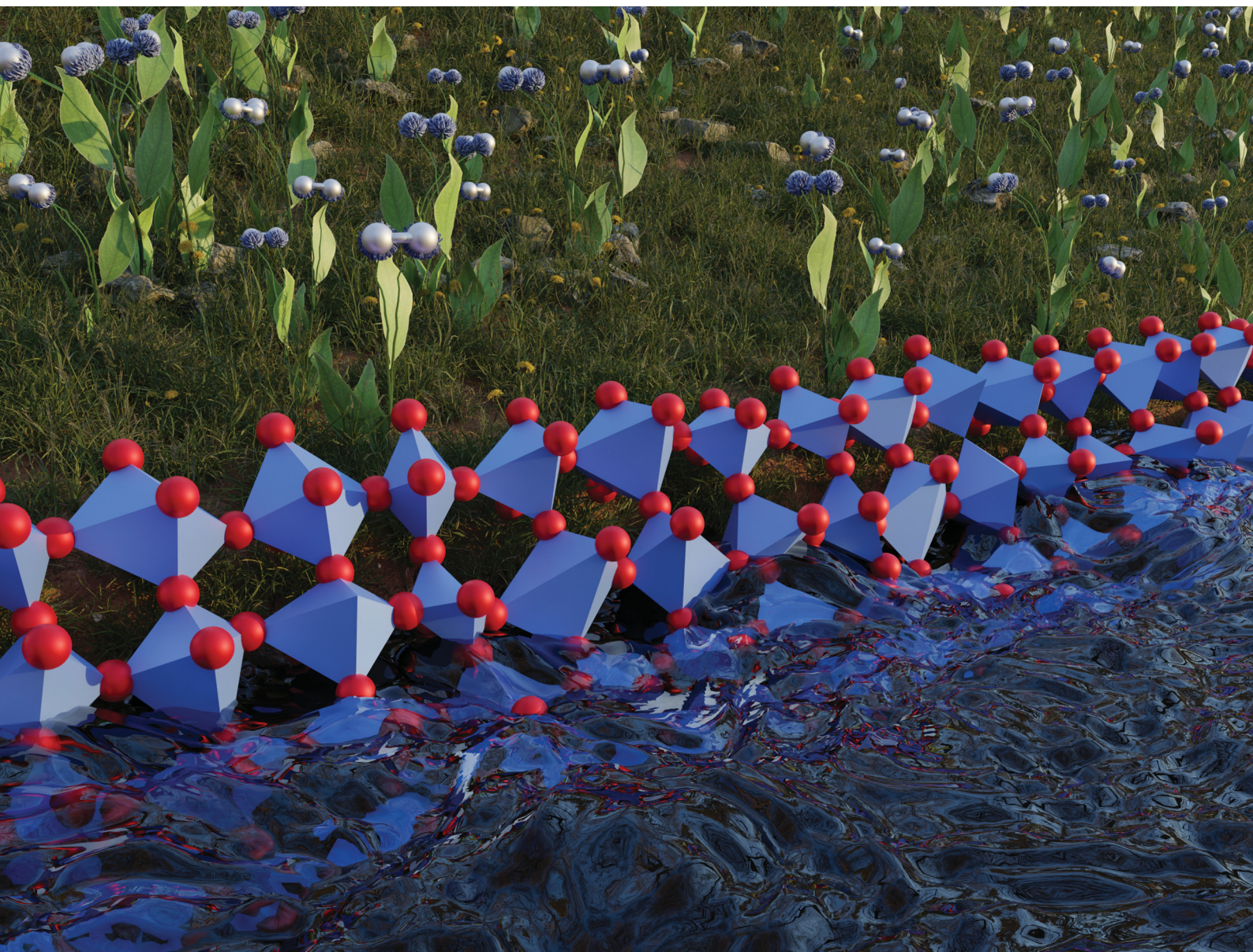


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FEATURE ARTICLE

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Deeper mechanistic insights into epitaxial nickelate electrocatalysts for the oxygen evolution reaction

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Mass production of green hydrogen via water electrolysis requires advancements in the performance of electrocatalysts, especially for the oxygen evolution reaction. In this feature article, we highlight how epitaxial nickelates act as model systems to identify atomic-level composition–structure–property–activity relationships, capture dynamic changes under operating conditions, and reveal reaction and failure mechanisms. These insights guide advanced electrocatalyst design with tailored functionality and superior performance. We conclude with an outlook for future developments via *operando* characterization and multilayer electrocatalyst design.

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1. Introduction

Mass production of green hydrogen through water electrolysis and electrochemical CO₂ reduction are widely anticipated pathways to reach carbon neutrality. Yet both hydrogen generation and CO₂ reduction require an oxidation reaction at the anode, which is typically the oxygen evolution reaction (OER). The OER is kinetically complex and often requires a high overpotential, necessitating highly-active electrocatalysts, which must be low cost and also stable under reaction conditions.^{1–5} To date, the understanding of the complicated reaction and failure mechanisms remains incomplete, which

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the characterization of the (electronic) structure of the pre-catalyst as well as in *operando* conditions to develop further understanding of the formation and stability of active sites in perovskite catalysts.



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impedes the development of electrocatalysts with tailored functionality and superior performance.

An attractive material class for OER electrocatalysts contains the perovskite oxides of the general formula ABO_3 , with rare earth or alkaline earth elements as A-site cations and transition metals (TMs) as B-site cations.⁶ Among perovskite oxides, nickelates ($RNiO_3$, where R represents a rare-earth lanthanide element) have garnered special attention, because of comparably high activity⁷ and suitable earth-abundance. Their excellent performance can be attributed to the following unique characteristics: (1) relatively weaker bond strength between Ni and OH^* compared to other first-row TMs,⁸ (2) e_g electron filling close to unity,⁹ (3) small or negative charge transfer energy,¹⁰ and (4) strong hybridization between Ni 3d and O 2p orbitals.¹¹ These electronic structure descriptors, to which we

will return below, identify perovskite nickelates as one of the most promising class of OER electrocatalysts.

Recent experimental observations have revealed that perovskite oxide electrocatalysts – including nickelates – show a range of dynamic changes rather than staying static during OER.^{12–15} The complicated modifications observed for both surfaces and bulk of nickelate electrocatalysts include the exchange of lattice oxygen and oxygen species between the electrocatalyst and the electrolyte (so-called lattice oxygen mechanisms), the formation and annihilation of ionic defects, which can also be regarded as ion (de-)intercalation processes similar to the electrode materials for aqueous batteries, as well as dynamic surface reconstructions. These dynamic changes during the OER can greatly impact the electrocatalytic activity and stability of nickelate electrocatalysts.



Luhan Wei

Luhan Wei received his BS degree in Functional Materials from Northeastern University in China in 2021. Currently, he is pursuing PhD degree under the supervision of Prof. Qiyang Lu at the School of Engineering of Westlake University. His research interests primarily lie in using spectro-electrochemistry, physical chemistry modeling and in situ/operando characterizations to examine the kinetics of cation (de-)intercalation behavior in

electrode materials. He is also interested in the connection between material properties, such as defects and surface reconstructions, and the electrocatalytic performance of oxygen evolution reaction (OER) in thin film nickelate systems.



Qiyang Lu

Dr Qiyang Lu is currently an assistant professor in School of Engineering at Westlake University. He received his bachelor's degree from Tsinghua University and his PhD degree from Massachusetts Institute of Technology, both in Materials Science and Engineering. He was the recipient of several awards, including the Best PhD Thesis Award from MIT and Ross Coffin Purdy award from American Ceramic Society. His current research interest is in the

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acterization and fundamental structure-function relations in model electrocatalysts. He received several awards and personal grants, including the Helmholtz Doctoral Prize (2017) and the ERC Starting Grant (2022).



This situation is further complicated by the observation that enhanced catalyst activity seemingly comes at the cost of a decreased stability and lifetime of the catalyst,^{15–20} which implies that good catalyst materials typically degrade very quickly, resulting in a rapid loss of the desired catalytic activity. This inverse correlation between stability and activity of catalyst materials involved in electrochemical processes presents a major obstacle for applications.

Researchers therefore face the challenge of identifying specific factors in the composition, crystal structure, and electronic structure of (nickelate) electrocatalysts that lead to a refined explanation of these dynamic processes, which would enable the design of catalysts with optimized activity *and* stability. Conventionally, electrocatalysts are fabricated as (nano) particles or electrodeposited thin films. These typically have heterogeneous surface composition, ill-defined crystallographic surface phase and exposed facets, which makes extracting intrinsic activity and stability trends difficult. In contrast, epitaxial thin films with well-defined microstructures and surfaces/interfaces offer a valuable platform for elucidating the origins of these dynamic processes.^{6,21,22}

In this feature article, we highlight the recent progress in the field on the mechanistic understanding obtained by using epitaxial nickelate OER electrocatalysts. We start by summarizing the current state-of-the-art regarding electrocatalyst activity trends, the role of lattice oxygen participation, and the formation of defects and new “active” phases. We introduce epitaxial thin films as a valuable and informative model platform to identify descriptive structure–property–functionality relationships. We further discuss the remaining unresolved questions and challenges confronting the utilization of the epitaxial nickelate system. We end this review by projecting future directions that enable deeper insights into the dynamic changes of OER electrocatalysts through *operando* characterization, and ultimate tuning of material properties and functionality using multilayer approaches.

2. The quest for mechanistic understanding of dynamic changes during OER

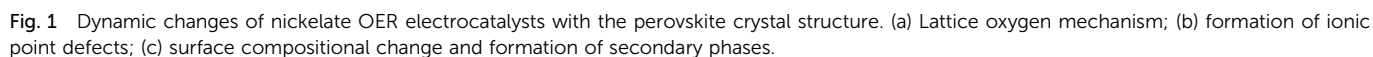
The classical empirical description of electrocatalytic reactions including the OER assumes a reaction at a solid electrode/liquid electrolyte interface with static composition and structure of the solid. Only little attention has been paid to the “internal life” of the electrocatalysts, *i.e.*, the composition and electronic structure of the surface and subsurface, which may change as a function of potential and time, especially for TM oxide (TMO) based electrocatalysts. There has been mounting evidence that shows the surface and the “bulk” (at least several nanometers from the interface into the electrocatalysts) can participate in the electrochemical reaction, and often determines the kinetics and performance of these electrocatalysts.^{15,23–27} Therefore, a holistic picture considering the solid/liquid interfaces, as well as the constituent ions and ionic

defects of TMOs, becomes important for understanding the reaction mechanism and guiding the predictive design of nickelate OER electrocatalysts. Due to the participation of electrocatalyst “bulk” during the electrochemical reactions, a wide range of dynamic mechanisms and phenomena have been observed. These dynamic behaviors of nickelate electrocatalysts indicate that at the OER condition (*e.g.*, $E \geq 1.55$ V vs. RHE (Reversible Hydrogen Electrode)), both the surface and the near-surface region of these electrocatalysts can be very different from the “pre-catalyst” (the parent perovskite oxide before any electrochemical treatment) in both chemical composition and crystal structure. During extended operation, the compositional or structural dynamic changes may further evolve. These dynamic changes, potentially driven by the reorganization of cationic and anionic defects, will drastically alter the electronic structure and active sites of the electrocatalysts. In this section, we will first briefly summarize bulk electronic descriptors of the OER activity that have been shown to be relevant for perovskite oxides. Next, we will review three important aspects regarding the dynamic changes of nickelate electrocatalysts, which are (1) the role of lattice oxygen in OER mechanisms (so-called lattice oxygen mechanism); (2) formation of ionic point defects (oxygen vacancies ($V_{\text{O}}^{\bullet\bullet}$)/protons (H^+)); (3) formation of secondary phases at the near-surface region. Schematics of these three dynamic behaviors are summarized in Fig. 1. To conclude the section, we describe why the use of epitaxial thin films as model systems can help answer unresolved questions in the field.

2.1 Bulk descriptors of the OER

As the OER activity and reaction kinetics depend on the electronic structure of the perovskite oxide electrocatalysts, several approximate descriptors relating bulk electronic structure and catalytic activity have been identified, such as the orbital filling of the frontier orbitals and relative orbital positions.^{9,10,28,29} For example, the bonding strength of intermediates is determined by the filling of the antibonding orbital formed between the oxygen species of the adsorbates and TM.²⁹ The formation and filling of this antibonding orbital are highly dependent on the e_g orbital filling of the TM cations. Hence, the activity of perovskite oxides towards the OER was proposed to follow a volcano-like dependence on the e_g orbital filling, with the optimum close to unity, following the Sabatier principle.^{9,29} Not only the occupancy of the e_g orbitals influences the binding of intermediates, their chemisorption is also determined by the geometry of the occupied orbitals. The $d_{3z^2-r^2}$ orbital points towards the adsorbates leading to more spatial overlap with the adsorbate O 2p orbitals compared to the $d_{x^2-y^2}$ orbitals.³⁰ Hence, a preferred occupancy of these orbitals, *e.g.* through orbital polarization lifting the degeneracy of the e_g energy states, will strongly influence the chemisorption and the OER activity, as will be discussed later. In addition to the occupancy and degeneracy of the e_g bands, their relative positions also influence the chemisorption and OER activity. For example, suppressing Jahn–Teller distortions in Mn-containing catalysts with spinel structure lifts up the





Experimental evidence shows that nickelates always contain non-negligible amounts of $V_{\text{O}}^{\bullet\bullet}$, and that oxygen exchange can occur under sufficient electrochemical driving forces.³⁷ Compared to $V_{\text{O}}^{\bullet\bullet}$, H^+ incorporation (protonation) can occur more readily in nickelates in aqueous solution since the hydration process is spontaneous and can compensate the total

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LaAlO₃, NdGaO₃, and SrTiO₃. For these substrates, the in-plane misfit strain of NdNiO₃ films varies from −1.39% (compressive) to +2.49% (tensile) depending on the substrate, as deduced from the pseudocubic lattice constants of bulk NdNiO₃ and the four substrates (Fig. 2a). A typical reciprocal space map shown in the inset of Fig. 2c reveals a coherent growth of NdNiO₃ films on these substrates. Fig. 2b shows the X-ray diffraction (XRD) θ – 2θ scans around (002) peaks of NdNiO₃ films and the respective substrates. The peak shift as a function of substrate lattice parameter indicates that the substrate-induced in-plane misfit strain is accommodated by the elastic deformation (out-of-plane expansion or contraction) of the NdNiO₃ films. Fig. 2c summarizes the experimentally obtained and calculated out-of-plane lattice constants of NdNiO₃ films as a function of strain. It can be seen that the calculated out-of-plane lattice constant of NdNiO₃ matches well with the experimental value for the film grown on LaAlO₃, *i.e.* the substrate inducing the minimum in-plane strain. This indicates a very low concentration of point defects such as $V_{\text{O}}^{\bullet\bullet}$ exist in NdNiO₃ on LaAlO₃. On the other hand, the experimental out-of-plane lattice constants of NdNiO₃ films grown on the remaining substrates are larger than the calculated values which suggests the formation of point defects due to the larger lattice

mismatch. Besides showing the largest difference between the experimental and calculated out-of-plane lattice constants, NdNiO₃ on SrTiO₃ exhibits the highest resistivity at room temperature and the lowest intensity of the O K pre-edge observed in X-ray absorption spectroscopy, as shown in Fig. 2d. These results suggest the highest $V_{\text{O}}^{\bullet\bullet}$ concentration is present in NdNiO₃ on SrTiO₃ (Fig. 2d). The orbital occupancy of strained NdNiO₃ films was probed by X-ray linear dichroism (XLD = $E_{\text{ab}} - E_{\text{c}}$), a technique that uses differential absorption of horizontally and vertically linear polarized light to examine electronic properties. Fig. 2e shows the XLD results of NdNiO₃ films as a function of strain. For the NdNiO₃ films under compressive strain, a positive XLD value was obtained, indicating preferential $d_{3z^2-r^2}$ orbital occupancy. The negative integrated XLD intensity for NdNiO₃ films under tensile strain indicates the preferred occupancy of the $d_{x^2-y^2}$ orbital, resulting in stronger Ni–O chemisorption and lower OER activity (Fig. 2f). This is the reason why the NdNiO₃ films under compressive strain show higher OER activity than the NdNiO₃ films under tensile strain. Bak *et al.*³³ probed the effect of octahedral distortions on the OER activity of perovskite nickelates, which also depend on the strain. They found that strong distortion of oxygen octahedra results in a considerable increase in electronic

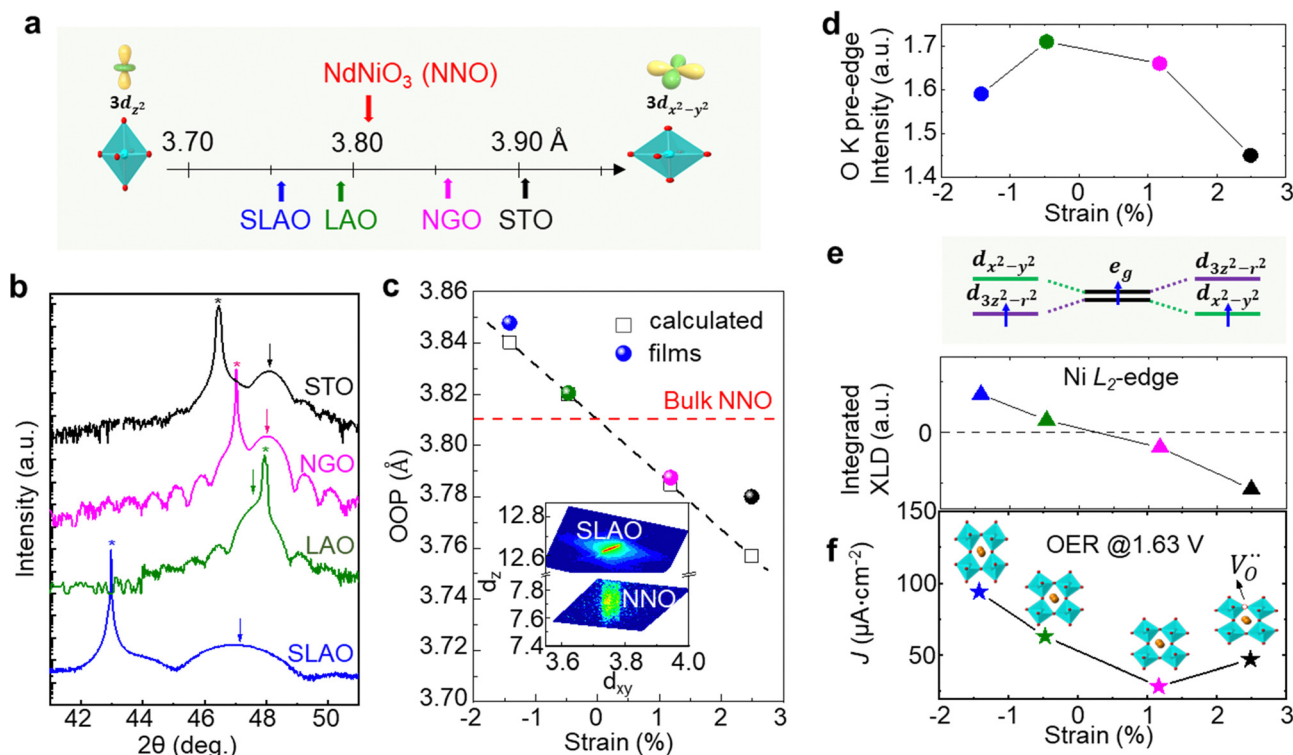


Fig. 2 (a) Pseudo-cubic lattice parameters for bulk NdNiO₃ and single crystalline substrates, including SrLaAlO₄ (SLAO), LaAlO₃ (LAO), NdGaO₃ (NGO), and SrTiO₃ (STO). The inset shows a schematic diagram of octahedral distortion induced by bi-axial compressive and tensile strain. (b) XRD θ – 2θ scans around the (002) diffraction peak of 5 nm NNO films deposited on different substrates. Film and substrate peaks are noted by arrows and stars, respectively. (c) Experimentally obtained out-of-plane lattice parameter values (colored circles) of NdNiO₃ films as a function of strain. Strained out-of-plane lattice parameters of NdNiO₃ films estimated from the Young's modulus are presented by black open squares. The inset displays a reciprocal space map of NdNiO₃ on SLAO. (d) O K pre-edge intensity of NdNiO₃ films as a function of strain. (e) Schematic electronic configuration of e_g orbital and integrated XLD as a function of strain. (f) OER current density at 1.63 V vs. RHE of NdNiO₃ films under different biaxial strains. The inset in (f) shows schematic illustrations of octahedral distortions induced by strain. Reprinted (adapted) with permission from ref. 41. Copyright 2019, American Chemical Society.

states near the Fermi level (E_F), making the charge transfer between TM and oxygen much easier, thereby enhancing OER activity.³³ This is different for Mn-containing catalysts with spinel structure, in which the OER activity increases with the suppression of the Jahn–Teller distortion.^{31,32} On the other hand, when a tensile strain large enough to generate $V_{\text{O}}^{\bullet\bullet}$ is applied, the Ni valence can be reduced from Ni^{3+} to Ni^{2+} . This leads to e_g filling slightly larger than one, which can contribute to the enhanced OER activity observed in NdNiO_3 on SrTiO_3 . Similar experiments were also performed on other TMOs, demonstrating that strain-induced structural distortion and oxygen deficiencies modify the OER activity of epitaxial TMO films.^{42,45}

3.2 Tuning surface termination towards active surface phase formation

As discussed in Part 2, nickelate OER electrocatalysts often go through dynamic changes of the structure and chemical composition, especially at the electrochemical (solid/liquid) interface and the near-surface region of the oxide. While conventional particulate electrocatalysts (even nanoparticles) can be difficult to control precisely, our recent work (Baeumer *et al.*¹⁴) shows that epitaxial nickelate thin films, with the capability of controlling the surface termination and composition

with atomic precision, can be a powerful platform to obtain detailed understanding on the dynamic changes during the OER. We employed standing-wave X-ray photoemission spectroscopy (SW-XPS), which is an emerging technique capable of depth-profiling the chemical environment in the near-surface region with 1–2 Å depth resolution, to reveal details of the surface chemical composition of LaNiO_3 . Epitaxial layers are an ideal system for this spectroscopic technique because of the opportunity to create smooth films supported superlattices functioning as X-ray mirrors (Fig. 3a). SW-XPS analysis of LaNiO_3 prepared in different growth conditions revealed predominant NiO_2 and LaO termination in Fig. 3b and c, respectively. Electrochemical characterization of the same samples revealed that NiO_2 -terminated LaNiO_3 thin films show much higher OER activity compared to LaNiO_3 samples with LaO -termination (Fig. 3e). Importantly, the surface morphology of samples before and after determining the OER activity was very similar, both showing atomically smooth terraces (Fig. 3d). Furthermore, redox peaks in cyclic voltammetry tests were only observed in the NiO_2 -terminated LaNiO_3 . Their peak area (which corresponds to the charge transferred across the solid/liquid interface) increases with Ni coverage of the first surface layer of LaNiO_3 . Combining experimental evidence from SW-XPS and electrochemical measurement showed that the

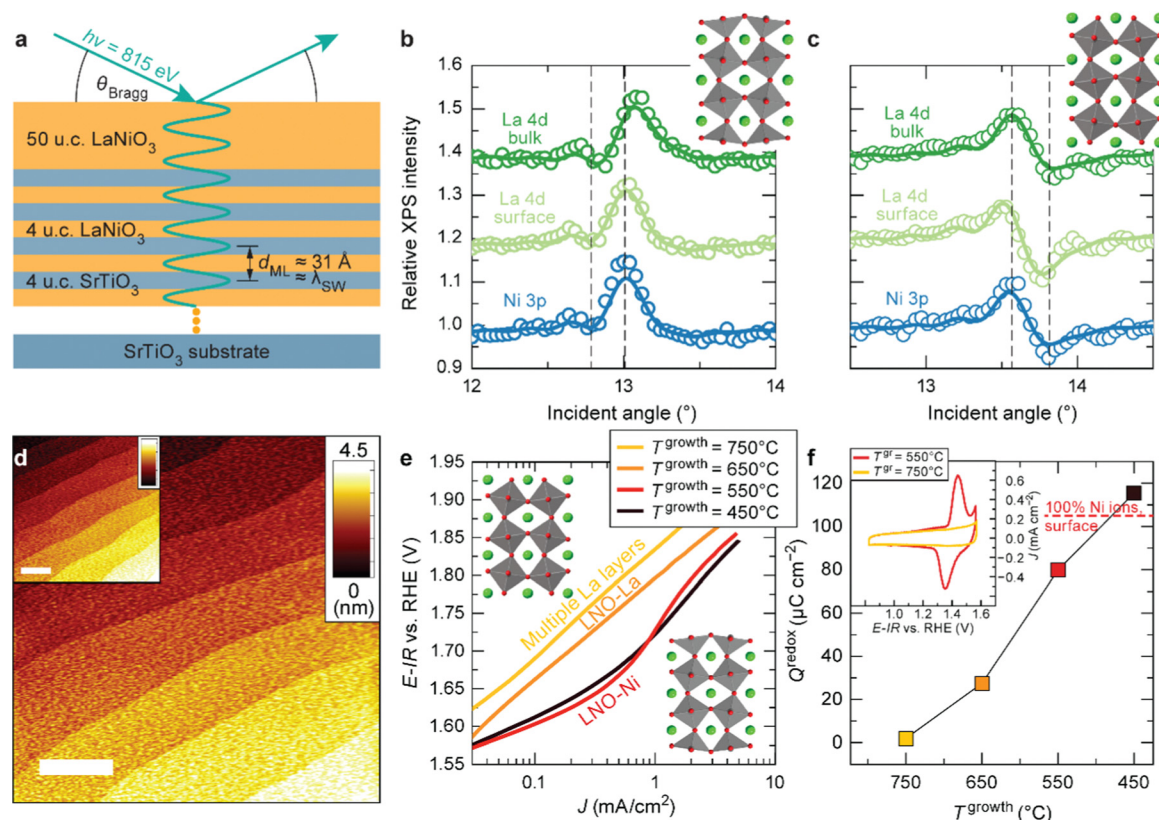


Fig. 3 (a) Schematic diagram of LaNiO_3 thin films on a superlattice of LaNiO_3 (4 unit cells (u.c.)) and SrTiO_3 (4 u.c.). SW-XPS rocking curves of La 4d and Ni 3p for LaNiO_3 top layers grown at (b) 450 and (c) 650 °C. Atomic force microscopy images for (d) as-deposited LaNiO_3 film (20 nm) grown at 550 °C and (inset) after cyclic voltammetry (CV). (e) Tafel-like plot for LaNiO_3 films with different surface termination. (f) Redox charge for conversion from Ni^{2+} to Ni^{3+} during CV. (inset) CV curves in the Ni^{2+} – Ni^{3+} redox area for LaNiO_3 films deposited at 550 and 750 °C. Reproduced with permission from ref. 10.



different activity can be directly related to the different composition of the surface termination layer. With the insights from both experimental evidence and computational support, the dynamic changes of LaNiO_3 surfaces were clarified. The difference in surface composition evolves to different surface secondary phases, *i.e.*, NiO_xH_y (oxy-hydroxide like) and $\text{La}(\text{OH})_3$ at sufficiently high potential, with the former much more active than the latter. Therefore, this work proves that a very subtle difference in chemical composition (only the first atomic surface layer) could lead to a very large difference in activity, which can be more readily captured by using well-controlled epitaxial thin films as model systems.

3.3 Optimizing electrocatalyst functionality *via* cation substitution

Cation substitution is a common strategy to tune the electronic structure of nickelates for optimizing OER activity. Taking LaNiO_3 (Fig. 4a) as an example, the cation substitution can be classified based on the doping sites, namely A-site, B-site, or dual sites. Although A-site cations in nickelates are not considered as active sites for OER, they can indirectly contribute to the OER by altering lattice distortion, $V_{\text{O}}^{\bullet\bullet}$ concentration, Ni

valence state, and the Ni 3d and O 2p hybridization. According to the doping elements, the A-site substitution can be divided to isovalent or aliovalent substitution. In 2018, we (Wang *et al.*⁴⁶) used PLD to synthesize a series of RNiO_3 (where R = La, $\text{La}_{0.5}\text{Nd}_{0.5}$, $\text{La}_{0.2}\text{Nd}_{0.8}$, Nd, $\text{Nd}_{0.5}\text{Sm}_{0.5}$, Sm, and Gd) thin films on SrTiO_3 substrates and investigated the effect of A-site isovalent substitution on OER activity. We found that decreasing the ionic radius of A-site elements in RNiO_3 leads to a decrease in the electronic conductivity, which is consistent with a decrease in Ni–O bond covalency due to bending of the Ni–O–Ni angle. Moreover, reducing the ionic radius of A-site elements induces the formation of $V_{\text{O}}^{\bullet\bullet}$ (the decrease of the O K pre-edge intensity), which increases the average occupancy of the antibonding e_g orbital and lowers E_F . This is favorable for the OER activity (Fig. 4c). One year later, we (Liu, Wang *et al.*⁴⁷) used MBE to deposit a set of $\text{La}_{1-x}\text{Sr}_x\text{NiO}_3$ ($x = 0, 0.12, 0.25, 0.5$) thin films on LaAlO_3 substrates and investigated the effect of A-site aliovalent substitution on the OER activity. Cyclic voltammetry curves of $\text{La}_{1-x}\text{Sr}_x\text{NiO}_3$ thin films in Fig. 4d show a clear trend towards improved OER activity as x increases, with $x = 0.5$ showing the most active OER activity. DFT calculations (Fig. 4e) clearly demonstrate that Sr doping in LaNiO_3 induces

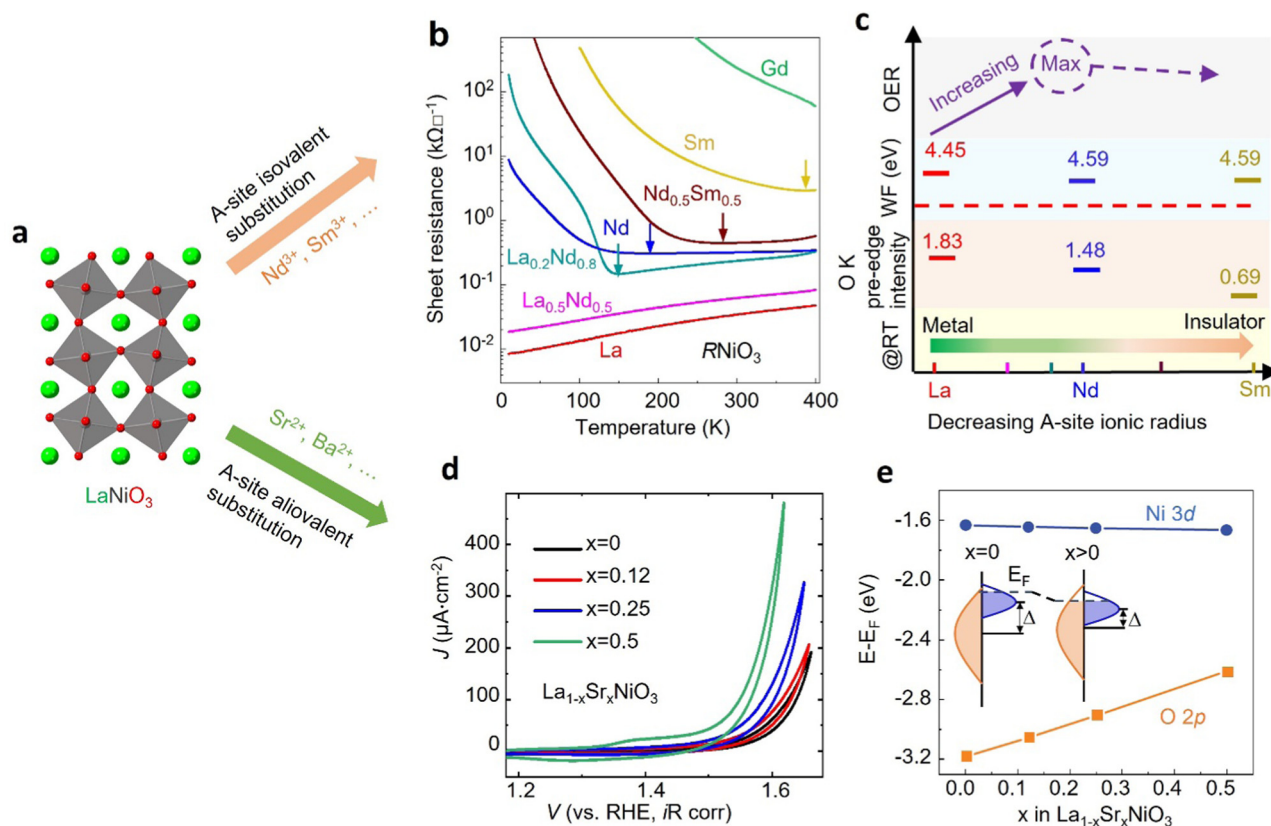


Fig. 4 (a) Schematic illustration of LaNiO_3 crystal structure. (b) Sheet resistance as a function of temperature for perovskite nickelate thin films with different A-site cations grown on SrTiO_3 substrate. (c) The trends in the OER activity, work function, O K pre-edge intensity, and room temperature conductivity with decreasing the ionic radius of A-site cations in nickelates. Reproduced with permission from ref. 43. Copyright 2018, Wiley-VCH. (d) CV curves of $\text{La}_{1-x}\text{Sr}_x\text{NiO}_3$ thin films with $x = 0, 0.12, 0.25$, and 0.5 . (e) Calculated average onsite energies of Ni 3d and O 2p orbitals with E_F as a reference. The inset shows a schematic energy band diagram of LaNiO_3 ($x = 0$) and $\text{La}_{1-x}\text{Sr}_x\text{NiO}_3$ ($x > 0$). Δ denotes the charge transfer energy. Reproduced with permission from ref. 44. Copyright 2019, Wiley-VCH.



Unlike A-site cations, the B-site cation, *i.e.*, the Ni site of RNiO_3 nickelates, is believed to directly participate in the electrochemical reaction, either as active site for OER or through the covalent interaction with the active oxygen site. Recently, we (Wang *et al.*⁴⁸) further explored the effect of B-site substitution, namely partially replacing Ni with other transition metals, on the OER activity. The electronegativity of the first-row transition metals increases when moving from left to right across the periodic table. Thus, Ni is the most electronegative element compared to other four cations Cr, Mn, Fe, and Co (Fig. 5a). Partially replacing Ni with Fe (Fig. 5b), or Cr, Mn, Co is expected to reduce the Ni valence state, which was verified in our work (Wang *et al.*⁴⁸). A whole set of epitaxial $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0, 0.12, 0.25, 0.33, 0.375, 0.5, 1$) solid solutions were synthesized by MBE. Chemical compositions and electronic structures were directly characterized by *in situ* XPS without air exposure. Fig. 5c clearly shows that, with doping Fe in LaNiO_3 , charge transfer from Fe to Ni occurs in these solid solutions, reducing Ni from Ni^{3+} to Ni^{2+} and oxidizing Fe from Fe^{3+} to Fe^{4+} . DFT calculations indicate the high-valent Fe^{4+} states can significantly contribute to the density of states around E_F (Fig. 5e), increasing the total TM 3d bandwidth *via* d-orbital

The potential beneficial effect of substitutional doping can be maximized using multiple elements on the same lattice site by using a solid-solution approach. Such multi-compositional perovskite oxides are frequently referred to as high-entropy perovskite oxides due to the increased configurational entropy induced by the mixing of several elements on the same crystallographic lattice site. These oxides may benefit from compositionally-fine-tuned electronic and atomic structure and the synergistic effects of multiple cations simultaneously/consecutively participating in electrocatalytic reactions. Furthermore, the high entropy may lead to phase stabilization according to the free energy of formation, resulting in increased stability against dissolution.⁵⁰ We recently found that (001)-oriented $\text{LaCr}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{O}_{3-\delta}$ epitaxial thin films outperformed the OER activity of all parent perovskites with single B-site cation

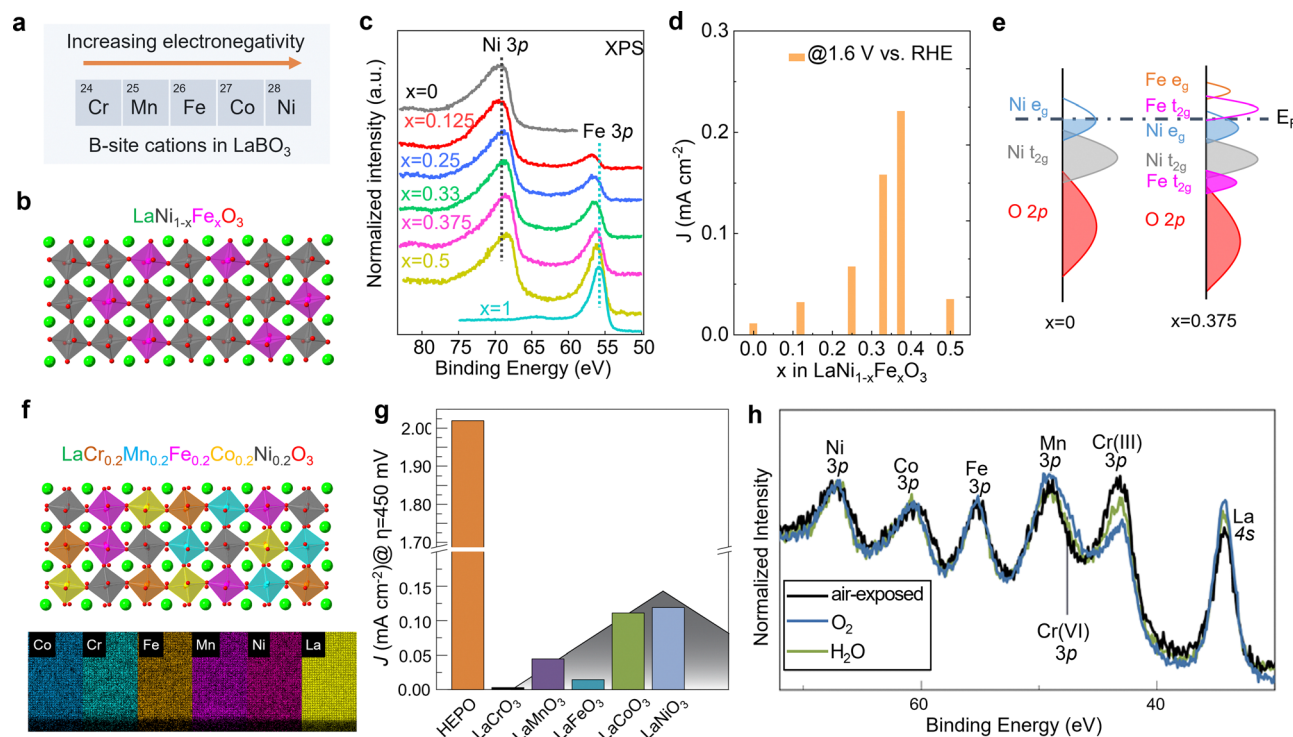


Fig. 5 (a) Five common first-row transition metals used as B-site cations in LaBO_3 and the trend of electronegativity. (b) Schematic illustration of $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ crystal structure. (c) *In situ* Ni 3p and Fe 3p core level XPS spectra of $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ films with $x = 0, 0.125, 0.25, 0.33, 0.375$, and 0.5 . (d) OER current density of $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ films measured at 1.6 V vs. RHE. (e) Schematic energy band diagram with corresponding electronic structure near E_F . Reprinted (adapted) with permission from ref. 32. Copyright 2021 American Chemical Society. (f) Schematic illustration of $\text{LaCr}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{O}_3$ and energy-dispersive X-ray spectroscopy maps of a $\text{LaCr}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{O}_3$ high entropy perovskite oxide (HEPO) thin film. Scale bar: 5 nm . (g) OER current density of HEPO and five parent perovskites thin films measured at 1.68 V vs. RHE. (h) TM 3p core level ambient pressure XPS spectra of the HEPO thin film in two different atmospheres. (f–h) Reprinted (adapted) with permission from ref. 49.

by a factor of 16 to 670 (Fig. 5g).⁴⁹ We speculated that this enhancement of electrocatalytic activity may be the result of the synergistic behavior of multiple cations, since the adsorption and binding of water molecules to the surface has been shown to induce an appreciable change in oxidation state of Cr, Co, and Ni simultaneously (Fig. 5h). The electronic structure descriptors discussed previously cannot explain the observed activity trend. Therefore, more experimental and theoretical work are needed to capture the complex composition–property–function relationships in this multi-dimensional space.⁵⁰

4. Outlook

4.1 *Operando* characterization for deeper mechanistic insights

Solid–solid, solid–gas and especially solid–liquid interfaces continuously evolve as a function of applied potentials, ionic concentrations, and time. For electrocatalysts, this implies that true active phases and reaction sites do not “pre-exist” in as-prepared “pre-catalyst” surfaces, but evolve under reaction conditions.⁵¹ This will be discussed below in more detail for the case of NiO₂-terminated LaNiO₃ from the example in Section 3.2. To achieve further understanding of the structure–property–function relationships governing electrocatalyst materials discovery, characterization of chemical composition, atomic arrangement and electronic structure of the interface under operating conditions is therefore necessary.

The term “*operando*” refers to measuring material properties under working conditions, *i.e.*, while the reaction of interest occurs, with simultaneous measurement of reaction rate.^{52,53} *Operando* characterization goes well beyond *in situ* or *ex situ* characterization of the as-prepared or even the operated surfaces because the catalyst changes reversibly or irreversibly as a function of potential. Therefore, only *operando* measurements can shed light on the surface properties actually giving rise to electrocatalytic activity. In this section, we will provide an overview of *operando* characterization techniques recently employed for epitaxial thin film electrocatalysts and techniques that exhibit high potential for impactful future use. We include a discussion why epitaxial thin-film samples are particularly useful to extract the relevant information.

Typical surface transformation giving rise to the electrocatalytic activity are confined to the surface,¹⁴ yet many *operando* characterization techniques are bulk-sensitive, *i.e.*, averaging the information from a thin surface layer with the underlying volume of the electrocatalyst. This hampers sensitivity to small structural or chemical changes in the surface layer. Fig. 6a and b shows a guiding principle to extract surface-sensitive information from a nominally bulk-sensitive technique, described in more detail in ref. 14 and 54. The relative intensity of a thin surface layer depends on the total thickness of the electrode. Using epitaxial thin films with unit-cell thickness control, one can extract the surface signal from a series of *operando* experiments with various sample thicknesses. We employed this technique successfully using bulk-sensitive UV-Vis spectroscopy

in transmission geometry (Fig. 6c). The optical density of the electrocatalyst at a characteristic photon wavelength changes reversibly at the previously discussed Ni redox potential. Comparison to reference samples and systematic thickness-dependent measurements revealed a phase transition of a unit-cell-thin layer to a Ni oxyhydroxide-like layer.¹⁴ This transformation towards an edge-sharing octahedral arrangement of the Ni atoms in a sub-nanometer surface layer is key for the high electrocatalytic activity observed for NiO₂-termination because it does not occur for LaO-termination.

A similar approach to tune bulk-sensitive methods towards surface-sensitivity may be applied to X-ray absorption spectroscopy (XAS). XAS allows extraction of oxidation states, coordination geometry and number, and elemental composition from peak shapes, positions, intensities, and spin–orbit splitting.⁵⁶ In the past, *operando* XAS was already employed, for example, to track valence changes at OER-relevant voltages of a layered manganese oxide film prepared by electrodeposition (Fig. 6e).⁵⁵ X-ray absorption spectra revealed reversible yet hysteretic Mn redox. Oxidation to a mixed Mn^{3+/4+} valence preceded the oxygen evolution, and additional analysis of the O spectra showed changes in Mn–O hybridization with different applied potentials, where an *e_g* occupancy near one likely corresponds to the highest hybridization. In the future, *operando* XAS may therefore aid in identifying mechanistic OER activity trends based on the electronic structure of epitaxial nickelates under operating conditions. Yet, for epitaxial thin films, designing appropriate experimental cells is more challenging compared to conventional electrocatalyst materials because fabrication on X-ray-transparent membranes or a cell design with very thin liquid compartments are necessary to minimize attenuation of incoming and outgoing X-ray, as discussed in more detail elsewhere.⁵¹

In addition to studying activity trends, characterization of degradation pathways becomes increasingly important for selecting ideal electrocatalyst materials since an inverse activity–stability relationship seems to exist as introduced previously. Akbashev *et al.*⁵⁷ recently investigated the degradation of SrIrO₃, a highly active electrocatalyst, during the oxygen evolution reaction (OER) using *operando* electrochemical atomic force microscopy (EC-AFM). This material serves as a model system for degradation studies of perovskite ABO₃ oxides, exhibiting both A-site cation leaching and transition metal (B-site) dissolution. EC-AFM can track surface morphology changes and dissolution, and epitaxial thin films are particularly suited for mechanistic studies because they provide a smooth, step-terraced surface morphology with unit-cell precise thickness control of the as-prepared state. For the epitaxial SrIrO₃, the thickness remained identical during operation in H₂SO₄ up to 2 V vs. RHE, implying that no dissolution occurred in these conditions and in contrast to severe dissolution in alkaline media.⁵⁸ In H₂SO₄, particulates appear at ~1.17 V vs. RHE and disappear at 1.5–1.6 V vs. RHE, as shown in Fig. 6d. These particulates affect the surface roughness but the step-terraced morphology remains. The authors proposed that these particulates are SrSO₄, and discuss the formation and removal of the



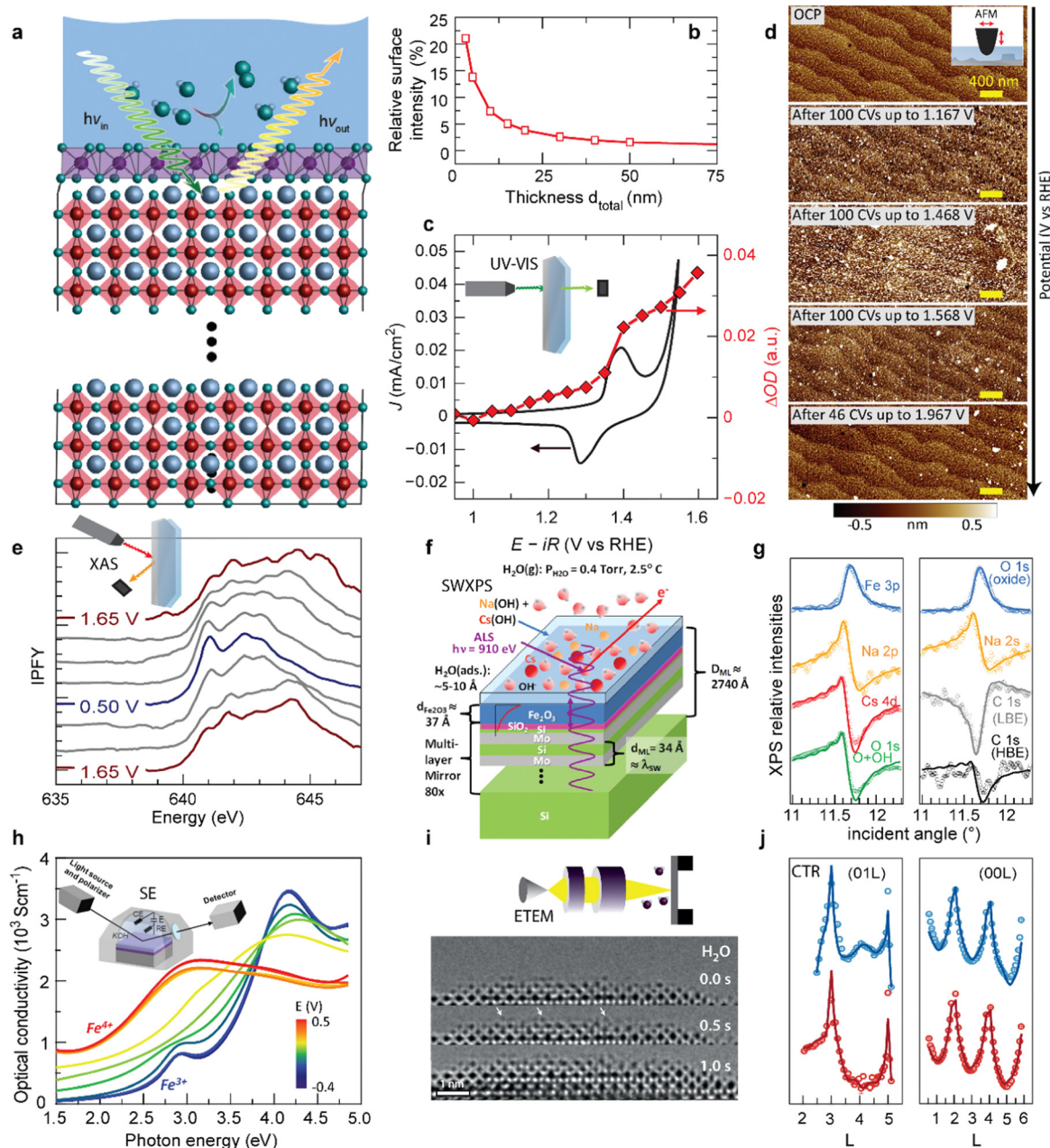


Fig. 6 (a) Schematic for extracting surface-sensitive information from bulk-sensitive techniques. A representative perovskite oxide electrocatalyst (red corner-sharing octahedra) exposed to an electrolyte develops a structurally and electronically different surface layer when a potential is applied to drive the oxygen evolution reaction (OER), in this example involving transformation of the top unit cell (violet edge-sharing octahedra), inspired by (ref. 10 and 49). (b) The relative intensity of a 0.8 nm surface layer measured by a bulk-sensitive technique like XAS or UV-Vis spectroscopy increases with decreasing total thickness of the electrode. Reprinted from C. Baeumer, *J. Appl. Phys.*, 2021, **129**, 170901, with the permission of AIP Publishing (c) cyclic voltammetry in the pre-OER region for Ni-terminated LaNiO_3 (LNO-Ni), along optical density change at $\lambda = 500$ nm during potential holds. Reproduced with permission from ref. 10. (d) Surface roughening during cycling up to increasingly higher potentials in and 0.5 M H_2SO_4 (scale bars are 400 nm). Used with permission of Royal Society of Chemistry, from "Probing the Stability of SrIrO_3 During Active Water Electrolysis via Operando Atomic Force Microscopy", A. R. Akbashev *et al.*, *Energy Environ. Sci.*, 2023, **14**. (e) Electrocatalyst changes with applied potential tracked by Mn L-edge XAS of electrodeposited MnO_x films in 0.1 M KOH cycled from 1.65 V to 0.50 V and back to 1.65 V vs. RHE. Reproduced (adapted) with permission from ref. 36. Copyright 2017, American Chemical Society. (f) Sample geometry used for SW-XPS analysis. (g) Comparison of experimental rocking curves for various XPS core-level intensities with calculations based on the optimized sample configuration, which allows extraction of sub-nanometer-resolution depth profiles of atomic concentrations. (f and g) Reproduced with permission from ref. 55. Copyright 2014, Springer Nature. (h) Optical conductivity spectra of a $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ thin film, recorded at various potentials. The inset shows a schematic representation of the chamber used for the measurements. Reprinted (adapted) with permission from Y. Q. Tang *et al.*, *ACS Appl. Mater. Interfaces*, 2022, **14**, 18486–18497. Copyright 2022 American Chemical Society. (i) ETEM investigation of the $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}/\text{H}_2\text{O}$ interface, showing a representative images of a time sequence in 0.5 Pa of H_2O . Highly mobile adatoms are highlighted by white arrows. Reproduced with permission from ref. 9. (j) (01L) and (00L) crystal truncation rods measured at 0.5 V (blue) and 1.5 V vs. RHE (red). Open points and solid lines denote the experimentally measured intensities and the best-fit results from the fitting process, respectively. Used with permission of Royal Society of Chemistry, from "Towards identifying the active sites on RuO_2 (110) in catalyzing oxygen evolution", R. R. Rao *et al.*, *Energy Environ. Sci.*, 2017, **10**, 2626–2637.



particulates in the context of Sr leaching observed by XPS and mass spectroscopy. Importantly, they also conclude that the stability of perovskite oxide electrocatalysts under operating conditions might be improved by suppressing A-site leaching a common degradation mechanism to which we will return below. For iridium based electrocatalysts, dissolution of the A-site element compared to Ir is highly dependent on their structure.⁵⁹ Electrocatalysts composed of strong edge- and face-sharing octahedra are more robust against A-site dissolution.⁶⁰ Furthermore, balancing A- and B-site dissolution by B-site substitution can help to maintain crystal structure and prevent catalyst degradation.⁶¹ *Operando* characterization may aid to identify these degradation mechanisms and related material properties to ultimately design more efficient and robust catalysts.

As previously discussed, the electrocatalytic performance is not only controlled by the surface but also by the defect chemistry of the underlying layer, which also changes during operation due to parasitic (de-)intercalation reactions. Therefore, *operando* probes for the type and concentration of point defects such as $V_{\text{O}}^{\bullet\bullet}$ and protons are needed. Tang *et al.*³⁸ recently developed an *operando* spectroscopic ellipsometry approach, allowing the tracking of the concentration of holes as a function of the intercalation potential (Fig. 6h). They characterized epitaxial $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ thin films and indirectly quantified the concentration of electron holes for different electrochemical potentials using the Fe oxidation state. Combining the experimental results with a defect chemistry model, they extracted estimates for the concentration of H^+ and $V_{\text{O}}^{\bullet\bullet}$ in the epitaxial layer as a function of potential. This approach may help to tune electrocatalyst properties through property-control by ionic intercalation, and can reveal the changes in electronic structure during electrochemical preconditioning.

We now turn towards future pathways for *operando* characterization that may lead to even deeper analysis or higher sensitivity and interface-specificity. As discussed in the previous section, SW-XPS is capable of depth-profiling the chemical environment in the near-surface region with 1–2 Å depth resolution. Nemšák *et al.*⁶² reported a strategy to extend SW-XPS to solid–liquid interfaces using an ~ 1 nm thick hydrated layer on $\alpha\text{-Fe}_2\text{O}_3$, combining ambient-pressure XPS and SW-XPS. They found that SW-XPS at the solid–liquid interface allows sub-nm resolution of the spatial arrangement of chemical species, in this case the position of Cs and Na cations in the hydrated layer, as well as local potential energy variations along the direction perpendicular to the interface (Fig. 6f and g). Later, the same research group followed up with a pioneering *operando* study, revealing that SW-XPS is even possible in the presence of an electrolyte meniscus with ~ 20 nm thickness while applying electrochemical potentials.⁶³ In this example, they demonstrated the oxidation and hydroxylation of an 8 nm thick Ni film while maintaining sub-nanometer depth resolution using the increasingly popular dip-and-pull geometry, which was introduced in the seminal paper by Axnanda, Crumlin *et al.*⁶⁴ The same depth resolution can be now achieved using near total reflection geometry, which is especially attractive because it provides all the strengths of a standard SW-XPS without the need of an

artificial multilayer mirror, making the technique more broadly applicable.⁶⁵

For atomic-level spatial resolution, environmental transmission electron microscopy (ETEM) is a key development as it enables the direct imaging of surface processes on the atomic scale under exposure to ambient gases. When operated in H_2O conditions, a thin water layer condensates on the perovskite surface, as pioneered in the group of Jooss.⁶⁶ The primary electron beam of the TEM causes anodic polarization of the perovskite catalyst, resulting in close to relevant OER potentials. Weber *et al.*¹³ and Lole *et al.*⁶⁶ recently used this technique to reveal the dynamics at the $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}/\text{H}_2\text{O}$ and the $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_{3-\delta}/\text{H}_2\text{O}$ interfaces, where the TM ions are found to be highly mobile under OER potentials; a snapshot of the time sequence for this interface is shown in Fig. 6i.¹³ Such dynamics present an important future contribution for our understanding of electrocatalytic activity at continuously transforming electrocatalyst surfaces.

Lastly, we suspect that surface XRD and the investigation of crystal truncation rods (CTR) will lead to new fundamental insights when employed for epitaxial thin film electrocatalysts. CTR analysis was already successfully employed to study the surface structure and binding of reaction intermediates at single crystal surfaces, as showcased for the RuO_2 surface in Fig. 6j, where the diffraction data was fitted with a surface model including the presence of an $\ast\text{OO}$ intermediate on specific Ru sites.^{67,68} Such analyses, especially when combined with *ab initio* modelling and microkinetic modelling, may therefore lead to a more complete picture of the reaction intermediates preceding the rate determining step and potential-dependent surface structures and coverages, all of which are urgently needed for enhanced mechanistic understanding of OER electrocatalysts.

4.2 Layer-by-layer control of functionality and performance

To further enhance the performance of nickelates and perovskite electrocatalysts in general, both the activity and stability must be considered because of the typically-observed inverse activity–stability relationship. As stated before, epitaxial thin films are a valuable platform to develop structure–property–function relationships that might provide design rules to optimize both activity and stability simultaneously. It was recently shown that this inverse activity–stability relationship is not universal and can be overcome by careful inspection of facet-dependent activity and stability. For example, for LaNiO_3 , the (111) facet is both more active and more stable than other facets, a trend that could be revealed studying epitaxial thin films synthesized on differently oriented substrates.⁶⁹ Epitaxial thin films also enable the fabrication of material combinations with hybrid properties by interfacing different perovskite oxides with unit cell thickness control.²² Such heterostructures offer even more degrees of freedom to engineer stable and active electrocatalysts that overcome the inverse stability–activity relationship.

As previously discussed, the electrochemical properties of epitaxial thin films are influenced by the surface layer as well as



the subsurface layer. Engineering of the subsurface layer allows for optimization of the activity and stability. For example, electronic transport in thin film or heterostructure electrodes can be manipulated by engineering the interfacial depletion layers and corresponding potential barriers. Baniecki *et al.*⁷⁰ showed that buried epitaxial layers can be exploited to engineer the depletion layer and enhance the overall performance of epitaxial catalysts. Heterostructures of La-doped BaSnO₃ and La-doped SrTiO₃ on Nb-doped SrTiO₃ substrates were used as support of few-unit-cell thin La_{0.7}Sr_{0.3}CoO_{3-δ} catalysts layers. The introduction of La-doped BaSnO₃ and La-doped SrTiO₃ underneath the electrochemically active La_{0.7}Sr_{0.3}CoO_{3-δ} results in a narrower depletion layer and facilitates p-type character in the catalyst that greatly enhances its activity. This results in fast transport kinetics, even accompanied by enhanced stability as shown in Fig. 7c and d. Furthermore, engineering of the band edge has also been found to greatly enhance the performance of photoanodes in photoelectrochemical water-splitting. For example, the introduction of subsurface dipoles by placement of 1 unit cell LaAlO₃ in SrTiO₃ leads to improved efficiency.⁷¹

In addition to the manipulation of band bending at the solid/liquid interface, electronic properties of the active surface can be tuned in epitaxial multilayers as schematically shown in Fig. 7e. In our work (Heymann *et al.*⁷²), we showed that the enhanced Co–O covalency at the surface of hybrid epitaxial bilayers of La_{0.6}Sr_{0.4}CoO₃ and LaCoO₃ influences its activity. We evaluated valence band spectra of hybrid bilayers of 2–8 unit cells LaCoO₃ on top of 20 nm La_{0.6}Sr_{0.4}CoO₃ and their parent compounds, as shown in Fig. 7f. The valence band of La_{0.6}Sr_{0.4}CoO₃ shows more overlap between the O 2p (blue) and Co 3d (red) contribution compared to LaCoO₃, which indicates higher Co–O covalency for La_{0.6}Sr_{0.4}CoO₃. The spectra obtained for the hybrid bilayers also show large overlap between O 2p and Co 3d bands (more than expected based on a linear combination of the parent spectra) indicating interfacial hybridization in the bilayer catalysts. As Mott–Schottky analysis indicates hole accumulation for all investigated bilayers and both parent compounds in the OER regime, the observed activity of the fabricated bilayers is attributed to the increased Co–O covalency obtained by interfacial hybridization, rather than band bending at the solid/liquid interface.

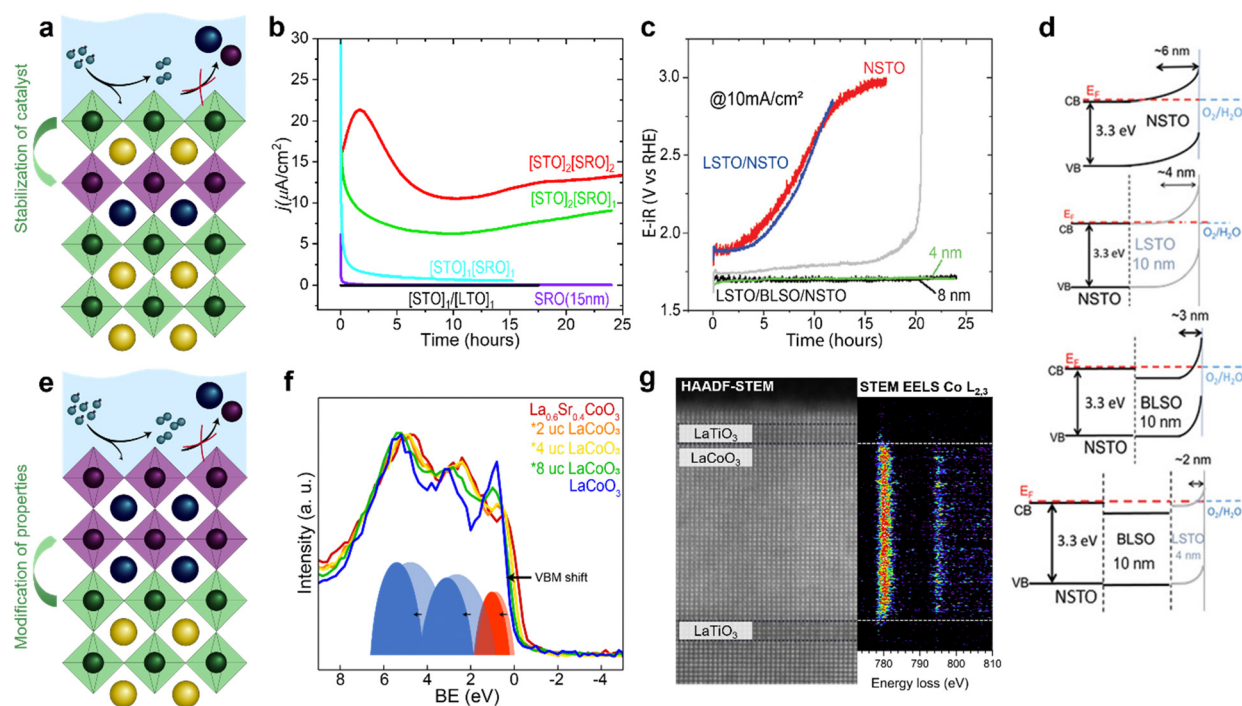


Fig. 7 Epitaxial multilayers offer opportunities to engineer both active and stable OER catalysts using various methods. (a) Hybrid structures can prevent catalyst dissolution. (b) Subsurface layers of SrRuO₃ (SRO) can activate SrTiO₃ (STO). Subscripts indicate the number of unit cells of STO (SRO) in the surface (subsurface). The current density of SrTiO₃ with an inactive subsurface layer of LaTiO₃ (LTO) and of a thin film of SrRuO₃ over time are shown for comparison. Used with permission of Royal Society of Chemistry, from "Activation of ultrathin SrTiO₃ with subsurface SrRuO₃ for the oxygen evolution reaction", A. R. Akbashev *et al.*, *Energy Environ. Sci.*, 2018, **11**, 1762–1769 (ref. 54). (c and d) Band engineering using layers of La doped BaSnO₃ (BLSO) and La-doped SrTiO₃ (LSTO) facilitates charge transport and enhances the lifetime of epitaxial catalysts grown on Nb-doped SrTiO₃ (NSTO). Reproduced with permission from ref. 63. Copyright 2019, Wiley-VCH. (e) Interfacial engineering allows for modification of surface properties without changing the chemical composition of the catalyst. (f) Interfacial engineering tunes the Co–O covalency of hybrid bilayers of 2–8 unit cells (u.c.) LaCoO₃ on 20 nm La_{0.6}Sr_{0.4}CoO₃ as shown using X-ray photoelectron of the valence band. Reproduced with permission from ref. 65. (g) Interfacial engineering results in a change in Co oxidation state near an epitaxial interface as observed with high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) with electron energy loss spectroscopy (EELS). Reprinted figure with permission from Araizi-Kanoutas *et al.*, *Phys. Rev. Mater.*, 2020, **4**, 026001. Copyright 2020 by the American Physical Society (ref. 68).

In addition to the stabilization of active catalysts by the prevention of dissolution with capping layers, or activation of inactive catalysts by placement of more active subsurface layers, as shown in Fig. 7a, interfacial engineering offers even more opportunities to tune the properties of stable catalysts to enhance activity, as shown in Fig. 7e. For example, the oxidation state of B-site atoms in epitaxial perovskites changes near the interface of perovskites with a different B-site atom, as shown in Fig. 7g.⁷⁵ This offers opportunities to manipulate the oxidation state, structural distortions, orbital filling and covalency of ultrathin catalytic layers without changing their chemical composition. As the chemical composition remains unchanged, this is a promising strategy to overcome the observed inverse activity–stability relationship by activating chemically stable surfaces through remote doping, which may be extended from these Co- and Ru-based examples to epitaxial nickelate layers. Due to the control of the growth of epitaxial multilayers, these films serve as promising model systems to

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