Li, Y., & Kallio, T. (2022). Two orders of magnitude enhancement in oxygen evolution reactivity of La<sub>0.7</sub> Sr<sub>0.3</sub> Fe<sub>1-x</sub> Ni<sub>x</sub> O<sub>3-δ</sub> by improving the electrical conductivity. *Nano Energy*, *93*, Article 106794. https://doi.org/10.1016/j.nanoen.2021.106794

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.



Contents lists available at ScienceDirect

# Nano Energy



journal homepage: www.elsevier.com/locate/nanoen

# Two orders of magnitude enhancement in oxygen evolution reactivity of $La_{0.7}Sr_{0.3}Fe_{1-x}Ni_xO_{3-\delta}$ by improving the electrical conductivity

Lijun Fan<sup>a,b</sup>, Eeva Leena Rautama<sup>a</sup>, Johan Lindén<sup>c</sup>, Jani Sainio<sup>d</sup>, Hua Jiang<sup>d</sup>, Olli Sorsa<sup>a</sup>, Nana Han<sup>a</sup>, Cristina Flox<sup>a</sup>, Yicheng Zhao<sup>b</sup>, Yongdan Li<sup>b,e</sup>, Tanja Kallio<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry and Materials Science, School of Chemical Engineering, Aalto University, FI-00076 Aalto, Finland

<sup>b</sup> Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), State Key Laboratory of Chemical Engineering (Tianjin University), Tianjin Key

Laboratory of Applied Catalysis Science and Technology, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

<sup>c</sup> Faculty of Science and Engineering/ Physics, Åbo Akademi University, FI-20500 Turku, Finland

<sup>d</sup> Department of Applied Physics, School of Science, Aalto University, FI-00076 Aalto, Finland

e Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, FI-00076 Aalto, Finland

ARTICLE INFO

Keywords: Oxygen evolution reaction (OER) Perovskite oxides Structural transition Electrical conductivity Oxygen vacancy

#### ABSTRACT

Developing highly efficient and robust electrocatalysts for oxygen evolution reaction (OER) is critical to renewable energy technologies. Here, we report an effective strategy to enhance the OER activity of a perovskite electrocatalyst through improving the electrical conductivity introduced by the structural transition.  $La_{0.7}Sr_{0.3}Fe_{1-x}Ni_xO_{3-\delta}$  (denoted as LSFN-x) with increasing Ni content is found to crystallize in a higher symmetry structure and exhibit improved OER catalytic performance. The optimized cubic LSFN-0.4 catalyst delivers a 90-times higher specific activity than its non-doped parent rhombohedral compound  $La_{0.7}Sr_{0.3}FeO_{3-\delta}$  at an overpotential of 340 mV, with an overpotential of only 320 mV for 10 mA cm<sup>-2</sup> and a low Tafel slope of 35 mV dec<sup>-1</sup> in 0.1 M KOH, while maintaining excellent durability during 1000 continuous cycles and 50 h-water-splitting in a laboratory-scale electrolyzer. The enhanced OER catalytic performance of LSFN-0.4 is highly correlated with its increased conductivity as well as the increased oxygen vacancy concentration.

## 1. Introduction

The rising awareness of the global environmental problems and growing demand for renewable energy have stimulated intense interest to develop advanced energy conversion and storage systems. Oxygen evolution reaction (OER,  $4OH^- \rightarrow 2 H_2O + O_2 + 4e^-$  in alkaline media) is the vital step for many renewable-energy technologies such as rechargeable metal-air batteries and solar/electricity-driven water splitting [1,2]. However, this reaction is intrinsically sluggish because of the complex nature of the four-electron oxidation process, requiring a relatively high overpotential (n) [1,3,4]. Therefore, developing highly efficient OER catalysts is crucial to achieving fast kinetics. Currently, noble metal oxides (IrO2 and RuO2) are typically regarded as the benchmark OER catalysts, but the low abundance and high cost severely prohibit their large-scale applications [5]. Accordingly, low-cost transition metal-based OER catalysts, such as spinels [6-8], oxides [5,9], hydroxides [2,10], perovskites [11-13] and sulfides [14,15] have been widely investigated.

Perovskite oxides with a general formula of ABO3 where A is a rareearth or alkaline earth element and B is a transition metal element (TM), have attracted renewed interest owing to their high intrinsic activities and good structural stability towards OER [4]. To date, under the compositional and structural flexibility, a series of perovskite catalysts with various OER active sites and several activity descriptors have been developed [4,16]. For example, based on the conventional adsorbate evolution mechanism (AEM), Shao-Horn et. al [1] proposed a descriptor of the  $e_g$  filling of the transition metal cations for the OER activity. The perovskite with an eg orbital of 1.2 is expected to display a superior OER activity. This design principle has been widely accepted and has led to identification of the highly active OER the catalyst  $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$  (BSCF). However, to determine the  $e_{\sigma}$  occupancy of the active sites accurately is difficult when the surface spin state is not well known [17]. Moreover, some experiments have shown that different perovskites with the same optimal eg orbital exhibit significant differences in their activities [18,19]. Besides the eg occupancy, other descriptors such as the p-band center of bulk O, and oxygen

https://doi.org/10.1016/j.nanoen.2021.106794

Received 22 August 2021; Received in revised form 29 November 2021; Accepted 30 November 2021 Available online 3 December 2021

2211-2855/© 2021 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

<sup>\*</sup> Corresponding author. *E-mail address:* tanja.kallio@aalto.fi (T. Kallio).

vacancies have been also proposed [13,20]. Recent findings showed that the intrinsic OER activity of a perovskite is also related to its electrical conductivity [21], especially for the electrocatalyst via the newly proposed more efficient lattice-oxygen oxidation mechanism (LOM). For instance, Si-incorporated SrCoO<sub>3- $\delta$ </sub> (Si-SCO, 198 S cm<sup>-1</sup>) with a higher electrical conductivity demonstrates its lattice oxygen being more likely to participate in OER than the pristine SCO (2 S cm<sup>-1</sup>) [22]. The reason might be that the higher electrical conductivity can provide more internal pathways and improve energy efficiency, which is more critical for the oxide lattice participation process [11,23,24]. Nevertheless, the electrical conductivity has not received as much attention as other descriptors [4].

So far, A-site and O-site doping strategies and electron injections by hydrogen treatment have been intensively used to improve the electrical conductivity of the perovskite OER catalysts [25,26]. For example, Cheng et. al [21] reported that Sr doped LaCoO<sub>3</sub> (LCO) shows a clearly higher electrical conductivity than the parent perovskite LCO and therefore exhibited improved OER activity. Zhu et. al [27] found that P-doping in SCO enables a significant enhancement in the electrical conductivity as well as intrinsic activity. Wang et. al [28] demonstrated that anion F-doping is also beneficial for increasing the conductivity and the resulting electrochemical performance. Guo et al. [26] found that the conductivity and OER electrocatalytic activity of Ca<sub>0.9</sub>Yb<sub>0.1</sub>MnO<sub>3</sub> after H<sub>2</sub> treatment at 350 °C increase by 2.5 times and 100 times, respectively. In addition, also B-site doping has been found to effectively improve conductivity [29]. For example, Ru<sup>5+</sup> doped SCO (60 S cm<sup>-1</sup> at room temperature) has a higher electrical conductivity than the pristine SCO ( $\sim 2$  S cm<sup>-1</sup>), consequently, it shows an enhanced OER activity [24]. However, the  $Co^{3+}/Co^{4+}$ ,  $Ru^{5+}$  and active oxygen species of  $Ru^{5+}$ doped SCO also show high activity toward OER, which makes it difficult to distinguish the real contribution of the enhanced conductivity. The inclusion of Si into the SCO lattice also leads to an increase in surface oxygen vacancies and electrical conductivity, but the Si-incorporated SCO is subject to rapid surface reconstruction and amorphization during potential cycling [22].

Higher crystal symmetry has been shown to enhance the overlap between the occupied O 2p valence bands and the unoccupied Co 3d conduction bands, thus increasing the electrical conductivity [25,27, 28]. On the other hand, the perovskite oxides with small lattice distortions and close to the ideal cubic symmetry tend to show higher OER stability [18,30,31]. Inspired by the above considerations, in this work, a B-site substitution strategy is reported to stabilize higher crystal symmetry for improving the electrical conductivity of a perovskite. The intrinsic OER activity of La<sub>0.7</sub>Sr<sub>0.3</sub>Fe<sub>1-x</sub>Ni<sub>x</sub>O<sub>3-δ</sub> (denoted as LSFN-x) improves by two orders of magnitude with increasing in conductivity, although the amount of Fe<sup>4+</sup> species, the active site based on AEM, is decreased. The optimized LSFN-0.4 catalyst exhibits an exceptional activity with an ultralow overpotential of 320 mV at 10 mA  $cm^{-2}$  and a Tafel slope of 35 mV dec<sup>-1</sup> in 0.1 M KOH. This activity is superior to those of the pristine LSF, benchmark IrO<sub>2</sub>, and most state-of-the-art perovskite catalysts reported. Furthermore, the LSFN-0.4 demonstrates excellent durability during 1000 consecutive cycles and 50 h-water splitting in a laboratory-scale electrolyzer. Finally, the variation in physicochemical properties and electronic configuration caused by Ni substitution are systematically explored and the crucial effect of conductivity on the OER performance of perovskite is determined.

#### 2. Results and discussion

# 2.1. Crystal structure and morphology

To gain insight into the composition-structure-reactivity relations of a potentially cost effective perovskite oxide oxygen evolution electrocatalyst, we have systematically studied the variation of crystal structure and physicochemical properties of La<sub>0.7</sub>Sr<sub>0.3</sub>Fe<sub>1-x</sub>Ni<sub>x</sub>O<sub>3- $\delta$ </sub> (LSFN-x, x = 0.2, 0.4 and 0.6) upon Ni substitution. La<sub>0.7</sub>Sr<sub>0.3</sub>FeO<sub>3- $\delta$ </sub> (LSF) has been selected as the parent phase because of its good structural flexibility, large surface area and excellent conductivity [29,32]. All samples were synthesized via the glycine-nitrate combustion method (for details see the section Material synthesis in Supporting information).

The structural transition of the perovskite series is first confirmed by X-ray diffraction (XRD) and Fig. 1a shows the XRD patterns of the LSF, LSFN-0.2, and LSFN-0.4 samples. As shown on the right-hand side magnified figure, the characteristic Bragg peaks of LSFN series shift toward higher angles with increasing Ni substitution (increasing x), revealing a lattice shrinkage, which is caused by the smaller radius of  $Ni^{3+}$  (VI coordinated, 0.56 Å) relative to  $Fe^{3+}$  (VI coordinated, 0.645 Å) [33,34]. The structure of all the samples is further analyzed by the Rietveld refinement method. As shown in Fig. S1 and Table S1, LSF and LSFN-0.2 feature a rhombohedral lattice with a space group of R-3c (#167), while LSFN-0.4 possesses a cubic structure (Pm-3m space group, #221). The phase transition is reflected in the drastic change of the bond structure, where the lattice parameters of the LSFN samples gradually decrease and the bond angle TM-O-TM (TM: Fe/Ni) increases up to  $180^{\circ}$  with the increasing of Ni content (Fig. 1b). As for x = 0.6, the sample still shows the cubic phase, but it has an obvious NiO secondary phase as shown in the XRD results (Fig. S1d and Table S1). Thus, this work mainly studies the pure phases LSF, LSFN-0.2 and LSFN-0.4.

The phase transition is further verified by the high-resolution transmission electron microscopy (HRTEM) images and corresponding Fourier transformation (FFT) patterns of the representative samples LSF and LSFN-0.4 (Fig. 2c and f). Obvious lattice fringes of 0.391 nm attributed to the (012) plane along  $[2\overline{2}1]$  zone axis is observed for LSF, while LSFN-0.4 shows a lattice space of 0.387 nm assigned to the (100) plane of the cubic structure along the [001] zone axis. The measured *d* spacings of these two samples are closely aligned with the corresponding theoretical values determined from the XRD data. The three key selected area electron diffraction (SAED) patterns of LSFN-0.4 along the [001], [ $\overline{1}20$ ] and [110] zone axes (Fig. 2g-i) further demonstrate its



Fig. 1. The structural transition of perovskites. (a) XRD patterns, with a magnified region of  $2\theta = 31.5-33.5^{\circ}$  shown on the right-hand side and (b) cell parameter and TM–O–TM angle of LSF, LSFN-0.2 and LSFN-0.4. The insets in (b) are the crystal structure of LSF (rhombohedral) and LSFN-0.4 (cubic), respectively.



Fig. 2. Structure and morphology characterization of perovskites. (a) SEM image, (b) TEM image, (c) HRTEM image and the corresponding FFT pattern (inset) along [221] zone axis of LSF. (d) SEM image, (e) TEM image, (f) HRTEM image and the corresponding FFT pattern (insert) along [001] zone axis, and SAED patterns obtained along (g) [001], (h) [120] and (i) [110] zone axes of LSFN-0.4.

perovskite structure, which can be well indexed in terms of a cubic unit cell, allowing the lattice planes to be identified.

The scanning electron microscope (SEM, Fig. 2a, d and Fig. S2) and TEM (Fig. 2b and e) images of these LSFN samples show an agglomerated nanoparticles morphology with the particle size range of 10–100 nm. The particle sizes of LSFN are decreasing with partial substitution of Fe by Ni, which is consistent with the average grain sizes trend calculated by the Scherrer equation (Table 1). Accordingly, the

# Table 1

Physical characteristics, and oxygen vacancy concentration ( $\delta$ ) and B-site ion oxidation state of LSF, LSFN-0.2, LSFN-0.4 and LSFN-0.6.

Perovskite	Particle size (nm)	BET surface area $(m^2 g^{-1})$	Oxygen vacancy concentration ( $\delta$ )	B-site ion oxidation state
LSF	28.93	11.2	$\textbf{0.072} \pm \textbf{0.004}$	$3.157 \pm 0.008$
LSFN-0.2	23.60	13.9	$0.094\pm0.002$	$3.113\pm0.004$
LSFN-0.4	15.84	19.2	$0.102\pm0.003$	$3.095\pm0.006$
LSFN-0.6	11.31	20.2	$\textbf{0.186} \pm \textbf{0.003}$	$\textbf{2.927} \pm \textbf{0.006}$

reduced particle size increases the specific surface area as calculated using the Brunauer-Emmett-Teller (BET) method of the perovskite oxide (Fig. S3 and Table 1), which would benefit OER due to the availability of more active sites [35–37].

The results of iodometric titrations indicate that the oxygen nonstoichiometry ( $\delta$ , representing the total oxygen vacancy) is slightly increased while the average B-site oxidation state decreased upon Ni substitution via the charge compensation (Table 1). The increase of oxygen vacancy is expected to facilitate oxygen absorption and release, thereby promoting oxygen electrocatalytic activity [30,36].

#### 2.2. Electrochemical performances

The OER activities of the perovskites and commercial  $IrO_2$  catalysts were evaluated on a rotating disc electrode (RDE) by performing linear sweep voltammetry (LSV) in O<sub>2</sub>-saturated 0.1 M KOH electrolyte at 1600 rpm in a typical three-electrode cell. All potentials are given relative to the reversible hydrogen electrode (RHE) and corrected for electrolyte resistance (~45  $\Omega$  for 0.1 M KOH). As shown in Fig. 3a, the



**Fig. 3. OER electrocatalytic activities and stabilities of catalysts.** (a) *IR*-corrected OER polarization curves of  $IrO_2$ , LSF, LSFN-0.2, LSFN-0.4 and LSFN-0.6 in  $O_2$  saturated 0.1 M KOH at a scan rate of 5 mVs<sup>-1</sup> with a rotation speed of 1600 rpm. These curves were averaged from three independent measurements. (b) Tafel plots corresponding to the polarization curves in (a). (c) EIS of the LSFN series catalysts recorded at 5 mA cm<sup>-2</sup>, the ohmic resistance has been subtracted. (d) Mass activities and specific activities (normalised to the BET surface area) of the LSFN series catalysts at 1.57 V vs. RHE derived from (a). (e) RRDE test of LSFN-0.4 in N<sub>2</sub>-saturated 0.1 M KOH to confirm that current is due to oxygen evolution, the inset displays the scheme of the RRDE detection for ORR on the Pt ring caused by OER on the disk. (f) *IR*-corrected OER polarization curves of LSFN-0.4 initially and after 1000 cycles between 1.2 and 1.65 V vs. RHE in O<sub>2</sub>-saturated 0.1 M KOH. All the error bars represent the s.d. from three independent measurements.

OER polarization curves of the Ni-doped samples exhibit smaller onset potentials and higher catalytic currents at a fixed potential compared to pristine LSF, implying higher OER activity. As a reference, the conductive carbon (Vulcan XC-72, VC) additives show a negligible activity contribution in the studied potential range (Fig. S4). The OER overpotential at a current density of 10 mA cm<sup>-2</sup> ( $\eta_{10}$ ) is a metric related to solar fuel synthesis [37]. Notably, LSFN-0.4 exhibits an ultra-low  $\eta_{10}$  of 320 mV, which is 20, 40 and 240 mV lower than those values of LSFN-0.6, LSFN-0.2, and LSF, and even surpasses that of the IrO2 catalyst (360 mV), indicating that LSFN-0.4 possesses the best OER activity among these investigated electrocatalysts. The excellent catalytic activity of LSFN-0.4 for OER is also considerably superior to most well-known perovskite-type OER electrocatalysts hitherto reported (Table S2). The enhanced kinetics of the LSFN catalysts toward OER was further proved by the Tafel plots (Fig. 3b), where the LSFN-0.4 catalyst exhibits the lowest Tafel slope of 35 mV  $dec^{-1}$ . This value is similar to those of  $La_5Ni_3CoO_{13-\delta}$  (35 mV dec<sup>-1</sup>) [38], nickel-iron layered double hydroxide (35 mV dec<sup>-1</sup>) [10] and Ni-Fe (Oxy)hydroxide (39.7 mV

 $dec^{-1}$ ) [39], which suggests the catalyst has moderate binding energy between the OER intermediates and the active site (either oxidized metal cation center or electrophilic lattice oxygen) [39–41].

Fig. 3c shows the electrochemical impedance spectroscopy (EIS) results of those catalysts, and the ohmic resistance has been subtracted for clarity. The Nyquist plots are fitted with an equivalent circuit  $R_o(R_{ct}CPE_{ct})$ , where  $R_o$ ,  $R_{ct}$  and  $CPE_{ct}$  are the ohmic resistances, charge transfer resistance and charge transfer constant phase elements, respectively [26,28,42]. The LSFN-0.4 has the smallest  $R_{ct}$  value among all the samples, indicating that LSFN-0.4 possesses the fastest charger transfer ability in agreement with the LSV results (Table S3) [28]. Besides, the capacitances of LSFN determined by the EIS have the same trend as those obtained by the cyclic voltammetry (CV) scan, although their values deviate (Fig. S5) [42].

Fig. 3d plots the mass activity (MA, normalized to the oxide mass loading) and specific activity (SA, normalized to the BET specific surface area) of the perovskite electrocatalysts at 1.57 V vs. RHE, both of which exhibit a volcano-like dependence on the Ni content. The peak MA (148

 $Ag_{oxide}^{-1}$ ) and SA (7.70  $Am_{oxide}^{-2}$ ) of LSFN-0.4 are 155 times and 90 times higher than those of LSF. These results reveal that LSFN-0.4 generates an outstanding mass activity, a very important parameter in practical applications which can be further enhanced by nano-structure optimization. The catalytic activities normalized to the electrochemically active surface area (ECSA) are also compared and exhibit the same trend as the BET normalized SA (Fig. S5 and S6).

To ensure that the measured current for LSFN-0.4 is only due to OER and not corrosion of the conductive carbon or other side reactions, the rotating ring-disk electrode (RRDE) measurement technique in N<sub>2</sub>saturated 0.1 M KOH has been carried out as shown in Fig. 3e. In this technique, the O<sub>2</sub> gas generated from LSFN-0.4 on the GC disk is collected and reduced at the Pt ring at a constant potential of 0.4 V vs. RHE. The Faradaic efficiency ( $\varepsilon$ ) of O<sub>2</sub> production estimated from Fig. 3e is about 98% on the LSFN-0.4 electrode, suggesting that the oxidation current from LSFN-0.4 could be attributed to the OER through a fourelectron transfer pathway [9,43]. It is worth noting that the calculated  $\varepsilon$ slightly deviates from the 100% efficiency. This could be due to the formation of oxygen bubbles leading to a decrease in the collection efficiency of the RRDE, and the non-uniformity of the catalyst film causes an error in the measured geometric surface area of the disk [34,43].

The long-term stability, another critical criterion for practical application considerations, was first investigated by continuous CV between 1.2 and 1.65 V vs. RHE in O<sub>2</sub>-saturated 0.1 M KOH at a scan rate of 50 mV s<sup>-1</sup>. As depicted in Fig. 3f, the OER activity of LSFN-0.4 is almost completely preserved after 1000 cycles, revealing its excellent stability during the OER cycling conditions. In contrast, the sample La<sub>0.8</sub>Sr<sub>0.2</sub>FeO<sub>2.96</sub> with a similar composition to the pristine LSF shows an increase in  $\eta_{10}$  by 11.02 mV after 20 cycles [30]. Moreover, no visible change in the structure of LSFN-0.4 is detected after the 1000 cycles

(Fig. S7). On the contrary, an amorphous phase formation has been observed for the state-of-the-art perovskite catalysts such as BSCF and Si-SCO [22,44,45].

The OER stability of LSFN-0.4 was further verified by carrying out chronoamperometry measurement in 0.1 M KOH. As can be seen in Fig. S8a, the current density remains stable during the 15 h-test, apart from a small fluctuation in the current due to the temporary deactivation of the catalyst that comes from the blocking of the active surface by the generated O<sub>2</sub> bubbles [46]. It is also worth noting that the activity obtained on a woven carbon cloth is slightly lower than that on the RDE (Fig. S8b), indicating inefficient utilization of the catalyst, which is probably due to the higher mass loadings and mass transfer limitations in the absence of the rotation [34,46]. All the above electrochemical analysis reveals that Ni doping plays a vital role to enhance the activity of the LSFN catalysts.

## 2.3. Anion exchange membrane electrolyzer performance

To further evaluate the performance of LSFN-0.4 in the practical application, an anion exchange membrane electrolyzer with the sandwiched structure of 50 wt% LSFN-0.4/VC (anode)| FAA-3–PPS-130 membrane| 40 wt% Pt/C (cathode) was assembled and tested in a homemade apparatus in 0.1 M KOH at room temperature (Fig. S9). As shown in Fig. 4a, the electrolyzer can generate the common benchmark current density of 10 mA cm<sup>-2</sup> at a low cell voltage of 1.64 V, which is comparable with the results reported in the literature [47]. As for the electrochemical durability under a constant voltage of 1.64 V for 50 h, it yields the electrolyzing current density of  $\sim$ 11 mA cm<sup>-2</sup> in the beginning, then slowly decays and stabilizes to 9.3 mA cm<sup>-2</sup> after 36 h (Fig. 4b). The LSV curves obtained after the stability test with efficient



Fig. 4. Water-splitting in an anion exchange membrane electrolyzer with the sandwiched structure of 50 wt% LSFN-0.4/VC (anode)| FAA-3-PPS-130 membrane| 40 wt% Pt/C (cathode). (a) Current-voltage profiles before and after 50-h stability test in 0.1 M KOH at a scan rate of 5 mV s<sup>-1</sup>. The voltage is ohmic resistance-free. (b) Time-dependent current density response and (c) representative EIS measured at every 10-h interrupt during the chronoamperometric measurement at a constant potential of 1.64 V. Inset in (c) shows the used equivalent circuit. (d) Development of resistances during the chronoamperometric experiment derived from (c).

removal of  $H_2$  /O<sub>2</sub> bubbles almost overlaps the initial plot (Fig. 4a) indicating that the decay of current density is mainly due to the mass transport issues on the catalyst arising from the gradual accumulation of evolved bubbles, rather than the catalyst deactivation [48]. This is further evidenced by the EIS profiles evolution, where the mass transfer related low-frequency arcs increase, while the charge transfer related high-frequency ones remain constant during the stability test (Fig. 4c and d).

#### 2.4. Origin of the improved OER activity

To identify the origin of the OER electrocatalytic activity enhancement, we investigated the physicochemical properties and electronic structure evolution of the LSFN series caused by Ni substitution. Table S4 summarizes the surface compositions obtained by X-ray photoelectron spectroscopy (XPS, Fig. S10). Compared to the stoichiometric ratios, the amounts of Fe and Ni are constantly smaller than expected, indicating an A-site surface segregation, which is favoured by higher Ni substitution. The transition metal on the perovskite surface is generally considered to be the active site for catalyzing the OER. Therefore, such the A-site surface segregation is inevitably detrimental to the true catalytic properties [21,49].

The Fe 2p XPS spectra of all samples are presented in Fig. S11. The binding energy of Fe  $2p_{3/2}$  (710.2 eV) and the shape of the satellite at 718.7 eV are consistent with Fe<sup>3+</sup>, indicating that Fe<sup>3+</sup> is present in all samples [50]. However, because the Fe 2p region overlaps with the Ni LMM Auger peak, it is hard to accurately identify other oxidation states of Fe. Thus, the oxidation state of Fe was further analyzed by the Mössbauer spectroscopy, which is more sensitive to Fe characterization. Fig. 5a-c show the low-temperature Mössbauer spectra of LSF, LSFN-0.2 and LSFN-0.4, respectively, which can be fitted using four Fe<sup>3+</sup> sextets and one Fe<sup>4+</sup> sextet. The Fe<sup>3+</sup> sextets with different internal fields (*B*) and isomer shifts (*IS*) reflect the different strength of the coupling to the number of magnetic Fe or Ni next-neighboring atoms [51]. The dashed



Fig. 5. Chemical states and electronic structure of perovskites. Mössbauer spectra of (a) LSF measured at 77 K and (b) LSFN-0.2 measured at 6 K and (c) LSFN-0.4 measured at 6 K. (d) Relationship between specific activity and conductivity of LSF, LSFN-0.2 and LSFN-0.4. (e) O 1s and (f) Sr 3d XPS spectra of LSF, LSFN-0.2 and LSFN-0.4.

doublet in the spectra is assigned to the traces of Fe in the detector window. The hyperfine parameters obtained by the curve fitting are listed in Table S5. As shown in Table S5, the proportions of Fe<sup>4+</sup> species in LSF, LSFN-0.2 and LSFN-0.4 are 16.1%, 8.6% and 5.1%, respectively. According to AEM, Fe<sup>4+</sup> cations with an optimal eg orbital filling close to unity are widely accepted as the main contributor for the remarkable OER activity of perovskite [17,36,52]. Therefore, the trend of Fe<sup>4+</sup> content of the three perovskites, which is contrary to their OER activity, suggests that LSFN-0.4 with remarkable OER activity may follow the LOM pathway instead of AEM [22]. Fig. S12 shows the Ni 3p spectra of LSFN-0.2 and LSFN-0.4, which are fitted with two spin-orbit split doublets corresponding to  $Ni^{2+}$  and  $Ni^{3+}$ , and their  $3p_{3/2}$  peaks are set to 67.0 eV and 71.1 eV, respectively [34,35,53]. The calculated Ni<sup>3+</sup>/Ni<sup>2+</sup> ratio on the surface of LSFN-0.2 and LSFN-0.4 are 0.26 and 0.27, respectively. In literature, Ni<sup>3+</sup> is also predicted to be the active site for OER [35,54]. However, the effect of Ni substitution extends beyond increasing the oxidation state of Ni [35]. Although the Ni<sup>3+</sup>/Ni<sup>2+</sup> ratio is only slightly increased from LSFN-0.2 (0.26) to LSFN-0.4 (0.27), the  $\eta_{10}$ decreases 40 mV and the intrinsic activity (normalized by the BET surface area) at  $\eta = 340$  mV is improved by more than 5 times. The possible reason is that Ni substitution introduces and tunes the overlap between the Ni and Fe 3d bands and the O 2p band, consequently enhance charge-transfer interactions [34]. Therefore, it is reasonable to believe that the B-site cation is not the key contributor to the improved OER performance of LSFN. Instead, this improvement can be ascribed to the following two key factors.

First, the increase in the electrical conductivity induced by the structure transition. Fig. 5d shows the relationship between specific activity and the electrical conductivity of LSF, LSFN-0.2 and LSFN-0.4. As expected, the conductivity of LSFN increases significantly with increasing Ni concentration (Table S7). The conductivity of LSFN-0.4 (23 S cm<sup>-1</sup>) is almost three orders of magnitude higher than that of LSF  $(0.0035 \text{ S cm}^{-1})$ , indicating that the conductivity of the samples is greatly increased with the improvement of the lattice structure symmetry as a result of Ni substitution. This is mainly because the alignment of the TM-O-TM bands would broaden both the occupied O 2p valance band and the unoccupied TM 3d conduction bands, thus enhancing their overlap and increasing the electrical conductivity (Fig. 1b and Fig. S13) [21,23,25,28]. More importantly, the intrinsic OER activity strongly correlates with the electrical conductivity. Although the addition of conductive carbon can enhance the conduction pathway within the electrode, it cannot solve the conductivity problem of the electrocatalyst particles themselves [23]. The higher electrical conductivity of the perovskite can effectively extend the active zones and reduce polarization loss of OER [23,26,55]. Therefore, the increase in conductivity is the key factor being responsible for the significantly enhanced OER activity of the investigated perovskite electrocatalysts. This positive correlation is consistent with most previous studies [21,25,28], except for LaNiO<sub>3</sub> (LNO) with ultra-high conductivity (exceeding  $10^3$  S cm<sup>-1</sup>) [56], where OER activity increases, but electrical conductivity decreases upon Fe or Sr substitution [57,58], indicating such a descriptor is universal and applicable for other perovskites with different compositions and structures. The conductivity has little effect on the OER activity of the LNO samples, probably because it is already high enough to provide an effective internal pathway [59].

Second, the increase in oxygen vacancy concentration through Ni doping. Fig. 5e shows the O 1s XPS spectra of LSF, LSFN-0.2 and LSFN-0.4, which are fitted with three components. The component at 528.5 eV can be assigned to lattice oxygen species ( $O_{latt}$ ), the one located at 529.7 eV can be tentatively assigned to the perovskite lattice termination layer (M–O), and the third component with the highest binding energy (531.3 eV) is related to the surface species ( $O_{surf}$ ), such as highly oxidative oxygen species, hydroxides and carbonates [21,60]. The percentages of these three distinct oxygen species have been calculated and summarized in Table S6. It can be seen that the amount of  $O_{surf}$  increases with increasing nickel concentration, which could at least be partially

related to the increase in the surface oxygen vacancy concentration and consistent with that in the bulk (Table 1) [61]. This is mainly attributed to the enhanced TM-O covalency via decreasing the formatting energy of oxygen vacancy (Fig. S13). The increase in the surface oxygen vacancy concentration occurring concomitantly with the rise in the electrical conductivity can promote OER to occur via LOM [22,27], which is energetically favourable compared to AEM [12,59], enabling LSFN-0.4 to show the highest OER activity. It is worth noting that, compared with the changes in the literature [22,30,52], the increase in surface oxygen vacancy content from LSF (34.9%) to LSFN-0.2 (37.2%) is moderate. However, the OER activity of LSFN-0.2 is remarkably enhanced due to the significant increase in its electrical conductivity, further indicating that the electrical conductivity has a crucial effect on the OER performance of the studied perovskite. The increased surface oxygen vacancy concentration is also proved by the Sr 3d and C 1s XPS results (Fig. 5f, Fig. S14 and Table S6), in which the surface Sr species (Sr<sub>surf</sub>), mainly driven by the elastic and electrostatic interactions of oxygen vacancies, are found to increase with the increasing nickel content [60,62]. Meanwhile, these surface Sr species can be dissolved after immersion in the electrolyte, and exposing a surface rich in active B sites [63]. The La 3d XPS spectra of the perovskites are shown in Fig. S15. The strong overlap with the Ni 2p region at energies 850-870 eV makes it impossible to determine La 3d binding energy position accurately enough to probe its electronic structure. The La  $3d_{5/2}$ peak at lower binding energy (833.4 eV) is typical for the perovskite structure and the La 3d<sub>5/2</sub> peak does not change much with the increasing nickel content [53,64].

In addition, although LSFN-0.6 shows the highest BET surface area, oxygen vacancy concentration and electrical conductivity among the LSFN series (Table 1, Fig. S16, Table S6 and S7), it exhibits a lower intrinsic OER activity than LSFN-0.4. Such difference may be due to the presence of the NiO impurity in LSFN-0.6, with a proportion of 12.63% (Fig. S1 and Table 1), blocking the reactions on the perovskite active sites [29,65,66]. Similar detrimental effects of impurities, such as NiO [65–67],  $Co_3O_4$  [21] and  $Fe_2O_3$  [36] on the OER activity of a perovskite have been observed in the literature, indicating that the precise control of the composition is also essential for optimizing the OER activity of perovskites.

# 3. Conclusion

In this work, we demonstrated a simple strategy to increase the OER activity of LSFN by increasing the conductivity introduced by the structural transformation. Gradual substitution of Fe by Ni realizes the phase transition from rhombohedral to cubic structure, and then significantly improve the OER catalytic performance. The most active electrocatalyst LSFN-0.4 delivers a 90-times higher specific activity than the parent LSF at  $\eta = 340$  mV, with an ultra-low overpotential of 320 mV at 10 mA cm<sup>-2</sup> and Tafel slope of 35 mV dec<sup>-1</sup> in 0.1 M KOH. Furthermore, LSFN-0.4 maintains excellent durability during 1000 consecutive cycles and 50 h-water splitting in a laboratory-scale electrolyzer. The increased intrinsic OER activity of LSFN-0.4 is strongly correlated to the increased electrical conductivity, which together with the increase in the oxygen vacancy concentration may synergistically activate the participation of reversible lattice oxygen in OER. This work not only introduces a highly efficient and durable OER electrocatalyst, but also highlights the crucial effect of the electrical conductivity of perovskites on OER catalysis for the first time, which may disclose a new perspective in developing more efficient perovskite OER catalysts.

# CRediT authorship contribution statement

Lijun Fan: Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft, Writing – review & editing. Eeva Leena Rautama: Investigation, Formal analysis, Writing – review & editing. Johan Lindén: Investigation, Formal analysis, Writing – original draft. Jani Sainio: Investigation, Formal analysis, Writing original draft. Hua Jiang: Investigation, Writing – review & editing. Olli Sorsa: Investigation, Writing – review & editing. Nana Han: Writing – review & editing. Yongdan Li: Supervision, Writing – review & editing. Cristina Flox: Writing – review & editing. Yongdan Li: Supervision, Writing – review & editing. Yicheng Zhao: Writing – review & editing. Yongdan Li: Supervision, Writing – review & editing. Supervision, Funding acquisition, Conceptualization, Writing – review & editing.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgements

This work was supported by the Academy of Finland (the Profi 5 project). This work made use of the Aalto University RawMaterials (Aalto-RAMI) and Nanomicroscopy Center (Aalto-NMC) infrastructures. Mr. Lijun Fan acknowledges the financial support from the China Scholarship Council (No. 201806250102). The authors would like to thank Dr. Hongjiao Li for fruitful discussions.

#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2021.106794.

#### References

- J. Suntivich, K.J. May, H.A. Gasteiger, J.B. Goodenough, Y. Shao-Horn, A. Perovskite, Oxide Optimized for Oxygen Evolution Catalysis from Molecular Orbital Principles, Science 334 (2011) 1383–1385.
- [2] D. Zhou, P. Li, X. Lin, A. McKinley, Y. Kuang, W. Liu, W.F. Lin, X. Sun, X. Duan, Layered double hydroxide-based electrocatalysts for the oxygen evolution reaction: identification and tailoring of active sites, and superaerophobic nanoarray electrode assembly, Chem. Soc. Rev. 50 (2021) 8790–8817.
- [3] S. She, Y. Zhu, Y. Chen, Q. Lu, W. Zhou, Z. Shao, Realizing Ultrafast Oxygen Evolution by Introducing Proton Acceptor into Perovskites, Adv. Energy Mater. 9 (2019) 1900429–1900434.
- [4] J. Liu, H. Liu, H. Chen, X. Du, B. Zhang, Z. Hong, S. Sun, W. Wang, Progress and Challenges Toward the Rational Design of Oxygen Electrocatalysts Based on a Descriptor Approach, Adv. Sci. 7 (2020) 1901614.
- [5] F.A. Garcés-Pineda, M. Blasco-Ahicart, D. Nieto-Castro, N. López, J.R. Galán-Mascarós, Direct magnetic enhancement of electrocatalytic water oxidation in alkaline media, Nat. Energy 4 (2019) 519–525.
- [6] C. Li, X. Han, F. Cheng, Y. Hu, C. Chen, J. Chen, Phase and composition controllable synthesis of cobalt manganese spinel nanoparticles towards efficient oxygen electrocatalysis, Nat. Commun. 6 (2015) 7345.
- [7] Z. Chen, B. Zhao, Y.-C. He, H.-R. Wen, X.-Z. Fu, R. Sun, C.-P. Wong, NiCo<sub>2</sub>O<sub>4</sub> nanoframes with a nanosheet surface as efficient electrocatalysts for the oxygen evolution reaction, Mater. Chem. Front. 2 (2018) 1155–1164.
- [8] F.A. Garces-Pineda, H. Chuong Nguyen, M. Blasco-Ahicart, M. Garcia-Tecedor, M. de Fez Febre, P.Y. Tang, J. Arbiol, S. Gimenez, J.R. Galan-Mascaros, N. Lopez, Push-Pull Electronic Effects in Surface-Active Sites Enhance Electrocatalytic Oxygen Evolution on Transition Metal Oxides, ChemSusChem 14 (2021) 1595–1601.
- [9] F. Davodi, E. Muhlhausen, M. Tavakkoli, J. Sainio, H. Jiang, B. Gokce, G. Marzun, T. Kallio, Catalyst Support Effect on the Activity and Durability of Magnetic Nanoparticles: toward Design of Advanced Electrocatalyst for Full Water Splitting, ACS Appl. Mater. Interfaces 10 (2018) 31300–31311.
- [10] M. Gong, Y. Li, H. Wang, Y. Liang, J.Z. Wu, J. Zhou, J. Wang, T. Regier, F. Wei, H. Dai, An advanced Ni-Fe layered double hydroxide electrocatalyst for water oxidation, J. Am. Chem. Soc. 135 (2013) 8452–8455.
- [11] A. Grimaud, O. Diaz-Morales, B. Han, W.T. Hong, Y.L. Lee, L. Giordano, K. A. Stoerzinger, M.T.M. Koper, Y. Shao-Horn, Activating lattice oxygen redox reactions in metal oxides to catalyse oxygen evolution, Nat. Chem. 9 (2017) 457–465.
- [12] J.S. Yoo, X. Rong, Y. Liu, A.M. Kolpak, Role of Lattice Oxygen Participation in Understanding Trends in the Oxygen Evolution Reaction on Perovskites, ACS Catal. 8 (2018) 4628–4636.
- [13] J.T. Mefford, X. Rong, A.M. Abakumov, W.G. Hardin, S. Dai, A.M. Kolpak, K. P. Johnston, K.J. Stevenson, Water electrolysis on La<sub>1-x</sub>Sr<sub>x</sub>CoO<sub>3-δ</sub> perovskite electrocatalysts, Nat. Commun. 7 (2016) 11053.

- [14] G. Solomon, M.G. Kohan, M. Vagin, F. Rigoni, R. Mazzaro, M.M. Natile, S. You, V. Morandi, I. Concina, A. Vomiero, Decorating vertically aligned MoS<sub>2</sub> nanoflakes with silver nanoparticles for inducing a bifunctional electrocatalyst towards oxygen evolution and oxygen reduction reaction, Nano Energy 81 (2021), 105664.
- [15] Y. Guo, J. Tang, Z. Wang, Y.-M. Kang, Y. Bando, Y. Yamauchi, Elaborately assembled core-shell structured metal sulfides as a bifunctional catalyst for highly efficient electrochemical overall water splitting, Nano Energy 47 (2018) 494–502.
- [16] R. Pittkowski, P. Krtil, J. Rossmeisl, Rationality in the new oxygen evolution catalyst development, Curr. Opin. Electrochem. 12 (2018) 218–224.
- [17] J. Hwang, R.R. Rao, L. Giordano, Y. Katayama, Y. Yu, Y. Shao-Horn, Perovskites in catalysis and electrocatalysis, Science 358 (2017) 751–756.
- [18] Y. Zhu, W. Zhou, Z.-G. Chen, Y. Chen, C. Su, M.O. Tade, Z. Shao, SrNb<sub>0.1</sub>Co<sub>0.7</sub>Fe<sub>0.2</sub>O<sub>3-8</sub> Perovskite as a Next-Generation Electrocatalyst for Oxygen Evolution in Alkaline Solution, Angew. Chem. Int. Ed. 54 (2015) 3897–3901.
- [19] X. Rong, J. Parolin, A.M. Kolpak, A Fundamental Relationship between Reaction Mechanism and Stability in Metal Oxide Catalysts for Oxygen Evolution, ACS Catal. 6 (2016) 1153–1158.
- [20] K.Y. Zhu, F. Shi, X.F. Zhu, W.S. Yang, The roles of oxygen vacancies in electrocatalytic oxygen evolution reaction, Nano Energy 73 (2020), 104761.
- [21] X. Cheng, E. Fabbri, M. Nachtegaal, I.E. Castelli, M. El Kazzi, R. Haumont, N. Marzari, T.J. Schmidt, Oxygen Evolution Reaction on La1-x5r<sub>2</sub>CoO<sub>2</sub> Perovskites: A Combined Experimental and Theoretical Study of Their Structural, Electronic, and Electrochemical Properties, Chem. Mater. 27 (2015) 7662-7672.
- [22] Y. Pan, X. Xu, Y. Zhong, L. Ge, Y. Chen, J.M. Veder, D. Guan, R. O'Hayre, M. Li, G. Wang, H. Wang, W. Zhou, Z. Shao, Direct evidence of boosted oxygen evolution over perovskite by enhanced lattice oxygen participation, Nat. Commun. 11 (2020) 2002.
- [23] L. Li, X. Feng, Y. Nie, S. Chen, F. Shi, K. Xiong, W. Ding, X. Qi, J. Hu, Z. Wei, L.-J. Wan, M. Xia, Insight into the Effect of Oxygen Vacancy Concentration on the Catalytic Performance of MnO<sub>2</sub>, ACS Catal. 5 (2015) 4825–4832.
- [24] J. Dai, Y. Zhu, Y. Yin, H.A. Tahini, D. Guan, F. Dong, Q. Lu, S.C. Smith, X. Zhang, H. Wang, W. Zhou, Z. Shao, Super-Exchange Interaction Induced Overall Optimization in Ferromagnetic Perovskite Oxides Enables Ultrafast Water Oxidation, Small 15 (2019), 1903120.
- [25] S.S. Pramana, A. Cavallaro, C. Li, A.D. Handoko, K.W. Chan, R.J. Walker, A. Regoutz, J.S. Herrin, B.S. Yeo, D.J. Payne, J.A. Kilner, M.P. Ryan, S.J. Skinner, Crystal structure and surface characteristics of Sr-doped GdBaCo<sub>2</sub>O<sub>6-δ</sub> double perovskites: oxygen evolution reaction and conductivity, J. Mater. Chem. A 6 (2018) 5335–5345.
- [26] Y. Guo, Y. Tong, P. Chen, K. Xu, J. Zhao, Y. Lin, W. Chu, Z. Peng, C. Wu, Y. Xie, Engineering the electronic state of a perovskite electrocatalyst for synergistically enhanced oxygen evolution reaction, Adv. Mater. 27 (2015) 5989–5994.
- [27] Y. Zhu, W. Zhou, J. Sunarso, Y. Zhong, Z. Shao, Phosphorus-Doped Perovskite Oxide as Highly Efficient Water Oxidation Electrocatalyst in Alkaline Solution, Adv. Funct. Mater. 26 (2016) 5862–5872.
- [28] W. Wang, Y. Yang, D. Huan, L. Wang, N. Shi, Y. Xie, C. Xia, R. Peng, Y. Lu, An excellent OER electrocatalyst of cubic SrCoO<sub>3-δ</sub> prepared by a simple F-doping strategy, J. Mater. Chem. A 7 (2019) 12538–12546.
- [29] R. Chiba, F. Yoshimura, Y. Sakurai, Properties of La<sub>1-y</sub>Sr<sub>y</sub>Ni<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> as a cathode material for a low-temperature operating SOFC, Solid State Ion. 152–153 (2002) 575–582.
- [30] S. She, J. Yu, W. Tang, Y. Zhu, Y. Chen, J. Sunarso, W. Zhou, Z. Shao, Systematic Study of Oxygen Evolution Activity and Stability on  $La_{1-x}Sr_xFeO_{3-\delta}$  Perovskite Electrocatalysts in Alkaline Media, ACS Appl. Mater. Interfaces 10 (2018) 11715–11721.
- [31] W. Zhou, J. Sunarso, Enhancing Bi-functional Electrocatalytic Activity of Perovskite by Temperature Shock: A Case Study of LaNiO<sub>3-& J</sub>. Phys. Chem. Lett. 4 (2013) 2982–2988.
- [32] W. Wang, B. Lin, H. Zhang, Y. Sun, X. Zhang, H. Yang, Synthesis, morphology and electrochemical performances of perovskite-type oxide La<sub>x</sub>Sr<sub>1-x</sub>FeO<sub>3</sub> nanofibers prepared by electrospinning, J. Phys. Chem. Solids 124 (2019) 144–150.
  [33] H. Wang, J. Wang, Y. Pi, Q. Shao, Y. Tan, X. Huang, Double Perovskite
- [33] H. Wang, J. Wang, Y. Pi, Q. Shao, Y. Tan, X. Huang, Double Perovskite LaFe<sub>x</sub>Ni<sub>1-x</sub>O<sub>3</sub> Nanorods Enable Efficient Oxygen Evolution Electrocatalysis, Angew. Chem. Int. Ed. 131 (2019) 2338–2342.
- [34] R.P. Forslund, W.G. Hardin, X. Rong, A.M. Abakumov, D. Filimonov, C. T. Alexander, J.T. Mefford, H. Iyer, A.M. Kolpak, K.P. Johnston, K.J. Stevenson, Exceptional electrocatalytic oxygen evolution via tunable charge transfer interactions in La<sub>0.5</sub>Sr<sub>1.5</sub>Ni<sub>1-x</sub>Fe<sub>x</sub>O<sub>4±δ</sub> Ruddlesden-Popper oxides, Nat. Commun. 9 (2018) 3150.
- [35] Z. Wang, Y. You, J. Yuan, Y.-X. Yin, Y.-T. Li, S. Xin, D. Zhang, Nickel-Doped La<sub>0.8</sub>Sr<sub>0.2</sub>Mn<sub>1-x</sub>Ni<sub>x</sub>O<sub>3</sub> Nanoparticles Containing Abundant Oxygen Vacancies as an Optimized Bifunctional Catalyst for Oxygen Cathode in Rechargeable Lithium-Air Batteries, ACS Appl. Mater. Interfaces 8 (2016) 6520–6528.
- [36] Y.L. Zhu, W. Zhou, J. Yu, Y.B. Chen, M.L. Liu, Z.P. Shao, Enhancing Electrocatalytic Activity of Perovskite Oxides by Tuning Cation Deficiency for Oxygen Reduction and Evolution Reactions, Chem. Mater. 28 (2016) 1691–1697.
- [37] B. Zhao, L. Zhang, D. Zhen, S. Yoo, Y. Ding, D. Chen, Y. Chen, Q. Zhang, B. Doyle, X. Xiong, M. Liu, A tailored double perovskite nanofiber catalyst enables ultrafast oxygen evolution, Nat. Commun. 8 (2017) 14586.
- [38] S.R. Choi, J.-I. Lee, H. Park, S.W. Lee, D.Y. Kim, W.Y. An, J.H. Kim, J. Kim, H.-S. Cho, J.-Y. Park, Multiple perovskite layered lanthanum nickelate Ruddlesden-Popper systems as highly active bifunctional oxygen catalysts, Chem. Eng. J. 409 (2021), 128226.
- [39] H.B. Tao, Y. Xu, X. Huang, J. Chen, L. Pei, J. Zhang, J.G. Chen, B. Liu, A General Method to Probe Oxygen Evolution Intermediates at Operating Conditions, Joule 3 (2019) 1498–1509.

#### Nano Energy 93 (2022) 106794

- [40] T. Shinagawa, A.T. Garcia-Esparza, K. Takanabe, Insight on Tafel slopes from a microkinetic analysis of aqueous electrocatalysis for energy conversion, Sci. Rep. 5 (2015) 13801.
- [41] S. Liu, H. Luo, Y. Li, Q. Liu, J.-L. Luo, Structure-engineered electrocatalyst enables highly active and stable oxygen evolution reaction over layered perovskite LaSr<sub>3</sub>Co<sub>1.5</sub>Fe<sub>1.5</sub>O<sub>10-δ</sub>, Nano Energy 40 (2017) 115–121.
- [42] P. Connor, J. Schuch, B. Kaiser, W. Jaegermann, The Determination of Electrochemical Active Surface Area and Specific Capacity Revisited for the System MnO<sub>x</sub> as an Oxygen Evolution Catalyst, Z. Phys. Chem. 234 (2020) 979–994.
- [43] M. Tavakkoli, M. Nosek, J. Sainio, F. Davodi, T. Kallio, P.M. Joensuu, K. Laasonen, Functionalized Carbon Nanotubes with Ni(II) Bipyridine Complexes as Efficient Catalysts for the Alkaline Oxygen Evolution Reaction, ACS Catal. 7 (2017) 8033–8041.
- [44] K.J. May, C.E. Carlton, K.A. Stoerzinger, M. Risch, J. Suntivich, Y.-L. Lee, A. Grimaud, Y. Shao-Horn, Influence of Oxygen Evolution during Water Oxidation on the Surface of Perovskite Oxide Catalysts, J. Phys. Chem. Lett. 3 (2012) 3264–3270.
- [45] G. Chen, W. Zhou, D. Guan, J. Sunarso, Y. Zhu, X. Hu, W. Zhang, Z. Shao, Two orders of magnitude enhancement in oxygen evolution reactivity on amorphous  $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$  nanofilms with tunable oxidation state, Sci. Adv. 3 (2017), e1603206.
- [46] M. Tavakkoli, T. Kallio, O. Reynaud, A.G. Nasibulin, J. Sainio, H. Jiang, E. I. Kauppinen, K. Laasonen, Maghemite nanoparticles decorated on carbon nanotubes as efficient electrocatalysts for the oxygen evolution reaction, J. Mater. Chem. A 4 (2016) 5216–5222.
- [47] J. Hnát, M. Plevova, R.A. Tufa, J. Zitka, M. Paidar, K. Bouzek, Development and testing of a novel catalyst-coated membrane with platinum-free catalysts for alkaline water electrolysis, Int. J. Hydrogen Energy 44 (2019) 17493–17504.
- [48] G.-C. Chen, T.H. Wondimu, H.-C. Huang, K.-C. Wang, C.-H. Wang, Microwaveassisted facile synthesis of cobalt iron oxide nanocomposites for oxygen production using alkaline anion exchange membrane water electrolysis, Int. J. Hydrogen Energy 44 (2019) 10174–10181.
- [49] J. Yu, D. Chen, M. Saccoccio, K. Lam, F. Ciucci, Promotion of Oxygen Reduction with Both Amorphous and Crystalline MnO<sub>x</sub> through the Surface Engineering of La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3-δ</sub> Perovskite, ChemElectroChem 5 (2018) 1105–1112.
- [50] M.C. Biesinger, B.P. Payne, A.P. Grosvenor, L.W.M. Lau, A.R. Gerson, R.S.C. Smart, Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Cr, Mn, Fe, Co and Ni, Appl. Surf. Sci. 257 (2011) 2717–2730.
- **[51]** F. Menil, Systematic trends of the <sup>57</sup>Fe Mössbauer isomer shifts in (FeO<sub>n</sub>) and (FeF<sub>n</sub>) polyhedra. Evidence of a new correlation between the isomer shift and the inductive effect of the competing bond T- $X (\rightarrow$  Fe) (where X is O or F and T any element with a formal positive charge), J. Phys. Chem. Solids 46 (1985) 763–789.
- [52] Z. Li, L. Lv, J. Wang, X. Ao, Y. Ruan, D. Zha, G. Hong, Q. Wu, Y. Lan, C. Wang, J. Jiang, M. Liu, Engineering phosphorus-doped LaFeO<sub>3-δ</sub> perovskite oxide as robust bifunctional oxygen electrocatalysts in alkaline solutions, Nano Energy 47 (2018) 199–209.
- [53] L. Qiao, X. Bi, Direct observation of  $Ni^{3+}$  and  $Ni^{2+}$  in correlated LaNiO<sub>3-6</sub> films, EPL (Europhys. Lett. ) 93 (2011) 57002.

- [54] R. Pittkowski, S. Divanis, M. Klementová, R. Nebel, S. Nikman, H. Hoster, S. Mukerjee, J. Rossmeisl, P. Krtil, Engendering Unprecedented Activation of Oxygen Evolution via Rational Pinning of Ni Oxidation State in Prototypical Perovskite: Close Juxtaposition of Synthetic Approach and Theoretical Conception, ACS Catal. 11 (2021) 985–997.
- [55] G. Solomon, A. Landström, R. Mazzaro, M. Jugovac, P. Moras, E. Cattaruzza, V. Morandi, I. Concina, A. Vomiero, NiMoO<sub>4</sub>@Co<sub>3</sub>O<sub>4</sub> Core–Shell Nanorods: In Situ Catalyst Reconstruction toward High Efficiency Oxygen Evolution Reaction, Adv. Energy Mater. 11 (2021), 2101324.
- [56] J. Fowlie, M. Gibert, G. Tieri, A. Gloter, J. Iniguez, A. Filippetti, S. Catalano, S. Gariglio, A. Schober, M. Guennou, J. Kreisel, O. Stephan, J.M. Triscone, Conductivity and Local Structure of LaNiO<sub>3</sub> Thin Films, Adv. Mater. 29 (2017).
- [57] J. Liu, E. Jia, L. Wang, K.A. Stoerzinger, H. Zhou, C.S. Tang, X. Yin, X. He, E. Bousquet, M.E. Bowden, A.T.S. Wee, S.A. Chambers, Y. Du, Tuning the Electronic Structure of LaNiO<sub>3</sub> through Alloying with Strontium to Enhance Oxygen Evolution Activity, Adv. Sci. 6 (2019), 1901073.
- [58] L. Wang, P. Adiga, J. Zhao, W.S. Samarakoon, K.A. Stoerzinger, S.R. Spurgeon, B. E. Matthews, M.E. Bowden, P.V. Sushko, T.C. Kaspar, G.E. Sterbinsky, S.M. Heald, H. Wang, L.W. Wangoh, J. Wu, E.J. Guo, H. Qian, J. Wang, T. Varga, S. Thevuthasan, Z. Feng, W. Yang, Y. Du, S.A. Chambers, Understanding the Electronic Structure Evolution of Epitaxial LaNi<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> Thin Films for Water Oxidation, Nano Lett. 21 (2021) 8324–8331.
- [59] J. Liu, E. Jia, K.A. Stoerzinger, L. Wang, Y. Wang, Z. Yang, D. Shen, M. H. Engelhard, M.E. Bowden, Z. Zhu, S.A. Chambers, Y. Du, Dynamic Lattice Oxygen Participation on Perovskite LaNiO<sub>3</sub> during Oxygen Evolution Reaction, J. Phys. Chem. C. 124 (2020) 15386–15390.
- [60] E.J. Crumlin, E. Mutoro, Z. Liu, M.E. Grass, M.D. Biegalski, Y.-L. Lee, D. Morgan, H. M. Christen, H. Bluhm, Y. Shao-Horn, Surface strontium enrichment on highly active perovskites for oxygen electrocatalysis in solid oxide fuel cells, Energy Environ. Sci. 5 (2012) 6081–6088.
- [61] Q. Ji, L. Bi, J. Zhang, H. Cao, X.S. Zhao, The role of oxygen vacancies of ABO<sub>3</sub> perovskite oxides in the oxygen reduction reaction, Energy Environ. Sci. 13 (2020) 1408–1428.
- [62] B. Koo, K. Kim, J.K. Kim, H. Kwon, J.W. Han, W. Jung, Sr Segregation in Perovskite Oxides: Why It Happens and How It Exists, Joule 2 (2018) 1476–1499.
- [63] A. Boucly, E. Fabbri, L. Artiglia, X. Cheng, D. Pergolesi, M. Ammann, T.J. Schmidt, Surface Segregation Acts as Surface Engineering for the Oxygen Evolution Reaction on Perovskite Oxides in Alkaline Media, Chem. Mater. 32 (2020) 5256–5263.
- [64] P.A.W. van der Heide, Systematic x-ray photoelectron spectroscopic study of La<sub>1-x</sub>Sr<sub>x</sub>-based perovskite-type oxides, Surf. Interface Anal. 33 (2002) 414–425.
- [65] C.C. Wang, Y. Cheng, E. Ianni, S.P. Jiang, B. Lin, A highly active and stable La<sub>0.5</sub>Sr<sub>0.5</sub>Ni<sub>0.4</sub>Fe<sub>0.6</sub>O<sub>3-δ</sub> perovskite electrocatalyst for oxygen evolution reaction in alkaline media, Electrochim. Acta 246 (2017) 997–1003.
- [66] M. Retuerto, A.G. Pereira, F.J. Pérez-Alonso, M.A. Peña, J.L.G. Fierro, J.A. Alonso, M.T. Fernández-Díaz, L. Pascual, S. Rojas, Structural effects of LaNiO<sub>3</sub> as electrocatalyst for the oxygen reduction reaction, Appl. Catal., B 203 (2017) 363–371.