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# Ion Intercalation in Lanthanum Strontium Ferrite for Aqueous Electrochemical Energy Storage Devices

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12 KEYWORDS: Defect chemistry, thin films, ion intercalation, in-situ, spectroscopic ellipsometry,  
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14 liquid electrolyte  
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## 21 ABSTRACT 22 23 24

25 Ion intercalation of perovskite oxides in liquid electrolytes is a very promising method for  
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27 controlling their functional properties while storing charge, which opens the potential application  
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29 in different energy and information technologies. Although the role of defect chemistry in the  
30  
31 oxygen intercalation in a gaseous environment is well established, the mechanism of ion  
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33 intercalation in liquid electrolytes at room temperature is poorly understood. In this study, the  
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35 defect chemistry during ion intercalation of  $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$  thin films in alkaline electrolytes is  
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37 studied. Oxygen and proton intercalation into the LSF perovskite structure is observed at moderate  
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39 electrochemical potentials (0.5 V to -0.4 V), giving rise to a change in the oxidation state of Fe (as  
40  
41 a charge compensation mechanism). The variation of the concentration of holes as a function of  
42  
43 the intercalation potential was characterized by in-situ ellipsometry and the concentration of  
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45 electron holes was indirectly quantified for different electrochemical potentials. Finally, a dilute  
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47 defect chemistry model that describes the variation of defect species during ionic intercalation was  
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49 developed.  
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## INTRODUCTION

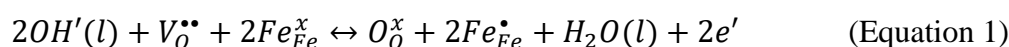
Transition metal oxides (TMOs) are promising electrode materials for room temperature energy conversion and storage applications based on ion intercalation, such as ion batteries,<sup>1,2</sup> supercapacitors<sup>3,4</sup> and pseudocapacitors.<sup>5,6</sup> In particular, perovskite oxides such as  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$  (LSM),  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  (LSC) and  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$  (LSF) are able to reversibly intercalate oxygen at room temperature in different liquid electrolytes, which raised the attention for their application as high energy density pseudocapacitors,<sup>7,8</sup> efficient catalyst in oxygen reduction reaction (ORR) and oxygen evolution reaction (OER),<sup>9-16</sup> rapid and efficient electrochromic windows and synaptic memories.<sup>17-19</sup> In these materials, ion intercalation is a complex phenomenon that involves redox reactions, ionic and electronic transfer through a liquid-solid interface and ionic transport.<sup>19</sup> Ion intercalation in perovskites oxides usually involves a change in the oxidation state of the B-site metal, which results in strong modifications of the electronic band structure of the oxide affecting its properties (electronic, thermal and optical conductivity etc.)<sup>18,20</sup> The oxygen anion exchange between the electrolyte and the perovskite may also induces a topotactic phase transformation between the oxidized perovskite and reduced brownmillerite phase,<sup>21,22</sup> favoring applications in resistive-switching memories and magnetoelectric and spintronic devices.<sup>23,24</sup>

A representative example of a pseudocapacitive behavior depending on point defects is found for non-stoichiometric  $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$  (LSF50).<sup>8</sup> LSF50 crystallizes in a perovskite structure where the Sr-substitution of La creates oxygen vacancies and/or electron holes to maintain electroneutrality. Moreover, insertion (or extraction) of oxygen anions into (or from) LSF50 generates changes in the concentration of  $\text{Fe}^{4+}$  holes and oxygen vacancies.<sup>8</sup> The increased concentration of oxygen vacancies in LSF50 not only causes a fast oxygen diffusion rate and an increased oxygen-anion-based pseudocapacitance,<sup>8</sup> but it also modifies the electrochemical

performance of the material.<sup>25–27</sup> Apart from the straightforward application in supercapacitors, the ability to intercalate ions at room temperature for LSF family was found to offer interesting application as rocking oxygen battery and synaptic memories.<sup>28,29</sup>

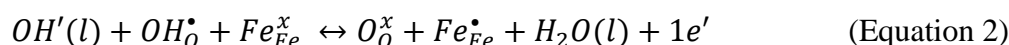
Despite this significant interest in low temperature ion intercalation in perovskite oxides, the exact mechanism and dynamics of ionic insertion are still unclear. For instance, different works show that the main species diffusing in and out LSF electrodes during intercalation in alkaline electrolytes are oxygen species,<sup>4,8,30</sup> while others proposed that protons are the main responsible for its pseudocapacitive behavior.<sup>10,31</sup> Moreover, ion intercalation in these materials is usually interpreted on the basis of pseudocapacitive Nernst behavior, where the effect of the different point defects is not taken into account.<sup>32</sup> In this sense, a comprehensive defect chemistry model considering both the intercalating species and the point defects in the perovskite oxide is still missing.

The common intercalation mechanism described in literature for explaining the electrochemical reactions in perovskite oxides cycled in alkaline electrolytes involves the incorporation of oxygen species through the annihilation of an oxygen vacancy ( $V_O^{\bullet\bullet}$ ) and the formation of two localized electronic holes ( $Fe_{Fe}^{\bullet}$ ), as:<sup>8,28</sup>

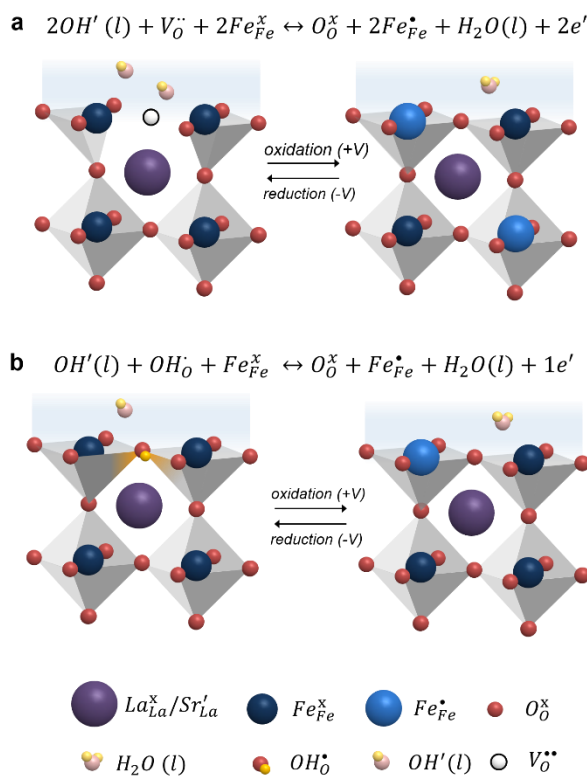


According to the Kröger-Vink notation,  $OH'$ ,  $Fe_{Fe}^x$ ,  $O_O^x$ , and  $e'$  represent the  $OH^-$  ions in the liquid electrolyte,  $Fe^{3+}$  and  $O^{2-}$  ions in the lattice of the perovskite structure and the electrons generated as a result of oxygen intercalation, respectively.

Nevertheless, an alternative pathway based on the incorporation of protons ( $OH_O^{\bullet}$ ) may also explain the changes of  $Fe^{4+}$ , as:<sup>10,18,33,34</sup>



In this case, protons are incorporated in the material through the dissociation of water. Protons are dissociated from the H<sub>2</sub>O molecules in the aqueous KOH electrolyte and intercalated into the LSF50 layer following an electrochemical reduction reaction with cathodic potentials ( $V < 0$ ). The incorporated protons are bonded with oxygen atoms in the lattice and form protonic defects  $OH'_O$  with a formal positive charge, reducing the oxidation state of iron as compensation mechanism. This reaction was alternatively proposed for explaining ion intercalation in perovskite oxides.<sup>31</sup> The two mechanisms are schematically illustrated in **Figure 1**.



**Figure 1.** Schematic representation of the oxygen (a) and protonic (b) intercalation mechanisms in alkaline electrolytes.

The present study investigates the mechanism of ion intercalation in LSF50 within liquid alkaline media at room temperature. LSF thin films are employed to ensure a well-defined geometry and an intimate contact with the substrate, which represents an advantage for

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3 understanding intrinsic materials properties<sup>35</sup>. However, the use of thin films prevents from  
4 employing conventional techniques such as coulometric titration for the determination of the  
5 concentration of relevant species (due to a reduced amount of material available). In this work, the  
6 concentration of electronic holes during the ion intercalation process was successfully measured  
7 by in-situ ellipsometry on thin films. This in-situ ellipsometry methodology has been recently  
8 proposed by the authors for successfully tracking defect chemistry and ion insertion in thin films  
9 under real electrochemical operation conditions.<sup>36,37</sup> Ellipsometry is a widely employed non-  
10 destructive spectroscopic technique, mainly used for the estimation of optical constants and  
11 thicknesses, which is based on the change of the polarization state of the light beam reflected on a  
12 thin film sample.<sup>36</sup> In combination with ellipsometry, the mechanism of ion intercalation in LSF  
13 was investigated using Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), Positron  
14 Annihilation Lifetime Spectroscopy (PALS) and ex-situ ellipsometry. These complementary  
15 analyses unambiguously determined that both oxygen and protons are intercalating in LSF in  
16 alkaline electrolyte. In addition, a dilute defect chemistry model that reproduces the electronic  
17 holes concentration during ion intercalation is proposed.  
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## 40 EXPERIMENTAL SECTION

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42 **Thin film deposition:**  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$  (LSM) and LSF50 thin films were sequentially  
43 deposited by Pulsed Laser Deposition (PLD) on a 10 mm × 10 mm (100)-oriented Nb doped STO  
44 (Nb:STO) substrate (Crystec GmbH) to build up LSF50/LSM/Nb:STO samples. Herein, the LSM  
45 interlayer was used for enhancing the electrical conductivity of the sample and creating a  
46 polarization in the LSF film.<sup>23,38</sup> LSF layers were deposited using a microfabricated Si mask that  
47 allowed the growth of a 5 mm × mm layer in the central area on the top of the LSM. Both layers  
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3 were deposited with an energy fluency of  $0.8 \text{ J cm}^{-2}$  at a frequency of 10 Hz using a large-area  
4 system from PVD products (PLD-5000) equipped with a KrF-248 nm excimer laser from Lambda  
5 Physik (COMPex PRO 205). The target-to-substrate distance was set to 90 mm and the substrate  
6 temperature was kept at 700 °C. The layers were grown in an oxidizing atmosphere with an oxygen  
7 partial pressure of 0.0067 mbar.  
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14 **Thin film characterization:** Structural analysis of the thin films was based on high-resolution  
15 X-Rays Diffraction (XRD) measurements carried out in  $\theta$ - $2\theta$  Bragg-Brentano geometry using a  
16 diffractometer PANalytical X'Pert-PRO MRD with a Cu  $K_{\alpha}$  radiation source and a combination  
17 of a parabolic mirror and a Ge monochromator with two reflections. Scanning Electron  
18 Microscopy coupled to Energy-Dispersive X-Ray (SEM-EDX) was carried out in a Zeiss Auriga  
19 microscope to characterize the morphology and the elemental composition of the thin films. In this  
20 way, the Sr/(La+Sr) ratio for the LSF50 thin film was obtained. The ionic species in the reduced  
21 and oxidized samples were investigated by ToF-SIMS depth profiling, using an IONTOF TOF-  
22 SIMS 5 instrument. The depth profiling analysis was obtained by alternating a 25 keV Bi<sup>+</sup> primary  
23 ion and a 2keV Cs<sup>+</sup> secondary ion beam. Negative secondary ions were detected in the burst  
24 alignment mode. The raster areas were 50  $\mu\text{m}$  x 50  $\mu\text{m}$  and 150  $\mu\text{m}$  x 150  $\mu\text{m}$  for the primary and  
25 secondary beams respectively. The open-volume defects in the post-annealed samples were  
26 studied by Variable Energy Positron Annihilation Lifetime Spectroscopy (VEPALS). VEPALS  
27 measurements were carried out at the Mono-energetic Positron Source (MePS) beamline at  
28 Helmholtz-Zentrum Dresden-Rossendorf (HZDR) in Germany.<sup>39</sup> Digital lifetime CrBr<sub>3</sub>  
29 scintillator detector coupled to a Hamamatsu R13089-100 PMT was utilized for acquisition of  
30 positron annihilation signals, which were evaluated using SPDevices ADQ14DC-2X digitizer with  
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3 14-bit vertical resolution and 2 GS/s horizontal resolution and with a time resolution function down  
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5 to about 0.230 ns.<sup>40</sup>  
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8 **Electrochemical characterization:** For ex-situ and in-situ experiments in liquid electrolyte,  
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10 LSF50 and LSM thin films were attached to a copper wire using graphite paste. The frame of the  
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12 sample and the graphite paste were covered by a robust epoxy resin glue from UHU to avoid  
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14 undesirable reactions. The final sample presents an active area of 11.7 mm<sup>2</sup>. The electrochemical  
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16 measurements were carried out on a three-electrode system in which: i) the encapsulated LSF50  
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18 thin film sample was the working electrode (WE); ii) an aqueous 0.1 M KOH solution was  
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20 employed as an electrolyte; iii) activated carbon and silver wires were introduced into the  
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22 electrolyte acting as a counter electrode (CE) and reference electrode (RE), respectively. Cyclic  
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24 Voltammetry (CV) experiments were performed at room temperature in the electrolyte of 0.1 M  
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26 KOH solution at a scan rate of 0.5 mV s<sup>-1</sup> using a SP-150 Biologic potentiostat.  
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31 **Spectroscopic ellipsometry measurements:** The optical properties of LSF50 thin films were  
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33 measured with a multi-wavelength spectroscopic ellipsometer (UVISEL, Horiba scientific). The  
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35 ex-situ ellipsometry experiments were performed in a range of photon energy from 0.6 eV to 5 eV  
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37 with a step of 0.05 eV whereas the in-situ ellipsometry spectra were recorded in a limited range of  
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39 photon energy from 1.5 eV to 4.85 eV because of the optical absorption of the liquid electrolyte.  
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41 The angle of the incident light was set at 70°. The obtained ellipsometry data were processed using  
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43 the DeltaPsi 2 software from Horiba Scientific. A thickness of 164±2 nm and 78±3 nm was  
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45 obtained for the LSF50 and LSM thin films, respectively.  
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50 For ex-situ measurements, four LSF50/LSM/Nb:STO samples were prepared. On the one hand,  
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52 two samples were annealed in dry pure oxygen and nitrogen (Nitrogen 5.0) atmospheres at 575 °C  
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54 for 5 hours using a Linkam thermal stage (THMS600). These samples were labelled as “O<sub>2</sub>-  
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annealed” and “N<sub>2</sub>-annealed”, respectively. After cooling down to room temperature, the optical properties of the annealed samples were characterized by spectroscopic ellipsometry in air. On the other hand, two different samples were oxidized and reduced in 0.1 M aqueous KOH electrolyte by applying DC potentials of 0.5 V and -0.4 V in a three-electrode configuration. These samples were labelled as “KOH-oxidized” and “KOH-reduced”, respectively.

In case of the in-situ ellipsometry, the measurements were carried out in a homemade 3D printed chamber fabricated in Acrylonitrile Butadiene Styrene (ABS). The chamber was equipped with two transparent optical windows perpendicularly tilted to the incident light beam of the ellipsometer. CE and RE were introduced into the chamber, which was filled with an aqueous electrolyte solution. Finally, LSF50 films under study were polarized by applying DC voltage bias ranging from 0.5 V to -0.4 V in three-electrode configuration. Electrochemical measurements were carried out using a potentiostat (Biologic SP-150). Individual spectroscopic ellipsometry spectra were recorded after each DC voltage step. The end of the intercalation process was ensured by monitoring the electrical current at each DC voltage bias.

## RESULTS AND DISCUSSION

**Structural and optical characterization of LSF50:** Fully dense and homogeneous La<sub>0.5</sub>Sr<sub>0.5</sub>FeO<sub>3-δ</sub> epitaxial thin films of 180 nm in thickness were successfully grown by PLD on La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3-δ</sub>/Nb:STO(100) substrates (see Supplementary Information **Figure S1**). Interlayers of LSM were included to improve the electrical conductivity of the sample.<sup>23,38</sup> Considering the potential range where the ion intercalation takes place,<sup>8</sup> LSF50 films were electrochemically cycled at room temperature in 0.1 M KOH aqueous solution from 0.5 to -0.4 V at a scan rate of 0.5 mV/s (see Experimental Section for more details). **Figure 2a** shows typical Cyclic

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3 Voltammetry (CV) curves for LSF50 thin films. In this figure, a pseudocapacitive behavior is  
4 clearly observed with redox reaction peaks centered at  $E_{1/2} = -0.15$  V, which is consistent with the  
5 results reported in the literature for the similar compound in powder form.<sup>8</sup> To discard  
6 contributions from the substrate, similar experiments were carried out for plain  
7 LSM/Nb:STO(100) samples and LSF50 layers on top of FTO substrates (see **Figure S2** and  
8 **Figure S3** in Supplementary Information, respectively), confirming that the observed redox pair  
9 is fully ascribable to the LSF50 layer. The asymmetric peaks observed in the CV scans are likely  
10 originated from kinetic limitations, different in cathodic and anodic directions and linked to the  
11 sluggish ionic diffusivity in the LSF50 bulk film at room temperature.

12  
13 In order to explore the origin of the redox reaction peaks, oxidized and reduced LSF50 samples  
14 were analyzed by ellipsometry and XRD. These samples were obtained after stabilization in KOH  
15 when applying a DC potential of 0.5 V (“KOH-oxidized”) and -0.4 V (“KOH-reduced”). **Figure**  
16 **2b** shows the optical conductivity of both films measured by spectroscopy ellipsometry (details on  
17 the data analysis can be found in **Section S4** in Supplementary Information), the optical  
18 conductivity of the thin films was calculated by **Equation S2** in Supplementary Information with  
19 the optical parameters measured by ellipsometry. KOH reduction clearly induces an intensity  
20 decrease of low-energy optical transitions (for *A*- and *B*-transitions with photon energies around 1  
21 eV and 3 eV, respectively) while amplification of the one in the high-energy range (*C*-transition  
22 with photon energy around 4.2 eV). This behavior has been previously assigned to a strong  
23 modification of the LSF band structure, associated with the change in the concentration of  $\text{Fe}^{4+}$   
24 holes, which induces a redistribution of the optical weight and the creation of new intra-gap states  
25 upon hole doping.<sup>36,41,42</sup> To independently confirm this hypothesis, the optical conductivity spectra  
26 of LSF50 thin films fully oxidized and reduced in a conventional way (employing oxygen and  
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3 nitrogen atmospheres at 575 °C)<sup>36,43,44</sup> were acquired and plotted in **Figure 2b** (named as “N<sub>2</sub>-  
4 annealed” and “O<sub>2</sub>-annealed”, respectively). In the N<sub>2</sub>-annealed sample electronic charges are  
5 compensated by electron holes ( $[Sr'_{La}] = [Fe'_{Fe}]$ ,  $[V''_O] \sim 0$ ), while in the O<sub>2</sub>-annealed sample  
6 electronic charges are compensated by oxygen vacancies ( $[Sr'_{La}] = 2[V''_O]$ ,  $[Fe'_{Fe}] \sim 0$ ). The change  
7 in optical conductivity observed for the O<sub>2</sub>-annealed and N<sub>2</sub>-annealed samples is consistent with  
8 the variation of holes in the LSF thin films, as observed in previous works.<sup>42,45</sup> Moreover, in our  
9 previous work we directly observed a univocal association between the optical conductivity of  
10 LSF thin films and the electron hole concentration, which allowed us to quantify the defect  
11 chemistry of these layers under a variety of different electrochemical conditions.<sup>36</sup> Thus,  
12 spectroscopic ellipsometry can be used to track the Fe<sup>4+</sup>/Fe<sup>3+</sup> transition through linking the optical  
13 conductivity with the concentration of electron holes. The similarity of the optical conductivity  
14 spectra observed for the LSF layers reduced and oxidized in the different environment confirms  
15 that the application of moderate electrochemical potentials in liquid KOH is able to completely  
16 oxidize and reduce the LSF. The optical conductivity spectra of the pristine LSF50 thin film is also  
17 present in the same figure. The optical conductivity of the pristine LSF50 layer is found between  
18 the fully oxidized film (KOH-oxidized or O<sub>2</sub>-annealed sample) and the fully-reduced sample  
19 (KOH-reduced or N<sub>2</sub>-annealed sample), indicating that the as deposited samples present a partial  
20 oxygen deficiency.

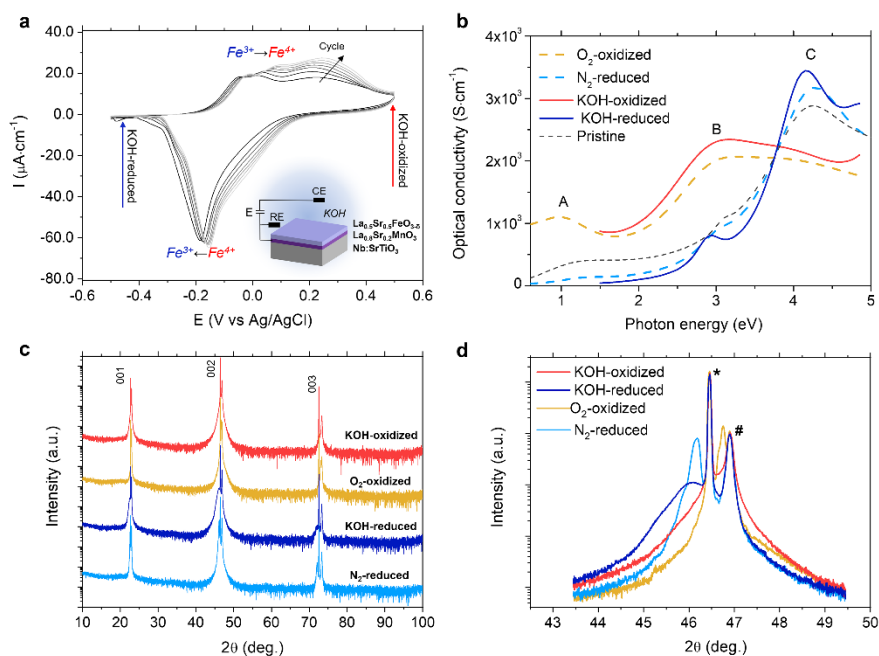
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45 High-resolution XRD was employed to retrieve the film structural parameters, and to characterize  
46 the chemical stability and volume expansion of the O<sub>2</sub>-annealed, N<sub>2</sub>-annealed, KOH-reduced and  
47 KOH-oxidized samples. The resulting XRD patterns are shown in **Figure 2c**. The whole set of  
48 films present a single (00l)-oriented perovskite structure without secondary phase formation and  
49 an excellent epitaxial nature, confirming the chemical stability of the LSF50 thin films after the  
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annealing treatments and ion intercalation reactions in alkaline electrolyte.<sup>46</sup> It is important to remark that any of the reduced films show transition to the brownmillerite phase, which is commonly observed for large Sr concentration.<sup>21,23,47,48</sup> The stability of the Nb:STO/LSM substrate is also remarkable as shown in **Figure 2d**, where the diffraction peaks associated to this substrate are always present. A displacement of the diffraction peak position of the N<sub>2</sub>-annealed LSF50 film from  $2\theta$  of 46.75 ° to 46.16 ° (with respect to the O<sub>2</sub>-annealed LSF50 film) implies a slight chemical expansion in the out-of-plane lattice parameter of the LSF50 film from 3.883 Å to 3.928 Å ( $\approx 2\%$ ), which is consistent with the increment in the LSF50 film thickness from 178 nm to 180 nm given by ellipsometry. This expansion is due to the reduction of Fe<sup>4+</sup> ions to Fe<sup>3+</sup> ions which have a larger ionic radius as a result of oxygen uptake from the perovskite structure.<sup>49</sup> The increased intensity in the XRD signal at  $2\theta \approx 46.7^\circ$  indicates the LSF50 diffraction peak for the KOH-oxidized sample, which is consistent with the LSF50 diffraction peak for the O<sub>2</sub>-annealed sample (see also the (004) diffraction peak in **Figure S5** of the supplementary information).

Comparable peak shift is also observed for KOH-reduced films, which suggests an analogous expansion behavior. Despite this similarity between conventionally- and KOH-reduced samples, a careful analysis of the Kiessig fringes<sup>47,50</sup>, which appear as a shoulder on the left side of the (200) diffraction peak of post-annealed LSF50 films while disappear for the KOH-cycled samples, indicates a certain loss of the film-substrate coherence during the ionic intercalation in liquid electrolytes. Furthermore, the broadening of the LSF50 diffraction peak for the KOH-oxidized sample indicates the decrement of crystallinity of the films. This is likely due to the foreseen creation of structural defects, as previously referred in the literature.<sup>51,52</sup> Regardless of this decrease of crystalline quality observed by XRD, the microstructural stability of the LSF50 films

in 0.1 M KOH solution is proved by SEM analysis of the morphology of the layers after cycling (see **Figure S6** in Supplementary Information), which remains crack-free and fully dense.

Overall, this section showed that the electrochemical cycling in KOH at room temperature leads to a reversible ion intercalation, resulting in a  $\text{Fe}^{4+}/\text{Fe}^{3+}$  transition as a charge compensation mechanism.



**Figure 2.** **a.** CV curve of the LSF50 thin film measured at room temperature using a scan rate of 0.5 mV/s. **b.** Optical conductivity spectra of the post-annealed LSF50 films (dash lines), KOH-reduced and KOH-oxidized LSF50 films (solid lines) obtained by ex-situ ellipsometry. **c.** XRD diagrams of the  $\text{O}_2$ -annealed,  $\text{N}_2$ -annealed, KOH-reduced and KOH-oxidized LSF50 samples. **d.** Magnification of the (002) diffraction peak. The diffraction peaks of Nb:STO and LSM are marked with star (\*) and hash (#) symbols, respectively. The observed shoulder on annealed samples correspond to Kiesel fringes characteristic of coherent and homogeneous epitaxial layers.

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3 **In-situ ellipsometry of LSF50 redox cycling in alkaline electrolytes:** A high sensitivity of the  
4 LSF optical properties to the concentration of electronic holes was reported in the previous section.  
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6 Here, in-situ ellipsometry acquired during the electrochemical reduction is employed for getting  
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8 more insights into the mechanism of ion intercalation. The measurements were carried out in a  
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10 three-electrode sample using a homemade chamber (see Experimental Section). In order to  
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12 measure the real equilibrium conditions, we focused on the reduction reaction at room temperature  
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14 applying DC voltage to the sample in stepwise from 0.5 V to -0.4 V, see **Figure 3a**. The  
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16 equilibrium was considered achieved when the electrochemical current, measured after each  
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18 polarization step, reached a value close to zero. The extracted optical conductivity spectra of the  
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20 LSF50 thin film measured at various intercalation potentials are shown in **Figure 3b** (see **Figure**  
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22 **S7** in Supplementary Information for the measured ellipsometry raw data and **Section S4** in  
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24 Supplementary Information for more details about the fitting model). The data shows a monotonic  
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26 variation in the intensity of the optical transitions “A”, “B” and “C”, consisting in a weakening of  
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28 low energy transition “A” and “B” together with a strengthening of UV transition “C” with  
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30 cathodic potential (*i.e.* with the reduction reaction). This trend implies a decrease of the hole  
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32 concentration in the LSF layer.<sup>42,45</sup>

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35 In our previous work, the concentration of electronic holes in LSF has been directly related to  
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37 the intensity of the low-energy transition “A”.<sup>36</sup> In this way, the low-energy transition “A” can be  
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39 used for calculating the hole concentration. However, the high optical absorption of the liquid  
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41 electrolyte in the infrared region hinders the application of the same procedure in this study. In  
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43 order to overcome such a limitation, we focus here on the variation of the LSF films’ optical  
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45 conductivity at the photon energy of 2 eV. In supplementary information **Section S7**, we  
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47 demonstrate that a linear relation with the Fe<sup>4+</sup> holes concentration is present. As a result,  
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3 motivated by this linear relation, the Fe<sup>4+</sup> holes concentration at different intercalation potentials  
4 can be readily quantified from the optical conductivity, see **Figure 3c**. The curve suggests a single  
5 electrochemical intercalation plateau (electronic transition Fe<sup>4+</sup>/Fe<sup>3+</sup>) during the reduction, as  
6 shown by the monotonic decrease of the iron valence. A pseudo-plateau for the Fe valence is  
7 observed around -0.05 V. The maximum capacity that can be extracted from the ionic intercalation  
8 in the LSF layers corresponds to the full reduction of the Fe valence from 4+ to 3+ and is  
9 determined by the total concentration of Sr<sub>La</sub>' dopant (around 55 mAh/g in the LSF50 film under  
10 study).

11 It is also interesting to compare the charge transferred after each voltage step (*i.e.* incremental  
12 capacity<sup>53</sup>) calculated by ellipsometry and by electrochemical method. Since the Fe<sup>4+</sup>/Fe<sup>3+</sup>  
13 transition is accompanied by charge transfer as:



15 The number of charge transferred in the reduction reaction can be calculated via the ellipsometry  
16 approach ( $Q_{ellipsometry}$ ) as:

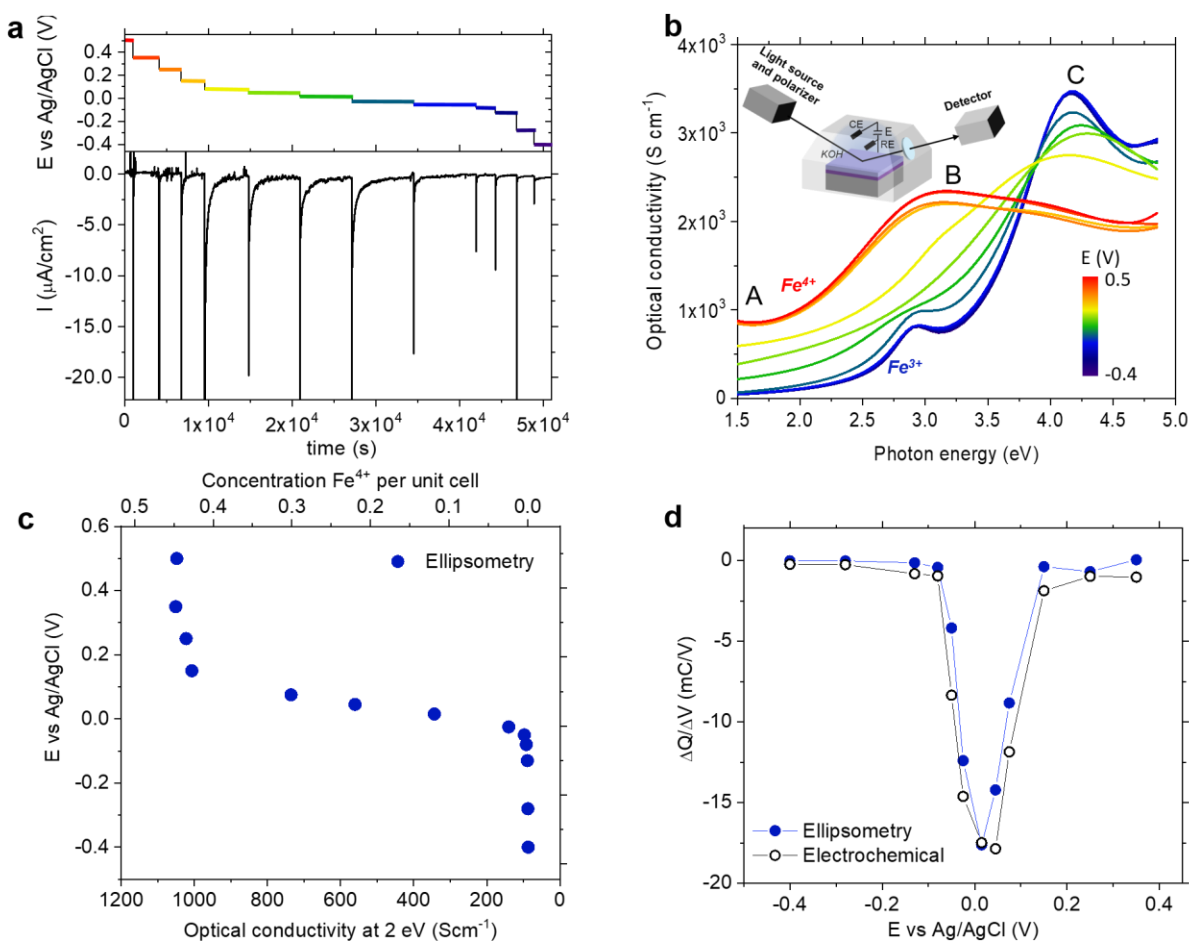
$$17 \quad Q_{ellipsometry} = n \cdot [Fe_{Fe}^{\bullet}] \cdot F \quad (\text{Equation 4})$$

18 Where  $n$  is the number of LSF50 cell (in mol) in the thin film and  $F$  is the Faraday constant. On  
19 the other hand, the charge transferred at each stepwise voltage can be obtained calculating the area  
20 under the I-t curves of **Figure 3a**, as:<sup>54</sup>

$$21 \quad Q_{electrochemical} = \int_{t_1}^{t_2} I(t) dt \quad (\text{Equation 5})$$

22 **Figure 3d** shows the incremental capacity obtained from the electrochemical and ellipsometry  
23 measurements employing **Equations 4** and **5**, respectively. A good agreement in the tendency of  
24 the incremental capacity obtained by the two approaches is observed, confirming the capability of  
25 ellipsometry to track the concentration of Fe<sup>4+</sup> in the layer. Nevertheless, the electrochemical  
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method shows a systematic larger value of charge transferred at each voltage step. This behavior can be ascribed to the electrochemical reactions (charge transfer) on the film surface caused, for instance, by oxygen reduction reaction (ORR).<sup>26,55</sup> Since in-situ ellipsometry is bulk-sensitive, it is able to differentiate the battery-like behavior linked to the ionic insertion from the electrochemical reactions taking place on the sample surface.<sup>37</sup> It is important to note that different fitting models were considered to fit the ellipsometry spectra and to derive the hole concentration at each potentials (see **Section S8** in Supplementary Information). Although a certain discrepancy in the thickness of the LSF layer was observed across the models, all of them led to the same concentration of  $\text{Fe}^{4+}$ , validating the presented in-situ ellipsometry approach.



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3 **Figure 3. a.** Evolution of the applied electrochemical potentials and of the current measured over  
4 time in the in-situ experiment. **b.** Optical conductivity spectra of the LSF50 thin film were recorded  
5 at various intercalation potentials (applied voltages). The inset shows a schematic representation  
6 of the chamber used for the measurements. **c.** Optical conductivity measured at 2 eV and  
7 corresponding  $\text{Fe}^{4+}$  concentration measured at each intercalation potential. **d.** Comparison of the  
8 incremental capacity of the LSF50 thin film obtained from the electrochemical and ellipsometry  
9 results.  
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22 **Ion intercalation mechanism in LSF50 cycled in an alkaline electrolyte:** As mentioned in  
23 the introductory section (and sketched in **Figure 1**), proton and oxide-ion incorporation pathways  
24 may be active separate or together. To unambiguously determine the active incorporation pathway,  
25 the redox process of LSF in liquid electrolyte was investigated by ToF-SIMS, PALS, and ex-situ  
26 ellipsometry measurements.  
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33 The possible proton incorporation was studied by ToF-SIMS in the KOH reduced sample, where,  
34 according to the protonic pathway shown in **Equation 2**, protons should compensate the reduction  
35 of oxidation state of iron atoms. **Figure 4a** shows the depth profiles of the  $\text{H}^+$  and  $\text{OH}^-$  intensities  
36 measured for the KOH-reduced sample. The thickness of the LSF, LSM and STO layers was  
37 obtained by monitoring the  $\text{FeO}^-$ ,  $\text{MnO}^-$  and  $\text{TiO}^-$  signals, respectively (**Figure S10** in  
38 Supplementary Information). An increased signal of the  $\text{H}^+$  and  $\text{OH}^-$  is visible in the LSF50 layer  
39 with respect to the background signal (STO layer). This experiment undoubtedly shows that an  
40 enhanced proton concentration is present in LSF as a consequence of incorporation during the  
41 electrochemical reduction in KOH electrolyte, proving that the protonic pathway is active. The  
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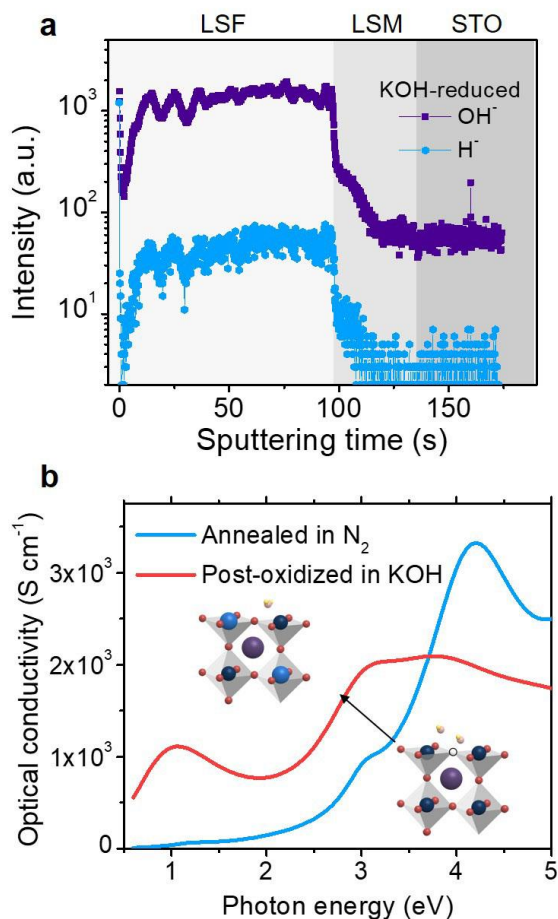
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3 sharp decrease of hydrogen species at the LSF/LSM interface suggests that, within the  
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5 electrochemical window studied, protons are not intercalated in the LSM layer.  
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8 The oxygen intercalation mechanism was studied by ex-situ ellipsometry. Since oxygen  
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10 vacancies cannot be straightforwardly measured in thin film oxides, we performed an indirect  
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12 measurement to verify the presence of oxygen intercalation in the LSF50 thin film. Considering  
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14 the high sensitivity of ellipsometry to the oxygen vacancy-related  $[Fe_{Fe}^{\cdot}]$  concentration reported  
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16 in our previous studies,<sup>36</sup> ellipsometry is a promising technique for detecting the oxygen  
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18 incorporation.  
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22 First, a LSF50 sample was annealed in dry N<sub>2</sub> at T=575 °C. As shown in the optical conductivity  
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24 of **Figure 4b**, the N<sub>2</sub>-annealed LSF50 film was fully reduced. Since a dry atmosphere was used,  
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26 no protons are expected in this state and the dopant is entirely compensated by oxygen vacancies  
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28 ( $[Fe_{Fe}^{\cdot}] \sim 0$ ,  $2[V_O^{\bullet\bullet}] \sim [Sr'_{La}]$ ). The sample was then oxidized in 0.1 M KOH electrolyte by applying  
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30 potentials of 0.5 V. After this treatment, the optical measurement shows that an almost complete  
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32 oxidation is achieved in the layer, highlighted by the large increase of optical conductivity in the  
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34 low energy region, see **Figure 4b**. According to the protonic pathway, positive bias should  
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36 decrease the concentration of protons in the layers. Since no protons were originally present in the  
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38 sample, the only possible explanation for the oxidation of the layer is that the oxygen pathway is  
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40 active and oxygen can enter in the reduced sample filling the oxygen vacancies and increasing the  
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42 oxidation state of Fe (see **Equation 1**).  
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47 An analogous experiment was also performed with a sample completely oxidized in dry O<sub>2</sub>  
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49 atmosphere (**Figure S11** in Supplementary Information). Also in this case, complete oxidation and  
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51 reduction was observed in the sample after electrochemical bias in KOH. It is also interesting to  
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53 notice that the CV of the two differently annealed samples (**Figure S11** in Supplementary  
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Information) are comparable and present the redox peak at the same voltage, despite starting from a very different oxygen vacancy (and electronic holes) concentration. This also suggests that a new equilibrium is achieved in liquid electrolytes, in which both oxygen and protonic species are intercalating in the layer.



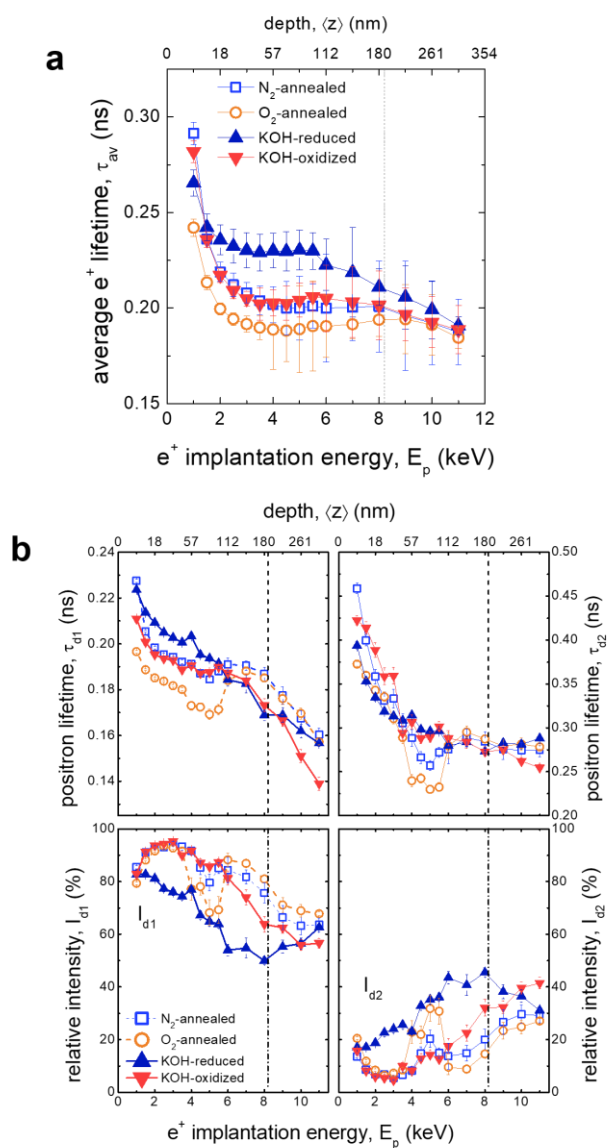
**Figure 4.** **a.** ToF-SIMS depth profiles of H<sup>+</sup> and OH<sup>-</sup> ions for the KOH-reduced sample. A clear increase of the protonic species intensity is observed in the LSF50 top-layer. **b.** Optical conductivity of a LSF50 layer reduced in dry N<sub>2</sub> followed by an oxidation in KOH. The increase of optical conductivity shows that the oxygen mechanism is also active in alkaline electrolytes.

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5 The LSF50 thin films subjected to the different redox treatments were also studied by Variable  
6 Energy Positron Annihilation Lifetime Spectroscopy (VEPALS) for direct analysis of defect type  
7 and concentration. PALS is particularly sensitive to localized vacancy-like defects (or close  
8 porosities) of a neutral or negative charge, which acts as annihilation sites for positrons. The  
9 positron lifetime is proportional to the size of the annihilating defect. By varying the positron  
10 implantation energy ( $E_p$ ), which is related to the mean positron implantation depth in the sample,  
11 one can obtain  $z$ -resolved information on defect type (from the positron lifetime  $\tau_i$ ) and relative  
12 concentration (from the relative intensity  $I_i$ ) with nominal nm-resolution (notwithstanding a certain  
13 signal broadening for increasing  $z$ ). The PALS analysis shown below is based on dedicated studies  
14 on a related perovskite, SrTiO<sub>3</sub> (STO), for the identification of the defect type based on the positron  
15 lifetime.<sup>56–58</sup> Although PALS cannot directly measure positive defects such as oxygen vacancies  
16 or protons, the technique is sensitive to their association with negative defects (e.g. cationic  
17 vacancies) resulting in the formation of an associate. A higher oxygen vacancy content is expected  
18 to lead to an increase of defect lifetime owing to the formation of larger open clusters.<sup>59,60</sup>  
19 Conversely, the effect of proton uptake depends on the defect site: the association of protons with  
20 a negatively charged vacancy leads to a contraction of the open volume and to lifetime decrease  
21 for proton incorporation as interstitials,<sup>61</sup> whereas protons bonded to oxygen may give rise to a  
22 displacement of oxygen from the equilibrium sites, resulting in a distorted structure and larger  
23 defect open volumes.<sup>51,62</sup> **Figure 5a** shows the average defects size positron lifetime ( $\tau_{av}$ ) obtained  
24 as a function of  $E_p$  for the KOH-oxidized and reduced samples as well as the O<sub>2</sub>-oxidized and the  
25 N<sub>2</sub>-reduced LSF50 thin films. Here,  $\tau_{av} = \sum_i \tau_i \cdot I_i$ , as obtained from deconvolution of the measured  
26 lifetime in two-lifetime components (cf. also experimental). The average defect size ( $\approx 200$  ps)  
27 obtained in the LSF50 film falls into the range of B-site vacancy.<sup>58</sup> The N<sub>2</sub>-annealed and KOH-

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3 reduced samples are characterized by a larger average positron lifetime  $\tau_{av}$  with respect to the  
4 oxidized counterpart (O<sub>2</sub>-annealed and KOH-oxidized, respectively), i.e., the reduction process  
5 induces the formation of larger defect clusters – arguably by increasing the concentration of  
6 oxygen vacancies. Interestingly, for the KOH-oxidized and reduced layers,  $\tau_{av}$  is larger than for  
7 the O<sub>2</sub>-annealed and N<sub>2</sub>-annealed samples, respectively, and  $\tau_{av}$  for the KOH-oxidized sample is  
8 about the same as for the N<sub>2</sub>-annealed sample, suggesting that a more defective structure is induced  
9 upon treatment in liquid, this defective structure might be attributed to the distorted structure and  
10 open-volume defects formed upon protons intercalation as discussed above. All layers present  
11 similar average lifetimes for the LSM interlayer, confirming that the different treatments do not  
12 affect this material. The subsurface layer ( $z < 20$  nm) is characterized by remarkably higher  $\tau_{av}$ ,  
13 indicating a large increase in defect size and concentration, which is related to the surface  
14 annihilation sites.

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31 An analysis of the single lifetime components ( $\tau_{d1}$  and  $\tau_{d2}$ ) and the relative intensities allow  
32 obtaining further insights, see **Figure 5b**. Comparing with literature values of STO,<sup>56</sup> the dominant  
33 defect component  $\tau_{d1}$  in the LSF50 film ( $I_{d1} > 60\%$ ,  $I_{d1} + I_{d2} = 100\%$ ) is found to be in the range of  
34 B-site vacancy ( $V_{Ti}^{''''}$ ) and a complex between Ti and oxygen vacancies (consistently with the  
35 average lifetime analysis, cf. panel a). Reducing the sample (both in KOH and in N<sub>2</sub>) is observed  
36 to increase the major defect lifetime  $\tau_{d1}$ , indicating the formation of larger  $V_{Ti}^{''''} - V_O^{\bullet\bullet}$  associates.  
37 The minority lifetime component  $\tau_{d2}$  is instead associated to defect clusters containing Sr-vacancies  
38 ( $V_{Sr}^{''}$ ), such as  $V_{Sr}^{''} + V_O^{\bullet\bullet}$  or full Schottky defects ( $V_{Sr}^{''} + V_{Ti}^{''''} + 3V_O^{\bullet\bullet}$ ).  $I_{d2}$  shows a considerable  
39 increment for the KOH-reduced sample (note that  $I_{d1}$  decreases accordingly). Here, an additional  
40 effect of proton uptake on lattice distortion and consequent increase of defect volume may be  
41 present. This hypothesis appears to be supported by the decrease of crystalline quality observed in  
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the XRD experiments (**Figure 2d**), possibly related to hydration-induced lattice distortions and LSF50 structure disorder.



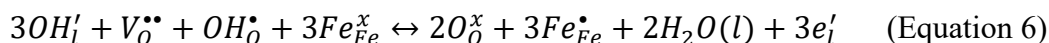
**Figure 5.** PALS parameters analysis for the  $O_2$ -annealed,  $N_2$ -annealed, KOH-reduced and KOH-oxidized samples. **a.** Average positron lifetime  $\tau_{av}$ . **b.** The first  $\tau_{d1}$  (left) and the second  $\tau_{d2}$  (right)



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3 components of the positron lifetime and their relative intensities  $I_{d1}$  and  $I_{d2}$ . The vertical line at  
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5  $E_p=8$  keV shows the position of the interface between LSF and LSM films.  
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10 In summary, according to the ex-situ measurements with different techniques, both proton and  
11 oxygen ions are intercalated into the LSF50 layers during the electrochemical experiments in  
12 alkaline electrolyte, giving rise to a variation of  $Fe^{4+}$  holes for electro-neutrality. At cathodic  
13 (negative) intercalation potentials, the electrical field causes oxygen anions to be pumped out from  
14 the LSF50 structure and protons from the liquid electrolyte to be incorporated into the LSF50  
15 structure, while the opposite reactions take place at anodic potentials.  
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26 **Defect chemistry modelling:** The results obtained in the previous sections suggest that: (i)  
27 Protons enter the LSF50 thin films upon electrochemical reduction. (ii) Oxygen is also exchanged  
28 during ionic intercalation with the electrolyte and the same equilibrium can be reached regardless  
29 of the initial defect concentration in the layer. (iii) A single electrochemical process is observed  
30 upon reduction, i.e. protons and oxygen are exchanged together. Therefore, ion intercalation can  
31 be described as a combination of oxygenation and hydrogenation reactions involving oxygen  
32 anions and protons. The global reaction can be written as a sum of the oxygenation reaction  
33 (**Equation 1**) and the hydration reaction (**Equation 2**) as:  
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45 Applying the Nernst equation, the potential for the ion intercalation for dilute non-interacting  
46 defects can be expressed as:  
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$$E = E_0 + \frac{RT}{3F} \ln \left( \frac{[O_O^x]^2 [Fe_{Fe}^{\bullet}]^3}{[V_O^{\bullet\bullet}] [OH_O^{\bullet}] [Fe_{Fe}^x]^3} \right) + \frac{RT}{3F} \ln \left( \frac{[H_2O]^2}{[OH']^3} \right) \quad (\text{Equation 7})$$

Where  $E_0$  is the standard potential of the ionic intercalation,  $R$  is the gas constant (8.314 Jmol<sup>-1</sup>K<sup>-1</sup>). The first logarithmic component on the right-hand side of the equation is linked to the concentration of the point defects in the LSF50 thin film, and the second logarithmic term is associated with the concentration of the ions in the liquid electrolyte with the activity coefficient assumed to be 1.<sup>63,64</sup> Thus, **Equation 7** can be rewritten as:

$$E = E_0 + \frac{RT}{3F} \ln \left( \frac{[O_{\dot{O}}^x]^2 [Fe_{Fe}^{\bullet}]^3}{[V_{\dot{O}}^{\bullet\bullet}] [OH_{\dot{O}}^{\bullet}] [Fe_{Fe}^x]^3} \right) + 0.16 V \quad (\text{Equation 8})$$

Because the electronic transition  $Fe^{3+}/Fe^{2+}$  was not detected in the studied potential window,<sup>8</sup> the  $Fe^{2+}$  electrons in the LSF50 are negligible. Thus, the charge equilibrium in the LSF50 film is:<sup>44,65,66</sup>

$$2[V_{\dot{O}}^{\bullet\bullet}] + [OH_{\dot{O}}^{\bullet}] + [Fe_{Fe}^{\bullet}] = [Sr'_{La}] \quad (\text{Equation 9})$$

$$[Fe_{Fe}^{\bullet}] + [Fe_{Fe}^x] = 1 \quad (\text{Equation 10})$$

The ratio between the concentration of oxygen vacancies  $V_{\dot{O}}^{\bullet\bullet}$  and  $OH_{\dot{O}}^{\bullet}$  ions can be determined by the hydration reaction:<sup>64,67,68</sup>



With the equilibrium constant  $K_w$ :

$$K_w = \frac{[OH_{\dot{O}}^{\bullet}]^2}{[H_2O_l][V_{\dot{O}}^{\bullet\bullet}][O_{\dot{O}}^x]} \quad (\text{Equation 12})$$

The hydration equilibrium constant depends on the material's properties and defines the total amount of protons that can be incorporated into the layer. The protonation mechanism of ferrites perovskites in high-temperature humid environment was studied in detail by Prof. Maier and co-workers.<sup>34,69-72</sup> Interestingly, they found that in the intermediate temperature range 250 °C - 500 °C LSF presents quite a low protonic concentration, especially when compared with Ba-doped ferrites. Nevertheless, the protonation mechanism (**Equation 11**) is regulated by an endothermic

reaction, meaning that the concentration of protons will be higher at lower temperatures. Considering the enthalpy and entropy of the hydration reaction measured for LSF,<sup>34,69–72</sup> a value of  $K_w$  around 0.1 can be extrapolated at room temperature, which is comparable with the protonation constant measured for a good protonic conductor such as  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.8}\text{Zn}_{0.2}\text{O}_{3-\delta}$  at 400 °C. Because of Matrix effects, no quantitative information on the concentration of protons in the reduced LSF50 thin films can be deduced from ToF-SIMS measurements. Thus, a value of  $K_w=0.1$  has been considered in this study. The set of **Equations 7-12** can be combined for obtaining an expression where the electrochemical potential of intercalation can be described as a function of  $\text{Fe}^{4+}$  holes concentration, as:

$$E = E_0 + \frac{RT}{3F} \ln \left( \frac{(2.55 + [V_{\text{O}}^{\bullet\bullet}] + [Fe_{\text{Fe}}^{\bullet}] )^2 [Fe_{\text{Fe}}^{\bullet}]^3}{[V_{\text{O}}^{\bullet\bullet}] (0.45 - 2[V_{\text{O}}^{\bullet\bullet}] - [Fe_{\text{Fe}}^{\bullet}]) (1 - [Fe_{\text{Fe}}^{\bullet}])^3} \right) + 0.16 \text{ V} \quad (\text{Equation 13})$$

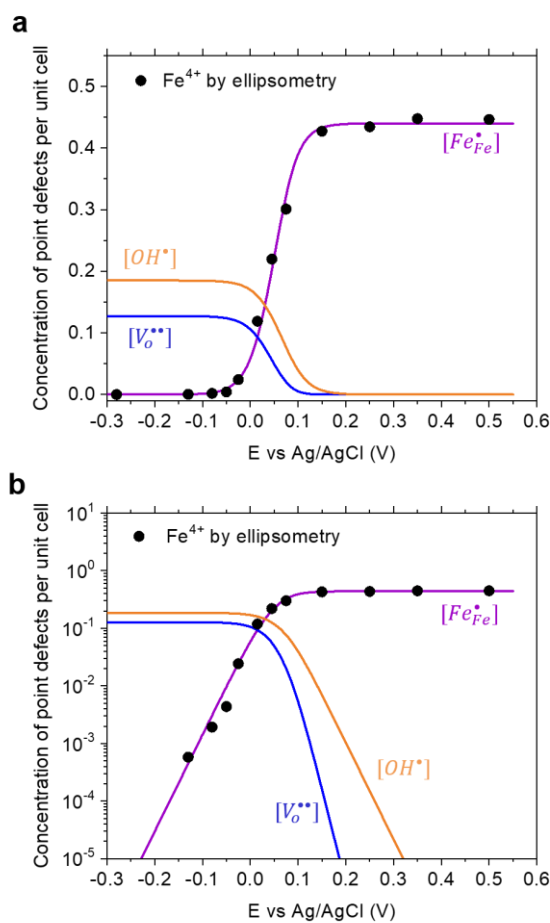
Where  $[V_{\text{O}}^{\bullet\bullet}]$  is the solution of the second-order equation:

$$2.55 + [V_{\text{O}}^{\bullet\bullet}] + [Fe_{\text{Fe}}^{\bullet}] = \frac{(0.45 - 2[V_{\text{O}}^{\bullet\bullet}] - [Fe_{\text{Fe}}^{\bullet}])^2}{K_w [V_{\text{O}}^{\bullet\bullet}]} \quad (\text{Equation 14})$$

With these equations, it is possible to fit the equilibrium  $\text{Fe}^{4+}$  concentration obtained at each electrochemical potential considering only  $E_0$  as a free parameter. **Figure 6** shows the results of the model obtained for a  $E_0 = 0.83 \text{ V}$  vs RHE (or  $-0.083 \text{ V}$  vs Hg/HgO). An excellent fit of the experimental data is obtained, suggesting that the proposed model is able to describe the mechanism of ionic intercalation in LSF50 thin films.

The model shows that the concentration of protons and oxygen vacancies increases while reducing the samples until the majority of holes is consumed. These results demonstrate that the ionic intercalation in LSF is dominated by bulk defect chemistry, which defines the potential and shape of the electrochemical response. In this sense, it is worth noting that the intercalation potential  $E_0$  is related to the oxidation constant commonly measured in these oxides at high temperature gaseous environment, which describes the equilibrium concentration of defects as a

function of the external oxygen chemical potential (varied either by the external oxygen partial pressure or by applying an electrochemical potential in a solid oxide cell).<sup>36,73</sup> Depending on the reducibility of the materials, the intercalation potential window in both liquid and gaseous environment is strongly modified. Finally, the effect of the hydration reaction on the defect chemistry of perovskite oxides in liquid electrolytes should be discussed. Depending on the capability of a certain material to host protons (*i.e.* on the value of the hydration constant  $K_w$ ), the oxygen or protonic electrochemical exchange mechanism will be dominating, giving rise to significant changes in the  $V_o^{\bullet\bullet} / OH^\bullet$  ratio in reducing conditions.



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3 **Figure 6.** Linear (a) and logarithmic (b) plots of the defects concentration obtained by defect  
4 chemistry modelling (lines) and of the Fe<sup>4+</sup> holes concentration measured by ellipsometry (points)  
5 for LSF50 thin films in 0.1 M KOH at room temperature.  
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## 10 11 12 13 14 15 16 17 CONCLUSIONS

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19 Ion intercalation phenomena for LSF50 thin films in liquid alkaline electrolyte were studied in  
20 this paper. One can conclude that, under an electrochemical field (induced by an applied voltage),  
21 ions from the liquid electrolyte intercalate into the LSF50 resulting in the Fe<sup>4+</sup>/Fe<sup>3+</sup> electronic  
22 transition. The intercalation mechanism was found to consist in a mixed oxygenation and hydration  
23 reactions (as determined by ex-situ XRD, ex-situ ellipsometry, SIMS and PALS techniques). It  
24 was possible to derive the concentration of Fe<sup>4+</sup> holes in the LSF50 film from the optical  
25 conductivity via the linear proportionality of the optical conductivity at the photon energy of 2 eV  
26 to the holes concentration. Like this, the evolution of Fe<sup>4+</sup> concentration with intercalation  
27 potential was satisfactorily described by a dilute defect chemistry model, which is highlighted by  
28 the importance of the oxygenation and hydration reactions in the intercalation mechanism. Overall,  
29 in-situ/operando ellipsometry approach got new insights into the defect chemistry of LSF50 oxide  
30 thin films along the ion intercalation in alkaline media, opening a new way to tailor the LSF50 thin  
31 film's functional properties for energy and information applications.  
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## 52 ASSOCIATED CONTENT

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3       **Supporting Information.** The following Supporting Information is available free of charge via  
4 the Internet at <https://pubs.acs.org/>.  
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8       XRD diagrams and SEM image of the as-deposited LSF50/LSM/Nb:STO sample, CV cycle for  
9 the LSF50 thin film grown on FTO substrates, in-situ ellipsometry measurements for LSM thin  
10 films, ellipsometry data analysis, SEM images of the morphology of the post-treated LSF50 thin  
11 films, ellipsometry raw data as a function of intercalation potential, linear relation between the  
12 optical conductivity and concentration of electron holes, models used for modelling the  
13 ellipsometry data, ToF-SIMS depth profiles of the ions in the KOH-reduced sample, ex-situ  
14 ellipsometry measurements. (PDF)  
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25 The manuscript was written through contributions of all authors. All authors have given approval  
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27 to the final version of the manuscript.  
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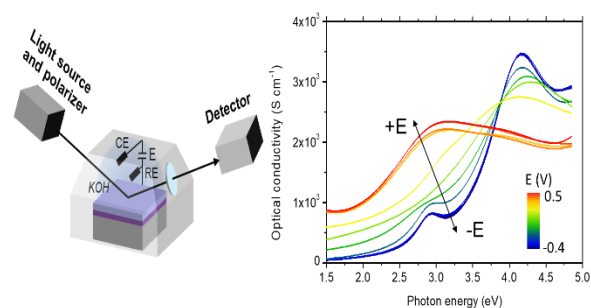
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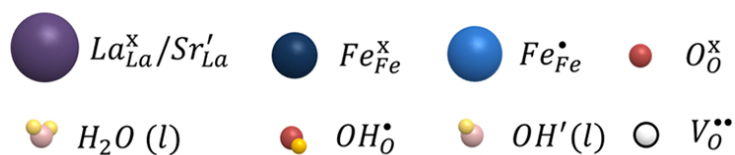
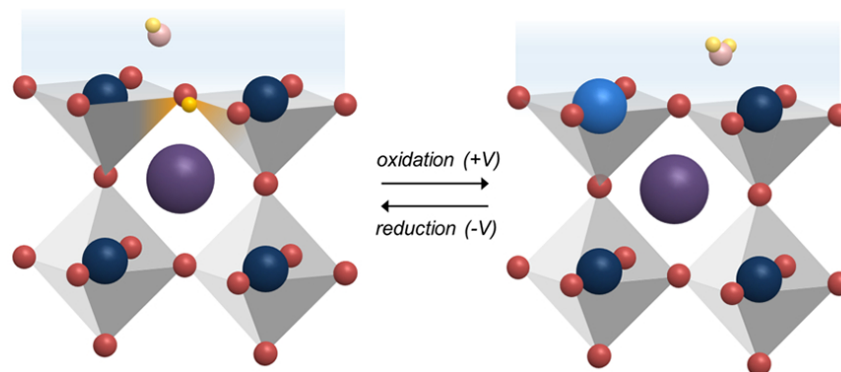
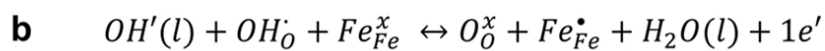
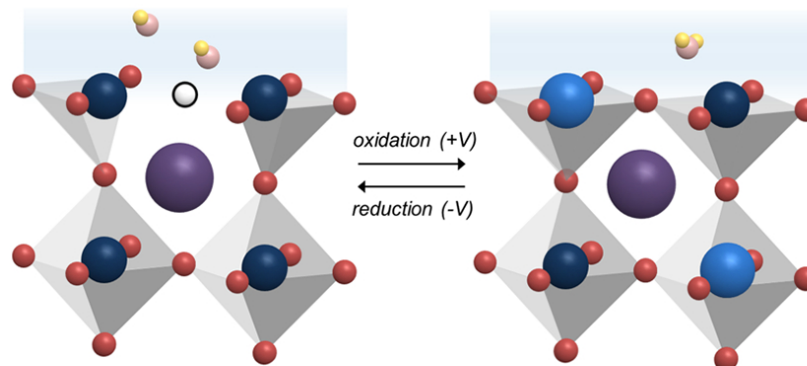
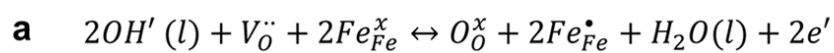
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## 14 Ion Intercalation in Lanthanum Strontium Ferrite for Aqueous Electrochemical Energy 15 16 Storage Devices 17

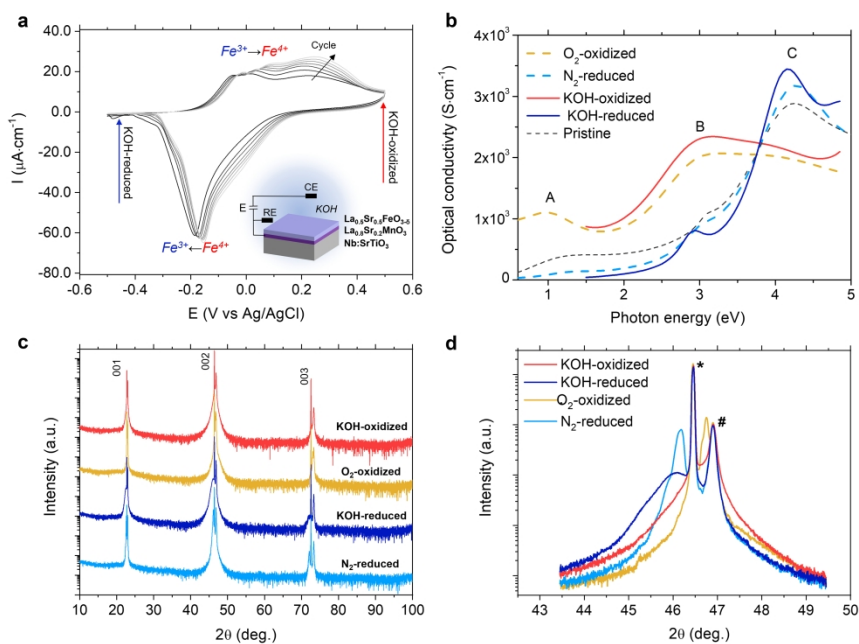
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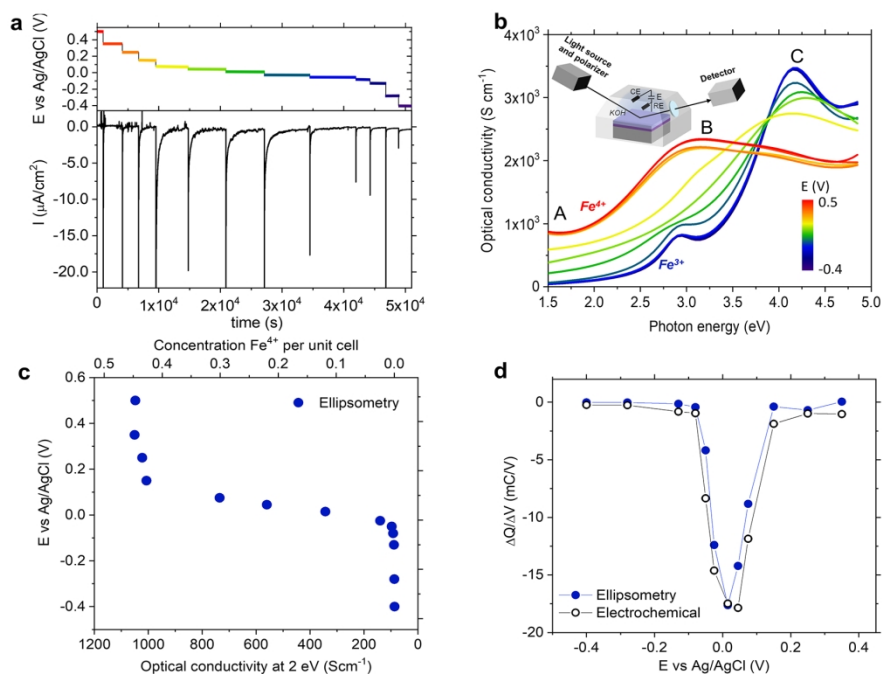
**Figure 1.** Schematic representation of the oxygen **(a)** and protonic **(b)** intercalation mechanisms in alkaline electrolytes.



**Figure 2. a.** CV curve of the LSF50 thin film measured at room temperature using a scan rate of 0.5 mV/s.

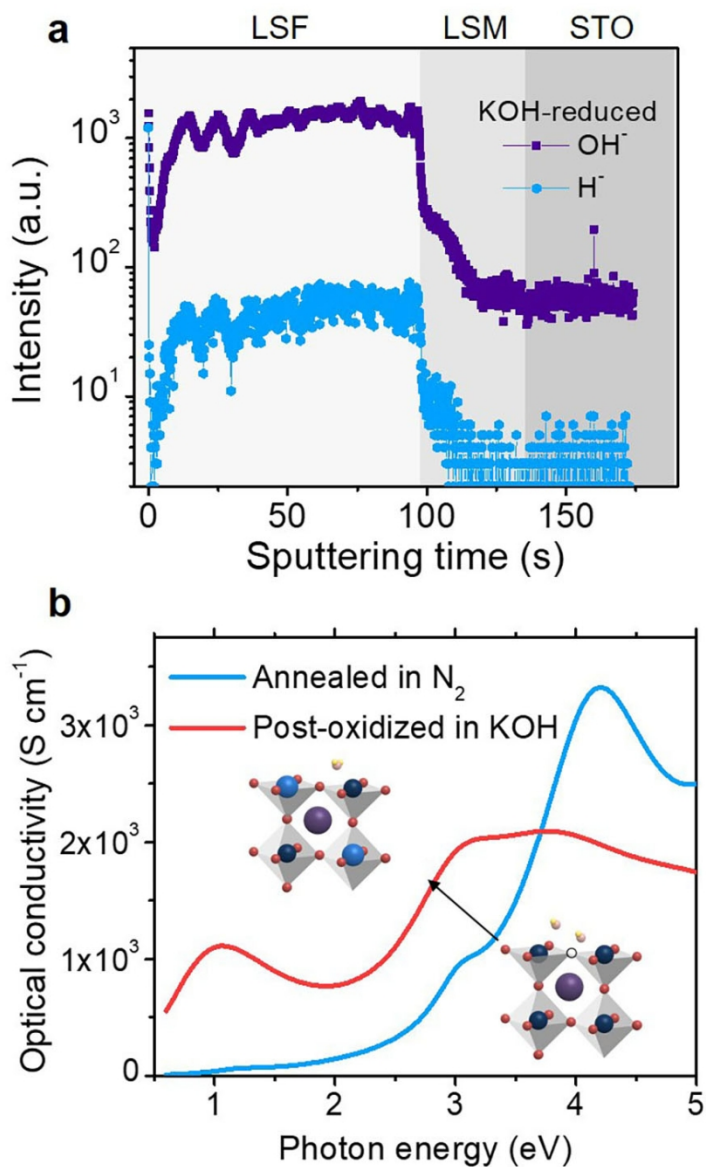
**b.** Optical conductivity spectra of the post-annealed LSF50 films (dash lines), KOH-reduced and KOH-oxidized LSF50 films (solid lines) obtained by ex-situ ellipsometry. **c.** XRD diagrams of the O<sub>2</sub>-annealed, N<sub>2</sub>-annealed, KOH-reduced and KOH-oxidized LSF50 samples. **d.** Magnification of the (002) diffraction peak. The diffraction peaks of Nb:STO and LSM are marked with star (\*) and hash (#) symbols, respectively. The observed shoulder on annealed samples correspond to Kossel fringes characteristic of coherent and homogeneous epitaxial layers.

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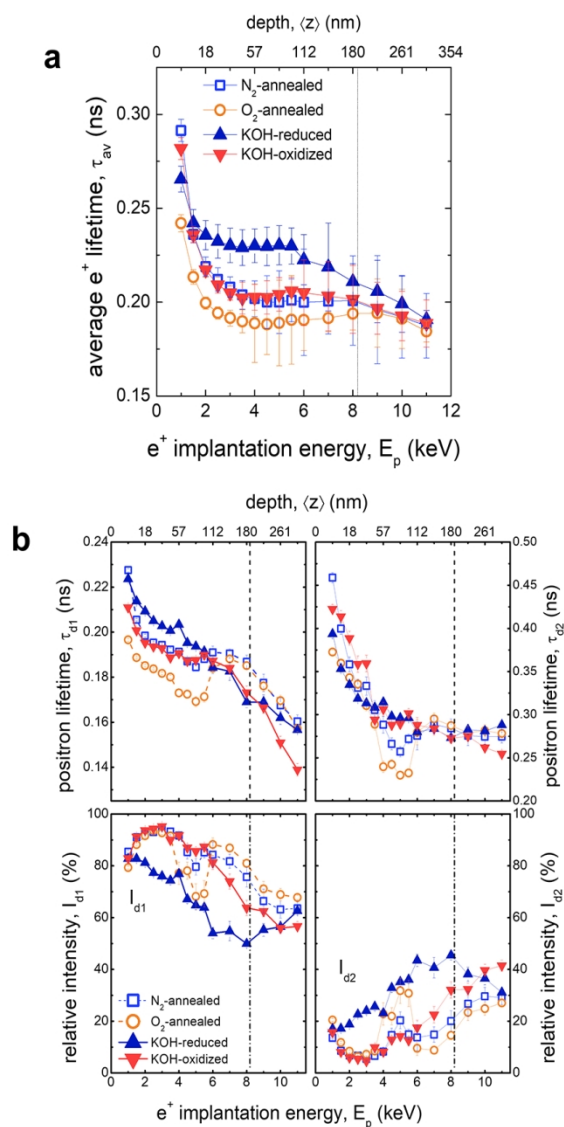


**Figure 3.** a. Evolution of the applied electrochemical potentials and of the current measured over time in the in-situ experiment. b. Optical conductivity spectra of the LSF50 thin film were recorded at various intercalation potentials (applied voltages). The inset shows a schematic representation of the chamber used for the measurements. c. Optical conductivity measured at 2 eV and corresponding  $Fe^{4+}$  concentration measured at each intercalation potential. d. Comparison of the incremental capacity of the LSF50 thin film obtained from the electrochemical and ellipsometry results.

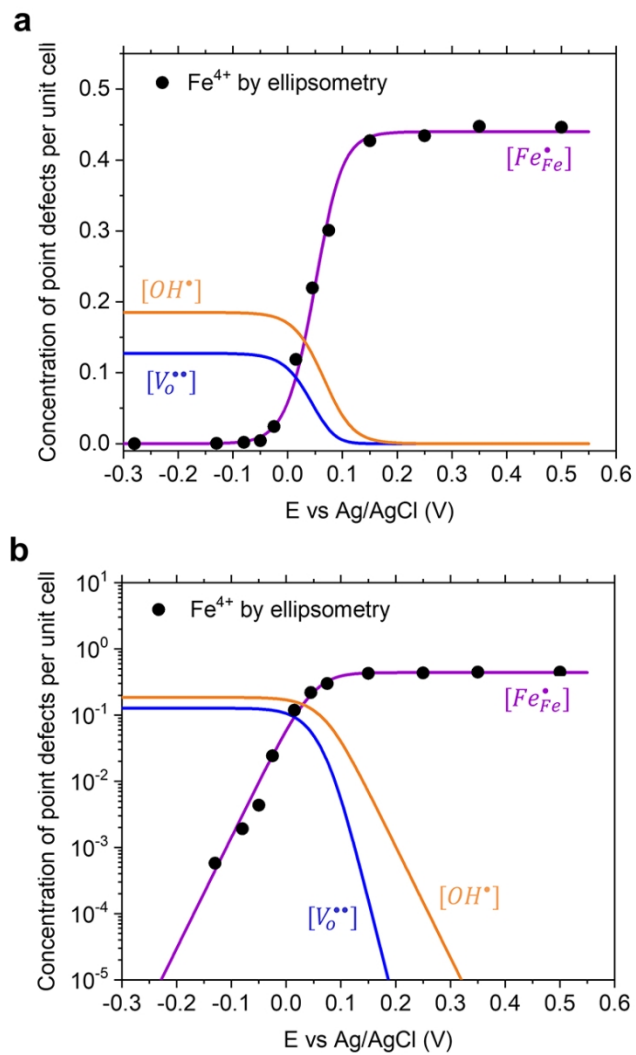




**Figure 4. a.** ToF-SIMS depth profiles of  $\text{H}^+$  and  $\text{OH}^-$  ions for the KOH-reduced sample. A clear increase of the protonic species intensity is observed in the LSF50 top-layer. **b.** Optical conductivity of a LSF50 layer reduced in dry  $\text{N}_2$  followed by an oxidation in KOH. The increase of optical conductivity shows that the oxygen mechanism is also active in alkaline electrolytes.

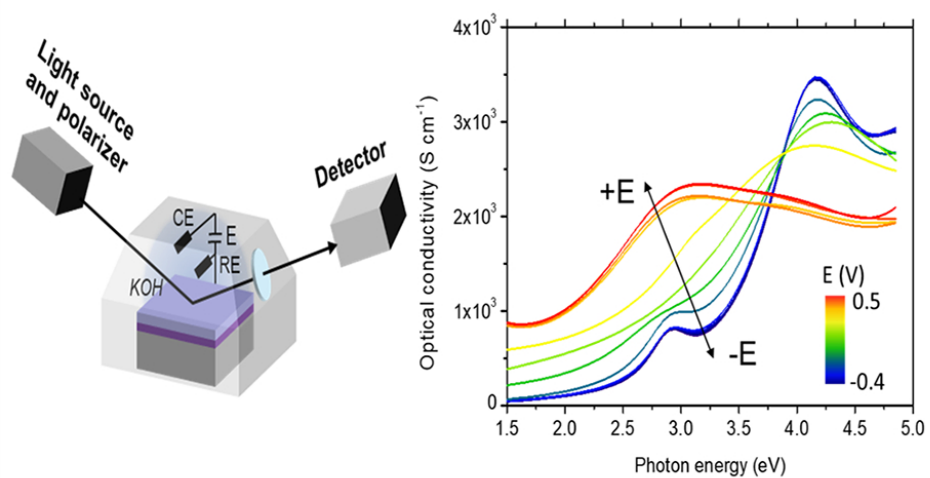


**Figure 5.** PALS parameters analysis for the O<sub>2</sub>-annealed, N<sub>2</sub>-annealed, KOH-reduced and KOH-oxidized samples. a. Average positron lifetime τ<sub>av</sub>. b. The first τ<sub>d1</sub> (left) and the second τ<sub>d2</sub> (right) components of the positron lifetime and their relative intensities I<sub>d1</sub> and I<sub>d2</sub>. The vertical line at E<sub>p</sub>=8 keV shows the position of the interface between LSF and LSM films.



**Figure 6.** Linear (a) and logarithmic (b) plots of the defects concentration obtained by defect chemistry modelling (lines) and of the  $Fe^{4+}$  holes concentration measured by ellipsometry (points) for LSF50 thin films in 0.1 M KOH at room temperature.

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