Trends of epitaxial perovskite oxide films catalyzing the oxygen evolution reaction in alkaline media

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Abstract

The oxygen evolution reaction (OER) is considered a key reaction for electrochemical energy conversion but slow kinetics hamper application in electrolyzers, metal-air batteries and other applications that rely on sustainable protons from water oxidation. In this review, the prospect of epitaxial perovskite oxides for the OER at room temperature in alkaline media is reviewed with respect to fundamental insight into systematic trends of the activity. First, we thoroughly define the perovskite structure and its parameter space. Then, the synthesis methods used to make electrocatalytic epitaxial perovskite oxide are surveyed, and we classify the different kinds of electrodes that can be assembled for electrocatalytic investigations. We discuss the semiconductor physics of epitaxial perovskite electrodes and their consequences for the interpretation of catalytic results. Prototypical mechanisms of the OER are introduced and comparatively discussed. OER investigations on epitaxial perovskite oxides are comprehensively surveyed and selected trends are graphically highlighted. The review concludes with a short perspective on opportunities for future electrocatalytic research on epitaxial perovskite oxide systems.

1. Introduction

Water splitting is the most important reaction for sustainable production of hydrogen equivalents (protons) [1–4]. These are used in one half reaction to make energy carriers (e.g. H₂, CH₃OH) [5–11], fertilizers (NH₃) [12–14] or feedstocks for the chemical industry (e.g. CH₂O) [15–17]. The supply of the much-needed hydrogen equivalents is limited by the half reaction of oxygen evolution from water, also known as water oxidation [18–20]. The oxygen evolution reaction (OER) suffers from large energy losses due to a high overpotential, which is rooted in the mechanism of transferring four electrons and four hydroxide molecules (in alkaline media) [21–24]. While much of our current knowledge of likely mechanisms is derived from theoretical work [21, 23, 25, 26], very few details of the mechanism are supported experimentally. A key concept in the rational design of better electrocatalysts is the so-called descriptor approach, i.e. property-activity relationships [23, 27–36]. The latter calls for systematic investigations of defined materials with tunable properties such as epitaxial perovskite oxides with the caveat that an intended change may be accompanied by unintended changes that also affect the activity.

The family of perovskite oxides is a popular choice for systematic investigations because the composition of the perovskites can be varied with little change to the structural framework in the best case [33, 37–40]. Over the last decade, the interest in epitaxially deposited perovskite oxides has increased considerably [41–44]. The preparation of epitaxial thin films and buried solid–solid interfaces since the late 1980s has led to a very mature understanding of the solid-state chemistry and oxide physics of perovskite oxides [45, 46]. These films have vast potential to further advance our understanding of the solid–liquid interface due to the controlled orientation of the films, their negligible roughness and the absence of additives, such as carbon or a binder, that are commonly added to composite electrodes based on powders. Therefore, epitaxial perovskite
oxides are the perfect choice for systematic investigations of electrocatalytic reactions and in particular of the ill-understood OER.

The scope of this review is a comprehensive overview of OER studies on epitaxial perovskite oxides. Firstly, the perovskite structure is rigorously and quantitatively defined. Then, synthesis methods for these films and the resulting physical properties are discussed and we survey how electrodes are made from the as-deposited films. The next section deals with charge transfer across buried solid–solid interfaces and across the solid–liquid interface, which must not limit catalysis. Prototypical mechanisms of the OER are introduced and comparatively discussed to lay the foundation for the descriptor approach. Subsequently, trends in the published works are identified and discussed based on the fundamentals introduced in earlier sections. In particular, we analyze how well an electronic and a structural descriptor describe the available activities of epitaxial perovskite oxides. The review is concluded by a summary of the current state of the small but burgeoning field and a perspective for future research directions.

2. What is a perovskite?

2.1. Ideal bulk perovskites

Perovskite oxides denote a family of compounds with the general structure ABO$_3$ named after the mineral CaTiO$_3$ which defines the prototypical structure [48]. Commonly, lanthanides or group II elements are found on the A-site and transition metals on the B-site. The term ‘perovskite’ is currently used ambiguously even though a precise definition exists. According to Breternitz and Schorr [49], three structural requirements must be met that define a general perovskite (including non-oxides):

R1) A stoichiometry of ABX$_3$, or at least a ratio A:B:X of 1:1:3
R2) The coordination of the B-site cation needs to be octahedral (or a distorted octahedra)
R3) The [BX$_6$] octahedra need to be organized in an all-corner sharing 3D network

The authors justify these rules based on the relationship between structure and properties where the properties would differ strongly, especially if the network of corner-sharing octahedra was lost. The ratio in requirement R1 includes double perovskites with the general formula A$_2$BB’X$_6$, for which this network is preserved. Herein, we would like to rephrase point 1 to ‘a ratio of A:B:X of near 1:1:3’ to include materials with anionic or cationic vacancies that still fulfill requirements R2 and R3, e.g. oxygen-vacancy ordered double perovskites with the formula AA’B$_2$O$_5$+$\delta$ or regular perovskites (fulfilling R2 and R3) that have a sizable number of vacancies, which are often important for the electronic and structural properties (see section 2.2).

The fulfilment of the above requirements naturally leads to quantitative definitions and requirements based on ionic radii. Goldschmidt [50] defined the tolerance factor as

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$

(1)

where $r_A$, $r_B$ and $r_O$ are the ionic radii of ions at the A-site, B-site and oxygen, respectively. Most commonly, specific values are taken from Shannon’s Table [51] or linearly extrapolated from these tabulated values to the appropriate coordination.

Li, Soh and Wu [52] found that the Goldschmidt tolerance factor is not sufficient to predict the formability of the perovskite structure, and they introduced the octahedral factor as a secondary requirement. The octahedral factor (of perovskite oxides) is defined as:

$$\mu = \frac{r_B}{r_O}$$

(2)

These definitions and their significance can be rationalized geometrically. The A-site cation exactly fits in the void between the B-O octahedra if the B-site cations sit on the corners of a cube and the size of the A-site cation matches the diagonal. This leads to a cubic bulk perovskite with tolerance factor very close to unity ($t \approx 1$; figure 1(b)). The octahedral cavity forms a regular cuboctahedron and the A-site is 12-fold coordinated. If the A-site cation is larger, it no longer fits in the octahedral void. This scenario is denoted SL (stretch limits) in figure 1(a) and illustrated in figure 1(c). In this case, requirements R2 and R3 need to be broken and non-perovskite crystal structures are observed. If the A-site is smaller than the octahedral cavity, the B-O octahedra tilt, rotate and often distort, which strongly affects the hybridization of electronic orbitals. Moreover, the A-site is moved out of the center of the octahedral void. The coordination of the A-site is reduced in this configuration. This scenario is denoted TL (tilt limits) in figure 1(a) and illustrated in figure 1(d). In these limits, the oxygen ions of neighboring octahedra touch and again requirement 3 cannot be not
Figure 1. (a) The theoretically derived stability region (solid blue area) of general perovskites $ABX_3$ in the parameter space defined by the tolerance and octahedral factors. The red outlined area indicates the parameter space of the electrocatalytic perovskite oxides studied herein. The shown limits are: chemical limits (CL1 and CL2), octahedral limit (OL), stretch limits (SL, SSL1 and SSL2), and tilt limits (TL1 and TL2). Further detail may be found in the text. Accompanying illustrations of (b) a cubic perovskite, (c) the stretch limit due to a large A-site, (d) the tilt limit due to small A-sites, and (e) the octahedral limit due to the relative size of the B-site and oxygen. Note that oxygen has similar ionic radius compared to common A-site cations (which is not the case in all illustrations on the right to emphasize the limits). Modified with permission from ref [47]. Copyright 2018 National Academy of Sciences.

fulfilled. The octahedral factor is limited by the case when the anions touch, i.e. when the B-site radius is small compared to the ionic radius of oxygen. It is denoted as OL (octahedral limit) in figure 1(a) and illustrated in figure 1(c). This limit is observed if $r_B = r_O \left(1 - \frac{1}{\sqrt{2}}\right) \leq 0.41$, which is smaller than the ionic radii of six-fold coordinated first-row transition metals [51]. However, stable perovskites were also found to the left of this boundary [47]. Finally, the upper boundary of the perovskite stability region in figure 1(a) is given by the ratio of the ionic radii of Cs (A-site) and F as the anion as well as Fr$^+$ and Ac$^{3+}$ as B-sites, which is denoted as CL (chemical limit).

For the perovskite oxides reviewed here as electrocatalysts for the OER, the largest A-site cation is Ba, the anion is O and the largest B-site is Ir$^{3+}$. The latter gives an upper octahedral factor of $\mu = 0.486$, and thus the stretch limit (SL) rather than chemistry (i.e. CL1) limits the tolerance factor to $t = 1.0$ for electrocatalytic perovskite oxides. The calculated tolerance factors of the perovskite oxides discussed herein range from $t = 0.958$ to $t = 1.053$ (table 1). About a third (28%) of all entries have a tolerance factor above $t_{SL} = 1.0$. The actual tolerance factors based on experimental bond distances may differ slightly. The limits discussed above are usually not strict, and stable perovskite oxides that fulfil the requirements of R1–3 can be observed experimentally also slightly outside the predicted ranges. The calculated octahedral factors range from $\mu = 0.371$ to $\mu = 0.456$, where again the lower boundary is very clearly outside the predicted stability boundary of $\mu_{OL} > (\sqrt{2} - 1) \approx 0.41$ [47]. In fact, 77% of all entries in table 1 have an octahedral factor below $\mu_{OL}$ and 28% of all entries have both octahedral factors below $\mu_{OL}$ and tolerance factors above $t_{SL}$, meaning all entries with $\mu < \mu_{OL}$ also show $t > t_{SL}$. Filip and Giustino [47] attribute their outliers to the simplicity of the used Goldschmidt model and found that values outside their predicted stability ranges may indicate polymorphism.

2.2. Realistic perovskites with defects: vacancies and segregation

Any real crystal must contain point defects in thermodynamic equilibrium as the associated entropy term minimizes the free energy of the crystal. Thus, point defects such as interstitials, antisites and vacancies should be expected in any real perovskites. The effect of interstitials in epitaxial perovskites is very rarely discussed in the context of the OER (to the best of our knowledge only in [76].). Likewise, the effect of antisites is not discussed. Thus, we only consider cation and oxygen vacancies since the latter are most frequently discussed. Higher dimensional defects such as dislocations [77] and twining [78] can also be expected for imperfect lattice match between the substrate and deposited film to release mechanical stress.
Table 1. Comprehensive overview of structural properties, fabrication methods and activity of 53 epitaxial films used as catalysts for the OER and additional films where the activity could not be evaluated.

| Material | Tolerance factor $(r)$ | Octahedral factor $(µ)$ | Substrate/Support | Synthesis method | Electrode type* | Conductivity (S cm$^{-1}$) | Orientation | E at 50 µA/cm$^{-2}$ (V vs RHE) | j at 1.6 V vs RHE (µA/cm$^{-2}$) | Tafel slope (mV dec$^{-1}$) | Electrochemical method | Reference |
|----------|------------------------|-------------------------|-------------------|------------------|-----------------|--------------------------|------------|-------------------------------|--------------------------------|--------------------------|---------------------------|-----------|
| SrIrO$_3$ | 0.992                  | 0.446                   | DyScO$_3$        | MBE              | RM              | $3 \times 10^5$          | (100)      | 1.53                          | 910                            | 41                       | CA, 0 rpm                 | [71]      |
| NdNiO$_3$ | 0.963                  | 0.400                   | LaSrAlO$_3$      | PLD              | RM              | $3 \times 10^5$          | (100)      | 1.61                          | 9                             | 68                       | CA, 0 rpm                 | [64]      |
| NdNiO$_3$ | 0.963                  | 0.400                   | LaAlO$_3$        | PLD              | RM              | $3 \times 10^5$          | (100)      | 1.65                          | 16                            | 100                      | CA, 0 rpm                 | [64]      |
| NdNiO$_3$ | 0.963                  | 0.400                   | NdGaO$_3$        | PLD              | RM              | $3 \times 10^5$          | (100)      | 1.66                          | 7                             | 132                      | CV, 0 rpm                 | [64]      |
| NdNiO$_3$ | 0.963                  | 0.400                   | SrTiO$_2$        | PLD              | RM              | $3 \times 10^5$          | (100)      | 1.64                          | 9                             | 139                      | CV, 0 rpm                 | [64]      |
| LaCoO$_3$ | 0.996*                 | 0.400                   | SrTiO$_2$        | PLD              | RM              | $3 \times 10^5$          | (100)      | 1.58                          | 114                           | 55                       | CA, 0 rpm                 | [72]      |
| LaCoO$_3$ | 0.996*                 | 0.400                   | LaAlO$_3$        | (Sr$_2$AlTaO$_6$)$_{0.3}$ | PLD | RM | $3 \times 10^5$          | (100)      | 1.58                          | 148                           | 64                       | CA, 0 rpm                 | [72]      |
| LaCoO$_3$ | 0.996*                 | 0.400                   | LaAlO$_3$        | (Sr$_2$AlTaO$_6$)$_{0.3}$ | PLD | RM | $3 \times 10^5$          | (100)      | 1.58                          | 148                           | 64                       | CA, 0 rpm                 | [72]      |
| LaCoO$_3$ | 0.996*                 | 0.400                   | LaAlO$_3$        | (Sr$_2$AlTaO$_6$)$_{0.3}$ | PLD | RM | $3 \times 10^5$          | (100)      | 1.58                          | 148                           | 64                       | CA, 0 rpm                 | [72]      |
| LaCoO$_3$ | 0.996*                 | 0.400                   | LaAlO$_3$        | (Sr$_2$AlTaO$_6$)$_{0.3}$ | PLD | RM | $3 \times 10^5$          | (100)      | 1.58                          | 148                           | 64                       | CA, 0 rpm                 | [72]      |

(Continued)
| Material | Tolerance factor (t) | Octahedral factor (µ) | Substrate/Support | Synthesis method | Electrode type* | Conductivity (S cm⁻¹) | Orientation | E at 50 μA/cm² ox (V vs RHE) | j at 1.6 V vs RHE (µA/cm² ox) | Tafel slope (mV dec⁻¹) | Electrochemical method | Reference |
|----------|---------------------|----------------------|-------------------|-----------------|----------------|----------------------|------------|----------------------------|-----------------------------|-----------------|----------------------|-----------|
| LaNiO₃   | 0.996               | 0.400                | LaSrAlO₄          | PLE             | DM             | 5.4*10⁻¹³          | (100)      | 1.63                       | 19                          | 56              | CV, 1600 rpm          | [78]       |
| LaNiO₃   | 0.996               | 0.400                | LaAlO₃            | PLE             | DM             | 6.0*10⁻¹⁵          | (100)      | 1.62                       | 21                          | 46              | CV, 1600 rpm          | [78]       |
| LaNiO₃   | 0.996               | 0.400                | (LaAlO₃)₀.₃ LaSrAlO₄₀.₇ | PLE             | DM             | 2.4*10⁻¹⁴          | (100)      | 1.63                       | 15                          | 68              | CV, 1600 rpm          | [78]       |
| LaNiO₃   | 0.996               | 0.400                | SrTiO₃            | PLE             | DM             | 1.6*10⁻¹⁵          | (100)      | 1.66                       | 8                           | 65              | CV, 1600 rpm          | [78]       |
| Ba₀.₅Sr₀.₅Co₀.₈Fe₀.₂O₃⁻δ on La₀.₈Sr₀.₂MnO₃ (0%) | 1.05³⁻bcd       | 0.404                | NbSrTiO₃          | PLD             | RM             | —         | (100)      | 1.68                       | 4                           | 69              | CV, 0 rpm             | [79]       |
| Ba₀.₅Sr₀.₅Co₀.₈Fe₀.₂O₃⁻δ on La₀.₈Sr₀.₂MnO₃ (48%) | 1.05³⁻bcd       | 0.404                | NbSrTiO₃          | PLD             | RM             | —         | (100)      | 1.54                       | 920                         | 50              | CV, 0 rpm             | [79]       |
| Ba₀.₅Sr₀.₅Co₀.₈Fe₀.₂O₃⁻δ on La₀.₈Sr₀.₂MnO₃ (94%) | 1.05³⁻bcd       | 0.404                | NbSrTiO₃          | PLD             | RM             | —         | (100)      | 1.51                       | 2500                        | 53              | CV, 0 rpm             | [79]       |
| Pr₀.₅Ba₀.₅Co₀.₈Fe₀.₂O₃⁻δ (Pr₀.₅Ba₀.₅Co₀.₈Fe₀.₂O₃⁻δ) | 1.044³⁻         | 0.400                | SrTiO₃            | PLD             | RM             | 3.6*10⁻¹⁵          | (100)      | 1.69                       | —                           | —               | CV, 0 rpm             | [80]       |
| Co₀.₅O₃⁻δ⁺m | 1.04³⁻         | 0.400                | SrTiO₃            | PLD             | RM             | 7.4*10⁻¹⁵          | (100)      | 1.67                       | —                           | —               | CV, 0 rpm             | [80]       |
| La₀.₇Sr₀.₃Co₀.₃ | 1.01³⁻     | 0.391                | NdGaO₃            | PLD             | RM             | 3.3*10⁻¹⁰          | (100)      | 1.48                       | 1280                        | —               | CV, 0 rpm             | [81]       |
| La₀.₈₈Sr₀.₁₂FeO₃ | 0.961       | 0.456                | NbSrTiO₃          | OPA-MBE         | RM             | 3.3*10⁻₂          | (100)      | 1.58                       | 97                          | —               | CV, 0 rpm             | [82]       |
| Material          | Tolerance factor (t) | Octahedral factor (μ) | Substrate/Support | Synthesis method | Electrode type* | Conductivity (S cm⁻¹) | Orientation | E at 50 μA/cm² (V vs RHE) | j at 1.6 V vs RHE (μA/cm²) | Tafel slope (mV dec⁻¹) | Electrochemical method | Reference  |
|-------------------|----------------------|-----------------------|-------------------|------------------|-----------------|----------------------|-------------|--------------------------|--------------------------|------------------------|-----------------------|------------|
| SrRuO₃            | 0.994                | 0.443                 | Nb:SrTiO₃         | RFMS             | DA              | —                   | (100)       | 1.43                      | —                        | —                      | CV, 1600 rpm           | [83]       |
| SrRuO₃            | 0.994                | 0.443                 | Nb:SrTiO₃         | RFMS             | DA              | —                   | (110)       | 1.32                      | —                        | —                      | CV, 1600 rpm           | [83]       |
| SrRuO₃            | 0.994                | 0.443                 | Nb:SrTiO₃         | RFMS             | DA              | —                   | (111)       | 1.30                      | —                        | —                      | CV, 1600 rpm           | [83]       |
| Pr₀.₃Ca₀.₇MnO₃    | 0.964                | 0.453                 | Nb:SrTiO₃         | IBS              | DA              | —                   | (100)       | 1.67                      | 4                        | —                      | CV, 0 rpm              | [84]       |
| Pr₀.₆Sr₀.₄MnO₃    | 0.974                | 0.434                 | Nb:SrTiO₃         | IBS              | DA              | —                   | (100)       | 1.64                      | 14                       | —                      | CV, 0 rpm              | [84]       |
| LaNiO₂            | 0.996                | 0.400                 | SrTiO₃            | Sol-gel          | RM              | —                   | (100)       | 1.61                      | 55                       | 69                     | CV, 0 rpm              | [85]       |
| LaNiO₂⁺            | 0.996               | 0.400                | SrTiO₃            | Sol-gel          | RM              | —                   | (100)       | 1.56                      | 575                      | 40                     | CV, 0 rpm              | [85]       |
| PrNiO₂            | 1.001                | 0.400                 | SrTiO₃            | Sol-gel          | RM              | —                   | (100)       | 1.56                      | 580                      | 37                     | CV, 0 rpm              | [85]       |
| PrNiO₂⁺            | 1.001               | 0.400                | SrTiO₃            | Sol-gel          | RM              | —                   | (100)       | 1.59                      | 55                       | 72                     | CV, 0 rpm              | [85]       |
| NdNiO₂            | 0.963                | 0.400                 | SrTiO₃            | Sol-gel          | RM              | —                   | (100)       | 1.59                      | 792                      | 36                     | CV, 0 rpm              | [85]       |
| NdNiO₂⁺            | 0.963               | 0.400                | SrTiO₃            | Sol-gel          | RM              | —                   | (100)       | 1.55                      | 792                      | 36                     | CV, 0 rpm              | [85]       |
| La₀.₂Sr₀.₈MnO₃     | 0.988                | 0.428                 | Nb:SrTiO₃         | IBS              | DA              | —                   | (100)       | 1.64                      | 13                       | —                      | CV, 1600 rpm           | [86]       |
| LaMnO₃            | 0.954                | 0.461                 | Nb:SrTiO₃         | PLD              | n/r             | —                   | (100)       | 1.72                      | —                        | —                      | CV, 0 rpm              | [29]       |
| SrRuO₃⁺            | 0.994               | 0.443                | Nb:SrTiO₃         | PLE               | RM              | —                   | (100)       | 4.5 × 10⁻³                 | —                        | 78                     | CV, 0 rpm              | [87]       |
| SrRuO₃⁺            | 0.994               | 0.443                | Nb:SrTiO₃         | PLE               | RM              | —                   | (100)       | 3.6 × 10⁻³                 | —                        | 109                    | CV, 0 rpm              | [87]       |
| LaCoO₃            | 0.996                | 0.400                 | LaAlO₃            | Sol-gel          | DM              | —                   | (100)       | 1.5 × 10⁻⁴                 | —                        | —                      | CV, 0 rpm              | [88]       |
| LaCoO₃⁺            | 0.996               | 0.400                | LaAlO₃            | Sol-gel          | DM              | —                   | (100)       | 2.3 × 10⁻⁴                 | —                        | —                      | CV, 0 rpm              | [88]       |
| LaCoO₃⁺            | 0.996               | 0.400                | LaAlO₃            | Sol-gel          | DM              | —                   | (110)       | 3.6 × 10⁻³                 | —                        | —                      | CV, 0 rpm              | [88]       |
| La₀.₈Sr₀.₂CoO₃     | 1.005                | 0.396                 | SrTiO₃            | PLD              | n/r             | —                   | (100)       | —                        | —                        | —                      | CV, 0 rpm              | [89]       |
| La₀.₈Sr₀.₂CoO₃     | 1.005                | 0.396                 | SrTiO₃            | PLD              | n/r             | —                   | (110)       | —                        | —                        | —                      | CV, 0 rpm              | [89]       |
| La₀.₈Sr₀.₂CoO₃     | 1.005                | 0.396                 | SrTiO₃            | PLD              | n/r             | —                   | (111)       | —                        | —                        | —                      | CV, 0 rpm              | [89]       |
| La₀.₈Sr₀.₂CoO₃     | 1.005                | 0.396                 | SrTiO₃            | PLD              | n/r             | —                   | (100)       | —                        | —                        | —                      | CV, 0 rpm              | [89]       |
| La₀.₈Sr₀.₂CoO₃     | 1.005                | 0.396                 | SrTiO₃            | PLD              | n/r             | —                   | (110)       | —                        | —                        | —                      | CV, 0 rpm              | [89]       |
| La₀.₈Sr₀.₂CoO₃     | 1.005                | 0.396                 | SrTiO₃            | PLD              | n/r             | —                   | (111)       | —                        | —                        | —                      | CV, 0 rpm              | [89]       |
| La₀.₈Sr₀.₂CoO₃     | 1.005                | 0.396                 | SrTiO₃            | PLD              | n/r             | —                   | (111)       | —                        | —                        | —                      | CV, 0 rpm              | [89]       |
| La₀.₈Sr₀.₂CoO₃     | 1.005                | 0.396                 | SrTiO₃            | PLD              | n/r             | —                   | (111)       | —                        | —                        | —                      | CV, 0 rpm              | [89]       |
| La₀.₈Sr₀.₂CoO₃     | 1.005                | 0.396                 | SrTiO₃            | PLD              | n/r             | —                   | (111)       | —                        | —                        | —                      | CV, 0 rpm              | [89]       |
| La₀.₈Sr₀.₂CoO₃     | 1.005                | 0.396                 | SrTiO₃            | PLD              | n/r             | —                   | (111)       | —                        | —                        | —                      | CV, 0 rpm              | [89]       |
| Material                      | Tolerance factor ($\delta$) | Octahedral factor ($\mu$) | Electrode type | Conductivity ($\sigma$) | Orientation | Electrocatalytic method | Reference |
|------------------------------|----------------------------|---------------------------|----------------|-------------------------|-------------|------------------------|-----------|
| SrCoO$_3$−δ                 | 1.036                      | 0.384                     | P/E            | 0.14                    | (100)       | DM                     |           |
| SrCoO$_3$−δ                 | 1.036                      | 0.384                     | P/E            | 1.11                    | (100)       | DM                     |           |
| SrCoO$_3$−δ                 | 1.034                      | 0.387                     | P/E            | 6.91                    | (100)       | DM                     |           |
| SrCoO$_3$−δ                 | 1.033                      | 0.389                     | K/P/E          | 8.91                    | (100)       | DM                     |           |

Note: Calculations are based on various methodologies and references cited in the original paper.

Abbreviations: RHE = reversible hydrogen electrode; CV = cyclic voltammetry; CA = chronoamperometry; P/E = pulsed electrode; DM = disk masked; DA = disk assembly; n/r = not reported.

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Strain due to lattice mismatch can also lead to segregation [79–82]. Finally, catalysis of the OER occurs on the perovskite surface, which is a discontinuity of the crystal lattice leading to structural distortions and localized electronic states.

The perovskite structure can stabilize a large number of vacancies and some compositions (e.g. La$_{0.66}$TiO$_3$, La$_{0.33}$NbO$_3$, La$_{1-x}$Sr$_x$CoO$_3$) are particularly prone to the formation of oxygen (ABO$_{3-\delta}$) or cation (A$_{1-x}$BO$_3$) vacancies [83–86]. In epitaxial films, oxygen vacancy formation is promoted by tensile strain, i.e. when the octahedra in the film are pulled apart, as discussed, e.g. by Wang et al [54]. Despite the likelihood of vacancies in the perovskite structure, it is often not reflected explicitly in the formula, which is written for the stoichiometric case (i.e. ABO$_3$). All values for $t$ and $\mu$ in table 1 were calculated assuming the stoichiometric case if non-stoichiometry was not explicit in the reported formula. The presence of oxygen vacancies reduces the coordination of the B-site and, to a lesser degree, that of the A-site, which reduces the ionic radius of these cations. Therefore, oxygen vacancies reduce $\mu$ and increase $t$. Cation vacancies reduce the coordination of oxygen and the other cation species as well as oxidize the B-site. Thus, they also lead to an increase in $t$ and decrease in $\mu$. Importantly, the presence of vacancies can drastically alter the material properties, such as the electronic conductivity [87] and the electrocatalytic activity [88], as well as lead to a change in the mechanism of the OER [88]. Unfortunately, this phenomenon has not yet been studied extensively for epitaxial films.

The presence of the aforementioned defects, in particular vacancies, may foster segregation, the enrichment of atoms in a microscopic region, often the surface, by minimizing interfacial energies and enhancing diffusion [79, 82, 89, 90]. As the diffusion coefficient generally increases with temperature, segregation is often discussed in the context of higher temperature devices for oxygen electrocatalysis such as solid oxide fuel cells and electrolyzers that are not covered here. However, the temperature during film deposition is comparable and may lead to segregation in an unoptimized deposition. Additionally, segregation may also be triggered by internal strain or by mismatch between the substrate and the perovskite film [81, 91]. Overall, the impact of segregation has not been investigated for the room temperature OER on perovskite oxides and there are only few reports overall, e.g. in [92].

In summary, the criteria for the definition of bulk perovskites are well defined. Yet, many perovskite oxides studied as catalysts for the OER fall outside the stability range predicted by the Goldschmidt model, where a third (28%) of all investigated perovskites are found in the top left corner of the red area in figure 1 and thus outside of the Goldschmidt model. While these make up only a small percentage of all possibly stable perovskites, a better model would be desirable for those perovskite oxides used as electrocatalysts for the OER. Additionally, tolerance and octahedral factors based on measured bond distances would be likewise desirable, particularly for epitaxial films where different values could arise due to defects, dislocations and strain between the substrate and film. Defects play an important role in the structure and properties of perovskite oxides, in particular epitaxial films. Their formation can be caused by several reasons, but the effect of defects (especially oxygen and cation vacancies) has not been studied extensively for low-temperature electrocatalysis.

3. Synthesis methods

Perovskite oxides can be epitaxially deposited by a multitude of thin film deposition methods. These can generally be classified by how the atoms for deposition are produced, namely using light, ballistics, heat or solvation, and by how these atoms react, namely, physically or chemically. The nature of production and deposition determines which substrates are suitable (e.g. conductive or insulating) and it affects the film properties and films of nominally identical composition may thus differ, e.g. in the type and concentration of defects or in morphology, when prepared by different methods. An in-depth discussion of epitaxial film deposition is beyond the scope of this review and the readers are referred to [93–100].

The epitaxial oxides reported as catalysts for the OER were made by mainly pulsed laser deposition (PLD; most general, i.e. any microstructure and crystallinity), pulsed laser epitaxy (PLE; epitaxial PLD) or pulsed reactive crossed-beam laser ablation (PRCLA), where the atoms are produced by laser ablation of a target and react physically with the substrate surface [98, 101, 102]. These methods amount to 64% of all entries in table 1. The next most popular methods for producing thin films are based on sputtering, namely ion-beam sputtering (IBS) and radio-frequency magnetron sputtering (RFMS). The atoms for deposition are produced ballistically by bombarding a target material with high-energy ions in IBS. In RFMS, the ions of an argon plasma are accelerated by a radio-frequency potential towards the target, and the sputtering yield is further increased by a magnetic field [93–96]. The atoms react physically upon deposition on the substrate. Epitaxial films were also made by molecular beam epitaxy (MBE) and oxygen plasma-assisted MBE (OPA-MBE), where molecular beams are directed towards the substrate. The atoms for deposition are usually produced
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from thermally evaporated elemental target materials. An oxygen plasma can be used to prepare oxide films by physical reactions with the substrate [95, 97].

Epitaxial thin films have also been made by chemical rather than physical methods. The sol-gel method can be used to obtain thin films with different orientations [68, 71]. The ions for deposition are dissolved homogeneously mixed soluble salts in solutions that are applied onto the substrate by spin-coating or similar techniques. The film forms upon chemical reaction of the dissolved ions with the substrate.

The wetting of the deposited ions on the substrate determines the microstructure and whether a closed film forms. In a simple model, the surface energy may be such that it is minimized by deposition of ions on the used substrate or that it is minimized by grouping multiple deposited ions. The former case will give monolayers and layer growth if the spreading is still favored (Frank–van der Merwe growth) and the latter case will give island growth (Volmer–Weber growth). Various microstructures have been reported for epitaxial oxides used as catalysts for the OER (figure 2). Most substrates are not cut exactly along the desired crystal orientation but have a slight misalignment. This produces a terraced surface, which usually requires an etching step [103] or a thermal treatment [104] for uniform sharp steps. In the best case, the epitaxially deposited film conforms to the well-defined morphology of the substrate (figure 2(a)). The growth of the epitaxial film may produce decorations on the terrace edges (figure 2(b)) or roughen the terrace edges (figure 2(c)). A smooth granular structure may also cover the (possibly present) terrace edges (figure 2(d)) or even produce a different microstructure, e.g. of micron-sized islands (figure 2(e)). The morphology is important for systematic investigations, where exposure of a single surface facet is highly desired. Any structural defect, such as step edges, kinks, vacancies, adatoms or islands, exposes secondary high-index facets. These defects, particularly step edges, have also been proposed as active sites for metal electrocatalysts [105, 106]. Despite their different morphologies, all films shown in figure 2 showed epitaxial growth by x-ray diffraction (XRD).

The perovskite oxide films herein were deposited mainly on SrTiO$_3$ (STO) with or without doping with Nb (often 0.5 wt%) to make the substrate conductive (66% of all entries in table 1). SrTiO$_3$ is a cubic perovskite ($t = 1.002, \mu = 0.432$) with a lattice parameter of $a_{\text{STO}} = 3.905$ Å [107]. Nb-doping changes this value insignificantly, e.g. [108]. Many perovskite oxides with first-row transition metal B-sites have similar pseudocubic lattice parameters and thus grow well on SrTiO$_3$, i.e. with small lattice mismatch. Pseudocubic means that the actual space group of the perovskite is orthorhombic or rhombohedral ($t < 1$), but the unit cell is translated and rotated to resemble a cubic one [109]. This pseudocubic unit cell may further be rotated with respect to the cubic unit cell of SrTiO$_3$ to minimize lattice mismatch. Other substrates include DyScO$_3$ (DSO), LaSrAlO$_3$ (LSAO), LaAlO$_3$ (LAO), NdGaO$_3$ (NGO) and (LaAlO$_3$)$_{0.3}$(Sr$_2$Ta$_2$O$_7$)$_{0.7}$ (LSAT) (or (LaAlO$_3$)$_{0.3}$(SrAl$_{0.5}$Ta$_{0.5}$O$_3$)$_{0.7}$, for which Petrie et al [61, 74] used the same abbreviation LSAT), where the most common shorthand notations are given in parentheses. These substrates are selected either to minimize the lattice mismatch (e.g. La$_{0.6}$Sr$_{0.4}$CoO$_3$ on NdGaO$_3$ [64]) or to study the effects of deliberate lattice mismatch, i.e. strain, where compressive strain increases the out-of-plane lattice parameter of the film and tensile strain decreases it.

Exemplary out-of-plane $\theta - 2\theta$ scans for NdNiO$_3$ on various substrates are shown in figure 3(a). The 002 reflection of NdNiO$_3$ is indicated by an arrow. A lower angle indicates a larger pseudocubic lattice parameter due to Bragg’s law [111]. In figure 3(b), the calculated lattice parameters (estimated from Young’s modulus using a Poisson ratio of $\nu = 0.23$ [54]) and experimental lattice parameters are compared to the bulk value of NdNiO$_3$ to determine if the strain is compressive (negative values) or tensile (positive values). The inset in figure 3(b) further shows a reciprocal space map of NdNiO$_3$ on SrLaAlO$_4$, which supports in-plane alignment of the (pseudocubic) lattice parameters of substrate and film. Strong strain effects can also be
observed for selection of dissimilar-sized A-site cations in figure 3(c). Yet, the extent of strain may be small for selection of similarly sized cations in the substrate and films, as well as for their mixtures, e.g. La (1.36 Å) and Sr (1.44 Å) [51], on a suitable substrate or buffer layer such as La0.8Sr0.2MnO3 for La1-xSrxCoxO3 deposition on SrTiO3 (figure 3(d)) [57]. Strain is an important parameter as it firstly determines whether epitaxy is possible at extreme values (depending on the composition of film and substrate) and, at less extreme values, what kind of distortions occur to reduce the surface energy of the mismatched interfaces. The coordination octahedra can distort and tilt (further), which affects bond lengths and angles. Electronically, the crystal field splitting is modified, and the covalence and charge transfer between the B-site transition metal and oxygen may change. It has been shown that these properties affect the electrocatalysis of oxygen, which is discussed in more detail below [27, 33, 34, 112–116]. Thus, epitaxially strained films offer a new degree of freedom for the design of electrocatalysts. The insight from these model systems may also be relevant, e.g. for core–shell nanoparticles or other bilayer or multilayer systems. In summary, the film properties depend on the synthesis or deposition method where similar ion sources and deposition mechanisms are expected to produce similar properties. There is no systematic study yet on how comparable nominally identical perovskite oxide films behave electrochemically, which would be a desirable multi-laboratory effort. For identical deposition methods, the growth mode depends on the composition and structural details of the substrate and deposited film. Various morphologies have been reported with different degrees of roughness that must match the desired research goal. Furthermore, epitaxial films offer another degree of freedom for the design of catalysts, namely the strain between the substrate and deposited film. The aspect has been well studied [54, 55, 61, 74], and the influence on the OER has been attributed to resulting changes in crystal field splitting due to octahedral distortion [61] and bond angles, i.e. hybridization [54, 74].

4. Assembly of electrodes for electrocatalytic investigations

Different approaches have been taken to assemble electrodes from epitaxial thin films for electrocatalytic investigations. In order of increasing complexity of the assembly, they range from immersed rectangular electrode assemblies (figure 4(a); ‘rectangular masked’) to square films in an assembly on a rotating disk (figure 4(b); ‘disk masked’) to fabrication of rotating disks for commercial electrode holders (figure 4(c); ‘disk assembly’). Most commonly, the substrate is connected to the working electrode lead of the potentiostat (‘back contact’), and Ti/Au or Ti/Pt metal contacts are fabricated to ensure ohmic contact with the electric contacts in the holders or with the used wire. Alternative connecting schemes are used when the substrate
required for epitaxy is not conductive. Details of the assembly and the advantages or disadvantages of the three approaches are discussed in the following paragraphs.

Rectangular masked electrodes are commonly made by attaching a suitable wire, often Ti, to an epitaxially deposited substrate (figure 4(a) i). This approach is used most frequently in electrocatalytic investigations with epitaxial oxides (70% of all entries in table 1). In addition to the aforementioned back contact, the wire can be connected to the active layer (‘front contact’) or to both the active layer and the substrate (‘side contact’). Initial fabrication steps often include cleaning of the contact area and wire and roughening of the contact areas. It should be noted that the latter procedure will likely expose the substrate and connect it electrically. Further fabrication steps include application of an In–Ga eutectic to make an ohmic contact between the oxide and metal, application of silver paint for fixation and finally masking the substrate back, sides and contact area using non-conductive chemically resistant epoxy. In an alternative approach [64], the rectangular sample is not masked by epoxy but by clamping a cover onto the surface (figure 4(a) ii). In this example, a 6 mm O-ring (not shown) is used to define the electrochemical surface exposed to the electrolyte. The advantages of these electrodes are the ease of fabrication and the compatibility with standard rectangular substrates of sizes 5 × 5, 5 × 10 or 10 × 10 mm². The limitations are the lack of control over charge transport, which is much less of an issue for the OER compared to other reactions such as the oxygen reduction reaction (ORR), and the difficulty in performing spectroscopic or microscopic post-mortem characterizations on masked samples. Yet, the latter point is alleviated by clamping the sample.

Rectangular epitaxial films can also be adapted to a rotating disk, either by gluing them to the surface (not shown) [61] or masking them with a circular aperture (figure 4(b)). We could not find further information on the glued samples, but this approach likely did not yield a circular electrochemical area and the analytical expression of the limiting current may be unknown. The masked setups are used by the Kan and Chueh groups [103, 117]. In the shown example, a 10 × 10 mm² substrate was masked by a cover with a 7 mm diameter aperture, which effectively converts the square film to a disk for electrocatalytic experiments. A back contact is the most natural connection in this approach. The home-made holder could then be mounted onto a conventional rotator and used akin to regular disks. While the OER in aqueous solutions is not limited by the reactants water or hydrogen, the forced convection by rotation removes bubbles from the surface. Additional advantages of this approach are the reusability of the epitaxial film for post-mortem investigations, and the control over mass transport. Disadvantages are possible contributions of stray resistance and capacitance of the covered film parts as well as the necessity to construct a holder.

Epitaxial films can also be deposited directly on circular substrates (figure 4(c)) [59, 66, 67, 69]. This approach is used by the Markovich [66], Shao-Horn [59], Jooss [59, 67, 76] and Risch [69] groups. For the latter three groups, these epitaxially deposited substrate disks are then connected by an In–Ga eutectic onto suitable conductive metal disks, e.g. made of stainless steel or aluminum. Additional fixation is provided by strips of double-sided carbon tape. The small gap between the support disk and the deposited substrate is finally filled with non-conductive epoxy. The disk electrodes assembled by this approach have been successfully mounted in commercial holders of rotating disk electrodes (RDE) and rotating ring-disk electrodes (RRDE) with 4 mm [59, 67, 69, 76] and 5 mm diameter [59, 66] in the same way a commercial metal disk or glassy carbon disk would be mounted. This approach also allows control over mass transport. Furthermore, the ring can be used to detect products such as oxygen, when mounted into an RRDE. The disadvantage is the complex assembly that only allows contacting on the back, which restricts it to conducting substrates, and the assembly complicates post-mortem analysis.
In summary, three different approaches for fabricating electrodes from epitaxial perovskite oxides have been discussed. Each has its own advantages and disadvantages as listed above, which can serve as a guide to new researchers in the field as to which preparation is best to achieve their research goals.

5. Semiconductor physics of epitaxial electrodes

The perovskite oxides reviewed herein are semiconductors and not metals, which is an important distinction for the necessary charge transfer from the solid to hydroxide/water in solution [118]. Yet, some perovskite oxides, e.g. La$_{1-x}$Sr$_x$CoO$_3$ [57], behave closely to p-type metals and should not be generally treated as classical semiconductors. On metals, charge transfer is possible within a bandwidth of a few $k_B T$ (~25 meV near room temperature) from the Fermi level, i.e. it is thermally activated. In contrast, the Fermi level in intrinsic semiconductors falls between the band gap and charge transfer can only occur from levels within the valence or conduction bands, which requires higher energy. Furthermore, the charge carrier concentration in metals is usually not a limiting factor, while it can be a severe limitation for semiconductors. For the latter, the distinction between the majority carrier and the minority carrier (i.e. electrons or holes) is important. An n-doped semiconductor is one with the Fermi level (or localized states such as surface states) near the conduction band where electrons are the majority carriers (e.g. Nb$^{5+}$ ions on Ti$^{4+}$ sites in Nb: SrTiO$_3$), while a p-doped semiconductor has the Fermi level near the valence band (VB) and holes are the majority carriers (e.g. La$_{0.88}$Sr$_{0.12}$FeO$_3$ in table 1). The concentration of the majority carriers may be similarly high to metals, while the concentration of minority carriers certainly limits the charge transfer rate. Since the desired reaction here is the oxidation of hydroxide/water to oxygen, the relevant charge transfer is that of a hole from the surface of the solid to adsorbed hydroxide/water and high hole concentration is desirable.

The OER requires the transfer of four electron holes from the perovskite surface to hydroxide (alkaline) or water (neutral/acid). The composite electrodes discussed here have a liquid–solid interface between the electrolyte and the surface of the active perovskite as well as at least one buried solid–solid interface between the active interface and either a buffer layer or the substrate (figure 5(a)). With the exception of La$_{0.88}$Sr$_{0.12}$FeO$_3$, all oxides in table 1 have bulk conductivities of at least 0.8 S cm$^{-1}$ and can thus be considered good conductors. Yet, charge transfer of some of composite electrodes is hindered at one of the interfaces, which is independent of bulk conductivity and instead depends on the band gaps, the alignment of the bands and the relative electron affinities on either side of the interface. Since electron holes are transferred, we focus on the VB. Three possible cases are shown in figure 5(a): (i) all ohmic contacts, where the holes can transfer across the internal interface and the surface; (ii) an ohmic contact at the internal interface, but a blocking Schottky contact at the surface that prevents hole transfer due to unfavorable band bending; and (iii) an ohmic contact at the surface, but a Schottky contact at the internal interface. Whether charge transfer across an interface or surface limits catalysis can be investigated using a fast redox couple with a single charge transfer as a charge acceptor simpler than the multi-step catalytic reactions, such as the OER.

A convenient choice for investigations of charge transfer in alkaline electrolytes is the ferri-/ferrocyanide (FCN) redox with reversible potential of $E^\circ \approx 1.2$ V vs. an RHE that is similar to the reversible potential of water oxidation of $E^\circ = 1.23$ V vs. RHE in alkaline media. (Note: $E^\circ$ of FCN depends on the pH on the RHE scale while that of the OER does not). The textbook example of the CV trace of a fast redox on a metal electrode is shown in figure 5(b). It is symmetric about the reversible potential between the oxidation and reduction peaks. If the CV on a semiconductor looks comparable to that in figure 5(b), then it behaves like a metal electrode that can both oxidize and reduce FCN, which cannot be assumed a priori for a semiconducting oxide. Additional complications may arise in epitaxial oxide films due to blocking behavior, as discussed above. The two peaks in the textbook example have approximately identical currents above the baseline before the onset of the catalytical rise, and the expected separation is 59 mV at 25 °C independent of slow sweep speeds (10’s of mV s$^{-1}$) [121, 122]. However, the latter value is rarely observed in aqueous solutions, even when using metal electrodes [123–125], possibly due to interactions between the surface and FCN [126–128]. The reported values on perovskite oxides are in the range of 90–115 mV for the reversible CVs [59, 110, 120] and are much larger if charge transfer across an interface is limiting.

The shape of the CV of FCN depends not only on the chemistry of the surface film, but also on its thickness and the choice of the substrate, where the latter two are specific to epitaxial oxide layers. In exemplary measurements on ANiO$_3$ (figure 5(c)), the peak currents of the FCN redox reduced in the order A = La, Nd, Sm, Gd. For Sm at the A-site, the shape is severely distorted with no discernable peaks, and no currents were detected for Gd at the A-site [58]. The authors show that SmNiO$_3$ and GdNiO$_3$ had the lowest bulk conductivities in the series. Yet, additional interfacial barriers may exist, which would be desirable to quantify.

The effect of the substrate composition on the FCN redox was investigated by Stoerzinger et al (figure 5(d)) [55]. An example is LaCoO$_3$ where the peak heights and separations increase from LSAT.
Figure 5. Influence of the band structure on electrochemical charge transfer. (a) Schematic band structures showing (i) a non-blocking contact for hole transfer, (ii) transfer blocked at the liquid–solid interface and (iii) transfer blocked at an internal solid–solid interface. (b) A textbook example of a fast redox couple recorded on an electrode with metallic conduction. The corresponding measurements on epitaxial perovskite oxides may differ due to blocking interfaces for unsuitable (c) composition, (d) substrate or (e) film thickness. Panels b, d were reproduced with permission from [55, 119]. Copyright American Chemical Society 2015, 2018. Panel c republished with permission of John Wiley and Sons from [58]. Panel e republished with permission of the Royal Society of Chemistry from [120].

$((\text{LaAlO}_3)_{0.3} (\text{Sr}_2\text{AlTaO}_6)_{0.7})$ to STO (SrTiO$_3$) to LAO (LaAlO$_3$). The curves remain symmetric, which indicates a reduction of available charge carriers rather than blocking due to bending bands at the surface. The authors argue that intermediate and high spin Co is formed due to tensile strain, as reported previously [129]. It is plausible that this affects the number of available charge carriers, which has not been investigated systematically.

Stoerzinger et al [120] also investigated the effect of LaMnO$_3$ film thickness on Nb-doped SrTiO$_3$ (figure 5(c)), where a 10 nm film showed the desired symmetric CV, while 5 nm films became slightly asymmetric with reduced currents, and films below 2 nm could not oxidize FCN and showed severely lowered onset and currents for reduction. The authors attribute the deactivation to a reduction of Mn$^{3+}$ (in the bulk of LaMnO$_3$) to Mn$^{2+}$ on the surface and band bending on the surface. Due to the bulk Fermi levels, an electron-rich space charge layer at the surface (i.e. a reduced surface) was expected, and the authors argue that only the space charge layer of the inactive Nb-doped SrTiO$_3$ formed for the thinnest LaMnO$_3$ films. While this sets a physical boundary to the minimal film thickness, the effect can be exploited to deposit very thin functional surface layers on active films, e.g. as demonstrated by Eom et al [130] and Akbashev et al [103].

In summary, we have discussed charge transfer from semiconducting electrodes to species in solution where blocking contacts or insufficient charge carriers may limit the charge transfer. This could mistakenly be attributed to the thermodynamics or kinetics of catalysis, and it is therefore an important aspect to investigate before the interpretation of catalytic measurements. The experiments and their interpretation are straightforward, and we urge everyone in the field to report this information for any new combination of perovskite film and substrate composition as well as the film thickness.

6. Electrocatalytic mechanisms of the oxygen evolution reaction

Very little is known conclusively about the mechanism of the OER on perovskites and oxide surfaces in general as the nature of the involved intermediates remains elusive. In both experimental and theoretical works, a mechanistic sequence is first proposed and then checked against the expected mechanistic parameters (defined below) or free energies. Thus, we take a similar approach in this section by first presenting elementary steps and prototypical mechanisms, which then are discussed in the context of available experimental and theoretical literature.
Figure 6. Proposed mechanisms for the oxygen evolution reaction in alkaline medium on oxides with perovskite structure: (a) adsorption mechanism, (b) oxygen coupling mechanism and (c) lattice oxygen mechanism.

The elementary processes of all mechanisms of oxygen evolution must be:

- P1) Adsorption of OH\(^{-}\) (alkaline) or H\(_2\)O (neutral, acid)
- P2) Formation of intermediates to aid charge transfer and lower catalytic barriers
- P3) Diffusion of adsorbed species and surface atoms in general
- P4) Transfer of electrons/holes and protons/hydroxide to/from the catalyst surface
- P5) Formation of the O–O bond
- P6) Release of O\(_2\)

We assumed a hydroxylated surface (M–OH) as the starting point of the catalytic cycles. This is supported by an in situ study of Stoerzinger et al.\([131]\), where the surface coverage of hydroxide was 50% or higher on LaBO\(_3\) perovskites already at 30% relative humidity. In contrast, a bare non-hydroxylated surface is often assumed as the starting point of the catalytic cycles in the literature. The argument in favor of a bare surface is that the slow processes, such as O–O bond formation, determine the surface coverage\([132]\) during a steady-state. However, this requires that nearly all sites on a surface are simultaneously active sites, which the authors deem unlikely. While there is no direct experimental evidence for epitaxial perovskite oxide films, catalytic hot spots have been observed for photocatalytic OER on TiO\(_2\)\([133]\) and for electrocatalytic hydrogen evolution on Pt(111)\([134]\). The implications of the choice of starting point on the mechanistic parameters are discussed below.

In alkaline solution, four hydroxide anions and four electrons (P4) need to be transferred to catalytically evolve oxygen. There is little to no discussion of the diffusion of adsorbed species and surface atoms (P3) but this process may occur, e.g. it was observed in water vapor\([135]\). The above processes do not necessarily occur in the order P1 to P6 and some processes may occur repeatedly, e.g. P4, as we discuss below for three prototypical oxygen evolution mechanisms.

The adsorbate mechanism is most commonly discussed for perovskite oxides (and other oxides). It focusses on the role of adsorbates on a single metal site (figure 6(a)). An early discussion can be found in the works of Kobussen and coworkers\([136, 137]\). Variants of this mechanism are also most frequently considered in density functional theory (DFT) calculations\([21, 23, 26]\). The mechanism works on a single metal site that is initially OH-covered. Then, it continues with the deprotonation of the OH surface group to M = O (step a1). Subsequently, OH species from the electrolyte form OOH on the metal site (a2), which is followed by deprotonation to M–OO (step a3). Finally, O\(_2\) is replaced by OH and thus released (step a4). Each interaction with a hydroxide from the electrolyte in steps a1–a4 is coupled to an electron transfer. The rate-limiting step is commonly assumed to be either the formation of the O–O bond (step a3) or the deprotonation of OOH (step a4)\([138]\).

The oxygen coupling mechanism avoids highly energetic hydroperoxide intermediates (figure 6(b)). While this has already been proposed by Bockris in the 1950s\([132]\), there has been little discussion of this mechanistic scenario in recent years. However, variants of this mechanism have been proposed\([139]\) for the amorphous transition metal (hydr)oxide layers that form on some perovskite oxides during the OER\([140–142]\). The resting state is again an OH-covered surface. Yet, the participation of at least two metal sites is required in contrast to the adsorption mechanism. The first step is the deprotonation of two OH groups and coupling of two M = O motifs to form the O–O bond (step b1). Molecular O\(_2\) is released and leaves two undercoordinated metal sites (step b2). These sites adsorb water molecules during the next step (step b3), followed by protonation of the latter (step b4). We again assumed that each hydroxide transfer is coupled to an electron transfer. Plausible rate-limiting steps are the meeting of two M = O motifs and/or their coupling (step b1). In the first case, diffusion must play an important role for this mechanism.
The oxygen vacancy mechanism also involves coupling but with participation of the lattice oxygen (figure 6(c)). Mass spectroscopic evidence for such a mechanism was reported early by Wohlfahrt-Mehrens and Heitbaum [143] for rutile RuO₂. It has recently received considerable attention as an alternative to the adsorbate mechanism in recent years due to the high activity of perovskite oxides with high-valent later transition metals, such as Pr₀.₅Ba₀.₅CoO₃₋ₓ [116], Ba₀.₅Sr₀.₅CoO₃₋ₓ [27], SrCoO₃₋ₓ [144] and strained LaNiO₃ [61], and in theoretical investigations [145–147]. The initial state is again assumed to be an OH-covered surface. The initial deprotonation during the first step is coupled with the formation of an O–O species, either in a terminal or bridging position, and the formation of an oxygen vacancy in the perovskite lattice (step c₁). The distance between coupling oxygen atoms is much smaller in step c₁ compared to step b₁ (of the previously discussed mechanism). Subsequently, O₂ is released and one of the two empty sites (terminal or bridging position) is replaced by OH from the electrolyte (step c₂). Then, another OH from the electrolyte occupies the vacancy in the bridging position (step c₃). Step c₃ may also occur before step c₂.

These last two steps are crucial to recover the catalyst without structural disintegration during the OER. Finally, the bridging site is deprotonated (step c₄). Grimaud et al [144] propose, based on the observed pH dependence, that either the deprotonation of the bridging oxygen (c₄) or a terminal oxygen (c₁) is rate-limiting. Here, it is important to note that it is the first step in their proposed mechanisms (in contrast to our prototypical mechanism in figure 6(c)). Diffusion of oxygen vacancies in the bulk, particularly towards the surface, may play an important role in this mechanism.

Microkinetic analysis can be used to obtain the electrochemical key parameters of the rate-limiting step, namely the Tafel slope ($b = \partial E/\partial \log(i)_{p,M}$) and the reaction order with respect to pH ($\nu = \partial \log(\nu_{p,M})/\partial \log(\nu_{p,M})_{E}$). The former is obtained by chronoamperometry or chronopotentiometry in a given range or sufficiently slow potential sweeping, while the latter requires the same measurements in electrolytes with different pH. A more comprehensive discussion of these parameters (and the related Nernst slope) can be found, e.g. in [148]. Many assumptions and approximations are made during the microkinetic analysis: the partial derivatives are not explicitly solved, the kinetic constants of the steps before the limiting one are assumed to be much faster than the rate-limiting step, and the limiting case of the surface coverage (meaning abundance of a specific intermediate) is evaluated. The results of the microkinetic analysis is usually found as tables in the literature, e.g. in Bockris and Otagawa [36], where $b = \text{RT}/2\text{F}$ (30 mV dec⁻¹ at standard conditions), $\nu = 3$ (on the standard hydrogen electrode (SHE) scale [149]) when step a₂ is limiting and $b = \text{RT}/5\text{F}$ (24 mV dec⁻¹), $\nu = 4$ when step a₃ is limiting, both under the assumption of negligible coverage (Langmuir isotherm) with the limiting intermediate (i.e. low current/overpotential) and a bare starting surface. When step b₁ is limiting, then $b = \text{RT}/4\text{F}$ (15 mV dec⁻¹), $\nu = 4$ using the same assumptions. The oxygen vacancy mechanism was not treated by Bockris and Otagawa. As the limiting step c₁ is an electrochemical one, a Tafel slope of 2RT/F (120 mV dec⁻¹) is expected and $\nu = 1$ as one hydroxide/proton transfer is involved.

These predicted Tafel slopes are rarely reported in the literature. The values of the Tafel slopes in table 1 range from 36 mV dec⁻¹ (NdNiO₃ on STO) to 141 mV dec⁻¹ (LaNiO₃ on LAO). A Tafel slope near 30 mV dec⁻¹ is reported for PrNiO₃ and NbNiO₃ on SrTiO₃ [68] but the reaction order is unknown. For PrNiO₃ on SrTiO₃, a Tafel slope of 139 mV dec⁻¹ is reported in a different study [54], which is closer to 120 mV dec⁻¹. Clearly, the assumptions and approximations are too restrictive to account for commonly observed values, and factors other than chemical composition (e.g. surface roughness) may play an important role. An improved treatment by Shinagawa et al [150] explicitly treats changes in surface coverage, and Fletcher [151] argues that some Tafel slopes may depend on the reorganization energy (from Marcus theory). We also note that electrochemical side reactions may influence the experimental Tafel slope and that it is preferable to obtain the Tafel slope of the OER using an oxygen sensitive detector [59, 148]. Catalytic cycles with a hydroxylated surface (i.e. M–OH, as in figure 6) have higher Tafel slopes (νₚ,M-OH = νₚ,M − 1) and lower reaction order ($ν_{p,M-OH} = ν_{p,M} − 1$) compared to those cycles with bare surfaces (denoted as M). Overall, the verification of mechanistic proposals by the experimentally accessible parameters of the Tafel slope and reaction order is highly ambiguous and should be complemented by in situ/operando spectroscopy and microscopy [57, 67, 152], or theoretical studies of the reaction thermochemistry or kinetics.

Much of the current atomistic understanding of the mechanism of the OER is based on theoretical work [21, 23, 25, 26] on the reaction thermodynamics, which is a field too vast to cover comprehensively here. Instead, we give a broad overview and refer the readers to an in-depth discussion elsewhere [153]. In most theoretical works on the OER, the energies of possible intermediates in a catalytic cycle are calculated by DFT. The free energy difference between the intermediates can be used to evaluate if a reaction will proceed along a given reaction path or another one with lower energy difference, i.e. thermodynamic barriers. Moreover, the analysis yields the potential-determining step (in analogy to the rate-determining step [154]). The thermodynamic equilibrium potential of oxygen evolution from adsorbed water/hydroxide is 1.23 V at standard conditions. Thus, thermodynamic barriers in an ideal catalyst are all 1.23 eV. Yet, in real catalysts the thermodynamic barrier heights were predicted to differ [23]. Furthermore, the reaction steps are not
independent as those intermediates, e.g. with single bonds (OH, OOH), interact identically with any surface due to so-called scaling relations [21, 155–158]. These scaling relations have two consequences. First, the free energy difference between these intermediates is fixed, and larger than $2 \times 1.23 \text{ eV}$ of the ideal catalyst, mostly values of around 3.2 to 3.4 eV, are calculated [23]. The energy difference to twice the value of the ideal catalyst imposes an additional overpotential on the OER of the order of 0.3 V, which is predicted to be lower for oxygen vacancy mechanisms [147]. The second consequence is that the free energy difference between intermediates with a single (M–OH) and double bond (M = O) is a surprisingly simple and universal descriptor of the OER in light of the (usually) four steps of the mechanism. A descriptor is a catalyst property that influences activity (and is consequently plotted on the x-axis of property-activity relationships), which will be discussed in detail in the next section. We need to point out that this descriptor was derived for the adsorbate mechanism (figure 6(a)) and gives different trends for the oxygen vacancy mechanism [147].

In summary, three prototypical mechanisms of the OER have been identified. Experimental mechanistic parameters were ambiguous, which calls for supporting in situ or operando spectroscopy and microscopy as well as atomic theoretical insight. Theoretical investigations of the thermodynamics and, in particular, the scaling relations have been an important reduction of complexity to understand the differences in activity among perovskite oxides (and other catalysts). While the trends can be compared qualitatively to experiments, a highly desirable quantitative comparison requires further interdisciplinary developments, not only of theoretical methods but also of well-defined experimental model systems, such as epitaxial perovskite oxide films. Current theoretical developments include an explicit prediction of the kinetics [146, 159, 160] so that currents (and Tafel slopes) can be compared to experiments. We hope that the data compiled in table 1 and analyzed in the next section is a fruitful starting point to identify the most promising model electrodes for combined theoretical–experimental insight into the complex processes during the OER on complex composite oxide systems, such as epitaxial perovskite oxides.

7. Activity trends

Table 1 comprehensively lists all investigations of the OER using epitaxial oxides with perovskite or double perovskite structures, for which the electron transfer across the surface was not limiting as either probed by FCN redox or evidenced by significant OER currents. The perovskite structure was experimentally verified for all entries in the table.

Common performance metrics of the OER are the currents normalized by the active area at a fixed voltage or the voltage, often overpotential, at fixed current density. All investigated films are very smooth so that the area exposed to the electrolyte can be taken as the oxide area, and this normalization is representative of the intrinsic activity. The best catalyst has high currents and low overpotential. We evaluated the overpotential at 50 $\mu$A cm$^{-2}$ $\text{ox}$ in our discussion, which has also been used previously for powders [27]. There is no benchmark voltage/overpotential for an intrinsically highly active catalyst evaluated at this current density (or any other current density per oxide area). Yet, benchmark targets exist for catalytic electrodes, which are normalized by the geometric area of the electrode (rather than that of the active oxide). The two most popular ones are 10 mA cm$^{-2}$ $\text{geo}$ [161], which matches the expected current density drawn by a solar water-splitting device with 10% efficiency under 1 sun illumination as well as 500 mA cm$^{-2}$ $\text{geo}$ for alkaline industrial electrolyzers [162]. However, both benchmark numbers use electrodes with high surface area to achieve these geometric current densities. Thus, we find them unsuitable for flat epitaxial perovskite oxides. Instead, the benchmark should arise from intrinsic properties of perovskites. We propose to use the boundary of the perovskite stability range ($t = 1.00(1)$ and $\mu = 0.41(1)$) as a fundamental reference for stable and active perovskite oxides. We define the 10th percentile (10% of all reported perovskites with these properties have lower overpotential and 90% higher overpotential) at 0.33 V for 50 $\mu$A cm$^{-2}$ $\text{ox}$ as a fundamental benchmark value that a good perovskite oxide catalyst can achieve and potentially retain for prolonged electrolysis. The value is similar to fundamental benchmarks in other contexts, namely the fundamental overpotential limit of 0.3–0.4 V predicted by the scaling relations (see above) and to the overpotential of ~0.3 V at which oxygen evolution in natural photosynthesis operates [163]. Significantly lower overpotentials may be at the cost of catalyst degradation (due to instability of the bulk perovskite structure), and higher overpotentials may indicate catalytic or semiconductor limitations.

The Tafel slope is also used as a performance metric as it presents the scaling of the overpotential with the drawn current, where a lower Tafel slope is desirable to minimize power losses (being the product of current and voltage) in devices. Both the Tafel slope as well as a pair of current and overpotential are required for general trends as the observed trends depend on the choice of the chosen reference current or voltage if the catalysts have different Tafel slopes (which is generally the case as in table 1). Some deviations in the trends discussed below may thus be due to differences in Tafel slopes among the catalysts.
There is a clear effect of the orientation of low index surfaces on the overpotential of the OER for SrRuO$_3$ films (table 1) [66], LaCoO$_3$ films [71] and La$_{0.8}$Sr$_{0.2}$CoO$_3$ films [72], as well as single crystals [73]. For SrRuO$_3$, the reported overpotentials with orientation increase in the order (111) $\gg$ (110) $>$ (100) but the measurements suffered from Sr and Ru dissolution, where the most active film dissolved the most cations. Nonetheless, the authors estimate about 90% Faradic efficiency using RRDE measurements. Interestingly, this trend is not confirmed on related investigations of epitaxial rutile RuO$_2$ films, where the reported current densities decrease with orientation in the order (100) $>$ (101) $>$ (110) $>$ (111) [164, 165]. It should also be noted that the trend of Ru dissolution differs, namely (111) $>$ (101) $>$ (100) $>$ (110) [166].

The orientation dependence of perovskite oxides with Co at the B-site has also been studied. The current density of LaCoO$_3$ decreased with pseudocubic orientation in the order (100) $>$ (110) $>$ (111) [71]. In contrast, Sr doping changes the trend on La$_{0.8}$Sr$_{0.2}$CoO$_3$ to (110) $>$ (100) $\approx$ (111) on both epitaxial films and single crystals [72].

Overall, there is no universal trend of activity with orientation of the epitaxial perovskite oxide, and it cannot be assumed a priori that the commonly used (100) orientation produces the most active surfaces. Based on the limited available data, both the A-site and B-site compositions may influence the activity trends with orientation. The defect concentrations, e.g. of oxygen vacancies, and film strain also depend on the orientation and may further affect the observed trends [167]. Furthermore, the trends with surface orientation also complicate comparisons with perovskite oxide powders, where multiple surface facets are present and the larger surface to volume ratio, especially of nanoparticles, fosters the formation of various defects to minimize the surface energy. Nonetheless, epitaxial films and powders with nominally identical composition have been compared where manganese-based perovskites, e.g. La$_{0.8}$Sr$_{0.2}$MnO$_3$ differed and cobalt-based perovskites, e.g. LaCoO$_3$, agreed well [29]. Therefore, all comparisons to powders (also by us below) should be evaluated critically. Further investigations are desirable to rationalize the observed trends with orientation and joint investigations of epitaxial films and powders to transfer the fundamental catalytic knowledge from flat epitaxial films to high surface area nanoparticles in composite electrodes (usually also containing additives to enhance conductivity and binders) for applications.

The reported B-site compositions on the most frequently reported (100)-oriented films mainly focus on transition metals of the first row, namely, Mn (9% in table 1), Fe (8% in table 1), Co (32% in table 1) and Ni (45% in table 1). No systematic series has been reported with identical A-sites, and thus we included several A-site compositions in the comparison (figure 7(a)). The lowest voltage was found for Co- and Fe-based perovskites at fixed A-site composition ($A = La$, La$_{0.8}$Sr$_{0.2}$ or La$_{0.8}$Sr$_{0.12}$), with the lowest overpotential of 0.34 V (1.57 V vs. RHE) on La$_{0.8}$Sr$_{0.2}$CoO$_3$, which is comparable to our definition of a good epitaxial perovskite catalyst for the OER. Perovskite oxides of Ir and Ru have also been reported, where (111)-oriented SrRuO$_3$ may have an even lower overpotential of 0.07 V (1.30 V vs. RHE; table 1) [66]. However, this comes at the cost of severe corrosion, which deactivates the film during the first cycle and may contribute to the current. The least active B-sites contain Mn. Earlier transition metals than Mn and later transition metals than Ni have not been reported yet, and extrapolating the reported trends suggests that they are also less active than B-sites of Co, Fe and Ni, which is also found in powder studies, e.g. in [27].

The majority of the studied A-site compositions contain La (26% in table 1) or La/Sr mixtures (25% in table 1). For the mixtures, the concentration of Sr$^{2+}$ at the A-site is often attributed to an increase in the concentration of M$^{4+}$ cations at the B-site, and thus the B-site valence. The trend with the composition of the A-site was studied by Liu $et$ $al$ [56] for La$_{1-x}$Sr$_x$NiO$_3$ (0.0$<x<0.5$) and by Stoerzinger $et$ $al$ [57] for La$_{1-x}$Sr$_x$CoO$_3$ (0.2$<x<0.6$), as summarized in figure 7(b). In both studies, the lowest overpotential was found between 40% and 50% of the divalent Sr on the A-site, for which a B-site valence of transition metals of the first row, namely, Mn (9% in table below) should be evaluated critically. Further investigations are desirable to rationalize the observed trends with orientation and joint investigations of epitaxial films and powders to transfer the fundamental catalytic knowledge from flat epitaxial films to high surface area nanoparticles in composite electrodes (usually also containing additives to enhance conductivity and binders) for applications.
the carrier concentration as well as mobility may depend on doping \([57]\) and the effective size of the A-site changes, which will modify the tolerance factor.

The influence of the size of the film’s A-site cation on the catalytic activity was studied by Wang et al for the perovskite oxides with ANiO\(_3\) deposited on Nb:STO (figure 7(c)). The highest overpotential of 0.41 V at 50 \(\mu\text{A cm}^{-2}\) was observed for LaNiO\(_3\). The overpotential decreases when La is systematically replaced by Nd, where the lowest overpotential was found for NdNiO\(_3\). An additional reduction of the overpotential to 0.37 V was achieved by replacing 50% of Nd with Sm. The authors attributed the observed trend to the reduction of Ni\(^{3+}\) (e.g. \(^1\)) to Ni\(^{2+}\) (e.g. \(^2\)) and the concomitant formation of oxygen vacancies. These substitutions also decrease the tolerance factor from La (\(t = 0.996\)) to Nd (\(t = 0.958\)) and thus make the more active perovskites less cubic. This puts a natural boundary on increasing the activity with this approach, and the activities in the study showed negligible effects when the effective A-site radius was below 1.28 Å, which suggests that the trend is not continued by further decreasing the effective A-site.

Strain between the substrate and epitaxial films affects many physical properties, including the concentration of oxygen vacancies \([166, 175–178]\), and likewise the catalytic activity, as investigated for various combinations of substrates and perovskite oxides based on Mn \([76]\), Co \([55, 74]\) and Ni \([54, 61]\) (figure 7(d)). In the shown example the lowest overpotential of LaNiO\(_3\) is found for the least strain, where the overpotential increases likely quadratically with positive and negative strain. Thus, minimal strain is strongly recommended for LaNiO\(_3\) films. Yet, for NdNiO\(_3\) films, the activity increases with either compressive or tensile strain \([54]\). The authors argue that the former is beneficial for OER due to an enhanced p-d hybridization \([179]\), and the latter is due to the formation of oxygen vacancies and the concomitant reduction of Ni, which increases the average \(e_g\) occupancy to slightly above unity, i.e. closer to the optimal value \([27]\). The effect of strained films has also been studied for Co at the B-site. Stoerzinger et al \([55]\) found that slightly tensile strain (+1.8%) resulted in the fastest kinetics for charge transfer (figure 5(d)) and also the highest OER activity. The authors argue that tensile strain increases the Co–O bond strength at fixed \(e_g\) occupancy. In contrast, Petrie et al \([61]\) found that the highest tensile strain of +4.2% resulted in the highest OER activity due to the formation of oxygen vacancies. In summary, the effect of strain depends on...
the active film and changes multiple material properties that had been previously correlated with OER activity. Some relaxed perovskite films may already have good properties for oxygen evolution (e.g. eg near 1), while other perovskite films may attain this property through strain (e.g. when the crystal field changes so that a frontier orbital becomes singly occupied). We point out that strain affects a multitude of possible OER descriptors. Therefore, the effect of strain is difficult to predict, and the compositional (e.g. oxygen vacancies) or electronic changes (e.g. hybridization) must be considered to identify the dominant effect on the OER.

The complex effect of seemingly simple substitutions in epitaxial perovskite oxide films on perovskite substrates has been discussed from various angles in this review. As stated above, we here focus on epitaxial systems which are not (strongly) limited by charge transfer. While perovskites are a good material system for systematic investigations, the caveat is that compositional changes affect multiple properties, which may all impact the OER. This is in line with the statistical evaluation of Hong et al [34] who likewise found that multiple properties must be considered for strong predictive relationships, where electron occupancy and metal–oxygen covalency are the dominant factors but structural influences such as M–O–M angles (i.e. octahedral tilt) and the tolerance factor also matter. In our examples in figure 6, the strongest effect on the OER was observed with B-site substitution (110 mV; figure 6(a)), then A-site composition and strain (both 70 mV; figures 6(b), (d)), and finally substitution of the A-site (40 mV; figure 6(c)). These trends agree with the ranking performed for systematic studies of perovskite oxides catalyzing the ORR, where electronic changes on the B-site also had the largest impact and changes on the A-site had the least impact [112]. Yet, these properties are not general enough to be easily transferred to other perovskites or other material classes, which motivates the search for predictive experimental descriptors of activity that relate to mechanistic details, most commonly hydroxide/water adsorption (P1 in section 6), which is a mandatory step for the OER.

Rational design of electrocatalysts for the OER requires fundamental insight into the microscopic origin of activity, which can be derived from structure–activity relationships. In oxygen electrocatalysis, this is frequently called the descriptor approach [23, 27–36], where some physical property of the material serves as the descriptor for catalytic activity. Many experimental descriptors have been proposed and tested for the OER. Popular choices include electronic properties, such as the number of d electrons [28], the number of outer electrons [31], the valence state, the number of eg electrons [27], the O-p band [116] and the metal–oxygen covalency [113, 180]. Similar to descriptors for the ORR [112], reports of structural descriptors [34, 181] and magnetic descriptors [34, 182] are very scarce. All of the experimental structure–activity relationships employ powders rather than epitaxial films, which naturally leads to the question: how well do popular descriptors of the OER work for epitaxial perovskite systems?

We selected the eg orbital occupancy and the ratio of the octahedral to the tolerance factor (µ t-1) as an electronic and a structural descriptor to plot the data in table 1 (figure 8). The analysis was limited to 0.1 M hydroxides to exclude pH effects that have been reported for perovskite oxides [144, 149, 183]. The eg occupancy was proposed by Suntivich et al for the ORR [114] and then also the OER [27] on perovskite oxides. It has since gained considerable popularity and also applies beyond the perovskite structure, e.g. for spinels [184]. The eg orbital points toward (end-on) adsorbed oxygen and thus correlates with oxygen adsorption as an elementary step in the mechanism of the OER. The ratio of the octahedral to the tolerance factor was recently proposed by Weng et al [181] based on symbolic regression. As these quantities are only defined for perovskites and related materials, the descriptor is less general than the eg occupancy and it does not clearly relate to hydroxide/water adsorption or another elementary mechanistic step. We believe that it most likely relates to tilting of the octahedra and, as such, to the metal–oxygen covalency and charge transfer. Nonetheless, its value can be easily calculated from readily available tables [51], and Weng et al [181] showed that it scales linearly with the OER activity.

We could not identify any apparent trend of the reported overpotentials at 50 µA cm-2 data with eg occupancy (figure 7(a)). The eg occupancy was calculated based on the reported stoichiometries (i.e. neglecting possibly present vacancies) where the most common spin state (high spin, hs, intermediate spin, is, or low spin, ls) was assumed, i.e. hs Mn3+, hs Fe3+, hs Fe4+, is Co3+, hs Co4+, ls Ni3+, ls Ni4+. In the shown representation, a V-shaped curve (inverted volcano) with the minimum near unity eg occupancy would be expected based on the previous works on perovskite oxide powders. However, no clear trend with the eg occupancy could be identified. Naturally, a large spread should be expected because the data were recorded by different groups with different protocols, because the films were made by different methods, producing different types and concentrations of defects (incuding vacancies) and most importantly because the aim of the investigations was often to demonstrate the effect of other parameters at nominally fixed eg occupancy, e.g. strain (different symbols in figure 7(a)). Our plot should not be misunderstood that the eg occupancy is unsuitable as a descriptor, which was proven for powders [27]. Instead it illustrates the limits of the eg descriptor. Many of the reports included in our plot discussed qualitative deviations from the formal valence [53–59, 61, 65, 67, 68], In that sense, the eg descriptor is not
very robust against guessing it from the formula, and it should be quantified consistently by measurement for films made by identical deposition methods to ensure similar (unavoidable) defects. As a final remark, the spread of the data at \( e_g \) occupancy of one (210 mV) compared to the span of overpotentials in figure 7(a) (190 mV) suggests that descriptors other than the \( e_g \) occupancy can have an equally large impact on the OER activity of epitaxial perovskite oxides, which is in contrast to powder studies [27, 112, 114].

We also plotted the same overpotentials at 50 \( \mu \text{A cm}^{-2} \) as a function of \( \mu t^{-1} \) (figure 7(b)). The tolerance (\( t \)) and octahedral (\( \mu \)) factors were calculated using equations (1) and (2) with the radii obtained from Shannon’s table [51]. Twelve-fold coordination was assumed for all A-sites. Surprisingly, the linear trend expected from the work of Weng et al [181] could also be found for epitaxial perovskite oxides on various substrates, albeit with large scattering. Overall, it can be concluded from our plot that a smaller \( \mu t^{-1} \) most likely leads to lower overpotentials for (mainly) first-row transition metals on the investigated substrates. Notable outliers are \( \text{La}_{0.88}\text{Sr}_{0.12}\text{FeO}_3 \) with low bulk conductivity and \( \text{SrIrO}_3 \). Upon closer inspection, the spread at selected values of \( \mu t^{-1} \) is still considerable, e.g. 140 mV at \( \mu t^{-1} = 0.40 \). We expect that it has similar origins as discussed above for the \( e_g \) descriptor, which results in modifications of the bond lengths due to strain and due to octahedral tilting (figures 1(a), (d)). In contrast to the \( e_g \) descriptor, the magnitude of the secondary effects (estimated as the spread of 140 mV at \( \mu t^{-1} = 0.40 \)) is smaller compared to the span of overpotentials in the dataset (210 mV). Experimental determination of the actual bond lengths and quantification of the defects would be desirable to obtain a more accurate \( \mu t^{-1} \) descriptor. In particular, the oxygen non-stoichiometry can lead to differences in \( t \) and \( \mu \) (discussed in section 2.2) as well as in \( e_g \). It is a great challenge to identify simple descriptors for a complex reaction such as the OER on a complex oxide, such as a perovskite, as the intended change in one parameter may affect other undesired properties that have an impact on the mechanism and thus the activity. Nonetheless, we found that the structural \( \mu t^{-1} \) descriptor was more robust against guessing its value from the formula and tabulated values compared to the popular electronic descriptor of \( e_g \) occupancy for epitaxial perovskite systems. A final reason for deviations from trends may be chemical or structural changes during the OER, which is still rarely reported. Stability of the perovskites at voltages below the onset of OER and during the OER is a topic too extensive to be covered herein. Instead, we give a brief overview. It has not been rigorously established that there is a perovskite surface that does not change during the OER. The reported modifications range from change in the surface chemistry with a retained perovskite framework to surface reconstruction to complete loss of crystalline structure [59, 76].

Currently there is no unified procedure to measure and compare the stability of perovskite oxides. Geiger et al [185] proposed the S-number as a stability parameter for Ir-containing oxides in acid. The S-number is defined as the ratio between the amount of evolved oxygen (calculated from the total charge \( Q_{\text{total}} \)) and the amount of dissolved transition metals (extracted from online ICP-MS data). Thus, it indicates the number of oxygen molecules that can be formed before a metal atom is dissolved into the electrolyte, which makes it analogous to the turnover number in homogeneous catalysis. The authors also show that the lifetime of the catalyst is proportional to the S-number divided by the current density. In their study, the predicted lifetimes range between a year for \( \text{IrO}_2 \) powder and only a month for an \( \text{IrO}_2 \) film in a laboratory setting. Pure
electrochemical approaches are used more commonly to evaluate stability as no specialized equipment is needed. They include testing at rather high fixed current density or potential, where OER performance can be observed, or performing a large number of voltage cycles during CV (usually around 100) [62, 63]. Bick et al. [186] report an end of service life test (ESLT), where the catalyst is cycled to 2.1 V vs. the RHE at 100 mV s⁻¹. A polycrystalline 100 nm film of Pr₀.2Ba₀.8CoO₃₋δ on Si lasted 40 ks (11.1 h), from which it was calculated that a 0.8 mm film would last ten years. Unfortunately, similar lifetime estimations are not yet available for epitaxial perovskite films at the time of writing. In summary, the discussed procedures provide a basic understanding of the changes in catalytic performance over time. Yet, they do not generally provide information about specific processes that occur in the material that may lead to a degradation or a loss of activity, for which post-mortem or in situ microscopy and spectroscopy is necessary.

Scholz et al. [59] reported that the surface of La₀.6Sr₀.4MnO₃ is enriched in La due to Mn and Sr dissolution. The surface remained in the perovskite structure, as observed by TEM. These films showed negligible changes in XRR, XRD and AFM. Weber et al. [64] also found a similar La enrichment on the surface of La₀.6Sr₀.4CoO₃ after electrocatalysis due to B-site (Co) and Sr leaching. Their data indicates a loss of the perovskite structure to an amorphous structure, as also reported for Co-based perovskite oxide powders [140, 141]. This transformation shows clear changes in both XRD and AFM. The induced changes depend on the number of cycles, i.e. the passed charge [62, 64], and the voltage range of the cycles [69].

Environmental TEM (ETEM) studies can give direct insight into surface changes but can currently only be performed in water vapor. Mildner et al. [187], Mierwaldt et al. [135] and Roddatis et al. [67] discuss the surface reconstructions of Pr₁₋ₓCaₓMnO₃ lamella when exposed to water vapor. Interestingly, the amorphization sometimes observed on the surface of perovskite oxides can be reversible, e.g. preparation-induced amorphous regions on the surface recrystallized in the presence of water on Pr₀.6⁰Sr₀.4⁰MnO₃ [67, 135, 187]. In contrast, Pr₀.9Ca₀.1MnO₃ remained crystalline in water vapor but showed cation dynamics on the surface [135].

The most extreme changes have been reported by Chang et al. [66] for some of the most active perovskites in table 1, namely SrRuO₃. Similar to La₀.6Sr₀.4MnO₃ and La₀.6Sr₀.4CoO₃, the B-site (Ru) and Sr are dissolved, while for the Ru-based perovskites drastic changes were evident from the cyclic voltammogram during the first cycle as the current becomes erratic soon after the exponential rise due to OER. Additionally, post-mortem analysis of the Bragg peaks (crystal truncation rods) corresponding to the surface shows dramatic changes that indicate severe roughening (i.e. extreme surface reconstruction).

In summary, leaching of the B-site transition metal and group II A-site cations appears to be common, but we caution that very few perovskites have been investigated. Enrichment of the surface with La was reported for those perovskites with La and Sr on the A-site. The degree of surface reorientation varies between reversible dynamic cation movement to complete irreversible loss of the perovskite structure, to which the more active perovskites are prone.

8. Concluding remarks and outlook

In this review, we have summarized the current state-of-the art investigations on epitaxial perovskite oxides catalyzing the OER. The perovskite structure is clearly defined, and the understanding of the physics and chemistry of epitaxial oxides is very mature. Likewise, electrocatalytic investigations are well established, even though there is a dire need for a unified testing protocol for OER investigations to make the results more comparable. The challenge lies in consolidating the knowledge in these two fields, and addressing the challenges that arise when epitaxial perovskite oxides are used as electrocatalysts for the OER. We introduced the prerequisites for charge transfer across interfaces, namely both a suitable alignment of the relevant energy levels and sufficient charge carriers. These parameters are not a concern for more classic electrochemical electrodes made of metals, but they are critical parameters for semiconductors such as perovskite oxides. These points are frequently discussed in the neighboring field of photoelectrocatalysis [188–193] but receive comparatively little attention in the electrocatalysis of the OER. It would also be desirable to include the effects of energy alignments and charge carriers in theoretical calculations of adsorption energies used as catalytic descriptors (e.g. ∆G of OH). It is conceivable that the surface with optimal adsorption energy of a key intermediate, such as OH, could have either unsuitable band edges for the OER or insufficient charge carriers. The need to align energy levels does not necessarily impact catalysis negatively. Eom et al. [130] and Akbashev et al. [103] used atomically controlled multilayers to optimize adsorption properties, stability and the alignment for optimal charge transfer. The prospects of these efforts have also been highlighted by Weber and Gunkel in this special issue [194].

Epitaxial perovskite oxides can be excellent model electrodes to gain fundamental insight into catalysis by property-activity relationships (i.e. descriptors) with the caveat that they are not free of undesired correlations between composition (of the film and substrate) and the resulting defects or strain. When this is
under control (or at least characterized), some perovskite oxides could be sufficiently understood to develop a solid–liquid interface that can be reasonably well approximated as an extended surface of a single facet with known composition to bridge between theoretical studies (e.g. by DFT) and experimental investigations for complementary atomic scale insight into active states and the mechanism. On the other hand, some perovskite oxides can be made as nanoparticles with nominally identical composition to epitaxial thin films, e.g. $\text{Ba}_0.5\text{Sr}_0.5\text{CoO}_3$, $\text{Fe}_0.5\text{O}_3$, $\text{Fe}_2\text{O}_3$, and $\text{Mn}_2\text{O}_3$ [195]. Yet, additional studies are required to bridge between epitaxial thin film studies and investigations of nanoparticles for use in electrolyzers. Building both bridges would allow a long-held dream of transferring atomic scale insight and control to applications.

In situ and operando spectroscopy and microscopy on epitaxial thin films is extremely challenging but desperately needed to address the key questions of the nature of the starting state of the mechanism, the active state for the OER, i.e. the intermediate before the rate-limiting step and its potential evolution during the OER. Ambient pressure x-ray photoelectron spectroscopy (AP-XPS) studies on epitaxial perovskite oxides have been key to understanding surface hydroxylation [57, 131, 196, 197]. In situ XRD has been used to study the structure and its evolution with potential for epitaxial oxides [198–200] but not perovskite oxides. In situ x-ray spectroscopy is used to elucidate the valence during OER for other catalysts but has not been used for epitaxial thin film oxides [201–204]. These in situ measurements are instrumental in enabling us to understand the OER on epitaxial perovskite oxides and fully harness their potential as model electrodes to derive guidelines to improve their electrocatalysis by optimizing the composition or by exploiting new concepts inherent to epitaxial layers.

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