

Engendering unprecedented activation of oxygen evolution via rational pinning of Ni oxidation state in prototypical perovskite: Close juxtaposition of synthetic approach and theoretical conception

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ABSTRACT: Rational optimization of OER activity of catalysts based on LaNiO₃ oxide is achieved by maximizing the presence of trivalent Ni in the surface structure. DFT investigations of the LaNiO₃ catalyst and surface structures related to it predict the improvement of OER activity for these materials to levels comparable with the top of the OER volcano if the La content is minimized while maintaining the oxidation state of Ni. These theoretically predicted structures of high intrinsic OER activity can be prepared by a templated spray-freeze freeze-drying synthesis followed by simple post-synthesis exfoliation-like treatment in acidic media. These nanocrystalline LaNiO₃ related materials confirm the theoretical predictions showing a dramatic improvement in OER activity. The exfoliated surfaces remain stable in OER catalysis as shown by an in-operando ICP-OES study. The unprecedented OER activation of the synthesized LaNiO₃-based materials is related to close juxtaposition of the theoretical conception of ideal structural motifs and the ability to engender such using a unique synthetic procedure, both principally related to stabilization and pinning of Ni oxidation state within the local coordination environment of the perovskite structure.

1. Introduction

Replacing fossil fuels as the main energy carrier by renewable electricity sources is one of the most urgent challenges for science and technology.¹ While the technologies for renewable electricity generation are relatively advanced, their intermittent nature brings up the question of the reversible storage of renewable electricity in chemical bonds.² “Green” hydrogen produced from water electrolysis is expected to play a major role as such an energy storage option.^{3,4} It is generally known that the efficiency of the water electrolysis is in fact controlled by a sluggish oxygen evolution (OER) while the hydrogen evolution reaction (HER) taking place at the cathode can be optimized and scaled up with less difficulty.⁵ Hence, the design of oxygen-evolving catalysts turned into one of the major topics in electrocatalysis. Although the most efficient water electrolyzers are based on polymer electrolyte membrane (PEM) cells operating in highly acidic media,^{4,6} their applicability is restricted by the lack of stable and feasible catalyst materials.^{7,8} This stresses the potential of the alkaline electrolyzers, which despite lower

efficiency can rely on catalysts based on more abundant transition metal oxides based on e.g. Mn, Ni, Fe, or Co.^{9–11}

Namely, the Ni-based catalysts became highly popular thanks to the abundance of nickel. The oxygen evolution on Ni-based compounds is inherently connected with the formation of trivalent nickel under *operando* conditions.^{12–15} Ni-based perovskite oxides with the stoichiometry ABO₃, where the A-sites are occupied by alkaline earth or rare-earth cations and the B-sites are occupied with Ni, represent in this context attractive candidates for the oxygen evolution catalysis in alkaline electrolytes.^{16–19} It ought to be stressed that the variability of the perovskite structure (i.e. possibility to combine different A-site and B site-cations) facilitates control of the oxidation state of the B site cation. Combining theory²⁰ and experiment²¹, one can predict the perovskite-based catalyst activity to follow its electronic structure, which – in the case of perovskite structure - can conveniently be controlled by a combination of A-site and B-site cations.²² In fact, perovskite-based catalysts represent a rather popular structural type of

catalysts in alkaline media.¹⁶ The highest activity among perovskite-based OER catalysts has been predicted for LaNiO_3 as well as for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ which both reside close to the top of the oxygen evolution activity volcano.^{20,21} Particularly LaNiO_3 is considered a prospective candidate for optimization. Several reports^{23–27} have shown that the synthetic route has a distinct influence on the morphology and electronic properties of lanthanum nickel oxide and consequently the activity in OER catalysis. Nanostructured LaNiO_3 particles of about 25 nm particle size were obtained using a freeze-drying technique and displayed very high OER activity if combined with conductive carbon support.²⁸ The actual crystal structure found in various LaNiO_3 perovskites is also reported to significantly affect OER activity. Directing the structure from rhombohedral to cubic is reported to improve the OER activity dramatically.²⁹ Strain effects have also been shown to influence the electrocatalytic properties of lanthanum nickel oxides.³⁰ The catalytic activity of lanthanum nickel perovskites can further be enhanced by introducing A-site vacancies affecting the overall redox properties of the material.³¹ Substitution in A-site^{32,33} and B-site^{34–36} of the perovskite structure was also reported to modulate the intrinsic catalytic activity of the material. Aside from the improvement of the catalyst's intrinsic activity, one may improve the feasibility of the catalyst by reducing its particle size^{37–40} to increase the catalytically active surface area. Alternatively, one can also explore the surface sensitivity of the oxygen evolution reaction by exposing facets of higher intrinsic

catalytic activity.^{41–43} Ideally, in exfoliation, both approaches can be explored simultaneously.^{44–47} It may be summarized that the optimization effects employed in the case of LaNiO_3 are based on exploring minor adjustments to the structure of the catalyst and/or on the maximization of the materials specific area without aspiring to improve the intrinsic activity of the catalyst on an atomary level.

In this paper, we report on a novel rational approach of the OER activity optimization of catalysts based on Ni oxides. Starting with LaNiO_3 perovskite as initial material, structural variations are computationally introduced to maximize the presence of the trivalent Ni in the surface structure. The initial model catalyst and its structural modifications are then systematically investigated by DFT to identify structural motifs with improved OER activity. These theoretically predicted catalytically active motifs are then synthesized by a novel approach combining a template spray-freeze freeze-drying approach^{48,49} followed by simple post-synthesis treatment. The experimental OER activity values are then compared with theoretical predictions.

2. Results and Discussion

Structural model evaluations

Theoretical assessment of new catalysts' OER activities relies on thermodynamic analysis based estimate of the limiting over-potential of the oxygen evolution reaction. This

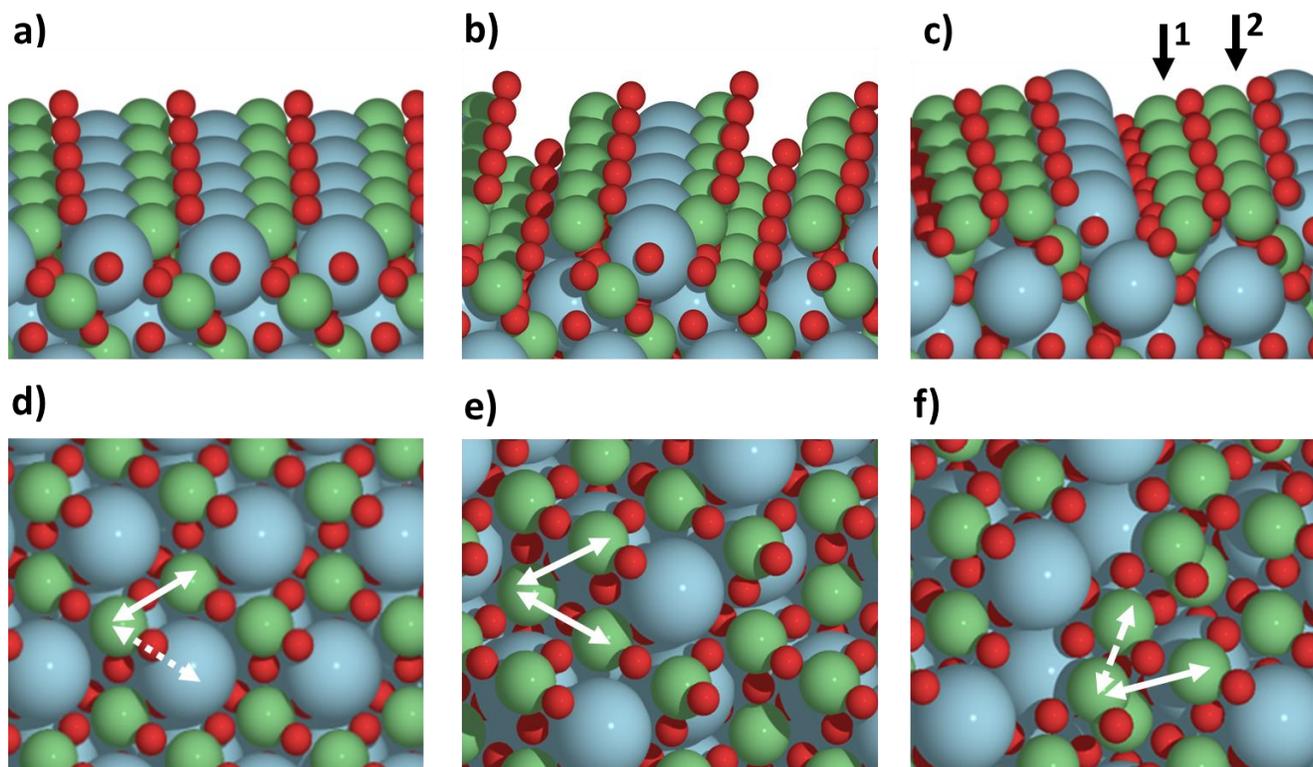
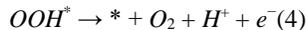
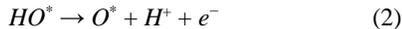
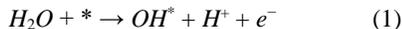


Figure 1 Geometry optimized structure of a) stoichiometric LaNiO_3 perovskite b) La-depleted LaNiO_3 structure before recombination c) La-depleted LaNiO_3 structure after recombination, Ni in two different arrangements (marked with arrows, 1 and 2) was tested as the active site for OER in this example. Surface structures of d) the stoichiometric LaNiO_3 perovskite, Ni-Ni (3.7 Å, solid arrow), La-Ni (3.3 Å, dotted arrow) e) the La-depleted surface before recombination Ni-Ni (3.5 Å, solid arrows), and f) the exposed Nickel surface after recombination, showing two different Ni-Ni distances: 2.8 Å (dashed arrow) and 3.5 Å (solid arrow).

is based on an assumption that the entire oxygen-evolving process is a sequence of four-electron proton transfer steps.²⁰ These electron-proton transfer steps are summarized as follows:



where the ‘*’ represents a binding site on the surface of the catalyst.

The scheme of the process depicted by equations (1) – (4) is valid regardless of the pH and may also be used to rationalize the behavior of the systems designed for alkaline media like, e.g. LaNiO₃.^{50,51} Oxygen may be evolved only if the overall reaction sequence is thermodynamically spontaneous, i.e. each of the reaction steps (1) – (4) is thermodynamically spontaneous. The step requiring the highest free energy to become thermodynamically spontaneous becomes the potential controlling step and the free energy associated with it is used to calculate the theoretical overpotential.

It may be also devised that the surface-confined active site(s) responsible for oxygen evolution has to be redox-active (i.e. capable of changing its oxidation state). Hence, one may assume that in the case of LaNiO₃ based catalysts the oxygen-evolving activity is primarily attributable to Ni, its oxidation state, and its local environment. It needs to be noted that the whole concept of the oxidation state is not native for DFT; hence, its change needs to be introduced by a modification of the local structure. Assuming LaNiO₃ perovskite as the initial well-defined structure (see **Figure 1a**), one can theoretically conceive a series of intermediate oxides derived from the perovskite LaNiO₃ containing a variable, yet decreased, amount of lanthanum near the surface (see **Figure 1b-c**).

The DFT-based energy optimization of the theoretically conceived structures depicted in **Figure 1a-c** suggests that the original perovskite arrangement features two types of metal-metal pairs¹ characterizing the surface structure; one relevant to pairs of neighboring Ni-Ni atoms at a distance of ca. 3.7 Å (solid arrow in **Figure 1d**) and the distance of neighboring Ni-La atoms (dotted arrow in **Figure 1d**) at a distance of ca. 3.3 Å. The perovskite structure responds to La removal in two principal ways: i) by cationic re-arrangement in the bulk of the structure and ii) by structural adjustment connected with a formation of new La free surface structures. Computational structure optimization predicts that the removal of La triggers a formation of Ni-enriched regions in the bulk where recombination of Ni atoms yields Ni pairs with an interatomic distance of ca. 3.5 Å (see arrows in **Figure 1e**). Recombination after the La leaching, however, also leads to

the formation of a new surface where the surface reconstruction leads to a completely new arrangement of Ni with Ni-Ni pairs at a distance of ca. 2.85 Å (see dashed arrow in **Figure 1f**). The average oxidation state of Ni remains III as follows from the average Ni-O distance of ca. 1.9 Å found in both proposed structural motifs reflecting the La removal

Regardless of whether these surface structures may actually exist they may be computationally assessed towards their activity in the oxygen evolution process. The theoretical OER over-potentials of the surface structures depicted in **Figure 1** were evaluated and compared with the generalized oxygen evolution volcano as shown in **Figure 2**. The DFT results summarized in **Figure 2** outline the striking difference between the behavior predicted for the stoichiometric LaNiO₃ and the surfaces created after La removal.

The La removal in principle forms either Ni-exposed or Ni-recombined surfaces, the catalytic behavior of which is fundamentally different from stoichiometric LaNiO₃. The theoretically conceived behavior of La-depleted La_xNiO₃ material shows smaller deviations from the ideal catalyst behavior (with all charge transfer steps driven with the same free energy) than the stoichiometric LaNiO₃. As shown in the data presented in **Figure 2**, the newly created Ni exposed surface (blue marker in **Figure 3**) shows significantly higher intrinsic activity than the conventional LaNiO₃ perovskite surface.

In contrast to the Ni exposed surface (see **Figure 1b** and **e**) which features only one type of possible active site, the Ni recombined surface shows two types of available Ni surface

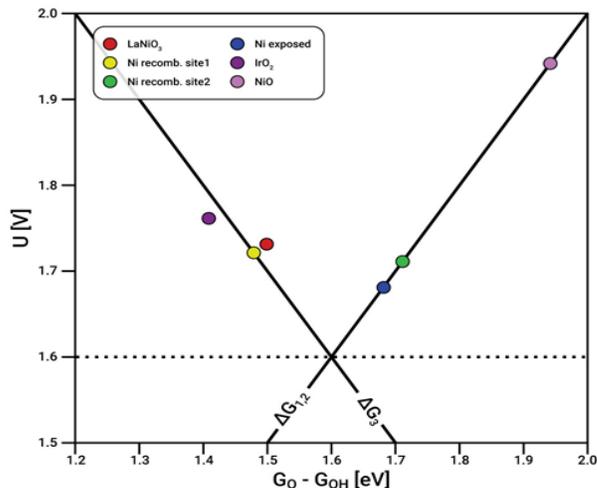


Figure 2 DFT-based activity volcano for the oxygen evolution reaction. The activity of the modified La-depleted surfaces is higher than the conventional stoichiometric surface.

sites. The reactivity of both available surface Ni sites (1 and 2, see **Figure 1c**) differs significantly, even though both types of surface Ni sites yield a similar theoretical OER overpotential. It also needs to be noted that the used descriptor – a difference of G_O and G_{OH} may be also taken as an approximation of the redox potential associated with oxidation/reduction to/from an active state in which the Ni stays in oxidation state III.

¹ It should be noted that the term *pair* in the text addresses essentially the distance at which specific atoms appear in the structure and its use does not suggest a direct bond formation between these atoms.

In this manner, one should expect the strongly binding Ni recombined site 1 to show a Ni(II) to Ni(III) transition in the interval 1.4-1.5 V. In contrast the weakly binding Ni recombined site 2 ought to show the same transition above 1.7 V coinciding with the oxygen evolution process.

While the Ni site 1 (see **Figure 1c** and yellow marker in **Figure 2**) can be easily oxidized and consequently resides on the strong binding branch of the volcano, the other available Ni surface site (site 2 in **Figure 1c** and green marker in **Figure 2**) shows greater resistance to the first electron transfer, which results in its position on the weak binding side of the OER volcano, making the binding of the *OH intermediate on the surface the potential determining step. Such a difference in reactivity of both Ni surface sites is not surprising given the proximity to the apex of the oxygen evolution volcano.

The activity of the recombined surface for both sites [site 1 (yellow marker) and site 2 (green marker), see **Figure 2**] is slightly lower than that of the Ni-exposed (i.e. non-recombined) surface (blue marker on the volcano), yet it remains closer to the apex of the volcano than the

stoichiometric LaNiO_3 . Although the thermodynamic analysis of the intrinsic OER activity for both types of La-depleted surfaces clearly favors the Ni exposed surface, the thermodynamic prediction does not automatically translate into superior practical activity of the Ni exposed surfaces. Given the thermodynamic nature of the analysis based on DFT calculations, the theoretical over-potentials are normalized per single active site. The predictions of practical OER activity, therefore, need to reflect the difference in density of the active sites on the surface. In fact, the Ni recombined surface has a higher density of active sites per surface area compared with other theoretically conceived surface structures, over the Ni exposed surface by a factor close to two. This higher active site density effectively brings the practical activity of Ni recombined surface up to the level of the Ni exposed surface which is superior to conventional LaNiO_3 .

The theoretical overpotential observed for the La depleted La_xNiO_3 oxides is about 50 mV lower than in the case of stoichiometric LaNiO_3 , which represents about an order of magnitude faster kinetics of the OER on La depleted materials. The results of the DFT modeling conclusively show that the

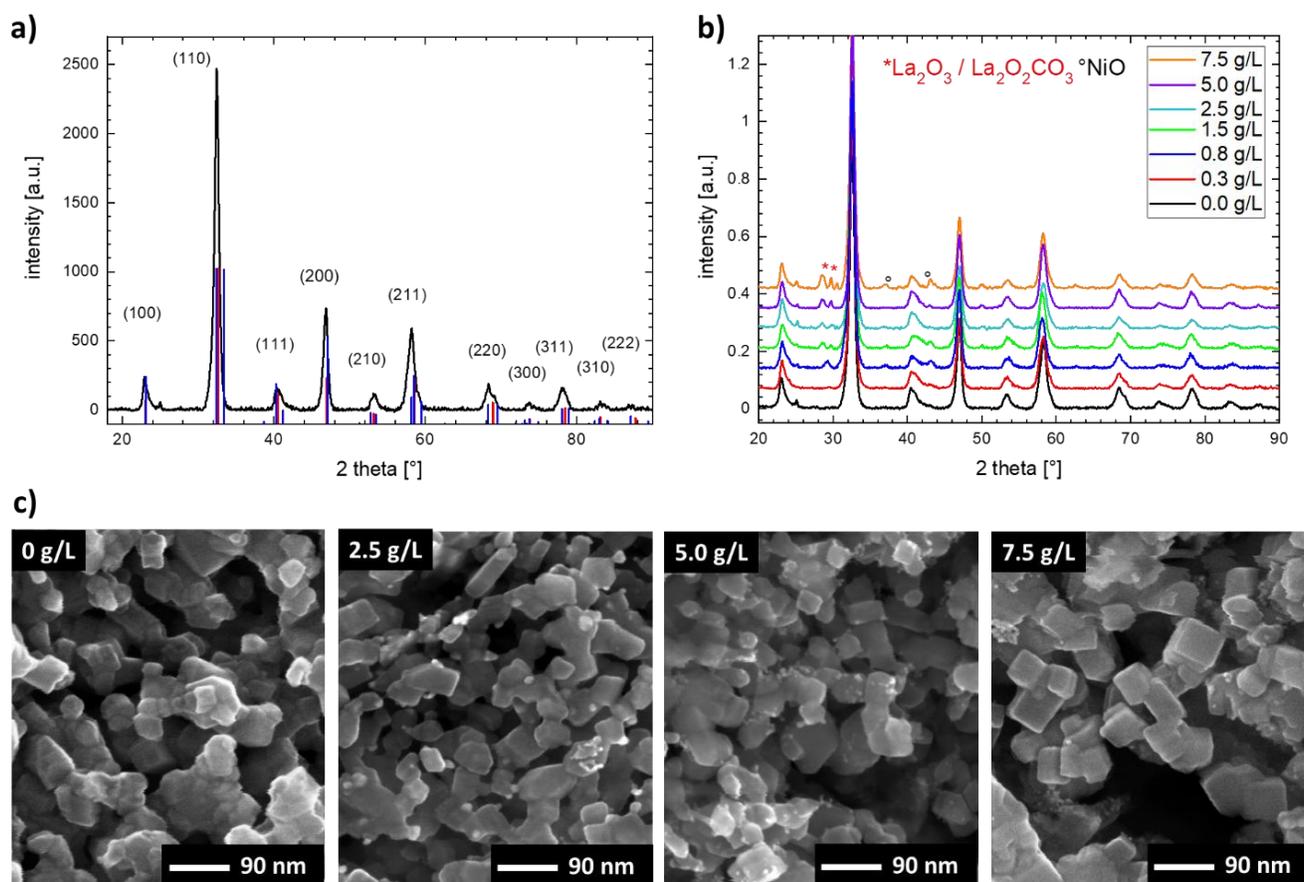


Figure 3 a) Powder diffraction pattern of lanthanum nickel oxide sample synthesized without added gelatin indexed with reference for cubic LaNiO_3 (red, Pm-3m, 221), for comparison the reference for rhombohedral LaNiO_3 (blue, R3c, 167) is added. **b)** Powder diffraction patterns of lanthanum nickel perovskites synthesized with different amounts of gelatin, peaks associated with lanthanum-based contaminations ($\text{La}_2\text{O}_3/\text{La}_2\text{O}_2\text{CO}_3$) are marked with an asterisks (*) and NiO (°). **c)** SEM micrographs of selected LaNiO_3 nanoparticles with varying gelatin concentrations.

activity of LaNiO_3 perovskites in oxygen evolution can in principle be significantly improved if one can stabilize La-free perovskite-related surface structures and prepare them on real catalysts.

Material synthesis

The synthesis of the structures theoretically identified as superior OER catalysts represents a significant challenge. Conventional synthetic approaches lead to the formation of stoichiometric LaNiO_3 . In the case of the spray-freeze freeze-drying process^{48,49} in the La-Ni system, an amorphous precursor is obtained which needs to be crystallized at elevated temperatures. The ternary lanthanum nickel oxide is formed at calcination temperatures as low as 700° C (see **Figure 3a**). The formed ternary lanthanum nickel oxide conforms to the perovskite structural type.

Detailed information on the structure of the prepared LaNiO_3 phases can be extracted from the Rietveld refinement of the experimental XRD patterns (see Supporting Information, **Figure S1**). Although the ideal perovskite structure is cubic, the variation in the sizes of the cations occupying both available types of cationic positions may trigger tetragonal or orthorhombic distortions. It needs to be noted that the precise structural determination of the materials prepared in the spray-freeze freeze-drying approach is complicated by the nanoparticulate nature, due to the poor quality of the diffraction data arising from the limited size of the coherent domains.

The refinement procedure of the experimental patterns gives the best convergence assuming that the prepared materials conform to the rhombohedral perovskite structure (R-3c, Space group 167), i.e. deviating from the ideal cubic perovskite (see **Figure S1b**).

A closer approach towards the theoretically predicted structures may be achieved by a combination of the spray-freeze freeze-drying synthesis in the presence of structure-directing gelatin^{52,53} followed by post-synthesis treatment. The synthesis in the presence of structure-directing gelatin leads to a formation of nano-crystalline phases which are apparently

identical with those synthesized in the absence of the structure-directing agent (see **Figure 3b**). The addition of structure-directing gelatin eventually leads to formation of secondary crystalline phases contaminating the produced materials. The diffraction signals of these secondary phases can be attributed to La-rich phases most likely La_2O_3 or $\text{La}_2\text{O}_2\text{CO}_3$. The La-rich contaminating phases are accompanied by a small fraction of NiO to maintain the stoichiometry of the reaction mixture. The amount of these additional phases, however, remains small, remains below 5% (2% of NiO) and their effect on the catalytic behavior can be neglected. Details of the Rietveld analysis are given in the Supporting Information (**Table S1** and **Figure S2**).

The structure-directing gelatin has a pronounced effect on the morphology of the synthesized materials as well as on the local structure (see **Figure 3c** and **Figure S3** of the Supporting Information). The LaNiO_3 materials prepared in the absence of gelatin show a random particle shape indicating a random orientation of the surface. The addition of gelatin directs the nanoparticle growth towards prisms with a rhombohedral base and with increasing gelatin content also prisms with a rectangular or square-like base. (see **Figure 3c**) The particle size analysis reveals very similar average particle sizes of around 35 nm for all samples, regardless of gelatin content (see details in the SI, **Figure S4**).

Electrocatalytic activity

Oxygen evolving activity of the prepared phases is reflected in cyclic voltammograms of the prepared LaNiO_3 nanocrystalline catalysts recorded in 0.1 M KOH solution in the potential range of 1.2 to 1.7 V vs RHE (**Figure 4**). To facilitate the reader's orientation, we will further use the potential necessary to drive the current density of 10 mA/cm² (of the projected electrode area) as a benchmark characteristic depicting the activity of the prepared materials. As follows from **Figure 4** there is no significant difference in the oxygen evolution activity which may be attributable to the surface orientation effects associated with the presence of gelatin in

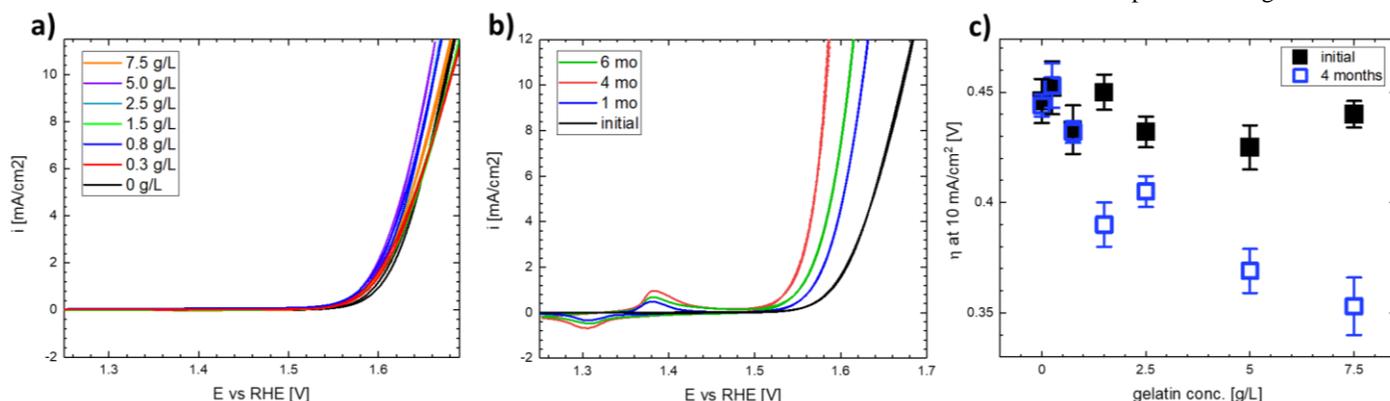


Figure 4 Cyclic voltammograms (CVs) of LaNiO_3 catalyst samples synthesized with varying amounts of gelatin, measured at 5 mV/s scan rate in 0.1M KOH, working electrode is the catalyst ink drop-cast onto GC-RDE support at 1600 rpm rotation rate. initial CVs of all synthesized samples b) CVs Cyclic voltammograms (CVs) of LaNiO_3 of the LaNiO_3 perovskite sample synthesized with a gelatin concentration of 7.5 g/L after different periods of ink aging and b) overpotential at a current density of 10 mA/cm² as a function of gelatin for initial samples (black) and after the post-synthesis ink aging for 4 months (blue).

the reaction mixture. All investigated materials show a comparable activity when the current density of 10 mA/cm² needs to be driven by over-potentials of 430-450 mV which are comparable with those of materials prepared by sol-gel synthesis.²⁵

A significant improvement of the catalytic activity is, however, observed for catalysts prepared in presence of gelatin if stored in the Nafion containing ink (see **Figure 4b**). The oxygen-evolving activity of the electrodes based on such materials improves with the amount of gelatin (see **Figure 4c**) and with storing time. The general behavior can be demonstrated on the sample of material prepared in the presence of gelatin in a concentration of 7.5 g/L, when aging of the electrochemical ink leads to a significant decrease of the overpotential needed to drive the current density of 10 mA/cm² from its initial value of 442 mV to 395 mV after one month and to 353 mV after 4 months (**Figure 4b**). Such overpotential is comparable to state-of-the-art perovskite OER catalysts in alkaline media, e.g. hexagonal -BSCF with η ca. 340 mV.⁵⁴ Further storage of the catalyst, however, leads to a pronounced drop in the oxygen-evolving activity (6 months, green curve in **Figure 4b**). The aging related increase of the catalyst activity might be in principle attributable to variations in catalysts loading due to a change of the ink concentration during the aging process. Such an explanation, however, cannot be accepted since the aging of the ink leads to a

significant structural development of the catalyst (see below). The observed behavior cannot be qualified using the XRD based structure and prompts more detailed structural characterization on a local level based on HRTEM and XAS.

Aside from the significant increase in OER activity one also finds a distinct redox feature characteristic for the Ni^{II}/Ni^{III} redox couple in voltammograms based on materials prepared in the presence of gelatin. This Ni^{II} to Ni^{III} transition is not observed in electrodes made from freshly prepared inks. It also needs to be noted that the signal attributable to a Ni^{II} → Ni^{III} transition is absent in the first anodic scan on a pristine electrode. This suggests that the electrodes originally do not contain any oxidizable Ni^{II} which gets formed only in-situ during the cathodic scan of the voltammetric experiment. The intensity of the Ni^{II}/Ni^{III} redox increases both with aging and, in general, also with the content of gelatin used in the synthesis. The intensity of the Ni^{II}/Ni^{III} redox feature yields a reasonable correlation with the measured activity (see Supporting Information, **Figure S5**).

It needs to be noted that the presence of the Ni(II) to Ni(III) at potentials slightly below 1.4 V vs. RHE shows a reasonable agreement with the theoretically conceived reactivity of the strongly binding (site 1) Ni on recombined surface presented in **Figure 2**. The observed experimental trend, when the resolved Ni(II) to Ni(III) transition signal increases with aging, is attributable to the increasing presence of the reconstructed

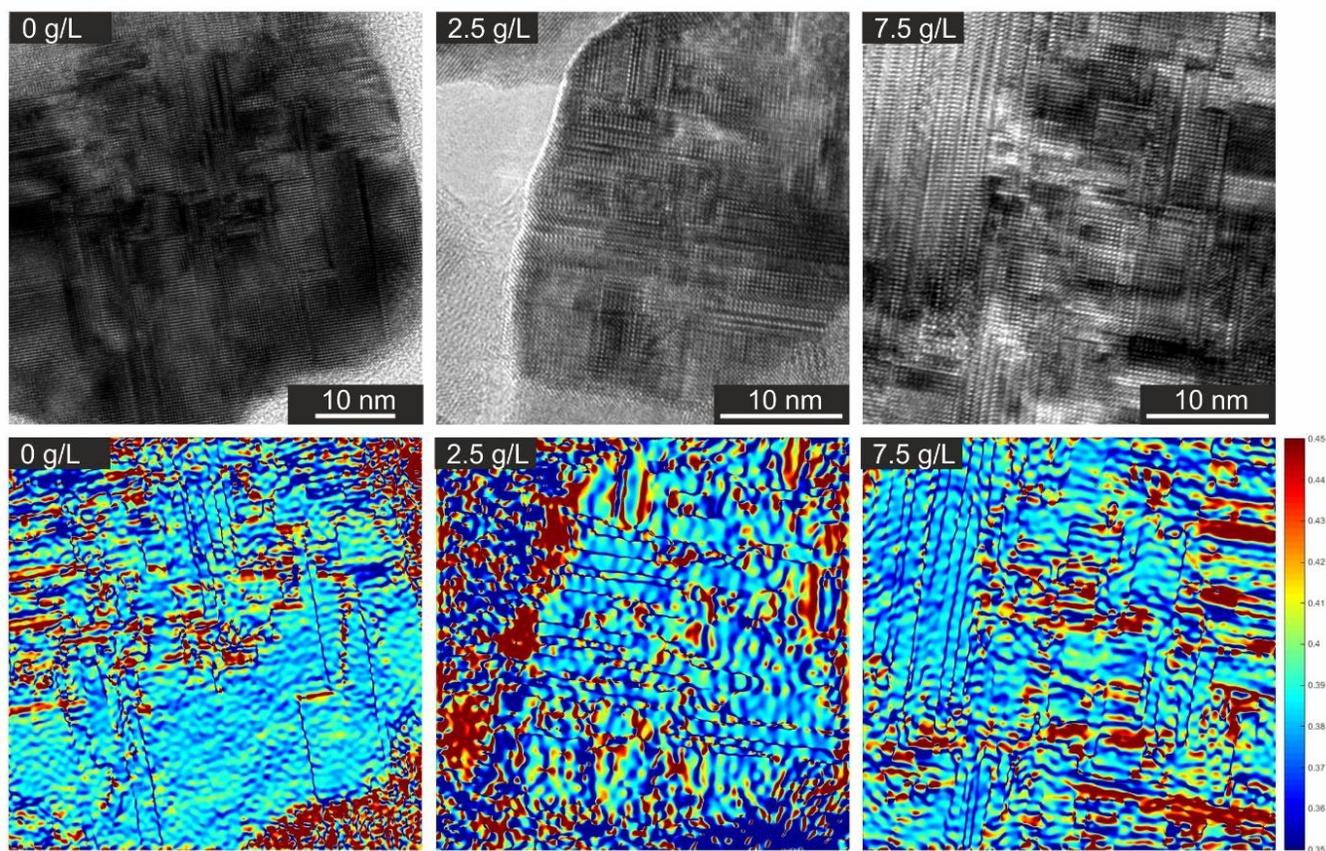


Figure 5 HR-TEM micrographs of selected LaNiO₃ nanoparticles with varying gelatin concentrations. The respective concentrations are given in the picture inset. Corresponding maps of d-spacing variation calculated by GPA are shown to outline the domain structure of the materials prepared in presence of gelatin.

Ni site at the surface. Since it is visible that the Ni^{II}/Ni^{III} redox charge correlates with increased activity, one may attribute the OER activity of the prepared materials to the strong binding sites of the Ni reconstructed active sites.

Local Structure Characterization

HR-TEM

High-resolution transmission electron microscopy (HR-TEM) data (see **Figure 5**) shows that all samples are composed of cuboid particles composed of rhombohedral LaNiO₃. The particles contain twinning domains compensating for the lower rhombohedral symmetry. The addition of gelatin leads to a decrease of the domain size and, therefore, an increase of the surface of domain boundaries. The formation of similar stacking faults has been reported in La-Ni-O materials previously.^{55,56} On the twinning boundaries, the formation of Ruddelsden-Popper (RP) faults, when the stacking NiO and LaO layers in the structure is broken and the formation of double LaO layers can be expected.^{55,56} It needs to be stressed that the formation of RP faults leads to a shift in the stacking of the layers by $a/2$ and causes a separation of La

and Ni on a sub-nanometer scale. The presence of the stacking faults is visualized in **Figure 5** by analysis of the d spacing variance which clearly distinguishes the density of the faults at the boundaries of the coherent domains which increases with increasing gelatin concentration.

This separation is, however, confined mostly to the bulk of the material and should not have an immediate effect on catalytic behavior as reflected in **Figure 4a**. A more detailed analysis of the HR-TEM data also yields additional structural information on materials phase composition confirming the presence of additional phases, identified also in XRD patterns. Detailed analysis of the local phase analysis is given in the Supporting Information (see **Figure S6**).

X-ray absorption spectroscopy

The X-ray absorption near edge structure (XANES) spectra of the Ni K-edge absorption spectra of prepared LaNiO₃ powders are shown in **Figure 6a**.

The absorption edge position of the lanthanum nickel samples appears at ca 8348 eV which is about 3 eV higher than that of the NiO reference (8345 eV). The Ni edge position obtained in LaNiO₃ is compatible with the projected oxidation

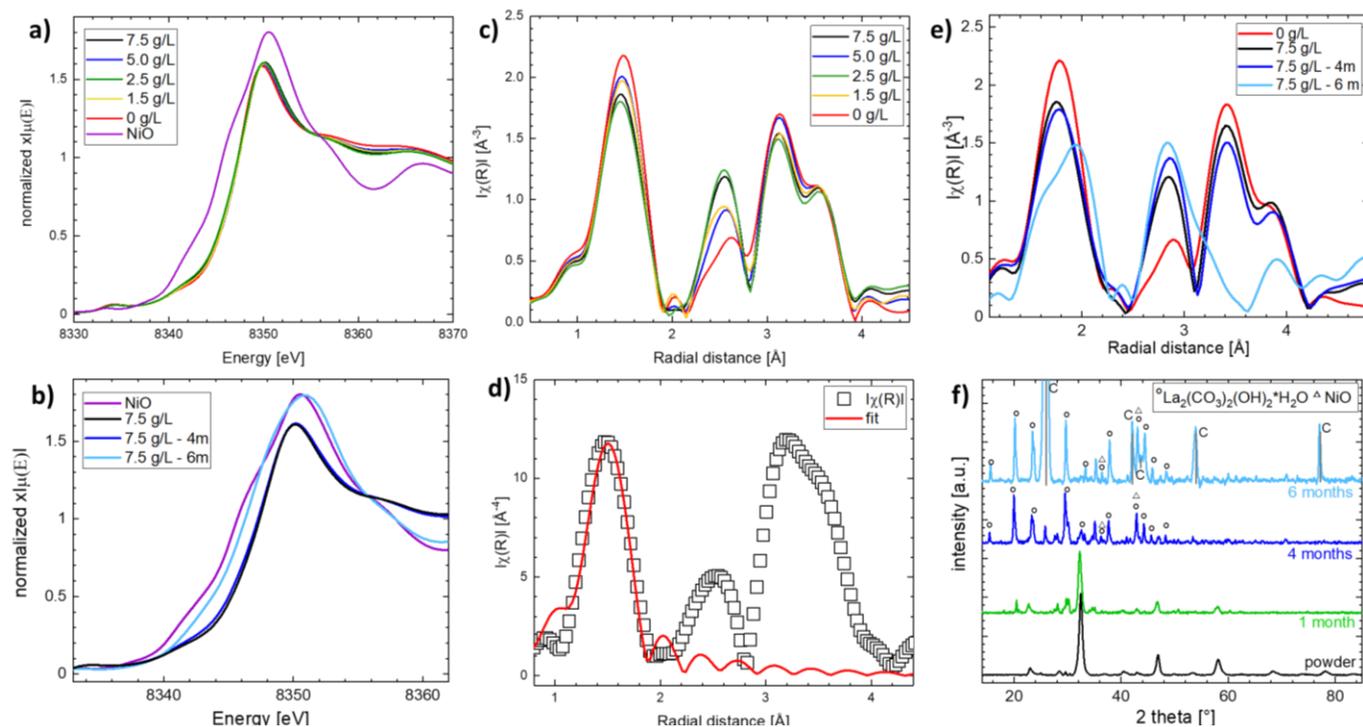


Figure 6 a) XANES spectra of the synthesized lanthanum nickel oxide powder samples and b) of the 7.5 g/L sample aged for different amounts of time (4 months – blue and 6 months -light blue) including the initial powder sample (black), measured at the Ni K-edge. The XANES spectra of NiO is included as a reference c) Fourier transformed EXAFS functions in R-space of the initial powder samples, weighed with k^2 , measured at the Ni K-edge, depicted with applied phase-correction. d) Typical NLLS fit (red line) of the theoretical model using a one-shell model of LaNiO₃ rhombohedral perovskite and NiOOH in a fitting range from 1.1 – 2 Å in R-space for the EXAFS function of the sample with 1.5 g/L gelatin concentration (\square) normalized with k^3 . e) Fourier transformed EXAFS functions in R-space of the 7.5 g/L sample aged for different amounts of times, weighed with k^2 , measured at the Ni K-edge, depicted with applied phase-correction. The 7.5 g/L and 0 g/L initial powder samples are included for comparison. f) XRD patterns of the LaNiO₃ sample prepared with 7.5 g/L gelatine collected after different ink aging times. The 6-month-old sample was prepared on graphite, the reflections that originate from the graphite substrate are marked in grey and indicated by C.

state of Ni^{III}.⁵⁷ The same oxidation state of Ni is also observed in catalysts subjected to aging in Nafion containing inks for less than 4 months (see blue curve in **Figure 6b** and SI, **Figure S7**). A longer aging of the catalysts, however, leads to a gradual decrease of the oxidation state of Ni to a lower oxidation state (see light blue curve in **Figure 6b**). The XANES based oxidation state of Ni is further corroborated by the average Ni-O bond length which remains close to 1.9 Å for all samples aged for less than 6 months. The lowered oxidation state of Ni suggested for materials aged for 6 months is matched by an elongation of the Ni-O distance which climbs above 2 Å for this material.

Since the high oxidation state of Ni is retained in all catalysts save for those aged in Nafion containing ink for more than 4 months, regardless of the different synthesis or aging conditions, one needs to seek additional structure-related information to qualify the observed changes of the oxygen-evolving activity of the prepared catalysts. This additional information can be extracted from the EXAFS based Ni local environment structure, which shows significant variability for different LaNiO₃ samples (see **Figure 6c**). Three distinct signals are identified in the Ni K EXAFS functions located at ca. 1.8 Å, 2.8 Å, and ca 3.4 Å. Assuming a rhombohedral perovskite structural model, one may expect the signal located at ca. 1.8 Å to reflect the direct Ni-O scattering in the first coordination shell. The pronounced signal located at ca. 3.4 Å can then be attributed to the cation-cation interaction between Ni in the B site and La located in the A-site of the perovskite structure. A relatively weak scattering signal, located near 2.8 Å, can be attributed to indirect scattering involving two of the Ni coordinating oxygens. This structural model works well for the Ni K-edge EXAFS functions of the LaNiO₃ prepared in the absence of gelatin (see **Figure S8** of the Supporting Information) but fails for the LaNiO₃ materials prepared in the presence of gelatin, namely, in the region near 2.8 Å.

The relative intensity of the feature located at 2.8 Å increases with increasing gelatin content and shows a different sensitivity to k normalization than in the case of LaNiO₃ prepared without gelatin (see SI - **Figure S9**). The observed behavior suggests that the signal located at 2.8 Å in the materials prepared with gelatin also integrates a metal-metal scattering interaction. The contribution from this metal-metal scattering increases with increasing gelatin content. The increase of this metal-metal scattering is accompanied also by

a decrease of the intensity of signals attributable to Ni-O scattering (ca. 1.8 Å) and Ni-La scattering (ca. 3.4 Å) (see **Figure 6c**).

Such a signal is typical for nickel-nickel arrangements typical for NiO⁵⁸ or other nickel oxo-compounds such as NiOOH.^{59,60} It may be, therefore, assumed that the Ni present in the materials prepared in presence of gelatin exists in two local arrangements one resembling a La-abated NiOOH-like environment (which introduces metal-metal scattering at ca. 2.8 Å) and perovskite local environment (introducing Ni-La scattering at 3.4 Å). One may, therefore, deconvolute the local structure data assuming the coexistence of these two local environments. The content of each Ni local environment was estimated from first-shell EXAFS function refinement (see **Figure 6d**) under the constraint that the Ni-O bonding distance and coordination number of Ni for both local environments remain constant ($r(\text{Ni-O})_{\text{NiOOH}} = 1.91 \text{ \AA}$ and $r(\text{Ni-O})_{\text{LaNiO}_3} = 1.93 \text{ \AA}$, respectively).

The fraction of the nickel-rich NiOOH-like environment increases with increasing gelatin content (see SI, **Table S2**). This trend is in agreement with the growing number of RP faults observed in HRTEM. It needs to be further stressed that the EXAFS based local structure analysis describes the situation in the materials' bulk and, as show the data presented in **Figure 4a**, gelatin content attributable variations of the Ni local arrangement have no immediate effect on the electrocatalytic activity. The aging of the LaNiO₃ catalysts in the Nafion based inks for up to 4 months has no qualitative effect on the Ni local structure of the prepared catalysts (see blue curve in **Figure 6e** and SI - **Figure S10**). The only discernible effect one observes is a slight increase in the presence of the Ni in a NiOOH-like environment.

The local structure, however, qualitatively changes for longer aging times (see light blue curve in **Figure 6e**) when the observed Ni EXAFS functions fail to show any scattering characteristic for La - Ni pairings with a distance of ca. 3.4 Å. The suppression of the signal characteristic for the perovskite environment is partially compensated by an increase of the metal-metal scattering with a distance of ca. 2.8 Å, characteristic for NiO or NiOOH.

This local structure development is complemented by a pronounced shift of the Ni absorption edge to lower energies (cf. **Figure 6b**) which identifies the local environment of Ni as the one typical for cubic NiO. The NiO structural model works

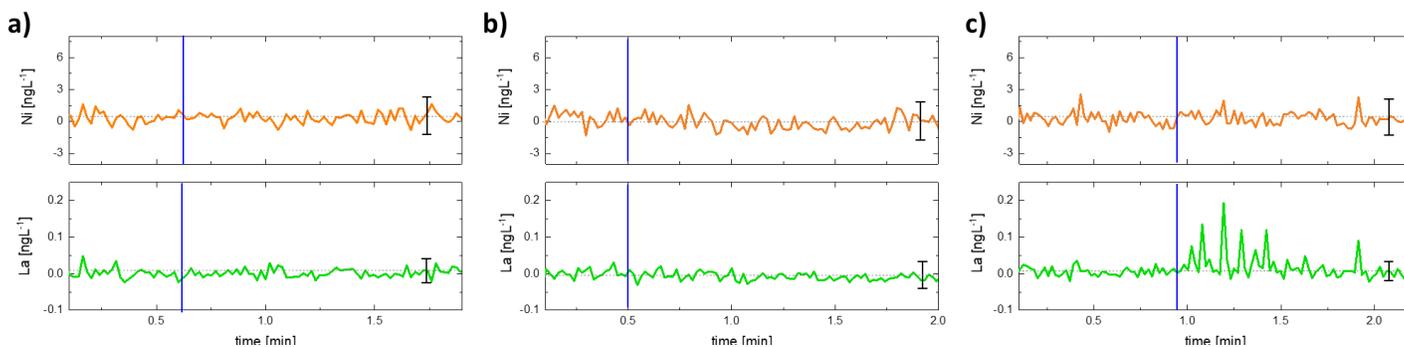


Figure 7 ICP-OES signals of lanthanum and nickel present in the 0.1M KOH electrolyte with no applied potential for a) freshly prepared ink with a gelatin concentration of 5.0 g/L b) aged ink synthesized without the addition of gelatin and c) aged ink with a gelatin concentration of 5.0 g/L. The contact time of the electrode with the electrolyte solution is indicated by the blue line. The detection limit is marked for each experiment as the black error bar.

well for the Ni K-edge EXAFS functions of 6-month aged inks (see **Figure S11** of the Supporting Information).

The local structure development of the aged LaNiO_3 catalysts is also indirectly reflected in the pronounced development of the diffraction patterns of the aged LaNiO_3 materials (see **Figure 6f**). As shown by the patterns presented in **Figure 6f**, the aging of the LaNiO_3 materials in Nafion based inks leads to the apparent destruction of the LaNiO_3 perovskite nanocrystals. The intensity of reflections typical for rhombohedral LaNiO_3 decreases with time and cannot practically be identified in the patterns of the materials aged for more than 4 months. The observed XRD patterns become dominated by La containing phases, namely by $\text{La}_2(\text{CO}_3)_2(\text{OH})_2 \cdot \text{H}_2\text{O}$ (PDF #00-046-0368). The observed diffraction patterns are further complemented with small contributions from NiO (the reflections of which, unfortunately, overlap with those of Lanthanum carbonate) and additional lanthanum phases such as LaO and La_2O_3 (see SI, Figure S12).

Combining the structural information based both on XRD and EXAFS data with the local arrangement information provided by HRTEM, one may conclude that the observed significant improvement of the OER activity is facilitated by specific action of the local structure forming gelatin. It may be also concluded that this effect is confined to a length scale inaccessible by conventional X-ray diffraction. Comparing the local structure of the LaNiO_3 prepared both in presence and absence of gelatin, one may propose that the gelatin, in fact, controls the distribution of the stress/strain connected with the A site and B site cations size in the LaNiO_3 perovskite. The materials prepared in absence of gelatin use the high entropy of the randomly oriented surface to release the stress/strain. The materials prepared in presence of the gelatin, which show a high degree of faceting and a relatively high orientation of the surface, locate the same stress/strain in the RP faults in the nanocrystals bulk. In fact, the RP faults facilitate exposing the Ni-rich structural motifs reflected in the EXAFS data (Ni-Ni scattering distance of 2.8 Å) to the surface. This may be achieved by selective leaching of the La confined in the RP stacking faults. Such a process is compatible with the identified formation of $\text{La}_2(\text{CO}_3)_2(\text{OH})_2 \cdot \text{H}_2\text{O}$ in the aged materials. The formed nanometer-to subnanometer perovskite-like domains are not reflected in the XRD patterns due to the limited ability of the conventional diffraction techniques to address structural features on nanometer or subnanometer lengthscale. This mechanism is further confirmed by selective removal of the perovskite stabilizing La, which can be followed by ICP-OES experiments (see **Figure 7**). The La leaching is recorded in ICP-OES experiments which clearly detects a transfer of La in the solution upon contact of the aged materials with the electrolyte solution (see **Figure 7**).

As follows from the ICP-OES data, contact with the electrolyte (0.1M KOH) does not trigger any visible leaching from the freshly prepared LaNiO_3 ink samples (**Figure 7a**). The same behavior is also observed for materials prepared without gelatin. (**Figure 7b**) Electrodes based on aged inks of catalysts prepared with gelatin, however, release lanthanum into solution immediately upon contact with the electrolyte solution (see **Figure 7c**). It needs to be noted that the signal of solution-based La in these experiments is rather discontinuous

which suggests lanthanum leaching rather from confined regions than from the entire bulk of the ternary phase. This leaching is facilitated by the presence of Nafion in the catalyst. The process, therefore, likely involves an increase of the overall surface area and can be viewed as an analog of an exfoliation. It needs to be noted that materials of similar structure indeed can be exfoliated in acid media.⁶¹ Similarly, it is known that immersion of the Nafion in aqueous solutions leads to a drop of the solution's pH by up to 2 pH units.⁶² In this context we may reasonably expect that the Nafion, aside of creating mild acid environment also facilitates stabilization of the exfoliated surface by preventing their clustering and re-assembly.⁶³ The improvement of the oxygen-evolving activity by aging is connected with creating acid conditions (attributable to the sulphonic groups of the Nafion) and cannot be achieved with another polymeric binder. (see Supporting Information, **Figure S13**). The oxygen evolution activity improvement then becomes proportional to the density of the RP faults in the prepared LaNiO_3 nanocrystals and becomes apparent only for materials prepared with a significant gelatin concentration (>1.5g/L) (cf **Fig 4c** and SI, **Fig S14**). This suggests that the observed behavior could be related to the Ni environment with a Ni-Ni pairing at 2.8 Å and its eventual exposure on the material's surface.

The observed improvement of the oxygen-evolving activity of the Nafion aged materials, is significant and apparently confirms the theoretical prediction presented in **Figure 4**. This agreement, however, needs to be taken with care as the experimental data can be described by an alternative interpretation. One needs to bear in mind that the aging of the catalysts causes an increase of the surface area, the effect of which may possibly overlap with the effect of the theoretically predicted intrinsic activity improvement. The quantitative effect of the electrode surface area, however, do not play a dominant role as can be deduced from the fact that the catalysts lose their activity immediately once the oxidation state of Ni starts to drop below III (cf. **Figure 4b**). In addition, the qualitative nature of the observed OER activity improvement is reflected also in the observed change of the Tafel slope (see Table 1). It should be stressed that the Tafel slope remains aging insensitive in the case of materials prepared without gelatin. On the other hand, the Tafel slope changes from ca. 55 mV/decade to ca. 40 mV/decade upon aging in Nafion containing ink (see Table 1). This trend reflects a change in the mechanism of the whole OER process and suggests a change of the kinetic control to the third electron transfer caused by aging. The significant difference between the Tafel slope of the LaNiO_3 prepared without gelatin and those of the aged LaNiO_3 synthesized in presence of gelatin also reflects the effect of the surface orientation which is quite heterogeneous for the materials prepared without gelatin. The random surface orientation explains in this case the rather high Tafel slope value observed experimentally (60 mV/decade) which differs from the fact that the DFT model (based on (100) surface orientation) predicts the third electron transfer as the potential controlling step which should result in Tafel slope close to 40 mV/decade.

The theoretical prediction of the third electron transfer to be the potential limiting step on the 1st type of the active site on the reconstructed surface (see Figure 2) seems to be, on the other hand, confirmed in the experimental values observed for

aged electrodes based on LaNiO_3 prepared in presence of gelatin. It also needs to be noted that the theoretical prediction assumes that the activity improvement requires the Ni to reside in the perovskite-like local environment. This implies that the complete leaching of La from the structure we apparently encounter in the samples aged for 6 months inevitably should lead to a drop in the OER activity. This drop in the OER activity is indeed observed and is also accompanied by an increase in the Tafel slope to ca. 60 mV/decade. The complex variations of the Tafel slope are difficult to explain and suggest that the catalytically active sites are in fact formed only under operando conditions. The prepared materials and their available structural information, therefore, describe just a precursory state and further in-situ XAS experiments would be needed to fully qualify the difference of the active sites formed on individual materials.

The observed OER activity data, nevertheless, confirm the theoretical prediction of the superior activity of La-depleted surface layers. It needs to be noted, however, that the observed change in oxygen-evolving activity is higher than that predicted theoretically for the La depletion of LaNiO_3 . This behavior is not surprising since the theoretical prediction of higher activity is based solely on intrinsic activity and/or crystallographic active site density. It remains insensitive to possible changes in the specific surface area caused by chemical processes like dissolution or exfoliation (see above).

Table 1 Slopes derived from the Tafel lines of the oxygen evolution on perovskite catalysts measured for initially prepared catalyst suspensions and after four months of aging of the ink suspensions, extracted from steady-state chronoamperometric measurements in 0.1 M KOH

Gelatin conc. [g/L]	Initial [mV/dec]	4 months [mV/dec]
0	65 ± 2	66 ± 3
1.5	55 ± 3	51 ± 2
2.5	57 ± 1	46 ± 4
5.0	52 ± 3	43 ± 4
7.5	52 ± 1	43 ± 1

As-prepared, as well as exfoliated LaNiO_3 related oxides, are reasonably stable under operando conditions as shown by ICP-OES experiments (see SI, **Figure S15**) and the catalysts seem to be stable up to a potential of 1.9 V vs. RHE. Exposure of the electrodes to higher potentials results in the rise of coinciding signals of La and Ni in the solution. This behavior indicates rather a disintegration of the electrodes when the whole particles are loosened from the electrode due to vigorous bubble formation rather than selective leaching of any component from the catalyst under operando conditions.

3. Conclusions

The rational design principle in electrocatalysis conventionally comprises the DFT screening of

thermodynamically stable phases as prospective catalysts. The data presented on the LaNiO_3 optimization, however, represent a qualitative improvement of this approach since they describe a combined theoretical and experimental approach towards the exploration of metastable phases which, based on theoretical analysis, have the potential to outperform materials populating the apex of the oxygen evolution volcano curve.

The spray-freeze freeze-drying approach in the presence of gelatin as a structure-directing agent demonstrates the potential to prepare and activate the phases conceived theoretically (i.e. without support in existing structures) as materials of superior OER activity. The control obtained with the structure-directing gelatin allows to prepare materials of identical XRD diffraction patterns differing, however, significantly on the local level. High-resolution transmission electron microscopy along with X-ray absorption spectroscopy apparently identifies a separation of La and Ni on the sub-nanometer level in the phases prepared, namely, if the synthesis of the materials was done in presence of gelatin. This defect local structure can be viewed as Ni-enriched regions separated by La-rich Ruddeldsen-Popper (RP) faults. The formation of these RP faults triggers cation redistribution in the Ni-rich domains leading to the arrangements predicted by DFT.

The Ni-rich regions contain Ni solely in the oxidation state III and are capable to significantly improve the OER activity of the prepared materials if exfoliated to the surface. It needs to be stressed, however, that although maintaining the Ni in a high oxidation state is necessary to retain high OER activity, the actual observed activity improvement is supported by a specific surface re-organization which enables - in agreement with the theoretical prediction - strong binding active sites shifting the be involvend in controlling step of the process. The observed drop in the overpotential needed to drive OER at the current density of 10 mA/cm² is as much as 100 mV, from 440 mV to 360 mV. The gelatin also directs the morphology of the prepared LaNiO_3 nanocrystals towards prismatic crystals with a rhombohedral and (if the concentration of gelatin increases) rectangular or square base, this morphology direction shows, however no effect on the oxygen-evolving properties of the prepared materials. The observed activity is comparable with that reported for the most active OER catalysts for oxygen evolution.

4. Methods

Density Functional Theory

The LaNiO_3 structures were optimized from the bulk using Density functional theory (DFT) calculations with the usage of the Grid-based Projector Augmented Wave (GPAW)^{64,65} with the Atomic Simulation Environment (ASE)⁶⁵ interface. The trigonal configuration of the perovskite unit cell (R-3c, 167) was used for the initial structure. Spin-polarized calculations were performed with a plane wave energy cut-off of 850 eV, a (10, 10, 10) k-point mesh, and the PBE⁶⁷ functional for describing the exchange and correlation effects were used to optimize the bulk structure. (100) LaNiO_3 surfaces were created from the optimized bulk structure. The generalized gradient approximation (GGA) was used by implementing the BEEF-vdW⁶⁸ functional to express the exchange and

correlation, with a grid spacing of $h=0.20 \text{ \AA}$. All the surface calculations were spin-polarized, the Brillouin zone was sampled with a k-point mesh of (4, 4, and 1), and the atomic positions were relaxed until the total forces were lower than 0.08 eV/\AA .

Synthesis

Lanthanum acetate hydrate ($\text{La}(\text{OOCCH}_3)_x \text{H}_2\text{O}$, Sigma Aldrich, 99.9 %), and nickel lactate tetrahydrate (98 %, Alfa Aesar) were used as metal precursor salts. The crystal water content x of the lanthanum acetate was thermally analyzed using a SetSys Evolution system (Setaram) coupled with a quadrupole mass spectrometer (QMG 700, Pfeiffer). The lanthanum acetate was heated in an open alumina crucible in an argon stream (60 mL min^{-1}) in a temperature range of $30 - 1000 \text{ }^\circ\text{C}$ at a rate of $10 \text{ }^\circ\text{C min}^{-1}$. The evolved gases were analyzed in multiple-ion detection mode (MID) when the intensity of individually selected fragments (mass-to-charge ratio) $m/z = 12, 16, 17, 18, 28,$ and 44 was followed as a function of temperature. The crystal water content was found to be $x = 1.3$.

The LaNiO_3 samples were synthesized by the spray-freeze freeze-drying method.^{48,49,69} The precursor solutions of lanthanum acetate and nickel lactate were prepared by dissolving the corresponding metal salts (ratio 1:1) as well as the respective gelatin amount (from 300 to 750 mg) in 100 ml of Milli-Q quality deionized water. The total metal concentration was kept at 10 mM in all syntheses. The solutions were heated to $80 \text{ }^\circ\text{C}$ to allow the dissolution of the gelatin and stirred for 30 minutes and left to cool off before the spray-freezing step. The ice-based precursor was prepared by spraying the starting solution into ca. 2 L of liquid nitrogen. The frozen solvent was removed in the freeze-drying step at reduced pressure (1 Pa) employing a FreeZone Triad Freeze Dry System 7400030 (Labconco). The following temperature protocol was employed in the procedure: $-30 \text{ }^\circ\text{C}$ during the evacuation of the cooling chamber, followed by gradual temperature increase ($-30 \text{ }^\circ\text{C}$ (2 h), $-25 \text{ }^\circ\text{C}$ (5 h), $-20 \text{ }^\circ\text{C}$ (4 h), $-15 \text{ }^\circ\text{C}$ (6 h), $+30 \text{ }^\circ\text{C}$ (4 h)). The dry, foam-like precursor was carefully removed from the freeze-dryer and annealed at $700 \text{ }^\circ\text{C}$ for 2 h in a tube furnace in air.

The crystallinity and phase purity of the synthesized materials were analyzed using powder X-ray diffraction (XRD). The diffraction patterns were recorded using a Rigaku Miniflex 600 powder X-ray diffractometer with $\text{Cu K}\alpha$ radiation operating at 30 kV and 10 mA. 10 scans were averaged to obtain data quality needed for Rietveld analysis. Rietveld refinements were performed to determine the unit cell parameter as well as contamination content with the Profex 3.13.0 software package.⁷⁰ Morphology and particle size of the prepared samples were analyzed using a Hitachi S4800 scanning electron microscope (SEM) equipped with a Nanotracer EDX detector (Thermo Electron). Transmission electron microscopy (TEM) was used to determine the defect nature of the prepared nanocrystals and was carried out on an FEI Tecnai TF20 X-twin microscope operated at 200 kV (FEG, 1.9 \AA point resolution) with an EDAX Energy Dispersive X-ray (EDX) detector attached. Images were recorded on a Gatan CCD camera with a resolution of 2048×2048 pixels using the Digital Micrograph software package. High resolution TEM (HR-TEM) micrographs were

treated by Geometrical Phase Analysis (GPA)⁷¹ performed by CrysTBox⁷². The powder samples were dispersed in isopropanol and the suspension was treated in ultrasound for 5 minutes. A drop of the diluted suspension was placed on a holey-carbon-coated copper grid and allowed to dry by evaporation at ambient temperature.

X-ray absorption spectroscopy

Ni K-edge and La LIII-edge X-ray absorption spectra (XAS) of all samples were collected at the Inner-Shell Spectroscopy (ISS 8-ID) of the National Synchrotron Light Source (NSLS) II, Brookhaven National Laboratory. The incident beam was monochromatized using a Si(111) cryogenically cooled double crystal monochromator. Spectra were measured in fluorescence mode using a Passivated Implanted Planar Silicon (PIPS) diode detector. The absorption spectra were collected at room temperature and ambient pressure. The X-ray absorption spectra of the freshly prepared materials were measured on BN-based pellets (150 mg) containing 5-10 mg of respective catalysts. Characterization of the catalysts relevant to their electrode-related behavior was performed on thin films prepared on rigid graphite carbon foil (0.125 mm , 99.95%, Good Fellow) substrates by drop-casting the catalyst inks (see below) to deposit a sufficient amount of catalyst (ca. 1-3 mg) on the substrate. Spectra were measured in an energy range of $8150 - 9150 \text{ eV}$ at the Ni K-edge and $5300 - 5800 \text{ eV}$ at the La LIII-edge. The absorption edge energies of the perovskite materials were determined from the X-ray absorption near edge structure (XANES) part of the collected spectra, using the maximum of the first derivative of the edge region. Extended X-ray absorption fine structure (EXAFS) data were analyzed using the Demeter program package based on the IFEFFIT libraries,^{73,74} which included energy calibration, background subtraction, and edge step normalization. For the fitting, the $\chi(k)$ functions were weighted with k^2 . The local structure parameters were refined from EXAFS functions by non-linear least square (NLS) fitting in the R-space in the range of $1.1 - 2 \text{ \AA}$. Details of the refinement (k-range, goodness of fit (R-factor), Debye-Waller factors σ , absorption edges E_0 , occupation, and refined values of the effective scattering paths) are listed in the respective tables.

Electrochemical characterization

The activity of the prepared materials in the oxygen evolution reaction was evaluated from linear sweep voltammograms recorded in alkaline media. A standard single-compartment three-electrode cell was used in all experiments with an Analytics Rotator AFMSRXE RDE-setup of Pine Instruments controlled by an Autolab PGSTAT30. Thin-film catalyst layers deposited on a glassy carbon RDE support were used as working electrodes. A platinum mesh was used as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All potentials were recalculated and are reported in the reversible hydrogen electrode (RHE) scale. The catalyst ink suspensions were prepared using 10 mg of perovskite catalyst, 1.0 mL of Milli-Q quality H_2O , 4.0 mL of isopropyl alcohol ($\geq 99.5 \%$, Sigma Aldrich), and $20 \text{ }\mu\text{L}$ of 5 wt. % Nafion solution (Nafion 117, Sigma Aldrich). The ink suspensions were sonicated for 30 min before depositing $10.0 \text{ }\mu\text{L}$ on a polished glassy carbon

disk electrode (0.196 cm²) to reach a total catalyst loading of 100 μg cm⁻².

The 0.1 M KOH electrolyte was prepared from KOH pellets (p.a., Lachema) by diluting with Milli-Q H₂O. Cyclic voltammograms were recorded at 5 mVs⁻¹ in the potential range of 1.1–1.7 V. Tafel lines were derived from steady-state chronoamperometric measurements, in which the potential was gradually stepped from 1.2 to 1.6 V while holding for one minute at each potential. All measurements were corrected for uncompensated resistance of the system. Electrochemical impedance spectroscopy measurements were recorded in the range from 15 kHz to 1 Hz with an amplitude of 10 mV (peak to peak) to determine the ohmic resistance of the system. The presented current densities are based on the geometric surface area of the glassy carbon disk electrode.

In-operando ICP-OES

Electrode dissolution was monitored during electrochemical experiments using a v-channel electrochemical flow cell (0.636 cm²) connected to an Agilent 5100 ICP-OES spectrometer by direct injection. The ICP-OES signals of lanthanum (379.477 nm) and nickel (352.453 nm) in 0.1 M KOH diluted from 38 wt% stock (VWR) were monitored as a function of time. Standard calibration curves were constructed from 0, 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 ppm (nickel) and 0, 0.13, 0.28, 0.55, 0.83, 1.1, and 1.4 ppm (lanthanum). The detection limit was estimated by calculating three times the standard deviation of the blank. The flow rate set by the peristaltic pump that supplied the ICP-OES was 1.5 mL min⁻¹ for all experiments. Glassy carbon plates of 2 mm thickness (Alfa Aesar) were used as catalyst substrates. The in-operando set-up of the electrochemical cell combined with an ICP-OES spectrometer allows analyzing the stability of catalyst particles under applied OER potential. The aged ink of 5.0 g/L gelatin concentration was chosen as a representative example. The potential was stepped from 1.4 V to 2.0 V vs RHE in 0.1 V increments while each potential step was held for five minutes.

ASSOCIATED CONTENT

Supporting Information. Details of the Rietveld refinement, SEM micrographs, Histograms of the statistical particles size analysis, SAED, R-space representations of EXAFS functions, and cyclic voltammograms and included in the Supporting Information (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>

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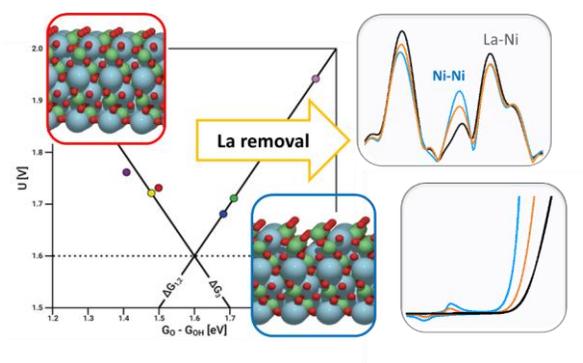
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Supporting Information

Engendering unprecedented activation of oxygen evolution via rational pinning of Ni oxidation state in prototypical perovskite: Close juxtaposition of synthetic approach and theoretical conception

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Figure S1 Rietveld refinement of lanthanum nickel perovskite synthesized without the addition of gelatin assuming a) cubic (Pm-3m, 221) ($R_{wp}=6.65\%$ $R_{exp}=3.27\%$ $\chi^2=4.1357$ GOF=2.0336) and b) rhombohedral (R3c, 167) ($R_{wp}=5.33\%$ $R_{exp}=3.27\%$ $\chi^2=2.6568$ GOF=1.6300) structural model.

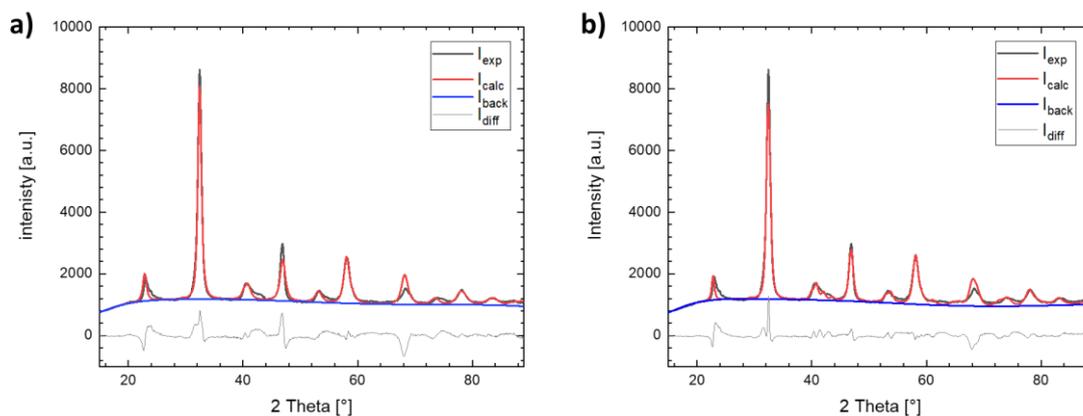


Figure S2 Typical full Rietveld refinement of lanthanum nickel oxide samples synthesized in presence of 7.5 g/L of gelatin calcined at 700 °C assuming NiO and La₂O₃ impurities. The figures of merit for the quality of the fit are $R_{wp}=4.78\%$, $R_{exp}=1.87\%$, $\chi^2=6.5339$ GOF=2.5561.

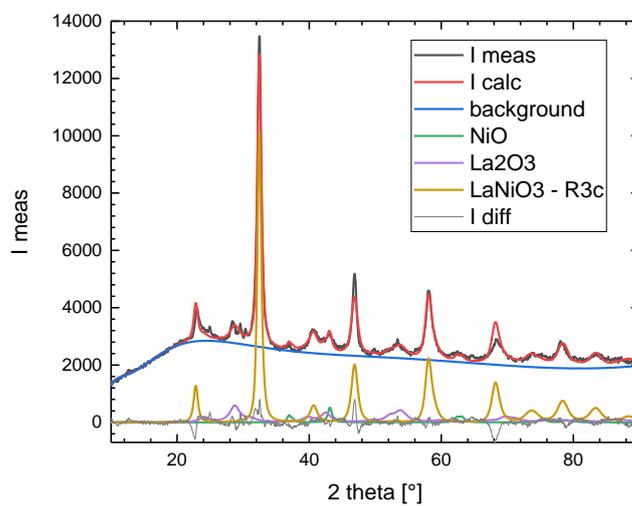


Table S1 Details of the full Rietveld refinement of the diffraction patterns of lanthanum nickel oxide perovskites synthesized with variable amount of gelatin.

	LaNiO ₃	ESD	NiO	ESD	La ₂ O ₃	ESD	
0 g/L	0.998	0.009	0.002	0.007	0	0	R _{wp} =7.85%, R _{exp} =3.29%, χ ² =5.6931 GOF=2.3860
0.3 g/L	0.989	0.003	0.011	0.001	0	0	R _{wp} =6.92% R _{exp} =2.8% χ ² =6.1080 GOF=2.4714
0.8 g/L	0.989	0.001	0.011	0.002	0	0	R _{wp} =7.69%, R _{exp} =2.88%, χ ² =7.1296 GOF=2.6701
1.5 g/L	0.988	0.002	0.012	0.001	0	0	R _{wp} =7.65%, R _{exp} =2.92%, χ ² =6.8637 GOF=2.6199
2.5 g/l	0.977	0.003	0.017	0.003	0.005	0.001	R _{wp} =4.6%, R _{exp} =2.17%, χ ² =4.4936 GOF=2.1198
5.0 g/L	0.945	0.002	0.017	0.002	0.038	0.006	R _{wp} =6.05%, R _{exp} =1.95%, χ ² =9.6259 GOF=3.1026
7.5 g/L	0.949	0.005	0.018	0.001	0.032	0.004	R _{wp} =4.78%, R _{exp} =1.87%, χ ² =6.5339, GOF=2.5561

Figure S3 SEM micrographs of lanthanum nickel oxide perovskite samples synthesized in presence of different gelatin contents.

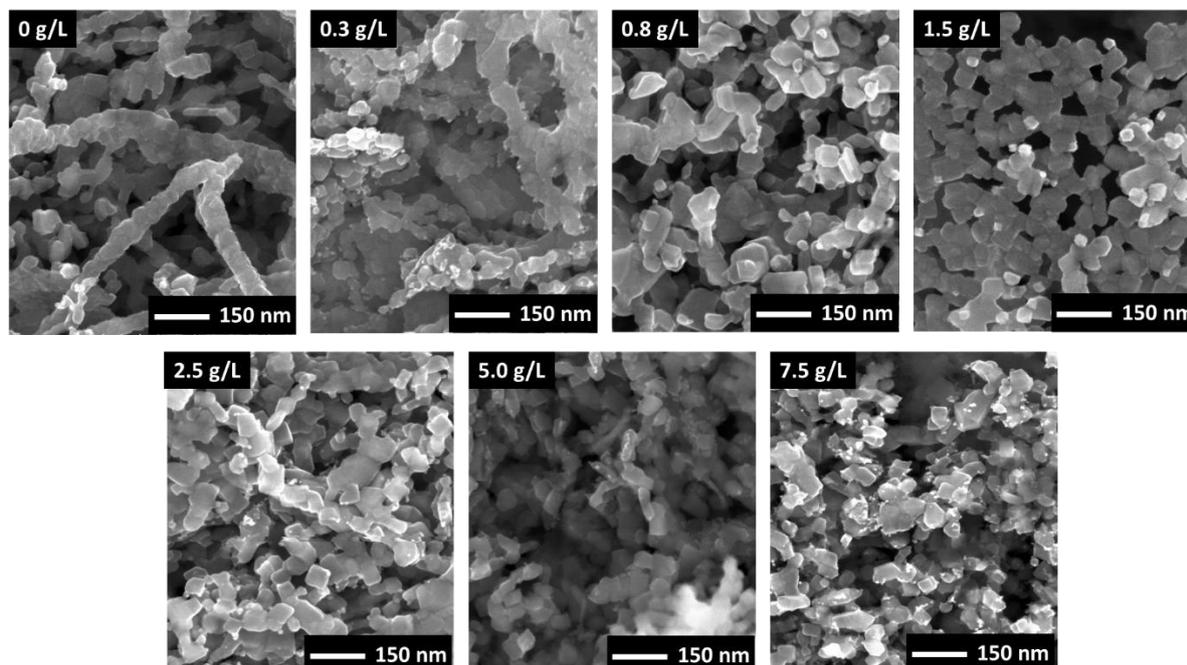


Figure S4 Statistical analysis of the particle size distribution in lanthanum nickel perovskite oxides synthesized with various gelatin concentrations. At least 400 data points were evaluated for each sample. The corresponding average particle sizes are given in the Figure legend.

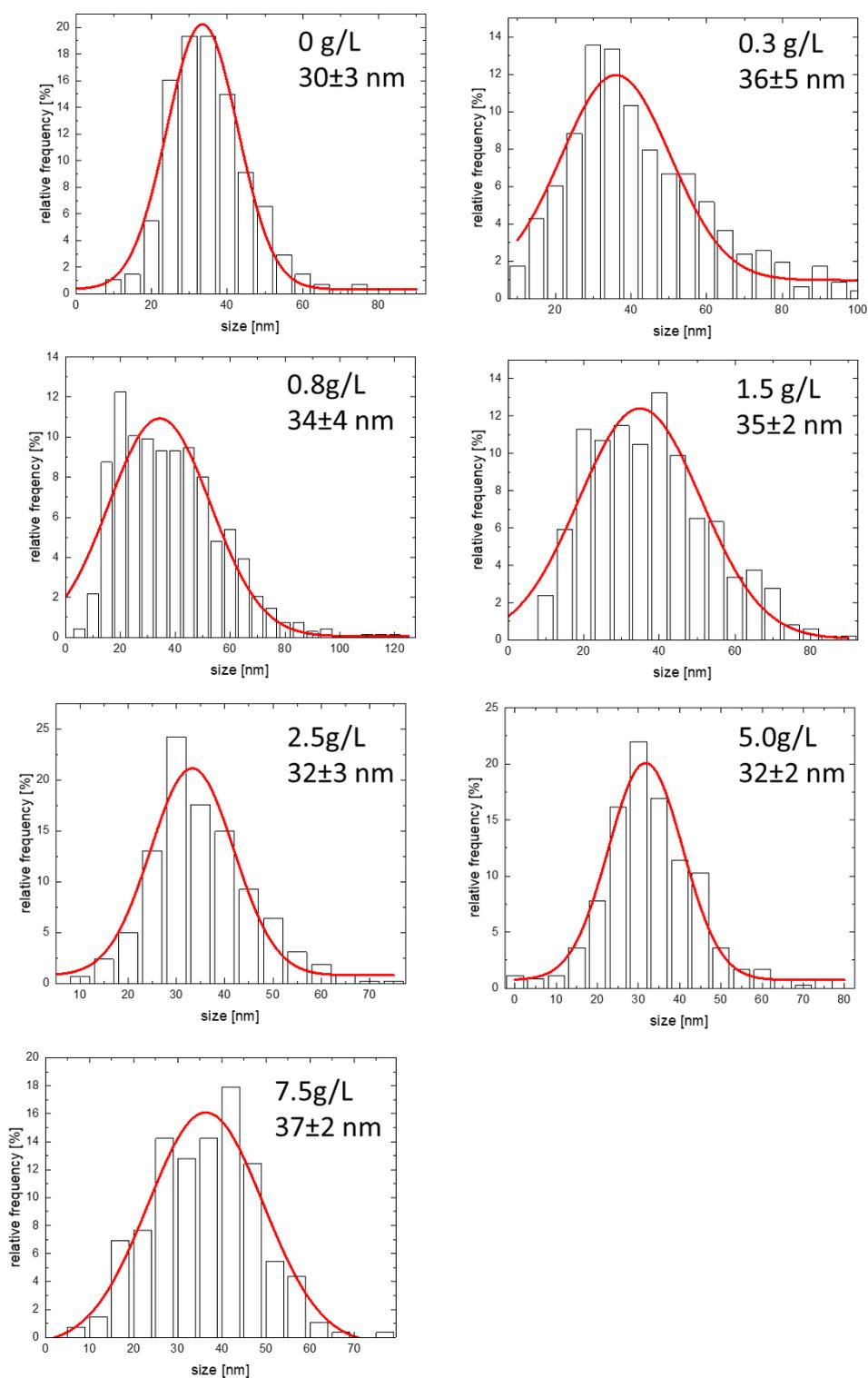


Figure S5 current density corresponding to the Ni^{III}/Ni^{II} redox feature as a function of the potential necessary to drive the reaction to a current density of 10 mA/cm².

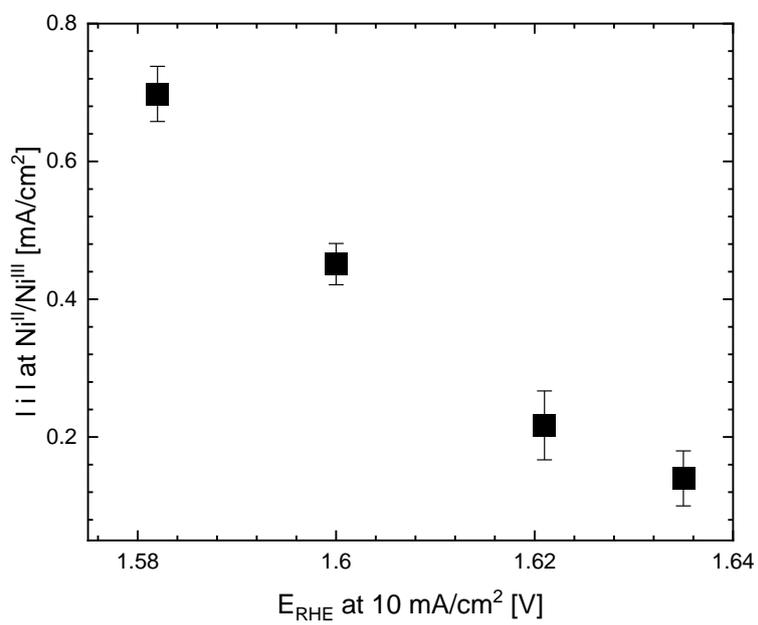


Figure S6 TEM observations of the lanthanum nickel oxide sample prepared in the presence of gelatin (7.5 g/L) as a structure-directing agent. **a)** low magnification image of sample with selected area electron diffraction (SAED) in the inset, **b)** interpretation of SAED confirming the presence of perovskite structured rhombohedral LaNiO_3 with minor admixtures of NiO and La_2NiO_4 , **c)** HRTEM image of rhombohedral particle showing domains with a 5 nm particle of NiO attached to the surface.

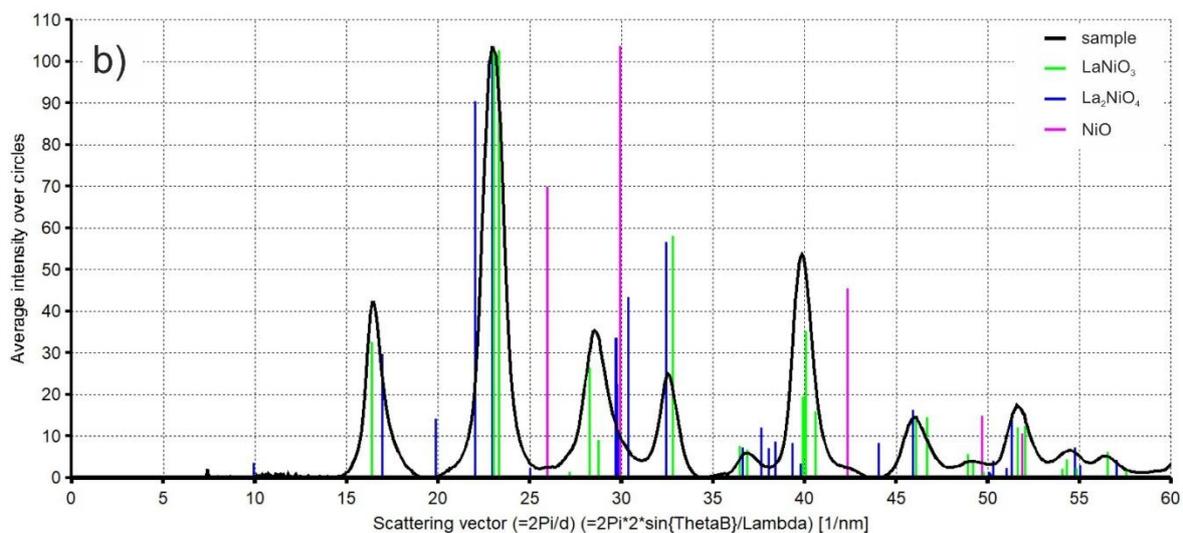
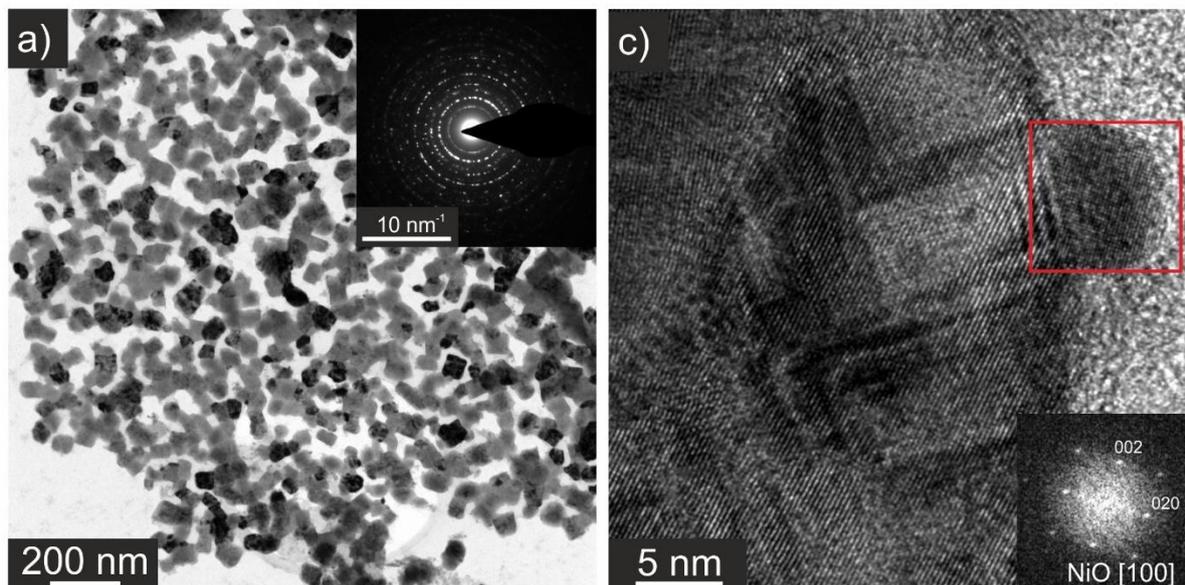


Figure S7 Ni K-edge XANES spectra of the lanthanum nickel oxide samples aged in Nafion containing ink for 4 months. The XANES spectrum of NiO is included as a reference.

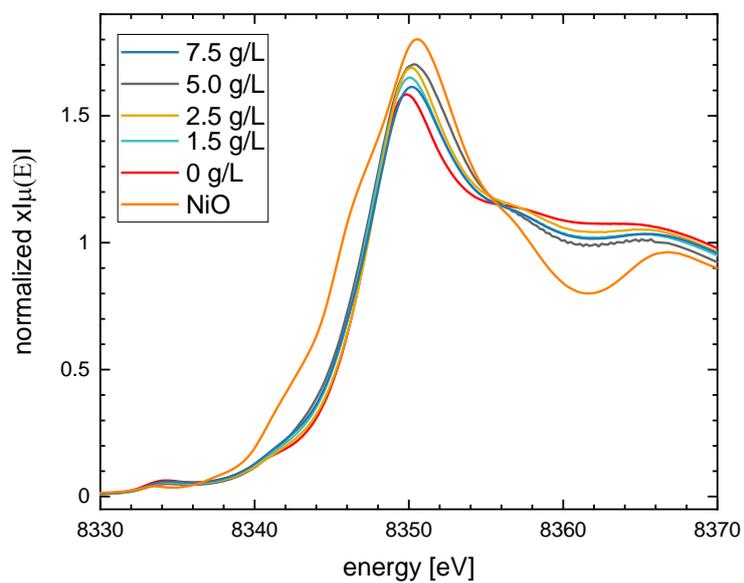


Figure S8 k^2 normalized Ni K-edge EXAFS function of the LaNiO_3 sample synthesized without gelatin (\square) and its NLLS fit (red line) assuming LaNiO_3 rhombohedral perovskites structural model.

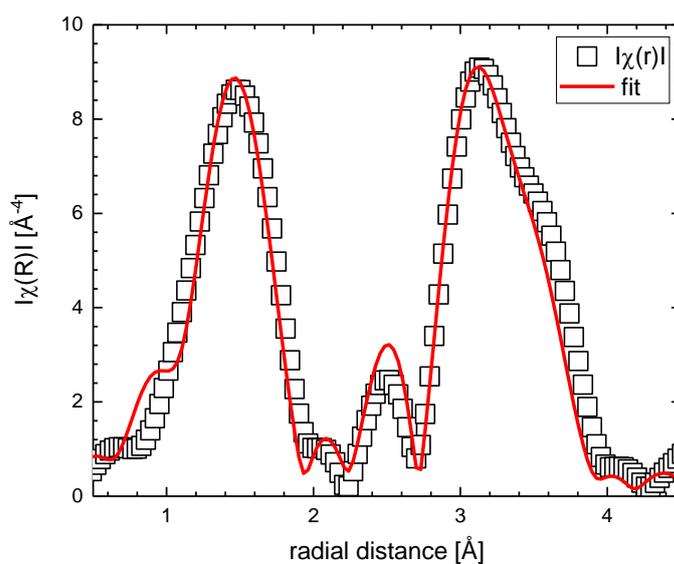


Figure S9 EXAFS function of the LaNiO_3 samples synthesized with different concentrations of gelatin measured at the Ni K-edge normalized with a) k , b) k^2 , and c) k^3 showing the difference in k -dependence for signal located at 2.8 \AA for the sample synthesized without gelatin in comparison with the samples synthesized in the presence of gelatin.

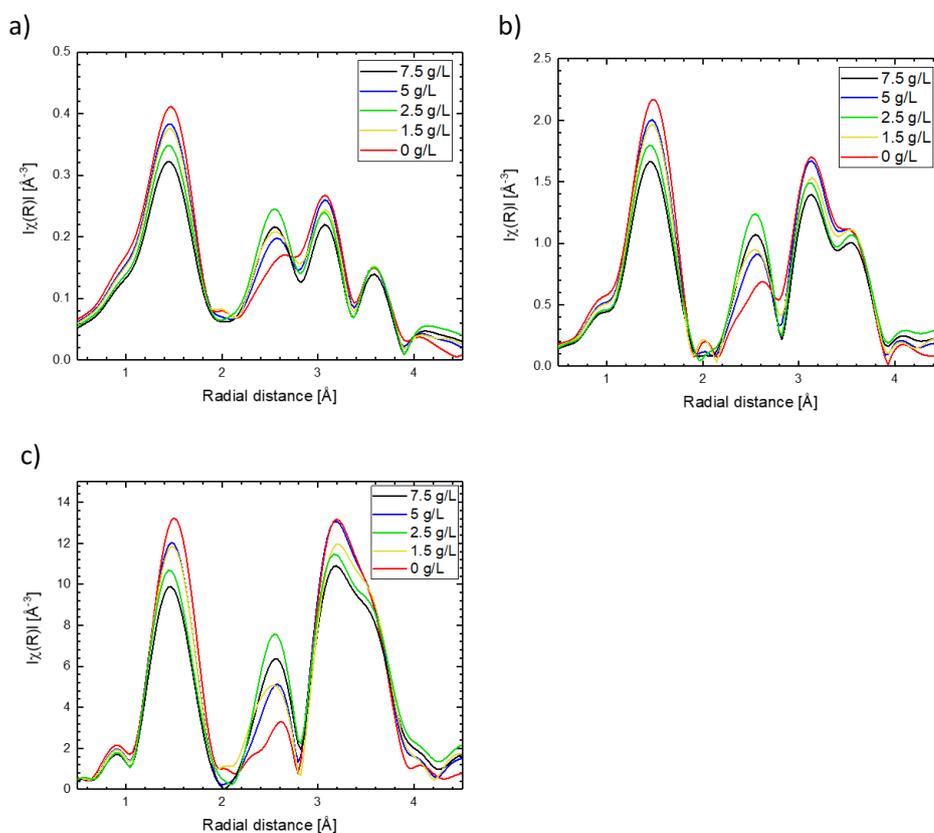


Table S2 Fraction x of NiOOH – like phase obtained from NLLS fits of the Ni K-edge EXAFS functions of initial powder samples assuming a coexistence of NiOOH like phase with Ni-O distance of 1.91 \AA , and LaNiO_3 phase with Ni-O of 1.93 \AA ($\sigma^2 = 0.004 \text{ \AA}^2$, $S_0^2 = 0.8$, k -range= $3\text{-}12 \text{ \AA}^{-1}$).

Sample (powder)	R	E_0 [eV]	X
1.5 g/L	0.008	8341.8 ± 0.8	0.04 ± 0.11
2.5 g/L	0.0255	8341.2 ± 1.6	0.10 ± 0.08
5.0 g/L	0.0105	8342.2 ± 0.9	0.11 ± 0.12
7.5 g/L	0.0102	8341.1 ± 0.9	0.30 ± 0.11

Figure S10 k^2 normalized Ni K-edge EXAFS functions of the lanthanum nickel samples prepared with different gelatin concentration aged for 4 months in Nafion containing ink. The EXAFS functions are present after phase-correction.

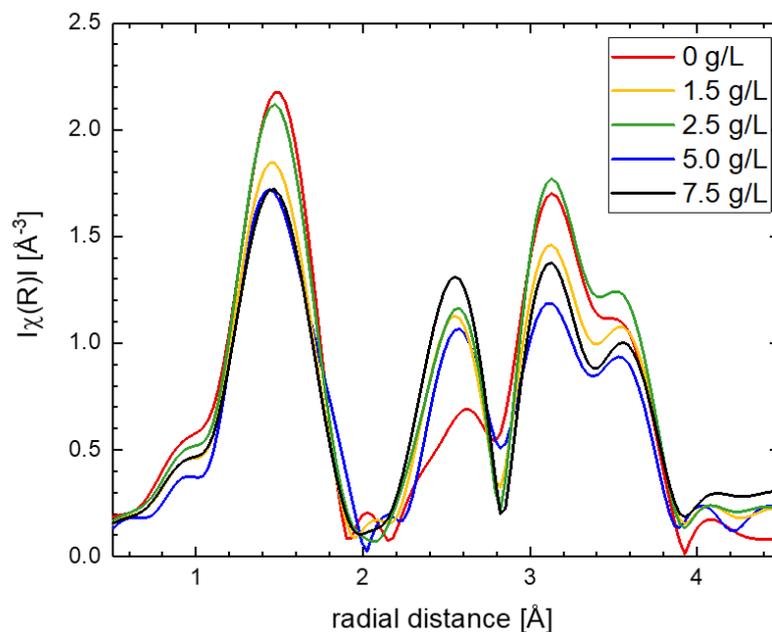


Figure S11 k^2 normalized Ni K edge EXAFS function of the lanthanum nickel sample prepared with 7.5 g/L of gelatin aged for 6 months in a Nafion based ink (\square) and its NLLS fit (red line) assuming a cubic NiO (rock salt) structural model.

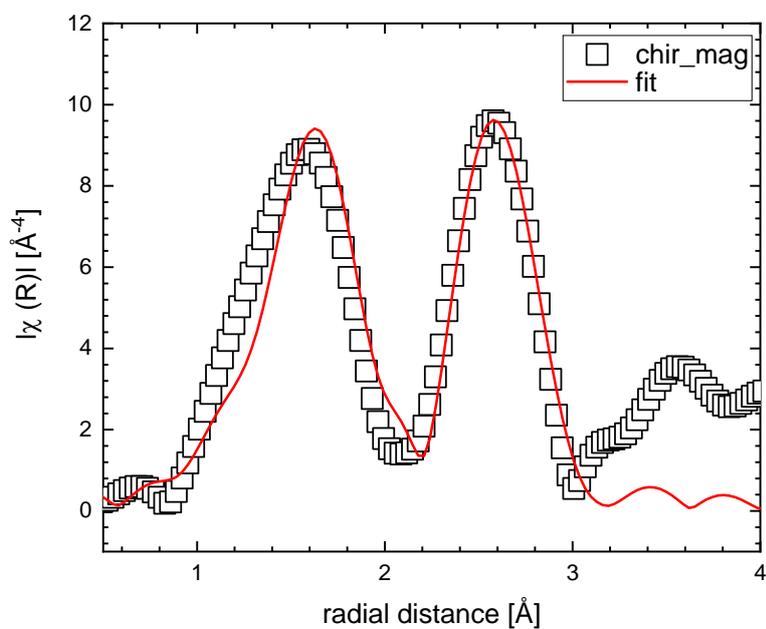


Figure S12 XRD pattern of lanthanum nickel oxide prepared in presence of 7.5 g/L of gelatin after 4 month of aging in a Nafion containing ink. The markers for the major co-existing phases ($\text{La}(\text{CO}_3)_2(\text{OH})_2$, La_2O_3 , LaO and LaOH , NiO and LaNiO_3) are given in the Figure legend.

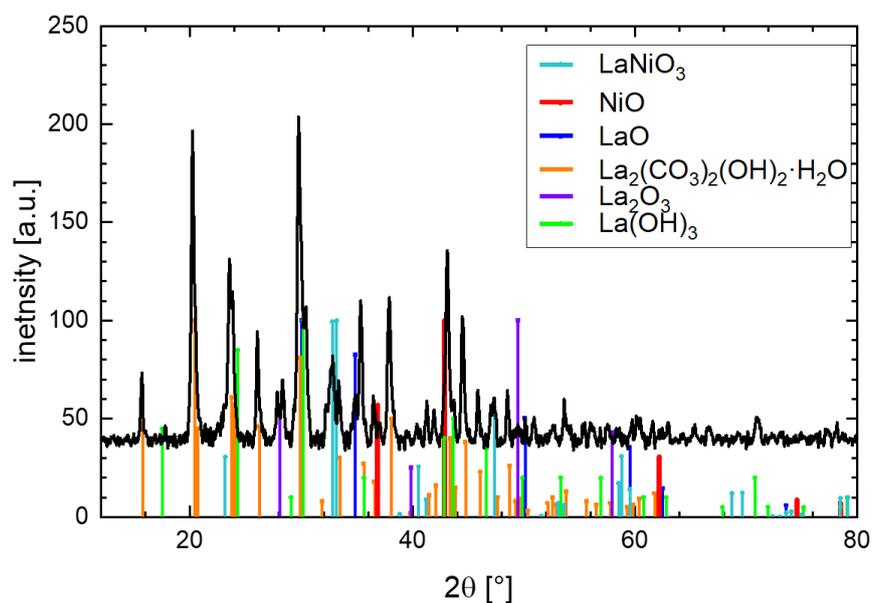


Figure S13 Cyclic voltammograms (CVs) of LaNiO_3 catalyst sample synthesized in presence of 7.5 g/L gelatin comparing the initial activity with that after 1 month of aging in an ink containing different binders. The assignment of the binders is given in the Figure legend. Measurements were performed at a 5 mV/s scan rate in 0.1M KOH, working electrode is the catalyst ink drop-cast onto GC-RDE support at 1600 rpm rotation rate

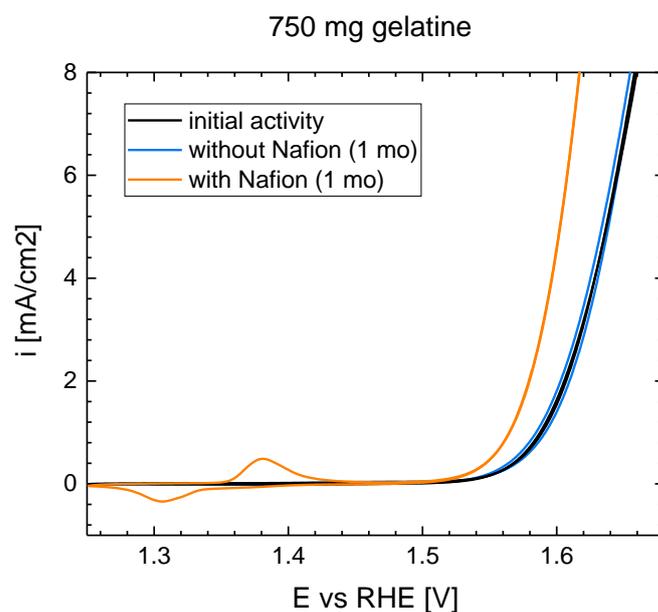


Figure S14 a) CVs of lanthanum nickel oxide samples prepared at high gelatin concentrations after 4 months aging in a Nafion based ink b) CVs of lanthanum nickel oxide samples prepared at low gelatin concentration before and after 4 months of aging in a Nafion based ink. The assignment of the curves is given in the Figure legend.

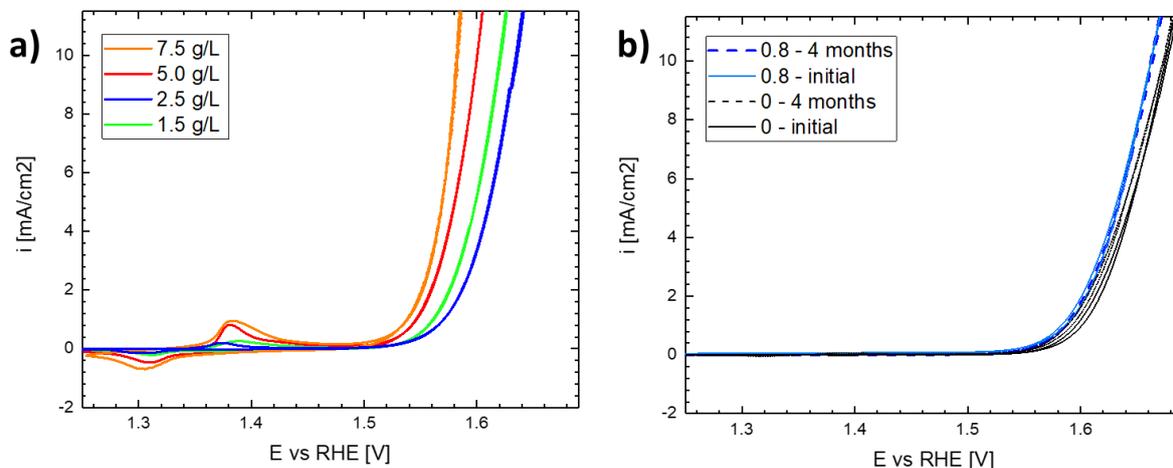


Figure S15 Typical stability behavior of lanthanum nickel oxide catalysts prepared in presence of gelation after aging in Nafion based ink for 4 months. The presented data were extracted from chronoamperometric experiment on a material prepared at gelatin concentration of 5.0 g/L. The chronoamperometric experiment was performed in 0.1M KOH by stepping the potential from 1.4 V to 2.0 V vs RHE while holding each potential step for 5 min. The potential (black) is accompanied by the ICP-OES based signals of La and Ni (blue and red, respectively) in solution.

