Epitaxial catalysts for oxygen evolution reaction: model systems and beyond

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Abstract

Epitaxy of complex perovskite oxides has arrived at atomic scale precision. This opens new chances and opportunities to the field of electrolysis and water splitting, where perovskite oxides show promising catalytic activity for the oxygen evolution reaction (OER). While representing ideal model systems for improving our scientific understanding of atomistic processes and scaling relations during OER, epitaxial heterostructures furthermore give access to atomic band engineering strategies and allow the generation of hybrid materials, which may combine beneficial properties of neighboring materials on the nanoscale. These strategies render novel opportunities to enhance chemical stability and to tune overpotentials of OER-active perovskite materials, not accessible in the bulk. Epitaxial catalysts can therefore play an important role in achieving new breakthroughs and guide lines in the field.

The production of chemical fuels is at the heart of sustainable hydrogen technologies. The chemical splitting of water molecules (H₂O) into their elemental compounds hydrogen (H₂) and oxygen (O₂) by electrolysis is the simplest chemical pathway to go. However, the process is typically inefficient and relies on available catalysts promoting hydrogen and oxygen evolution reaction. A major challenge in science and technology are particularly the overpotentials and losses generated in the oxygen evolution reaction (OER). These limits are partly resulting from physical limits of available catalyst materials. Moreover, however, these limits result from an incomplete atomistic understanding of oxygen evolution from complex catalyst surfaces and a limited ability to overcome classical scaling relations through the active control of catalyst properties, such as electronic structure, intrinsic conductivity, crystal orientation, or surface band alignment by purely chemical means.

Another challenge in the field is that the best OER catalysts known to date typically contain rare and expensive elements, such as Pt, Ru, or Ir, driving intensive search for more earth-abundant and cheap catalysts, which either reduce the volume fraction of these metals or fully replace them by more accessible elements such as Nickel or (with some limitations) Cobalt [1].

The materials screening approach of the community has identified perovskite oxides as promising candidates, particularly focusing on iridates, ruthenates, cobaltites, and nickelates [2–5], which (similar to pure metal compounds) group at the top of the volcano plot [6]. The beauty of these materials lies in the much lower volume concentration of metal ions as compared to pure metals, and even more in the wide range of chemical compositions and physical properties available within the family of perovskite oxides, and the extraordinary tunability of physical properties via the coupled ionic and electronic degrees of freedom in these materials. The electrochemistry of perovskites has been considered in the literature already quite some time ago [7, 8]. However, the atomistic details of OER processes, such as active site determination and associated activity and stability criteria, are still only partly understood. It is the same complexity of the chemistry of perovskites (containing 3–5 elements per unit cell) and their entangled electronic-ionic properties that make the search for distinct descriptors of catalytic activity and chemical stability difficult.

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Epitaxy of catalytic thin films is a huge opportunity to simplify and homogenize structural, electronic, and ionic properties of OER catalysts on the atomic level, delivering ideal model systems for understanding structure-property relations on the atomic scale and for complex catalyst compositions (Figure 1). Even more, by using epitaxial catalyst heterostructures and superlattices, atomic engineering strategies become available to the OER community, allowing to tailor physical properties of catalysts in a way not accessible to bulk-chemical methodology. Epitaxial catalysts therefore have the potential to pave ground for systematic understanding of OER processes on the atomic level, for reduced overpotentials and losses, and for enhanced chemical stability through atomic engineering.

Many materials now considered as potential OER catalysts have in a similar manner been utilized in the electronic and magnetic oxide community, where epitaxy and atomic precision plays a key role, e.g. for driving metal-to-insulator transitions or stabilizing high- and low-spin states in magnetic oxides [9–11]. Particularly for perovskite catalysts, such as iridates, ruthenates, cobalites, or nickelates, the electrochemical community can highly profit from the progress in those fields which pushed oxide heterostructure epitaxy towards single-unit-cell precision within the last decade. As such, we have learned to exploit oxide epitaxy and its degrees of freedom to control physical properties, strain, and crystal orientation in an atomically defined manner. In this way, atomically tailored dipoles can be used to manipulate band bending and charge transfer at surfaces and interfaces [12]. Even more, hybrid material properties can be generated by interfacing single unit cells of different compounds in atomically defined manner. Therefore, epitaxial OER catalysts provide a great opportunity for establishing better model catalysts and—beyond that—for driving enhanced functionality of the present OER catalysts.

Figure 1. Epitaxial perovskite catalysts for oxygen evolution reaction bear the chance to control properties via crystal orientation and strain, to test phase stability under OER conditions from a defined starting point, and to engineer hybrid materials and physical properties in heterostructures and superlattices.
Model systems with defined structural properties

Oxide epitaxy is accessible using various routes, such as sputtering, oxide molecular beam epitaxy, and pulsed laser deposition (PLD). For perovskites oxides, PLD is most commonly used as it allows to accommodate the complex stoichiometry of ternary and quaternary oxide catalysts, such as mixed A-site or B-site perovskites or double perovskites. In situ monitoring by electron diffraction techniques (reflection high energy electron diffraction, RHEED) allows the control of the epitaxial growth on the single unit cell level, enabling precise thickness control, but moreover, the combination of different materials on the atomic level.

In the coherent epitaxial growth process, the catalyst thin film adopts the crystal structure of the substrate, yielding single crystalline catalyst layers with atomically defined surface morphology, single crystal orientation, defined strain-state, and well-defined atomic structure (figure 1), yielding well-defined model systems for systematic OER studies. For complex oxide materials, however, the synthesis with unit-cell precision is at the edge of state-of-art epitaxy and requires the preparation of high-quality target materials and substrates, and the delicate optimization of growth conditions, controlling kinetic and thermodynamic processes in the growing layer. In recent literature, it was shown that it is possible to synthesize e.g. SrIrO$_3$ or (Pr,Ba)CoO$_{3-\delta}$ layers with a surface roughness below 2 nm at a layer thickness of about 100 nm [2, 13], while even subnanometer surface smoothness was achieved for (La,Sr)CoO$_{3-\delta}$ at a similar thickness [14]. The growth process can be monitored and controlled by means of electron diffraction techniques allowing layer deposition with single monolayer precision. As a result, complex catalysts in a fairly simple geometry, structure and morphology can be obtained. These may then serve as model systems for computational studies [15] or as templates for in situ/in-operando studies, including atomically resolved techniques such as scanning tunneling microscopy, yet widely limited to ideal metal surfaces.

Critical catalyst properties such as electrical conductivity and transport behavior can be measured as an independent property of the catalyst material in absence of chemical admixtures, and in a defined geometry allowing four-point-probe sheet resistance and Hall characterization [13, 14]. Starting from a defined single crystalline catalyst, phase stability and amorphization processes during OER may be monitored based on model catalysts (figure 1(B)). In [2], the authors show the formation of a stable surface phase during OER, which is formed and stabilized on epitaxial SrIrO$_3$ catalyst layers and results in increasing OER activity, rather than degradation over time. In [5], phase-sensitive catalytic activity was reported for SrRuO$_3$, while the different phases (tetragonal/orthorhombic) were obtained via defined control of the epitaxial growth process.

Comparability to powder catalysts

Up to now, a major drawback for epitaxial OER catalysts is that due to the limited sample size and layer thickness, appearing contact resistances, low active area/volume ratio and simplified level of technological cell integration only low current densities (typically in the range of $\mu$A cm$^{-2}$ up to a few mA cm$^{-2}$) can be applied to the catalyst, while technologically relevant cells work at exceedingly higher current density loads. This can make a direct comparison of model system and real catalyst system difficult. A few examples in the literature however show that even for epitaxial catalysts current densities exceeding 10 mA cm$^{-2}$ and approaching 100 mA cm$^{-2}$ [2, 14] can be achieved, while maintaining sufficiently stable performance, which now allows to couple and crosslink the behavior of epitaxial model systems to the properties of classical powder catalysts at comparable current density loads. As a result, chemical decomposition, leaching behavior, and physical degradation of catalysts can be studied under OER conditions based on defined epitaxial models systems. At the same time, physical material descriptors such as electrical conductivity can be monitored during operation.

Epitaxial degrees of freedom

Systematic comparison of epitaxial and powder catalyst allows us to benefit from the entire tool box of epitaxy to improve our understanding of the fundamental processes taking place on the atomic scale during OER. This includes to systematically vary the crystal orientation of the catalyst surface exposed to the electrolyte by the choice of the substrate and to study catalytic behavior for each crystal facet individually (figure 1(A)), such as reported for SrCoO$_{3-\delta}$ [16]. Moreover, the choice of different substrates allows to induce epitaxial strain into the catalyst material, when keeping the layer thickness below the critical thickness for strain relaxation (which can be up to tens and hundreds of nanometers depending on actual lattice mismatch and elastic parameters of the catalyst) [14]. Typically both compressive and tensile strain can be applied to the catalyst (figure 1(C)) [17]. In this way, interatomic distances and bond lengths can be varied in a defined way allowing us to control the energetics of adsorption on the catalytic surface. The defined geometry of epitaxial catalysts moreover allows to
track back potential strain effects on catalytic activity to specific physical properties of the material, such as electrical conductivity which in strongly correlated oxides often depends on strain, enabling the unambiguous separation of physical descriptors for OER activity from secondary effects.

**Defect structure of epitaxial perovskite catalysts**

Similar to all complex oxides, epitaxial thin film catalysts contain defects, even under ideal growth conditions. Typical defects range from oxygen and cation non-stoichiometry, but can also contain more extended defect structures, particularly stacking faults and dislocations, potentially arising from strain relaxation, non-ideal growth conditions, or as a thermodynamic requirement under applied growth conditions [13, 14]. The grade of defectiveness, however, can typically be systematically controlled through a variation of growth parameters, enabling to study the effect of a defined defect structure on the catalyst properties based on a model system approach [13].

**Generation of properties**

Exotic material states obtained via epitaxial strain, atomic engineering, or charge-transfer across atomically defined heterointerfaces can not only control electronic and structural properties of catalyst layers, but moreover give rise to new material properties emerging [12]. This may include fundamentally altered electronic structure, but also altered ionic structure. For one, epitaxial growth processes such as PLD allow to stabilize materials and phases away from thermodynamic equilibrium. In this way, for example, coherently ordered chains of oxygen vacancy defects have been controlled and stabilized in epitaxial double-perovskite OER catalysts, such as described in [13]. As could be shown, catalytic activity and overpotential of these compound is primarily decoupled from its polymorphous phase. Variations in overpotential and achieved current densities were found to result mainly from variation in the intrinsic electrical conductivity, rather than from structural ordering phenomena. Epitaxial heterostructuring also allows to tailor electronic (and ionic) band structure and band alignments by combining materials on the atomic scale (figure 1(D)). A proof-of-principle example for this is presented in [18], where the strong electric dipole associated with single monolayers of polar LaAlO3 layers inserted into an epitaxial catalyst system is used to engineer the flat band potential of SrTiO3-based photocatalytic anodes. Here, band engineering is employed to align electronic structure of the catalyst with the desired redox-potentials. A similar approach may be adopted to tailor the energy barrier for electron transfer reactions from catalyst to the electrolyte or vice versa in conventional electrolysis.

Ultimately, atomically defined layered structures can be utilized to generate hybrid materials, e.g. in form of superlattices and single-unit-cell heterostructures (figure 1(E)). Such as described by the authors in [19], single-unit-cell layering of two compounds allows to merge the electronic structure of neighboring materials, and to generate fundamentally new material properties. In this particular case, it was shown that combining SrRuO3—a highly active, but unstable OER catalyst—and SrTiO3—an inactive, but stable oxide under OER conditions—gives rise to a hybrid electronic structure in which Ru states merge and hybridize with the electronic states in SrTiO3, leaving behind an active and more stable catalyst layer. As the authors emphasize similar properties may be realized in core–shell geometries of engineered catalytic nanoparticles. The epitaxial approach chosen yields clear guide lines for their design, thus linking the epitaxy approach with neighboring fields in electrochemistry [19].

**Future perspective**

The examples discussed here already illustrate the chances and opportunities arising from the use of epitaxy and atomic engineering tools in understanding and tailoring catalytic processes and particularly oxygen evolution at complex oxide surfaces. Yet, epitaxial catalyst studies reflect only a small fraction of ongoing research in OER catalysis. However, improving our atomistic understanding of the catalytic process and generating enhanced functionality using this approach could lead to new breakthroughs in the field. Achieving continuous scientific and technological progress will require a cooperative and interdisciplinary approach between the oxide epitaxy community and the electrochemistry community. Following the above mentioned examples, however, epitaxial catalyst can surely play an important role in this process, as the precise combination of materials, tuning parameter, and engineering strategy may well be key in developing stable and efficient OER catalyst solutions.
References

[1] Vesborg P C K and Jaramillo T F 2012 RSC Adv. 2 7933
[2] Seitz L C et al 2016 Science 353 1011
[3] Mefford J T, Rong X, Abakumov A M, Hardin W G, Dai S, Kalpak A M, Johnston K P and Stevenson K J 2016 Nat. Commun. 7 11053
[4] Grimaud A, May K J, Carlton C E, Lee Y, Risch M, Hong W T, Zhou J and Shao-Horn Y 2013 Nat. Commun. 4 2439
[5] Lee S A et al 2017 Energy Environ. Sci. 10 924
[6] Man I, Su H-Y, Vallejo F, Hansen H, Martínez J, Inoglu N, Kitchin J, Jaramillo T, Nørskov J and Rossmeisl J 2011 ChemCatChem 3 1159
[7] Hoare J P 1969 J. Electrochem. Soc. 116 1168
[8] Bockris J O and Otagawa T 1984 J. Electrochem. Soc. 131 290
[9] Zubko P, Gariglio S, Gabay M, Ghosez P and Triscone J-M 2011 Annu. Rev. Condens. Matter Phys. 2 141
[10] Middey S, Chakhalian J, Mahadevan P, Freeland J, Millis A and Sarma D 2016 Annu. Rev. Mater. Res. 46 505
[11] Koster G, Klein L, Siemons W, Rijnders G, Dodge J S, Ezn M-C, Blank D H A and Beasley M R 2012 Rev. Mod. Phys. 84 253
[12] Hwang H Y, Iwasa Y, Kawasaki M, Keimer B, Nagaosa N and Tokura Y 2012 Nat. Mater. 11 105
[13] Gunkel F, Jia C, Bick D S, Jia C-L, Schneller T, Valov I, Waser R and Dittmann R 2017 ACS Catalysis 7 7029
[14] Weber M L, Baeumer C, Mueller D N, Jia C, Bick D S, Waser R, Dittmann R, Valov I and Gunkel F 2019 Chem. Mater. 31 2337–46
[15] Montoya J H, Garcia-Mota M, Nørskov J K and Vojvodic A 2015 Phys. Chem. Chem. Phys. 17 2634
[16] Jeen H, Bi Z, Choi W S, Chisholm M F, Bridges C A, Paranthaman M P and Lee H N 2013 Adv. Mater. 25 6459
[17] Stoerzinger K A, Choi W S, Jeen H, Lee H N and Shao-Horn Y 2015 J. Phys. Chem. Lett. 6 487
[18] Hikita Y, Nishio K, Seitz L C, Chakhtranont P, Tachikawa T, Jaramillo T F and Hwang H Y 2016 Adv. Energy Mater. 6 1502154
[19] Akbashev A R, Zhanga L, Mefford J T, Park J, Butz B, Luftman H, Chueh W C and Vojvodic A 2018 Energy Environ. Sci. 11 1762