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1 **The Stability-number as new metric for electrocatalyst stability benchmarking –**

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3
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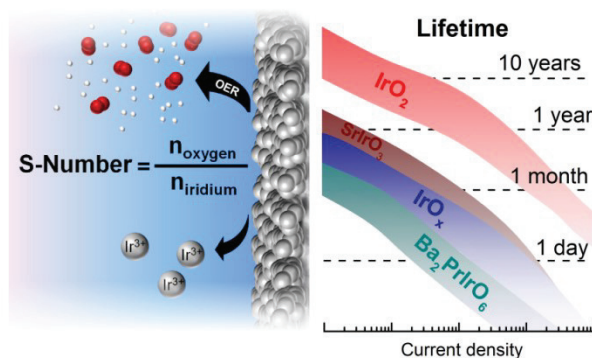
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30 Abstract

31 Reducing noble metal loading and increasing specific activity of oxygen evolution catalysts
32 are omnipresent challenges in proton exchange membrane (PEM) water electrolysis, which
33 have recently been tackled by utilizing mixed oxides of noble and non-noble elements (e.g.
34 perovskites, IrNiO_x, etc.). However, proper verification of the stability of these materials is
35 still pending. In this work dissolution processes of various iridium-based oxides are explored
36 by introducing a new metric, defined as the ratio between amount of evolved oxygen and
37 dissolved iridium. The so called Stability-number is independent of loading, surface area or
38 involved active sites and thus, provides a reasonable comparison of diverse materials with
39 respect to stability. Furthermore it can support the clarification of dissolution mechanisms and
40 the estimation of a catalyst's lifetime. The case study on iridium-based perovskites shows that
41 leaching of the non-noble elements in mixed oxides leads to formation of highly active
42 amorphous iridium oxide, the instability of which is explained by participation of activated
43 oxygen atoms, generating short-lived vacancies that favour dissolution. These insights are
44 considered to guide further research which should be devoted to increasing utilization of pure
45 crystalline iridium oxide, as it is the only known structure that guarantees a high durability in
46 acidic conditions. In case amorphous iridium oxides are used, solutions for stabilization are
47 needed.

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Graphical abstract

51

52 **Keywords:** oxygen evolution reaction, iridium, perovskites, stability-number, energy
53 conversion

54

55 1. Introduction

56 Electrochemical water splitting is considered to play a key role in the new energy scenario
57 for the production of hydrogen, which can act as central energy carrier and as raw material for
58 the chemical industry. Still, the persistent challenges of this concept are (i) slow kinetics of
59 the oxygen evolution reaction (OER) and (ii) need of expensive materials as catalysts or
60 related components. Especially for proton exchange membrane (PEM) electrolysis, the acidic
61 environment caused by the membrane itself together with high anodic potentials limits the
62 choice of catalyst materials to expensive noble metals. The best known catalysts for OER
63 contain high amounts of scarce iridium that hampers large scale implementation of this
64 technology. Smart catalyst design is needed to decrease noble metal loadings and increase
65 specific activity and stability.

66 Various iridium-based mixed oxides¹⁻⁸ have been investigated as potential catalyst
67 material to tackle the mentioned challenges by increased specific activity and lower
68 percentage of expensive noble metals. Enhanced activity and apparently decent stability was
69 demonstrated in comparison to IrO₂, Ir-black, or other benchmark materials. However, the
70 stability aspect needs more rigorous investigation. Especially non noble alkali or rare earth
71 elements are expected to be thermodynamically unstable in acidic electrolytes,⁹ favouring the
72 formation of amorphous iridium oxide structures after leaching. The latter have been shown to
73 degrade significantly in acidic electrolyte during OER,¹⁰⁻¹³ accentuating the need for further
74 understanding of degradation processes.

75 Most prominent examples are iridium-based perovskites recently investigated in acidic
76 electrolyte.^{1,2} Initial studies on the usage of this material class in electrocatalysis originate
77 from Bockris and Otagawa,^{14,15} who used alkaline electrolytes. Since then numerous studies
78 on the usage of perovskites for alkaline water splitting have been published.¹⁶⁻²⁵ Exceptionally
79 high OER activities were achieved for example by varying the occupancy of 3d orbitals of
80 surface transition metals¹⁸ or tuning oxygen vacancies by means of straining.²¹ However,
81 several groups brought up the important aspect of surface amorphization during OER.²⁶⁻²⁹
82 May *et al.*²⁶ indicated, that especially those materials with high amorphization are the ones
83 that show high activity, expressing the need of further investigations on the number of
84 involved active sites. Even more in acid environment catalyst stability and amorphization is
85 an issue. Therefore a thorough investigation of specific activity and dissolution processes of
86 iridium-based perovskites in 0.1 M HClO₄ is presented in this work.

87 In general, contemporary challenges to explore new electrocatalysts are, in addition to
88 increased activity: (i) the determination of the real electrochemical surface area (ECSA) by
89 identification and quantification of the active sites enabling a reliable comparison of different
90 materials and (ii) the investigation of degradation by thorough quantification of dissolution
91 products, assuming the latter as major degradation process of electrocatalysts. Both
92 parameters are important indicators of an electrocatalyst's performance. Our study aims to
93 clear these important gaps by cyclic voltammetry to quantify active centres for OER and in
94 situ dissolution data obtained by combining a scanning flow cell (SFC) with inductively
95 coupled plasma mass spectrometry (ICP-MS). The amount of dissolved iridium is presented
96 in relation to the evolved oxygen as new independent metric called Stability-number. The
97 latter is beneficial to estimate lifetimes and together with online electrochemical mass
98 spectrometry (OLEMS) underlines proposed dissolution mechanisms of the investigated
99 materials, namely double perovskite powders with $A_2B\text{IrO}_6$ structure ($A = \text{Ba, Sr; B} = \text{Nd, Pr,}$
100 Y), amorphous IrO_x powder, crystalline IrO_2 powder, SrIrO_3 perovskite films,
101 electrochemically formed hydrous IrO_x films and crystalline IrO_2 films. A general perspective
102 on the applicability of the mentioned iridium oxide structures towards acidic water splitting is
103 presented.

104

105 **2. Results and discussion**

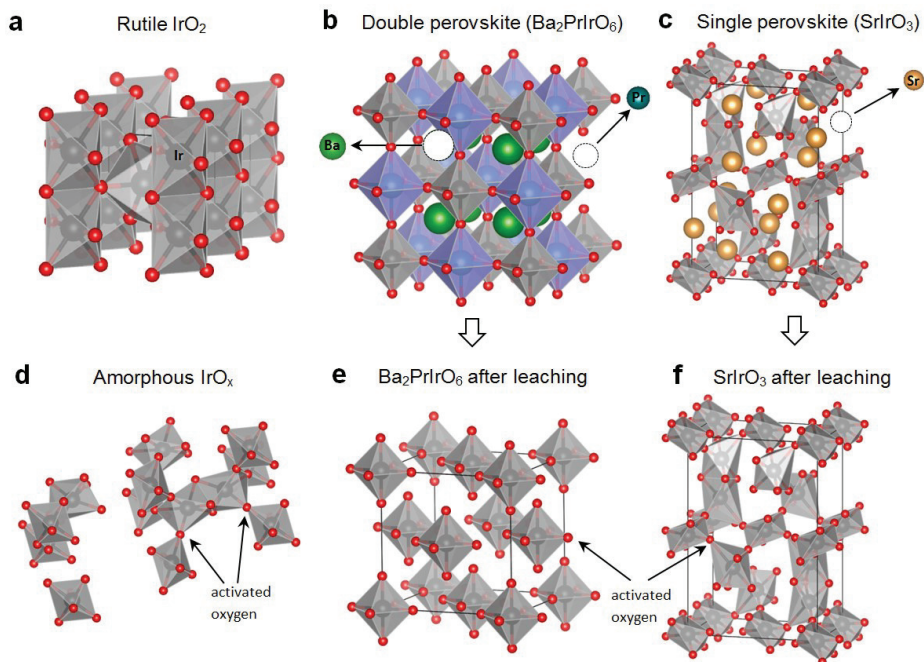
106 **Leaching processes in perovskites**

107 The catalyst composition on the surface is essential for exploring electrochemical
108 reactions at the catalyst-electrolyte interface. Therefore, the dissolution behaviour of all
109 materials was investigated during initial contact with 0.1 M HClO_4 at open circuit potential
110 (OCP). While crystalline IrO_2 and amorphous IrO_x do not dissolve initially, perovskites do
111 undergo intensive leaching. First of all the non-noble elements ($\text{Ba, Sr, Nd, Pr, and Y}$)
112 dissolve as expected from available thermodynamic data⁹ for single elements and related
113 experimental works^{1,2} (see Tab. S1 and Fig. S1, S3). However, in double-perovskites we
114 observed dissolution of iridium as well in the range of 30-40 w% from the initial value,
115 during 60 s of contact at OCP. This can be explained on the basis of the crystal structure
116 illustrated in Fig. 1b. As the component B (e.g. Pr) is part of the lattice, leaching of the latter
117 goes hand in hand with generation of isolated IrO_6 octahedra, which are prone to dissolve in
118 parallel. Furthermore we expect that the structure will collapse and reform in an amorphous
119 iridium oxide. To underline this statement one exemplary material of the double perovskite

120 family was examined during a prolonged leaching experiment. EDS analysis confirms
121 complete removal of Ba and Pr after keeping the powder for 14 days in 0.1 M HClO₄, leaving
122 behind an amorphous iridium oxide structure, demonstrated by selected area electron
123 diffraction (SAED) (see Fig. S2). The penetration depths of these methods are expected to be
124 higher than the diameter of the investigated particle, hence, leaching and formation of
125 amorphous iridium oxide is not restricted to the surface.

126 Single perovskites on the other hand consist of a coherent iridium oxide structure with
127 intercalated non-noble elements (see Fig. 1c). Thus, initial dissolution of a 20 nm SrIrO₃ film
128 is restricted to Sr (3.0 w%), while iridium oxide is fairly stable (0.01 w%) (see Fig. S3). The
129 leftover backbone of iridium oxide equals an anatase structure.^{1,30} However, no stable anatase
130 phase of iridium oxide has been reported to the best of our knowledge. It is therefore highly
131 probable that the structure will collapse as well into amorphous iridium oxide. Similar CV
132 shapes of electrochemically grown hydrous IrO_x and leached SrIrO₃ presented in Fig. 4d
133 supports this assumption. Based on the obtained dissolution data and simple calculation,
134 initial contact of SrIrO₃ with acid forms a 0.6 nm layer of hydrous iridium oxide, which
135 increases in thickness during prolonged OER measurements (see Fig. S3).

136



137

138 **Figure 1. Crystal structure of the investigated materials.** (a) rutile IrO₂; (b) double perovskite (e.g.
139 Ba₂PrIrO₆); (c) single perovskite (SrIrO₃); (d) assumed structure of amorphous iridium oxide, gaps are filled
140 with intercalated water molecules (not shown); (e) leached double perovskite showing isolated IrO₆ octahedra,
141 which will collapse into an amorphous structure; (f) leached SrIrO₃ resulting in an “anatase” iridium oxide
142 structure.

143 **The oxide structure and its relevance for activity and dissolution**

144 In order to understand the observed results on activity and stability presented later in
145 the manuscript we continue with a discussion on oxide structures and oxidation states before
146 and after the initial leaching process. In Fig. 1 the structures of rutile IrO_2 , amorphous IrO_x , a
147 double perovskite ($\text{Ba}_2\text{PrIrO}_6$), and a single perovskite (SrIrO_3) are presented. The dense
148 packing and edge sharing oxygen of the octahedra in the rutile structure are in contrast to
149 loose packing and corner sharing octahedra in $\text{Ba}_2\text{PrIrO}_6$ and SrIrO_3 generating lower
150 coordinated oxygen atoms (activated oxygen). Leaching of the non-noble elements A and B in
151 A_2BIrO_6 destroys the crystal structure of the double perovskite and pure octahedral elements
152 are linked together randomly inducing a high number of accessible “activated oxygen atoms”
153 and vacancies. Similar structures can be achieved by leaching Sr from SrIrO_3 or Ni from
154 IrNiO_x .^{3,4} Moreover, classical potential cycling of iridium metal³¹ or mild calcination of
155 iridium precursors^{11,32} are optional preparation methods.

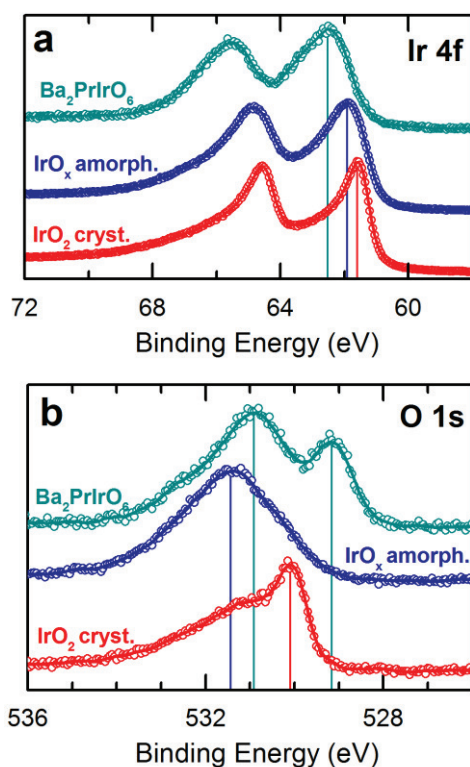
156 The binding energies of the 4f electrons of iridium and 1s electrons of oxygen
157 obtained via X-ray photoemission spectroscopy (XPS) are utilized for further analysis on the
158 chemical environment of iridium and oxygen in the structure. Based on a computational
159 model, Pfeifer *et al.*³³ studied the formation of an iridium vacancy in a supercell. According to
160 the calculations, this leads to the formation of $\text{O}^{\cdot-}$ and Ir^{III} species, which was supported by
161 XPS and NEXAFS investigations. Hereby, the authors explained the positive shift of the Ir 4f
162 binding energy³³ in amorphous IrO_x , which is shown in Fig. 2a. The Ir 4f peak of $\text{Ba}_2\text{PrIrO}_6$ is
163 shifted to even higher binding energies, however, the pristine structure rather indicates the
164 presence of Ir^{V} , which has a similar peak shift.³⁴ Still, Fu *et al.*³⁵ found a $\text{Pr}^{\text{IV}}/\text{Ir}^{\text{IV}}$ couple
165 present in $\text{Ba}_2\text{PrIrO}_6$, which is against the previous assumption. Consequently, based on XPS
166 data solely, a clear statement on the oxidation states cannot be made. However, XPS clearly
167 expresses the different environment of the iridium atoms in the respective structures. After
168 leaching of $\text{Ba}_2\text{PrIrO}_6$ in 0.1 M HClO_4 the spectrum is very similar to amorphous iridium
169 oxide (see Fig. S2c, d). This observation could be understood as a decreased amount of $\text{Ir}^{\text{VI/V}}$
170 and the formation of Ir^{III} by intensive leaching and creation of vacancies similar to the
171 theoretical model mentioned earlier in this section.

172 The O 1s spectra in Fig. 2b confirm that exclusively crystalline IrO_2 contains
173 oxygen atoms in the rutile lattice at a binding energy of ~ 530 eV. In perovskites and
174 amorphous oxide, the binding energy of the main peak is shifted to positive values, which is
175 usually assigned to hydroxyl groups.⁴ Alternatively, it could be attributed to oxygen atoms

176 with different environment, e.g. activated oxygen atoms. The shoulder at 529 eV for
177 $\text{Ba}_2\text{PrIrO}_6$ results from lattice oxygen bound to the Pr atom² and disappears after extensive
178 leaching (see Fig. S2). Similar absorption features were observed by Reier *et al.*⁴ in the case
179 of IrNiO_x and explained by “oxygen hole” states induced by substitution of Ir^{4+} with Ni^{2+} .³⁶

180 We suggest that the presence of activated oxygen atoms is crucial for the
181 explanation of the following results in activity and dissolution. The dense packing of the rutile
182 structure restricts the formation of activated oxygen atoms to the surface, which is
183 undercoordinated by definition. In contrast, for porous hydrous oxides with intercalated water
184 molecules^{37,38} iridium atoms inside the structure can participate in the reaction. These centres
185 are surrounded by a higher number of activated oxygen atoms and weaker in coordination
186 facilitating their instability (see discussion on mechanism and Stability-number).

187



188
189 **Figure 2. XPS results of pristine $\text{Ba}_2\text{PrIrO}_6$, amorphous IrO_x and crystalline IrO_2 .** (a) Ir 4f and (b) O 1s
190 spectra. Additional results of the leached $\text{Ba}_2\text{PrIrO}_6$ are presented in the supporting information (Fig. S2).

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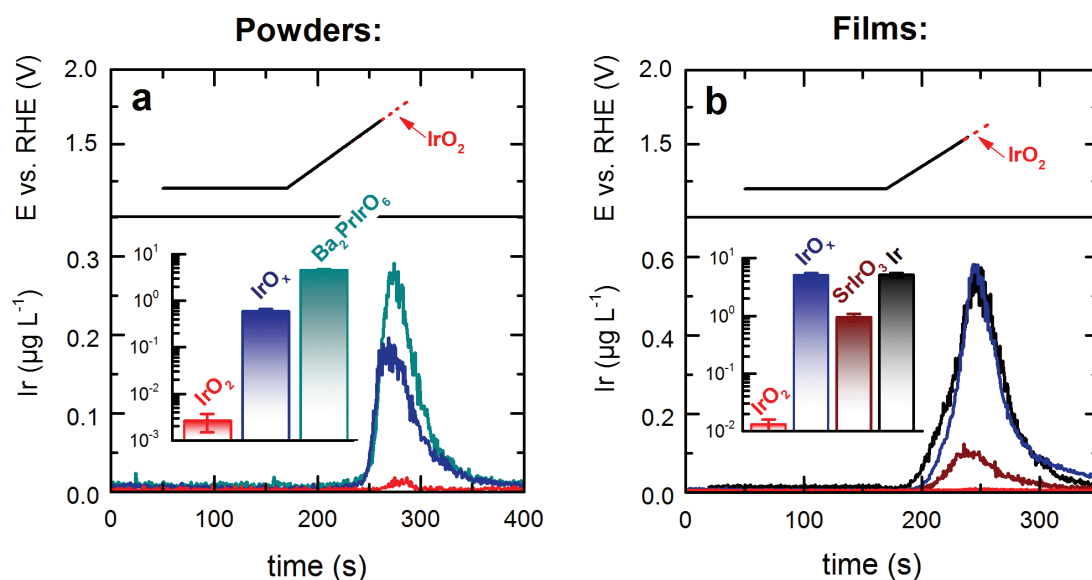
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196 Stability and activity with respect to OER

197 The SFC coupled to ICP-MS analytics enables in situ detection of dissolved iridium
198 ions during the oxygen evolution. This approach was used to investigate film and powder
199 materials by performing a linear sweep of potential at 5 mV s^{-1} , illustrated in Fig. 3a and 3b.
200 Potential and dissolution are plotted on the same time scale. The insets present the integrated
201 amount on a logarithmic scale. In line with previous reports we recorded orders of magnitude
202 higher dissolution for metallic iridium and hydrous iridium oxide in comparison to crystalline
203 iridium oxide.^{10,39} Perovskites, additionally studied in this work, show as well high
204 dissolution in the range of amorphous/hydrous oxide and therefore might not be suitable for
205 long time operation. Still, the high activity of the latter, demonstrated in the following, is of
206 importance to understand the clues on the synthesis of an improved OER catalyst.
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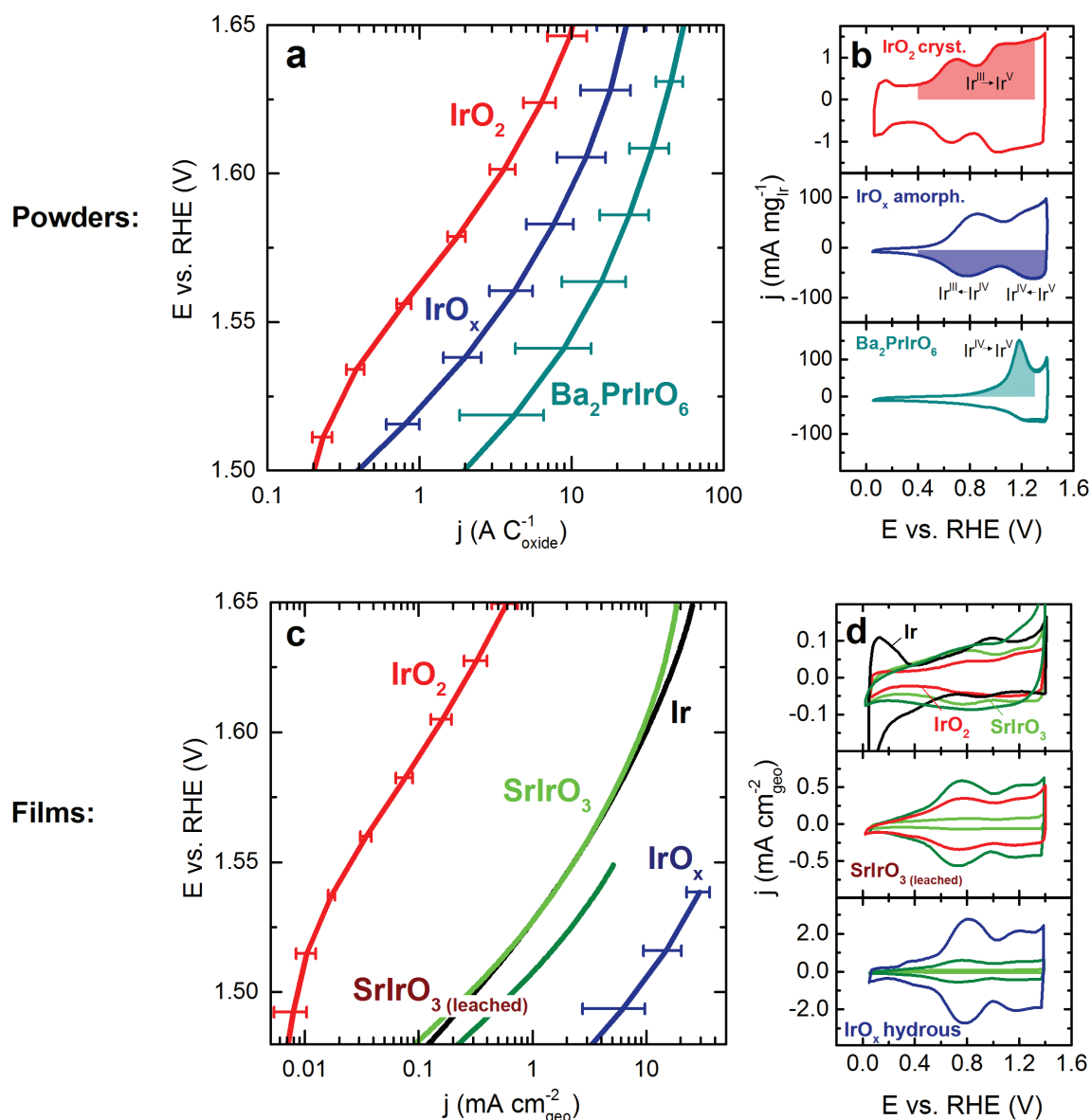
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209 **Figure 3. Investigation of iridium dissolution during OER.** (a) Detected iridium concentration in the
210 electrolyte during the 2nd linear scan of potential to 1.65 V vs. RHE for investigated powders. In case of IrO_2 a
211 higher loading was used and the potential was increased to 1.8 V vs. RHE in order to reach iridium
212 concentrations above the detection limit of the ICP-MS. Inset: integrated dissolution normalized by the actual
213 mass of iridium loaded given in $\text{ng } \mu\text{g}_{\text{Ir}}^{-1}$. (b) Detected iridium concentration in the electrolyte during a linear
214 scan of potential to 1.55 V vs. RHE for investigated films. In case of IrO_2 the potential was increased to 1.65 V
215 vs. RHE. Inset: integrated dissolution normalized to the geometric surface area given in ng cm^{-2} .

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220 In order to take into account the different active surface areas of the samples the
221 OER-current is normalized to the pseudocapacitive charge Q_{oxide} extracted from the cyclic
222 voltammograms in the range of 0.4 to 1.3 V vs. RHE (Fig. 4). Q_{oxide} is considered as a fair
223 approximation⁴⁰⁻⁴³ for the number of involved active sites, avoiding misinterpretation of data
224 on activity due to surface area effects. Based on the position of the redox peak in Fig. 4b we
225 assume that predominantly $\text{Ir}^{\text{IV}}/\text{Ir}^{\text{V}}$ transition^{37,44} appears in perovskites while $\text{Ir}^{\text{III}}/\text{Ir}^{\text{IV}}$ is
226 suppressed. In commercial amorphous IrO_x the $\text{Ir}^{\text{III}}/\text{Ir}^{\text{IV}}$ redox peak is much more pronounced
227 with a second wave indicating further oxidation to Ir^{V} . Assuming that Ir^{V} is essential for fast
228 OER kinetics, high presence of this species in perovskites could explain their superior activity
229 in comparison to IrO_x and IrO_2 . Alternatively the numerous activated oxygen atoms present in
230 $\text{Ba}_2\text{PrIrO}_6$ due to complete isolation of IrO_6 octahedral after leaching could be the reason for a
231 boost in specific activity. Normalization of OER activity to the actual mass of iridium is
232 shown in Fig. S5. Even though perovskite particles tested in this work are large in size (Fig.
233 S4), high activities were achieved, which is another indication on the formation of a very
234 active and highly porous layer.

235 In Fig. 4c and 4d the analogous procedure is illustrated for sputtered samples. Low
236 roughness of these films allows normalization to geometric surface area. Exceptions are
237 leached SrIrO_3 and electrochemically grown hydrous iridium oxide, investigated numerously
238 in the literature.^{31,45,46} Both show enhanced pseudo capacitance assigned to the formation of a
239 porous hydrous oxide layer. Almost identical CV shapes are indications on very similar
240 structures of the latter. The extraordinary activity of these porous 3D-structures is, inter alia,
241 related to the high number of accessible active sites. Normalization to pseudocapacitive
242 charge, as mentioned for powder samples, is necessary to reveal further insights on the
243 specific activity. The trend for specific activity is: $\text{Ba}_2\text{PrIrO}_6 > \text{SrIrO}_3 = \text{IrO}_x > \text{IrO}_2$,
244 presented and discussed in the supporting information (Figs. S6 –S8). Focusing on the flat
245 samples of iridium metal, crystalline IrO_2 and pristine SrIrO_3 with similar Q_{oxide} (Fig. 4d) one
246 can conclude that the specific OER activity on SrIrO_3 and metallic iridium is about two orders
247 of magnitude higher in comparison to crystalline IrO_2 , caused by a thin hydrated oxide layer
248 formed on SrIrO_3 via leaching and metallic iridium via surface oxidation during OER,⁴⁵
249 which is not present for crystalline iridium oxide.

250



251
 252 **Figure 4. Comparison of the investigated materials in terms of activity.** (a) OER-activity of the powder
 253 materials recorded with a linear scan of potential at 5 mV s⁻¹ (iR-drop corrected). The current is normalized to
 254 the pseudocapacitive charge in the anodic scan between 0.4 and 1.3 V_{RHE} at 200 mV s⁻¹. (b) Cyclic
 255 voltammograms recorded with 200 mV s⁻¹, the integrated area of the oxide charge used for normalization is
 256 highlighted. (c) OER-activity of the investigated films recorded with a linear scan of potential at 5 mV s⁻¹. The
 257 current is normalized to the geometric surface area. (d) Cyclic voltammograms recorded with 200 mV s⁻¹. All
 258 measurements were carried out in 0.1 M HClO₄ purged with argon.

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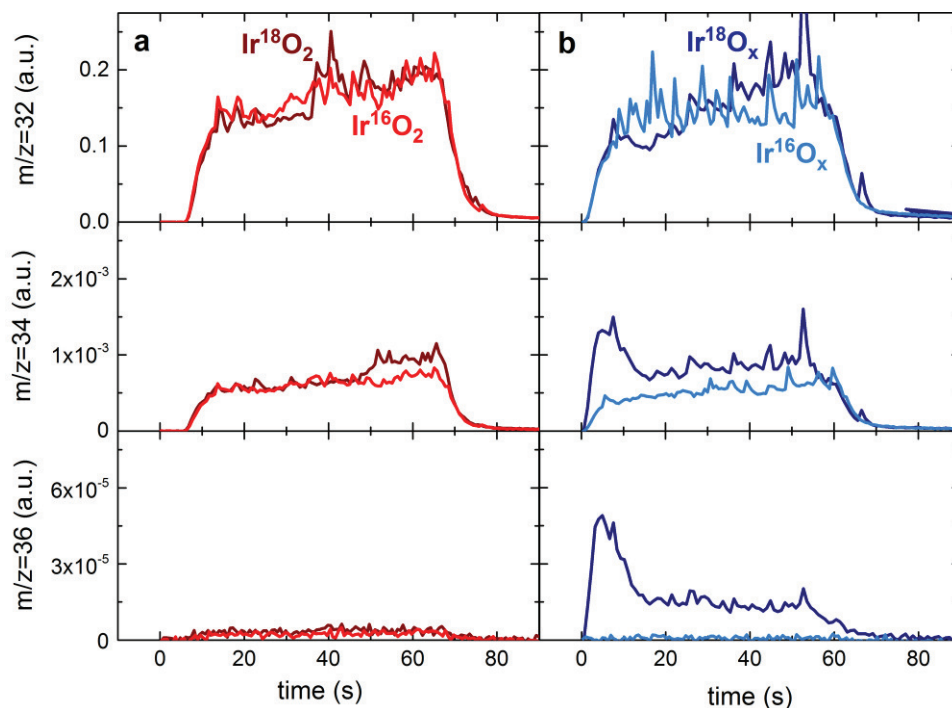
265 **Mechanistic insights**

266 With the gained understanding on structure, dissolution, and activity, we want to
267 combine existing mechanisms of the OER on iridium-based catalysts⁴⁷⁻⁵¹ with a mechanism
268 for simultaneous dissolution. Starting point is the differentiation of two oxygen species
269 present either in crystalline iridium oxide or amorphous, hydrated iridium oxides and the
270 significantly higher stability of the crystalline structure in comparison to the amorphous
271 hydrated structure as presented in Fig. 3.

272 The case of amorphous hydrous oxide merits special attention, as its structure is still
273 unknown. According to Pfeifer *et al.*,⁵¹⁻⁵³ enhanced activity of amorphous iridium oxide is
274 caused by electrophilic O⁻ species that are preferred for nucleophilic attack by water,
275 reducing the activation energy for the adsorption. Grimaud *et al.*²⁹ came to similar
276 conclusions using La₂LiIrO₆ as a model catalyst. There are several indications that the
277 “activated oxygen atoms” as described in this work and the abovementioned “O⁻ species” are
278 indeed interchangeable. The presence of O⁻ is, however, counterintuitive, as the high
279 electronegativity of oxygen in comparison to iridium should hardly allow the allocation of a
280 formal oxidation state of -1. Based on structural investigation of different amorphous iridium
281 oxides (e.g. hollandites), Willinger *et al.*⁵⁴ concluded that the ratio between corner- and edge-
282 sharing IrO₆ octahedra is determining the OER activity. Thus, a high number of corner
283 sharing oxygen atoms (activated oxygen) facilitates the OER. Regardless of the formal
284 oxidation state and termination, it was experimentally proven by ¹⁸O labelling for Co-based
285 perovskites, that activated oxygen can participate in the OER, which was taken as evidence
286 for oxygen redox chemistry.⁵⁰ Furthermore it is an important argument to explain the
287 instability of amorphous iridium oxides. In the following, the term lattice oxygen accounts
288 generally for all oxygen atoms that are part of the structure and is not exclusively limited to
289 the described oxygen atoms of the rutile lattice. Evidence for the participation of oxygen from
290 the lattice of iridium oxides is rare. One work of Fierro *et al.*⁵⁵ contains indications on a
291 participation, however, it focuses only on one type of oxide, the exact nature of which
292 remains unclear and therefore does not allow further generalization and conclusions.

293 In order to resolve the extent of lattice oxygen participation during OER on rutile and
294 amorphous iridium oxides (the final state for all unstable iridium-based oxides) in more detail
295 a method of isotope labelling combined with online electrochemical mass spectrometry was
296 used. The labelled Ir¹⁸O₂ and Ir¹⁸O_x films (for preparation see methods section) were
297 polarized galvanostatically in H₂¹⁶O-based electrolyte and formation of volatile species with

298 mass to charge ratios of 32 ($^{16}\text{O}^{16}\text{O}$), 34 ($^{16}\text{O}^{18}\text{O}$, and to a small extent $^{17}\text{O}^{17}\text{O}$) and 36
 299 ($^{18}\text{O}^{18}\text{O}$) were measured online (see Fig. 5). In order to compensate the influence of naturally
 300 occurring H_2^{18}O isotopes in the H_2^{16}O -based electrolyte, the same protocol was applied to
 301 unlabelled rutile Ir^{16}O_2 and hydrous Ir^{16}O_x prepared by identical procedures. During anodic
 302 polarization, both labelled and unlabelled rutile samples show similar formation of various
 303 oxygen products (Fig. 5a). This indicates that participation of lattice oxygen in the OER is
 304 absent or negligible. In contrast, the formation of $m/z=34$ and $m/z=36$ on Ir^{18}O_x is more
 305 intense in comparison to the unlabelled sample (Fig. 5b), denoting the instability of
 306 amorphous oxide lattice towards OER. However, the low measured intensities of $m/z=34$ and
 307 $m/z=36$ suggest that the major part of the evolved oxygen molecules is formed via water
 308 discharge. Gradual decrease of $m/z=34$ and $m/z=36$ signals on labelled Ir^{18}O_x indicates an
 309 exchange between lattice oxygen atoms and oxygen from water induced by the OER.
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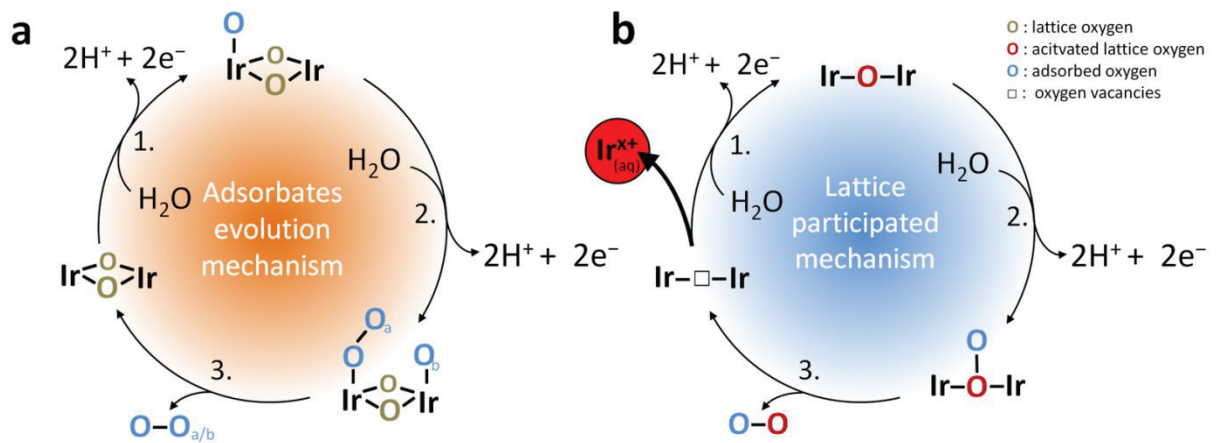
311
 312 **Figure 5. Online observation of lattice oxygen evolution on (a) rutile Ir^{18}O_2 / Ir^{16}O_2 and (b) hydrous Ir^{18}O_x /**
 313 **Ir^{16}O_x films during 60 s of anodic polarization at $25 \text{ mA cm}^{-2}_{\text{geo}}$. The signals from m/z of 32, 34 and 36**
 314 **correspond to $^{32}\text{O}_2$, $^{34}\text{O}_2$ and $^{36}\text{O}_2$, respectively. Electrolyte: 0.1 M HClO_4 in H_2^{16}O .**
 315

316 Based on the results shown in Fig. 5 and additional data presented in literature, we
 317 propose a summarized view on the OER mechanisms in Fig. 6. On the left side, the classical
 318 mechanism on crystalline iridium oxide is presented as adsorbates evolution mechanism.⁴⁷⁻⁴⁹
 319 The reaction can either happen on a single iridium site via an OOH intermediate^{34,56} (acid-

320 base)^{48,57} or by the coupling of two oxygen atoms from different sites (direct coupling).⁵⁸ For
321 the cycle on the right side, we base ourselves on the mechanism proposed by Grimaud *et al.*⁵⁰
322 and Rong *et al.*⁴⁹ Here, the reaction pathway differs by participation of activated (lattice)
323 oxygen in the reaction. It is assumed to be operative in the case of amorphous IrO_x and in
324 leached perovskites. The activated oxygen is attacked by water (step 2) and removed as O₂
325 from the surface (step 3) leaving behind an oxygen vacancy.^{49,50,59} This can either happen
326 with one lattice oxygen or by combining two lattice oxygen atoms as shown in Fig. 5b,
327 resulting in an iridium atom with two vacancies, which is highly probable to dissolve. The
328 latter scenario is less likely to happen for crystalline oxide. Participation of lattice oxygen, if
329 at all, is restricted to the outer surface while bulk oxygen will not participate and maintain a
330 high coordination of the iridium atom, resulting in a significantly lower probability for the
331 iridium atom to dissolve out of the structure. To close the cycle vacancies can be refilled by
332 adsorption of water or bulk oxygen migration²⁹ (step 1). We suggest the lower activation
333 energy for the adsorption of water in vacancies is further contributing to the higher activity of
334 amorphous oxide structures. Simultaneously, the weak bonding of iridium next to an oxygen
335 vacancy is considered as the reason for dissolution of iridium in amorphous iridium oxide
336 structures. In case more vacancies are created at the same time on one iridium atom,
337 dissolution becomes even more preferable. Dissolution itself might take place without
338 electron transfer Ir^{III}_(oxide) → Ir³⁺_(aq). A similar reaction pathway was proposed recently by our
339 group, in which the existence of an Ir^{III} intermediate in the OER cycle was linked to the
340 dissolution of hydrous iridium oxide.⁶⁰ Alternatively, additional electron transfer would lead
341 to formation of IrO₃ and IrO₄²⁻, described elsewhere.^{61,62}

342 As crystalline iridium oxide is assigned to the adsorbates evolution mechanism, its
343 very low but still measurable dissolution is not considered, yet. The constancy of the S-
344 number presented in the following section (Fig. 7c), suggests a direct relation between the
345 OER mechanism and the dissolution mechanism. The origin of the crystalline iridium oxide
346 dissolution might be some limited lattice oxygen participation on the surface similar to the
347 mechanism in Fig. 5b or other intermediates and dissolution pathways, e.g. formation of
348 volatile IrO₃.^{61,62} (see further discussion in the SI).

349 In conclusion, a catalyst's stability is determined by (i) the ratio between the two
350 presented mechanisms (a less stable material has a higher rate in the lattice participated
351 mechanism) and (ii) the stability of the intermediate itself, which can be higher for a rutile
352 structure in comparison to the amorphous oxide due to a more compact structure.



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356 **Figure 6. Sketch of the simplified OER reaction mechanism with dissolution pathway.** (a) Classical
 357 mechanism for crystalline IrO₂ without participation of lattice oxygen. Two possible pathways are presented:
 358 single site and double site. (b) Mechanism suggested for amorphous iridium oxide and leached perovskites with
 359 participation of activated oxygen in the reaction forming oxygen vacancies. Weakening the binding of iridium in
 360 the structure is taken as main reason for enhanced dissolution. To complete the cycle, vacancies can be filled
 361 again by adsorption of water. Octahedral configuration of iridium is not presented completely as well as
 362 nucleophilic attack of water and removal of proton is merged to one step to not overcrowd the scheme.

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365 **The Stability-number**

366 Significantly higher dissolution rates of iridium, but also higher OER rates were
 367 observed for amorphous IrO_x and perovskites in comparison to crystalline IrO₂. In order to
 368 take into account the possible effect of much higher amount of oxygen formed on amorphous
 369 and perovskite structures on dissolution, we introduce a metric characterizing the activity vs.
 370 stability performance of a given catalyst. The so called Stability-number (S-number) is
 371 defined as the ratio between the amount of evolved oxygen (calculated from Q_{total}) and the
 372 amount of dissolved iridium (extracted from ICP-MS data). The S-number describes how
 373 many oxygen molecules are formed per one iridium atom lost into the electrolyte.
 374 Consequently it is independent of the amount of involved active sites, surface area, or catalyst
 375 loading and gives an illustrative comparison of the stability of various materials. Moreover,
 376 unlike current efficiency, the S-number can be calculated without knowing the exact nature of
 377 the dissolved species and can be applied to neutral species. The higher the number, the more
 378 stable is the active centre of the electrocatalyst. Based on dissolution measurements presented
 379 in Fig. 3, the highest S-numbers were calculated for crystalline IrO₂ (Fig. S9). Perovskite

380 based iridium oxides possess the lowest S-numbers with two orders of magnitude less oxygen
381 evolved per dissolved iridium compared to rutile IrO₂. However, the influence of initially
382 dissolved iridium from defects as well as possible stabilization during longer operation should
383 not be overlooked in these short measurements (see discussion Fig. S10).

384 In order to demonstrate a more relevant study on stability of the investigated powders
385 and to gain further understanding on possible correlations of OER-mechanism and dissolution
386 mechanism, we varied the current per mass of iridium using galvanostatic steps of ~5-20 min
387 until a steady dissolution rate was observed (see Fig. S11). According to Fig. 7a the S-
388 numbers match the ones presented in the supporting information using a short linear scan of
389 potential. Over a wide range of current densities (0.01 to 1 A mg_{Ir}⁻¹) fairly constant S-
390 numbers were observed, indicating a direct relation between oxygen evolution and dissolution
391 for all materials. The difference in the absolute value of the S-number can be assigned to: (i) a
392 weaker bonding of the lattice oxygen in amorphous structures compared to crystalline ones,
393 enabling a direct participation in the OER with the formation of metastable, activated iridium
394 complexes that are more prone to dissolution, (ii) the amount of activated oxygen atoms
395 surrounding one iridium centre, which is assumed to be higher in the case of leached
396 Ba₂PrIrO₆ (see Fig. 1e) in comparison to amorphous iridium oxides and rutile IrO₂, enabling
397 the occurrence of instable iridium centres with two oxygen vacancies caused by
398 recombination of two activated oxygen atoms.⁵⁰ For crystalline IrO₂ the number of activated
399 oxygen atoms is restricted to the outer surface while bulk oxygen will not participate and
400 maintain a high coordination of the iridium atom resulting in a significantly lower probability
401 for the iridium atom to dissolve out of the structure.

402 The constancy of the S-number, observed over a wide range of current densities allows
403 a relation of dissolution and lifetime of the catalyst using equation 1, presented in Fig. 7b.

$$t = \frac{S \cdot z \cdot F \cdot m}{j \cdot M} \quad (1)$$

404 t = lifetime of the catalyst (s), S = Stability-number, z = electrons per transferred O₂,
405 F = Faraday constant (96485 C mol⁻¹), m = loaded mass of iridium (g cm⁻²), j = applied
406 current density (A cm⁻²), M = molar mass of iridium (192.2 g mol⁻¹).

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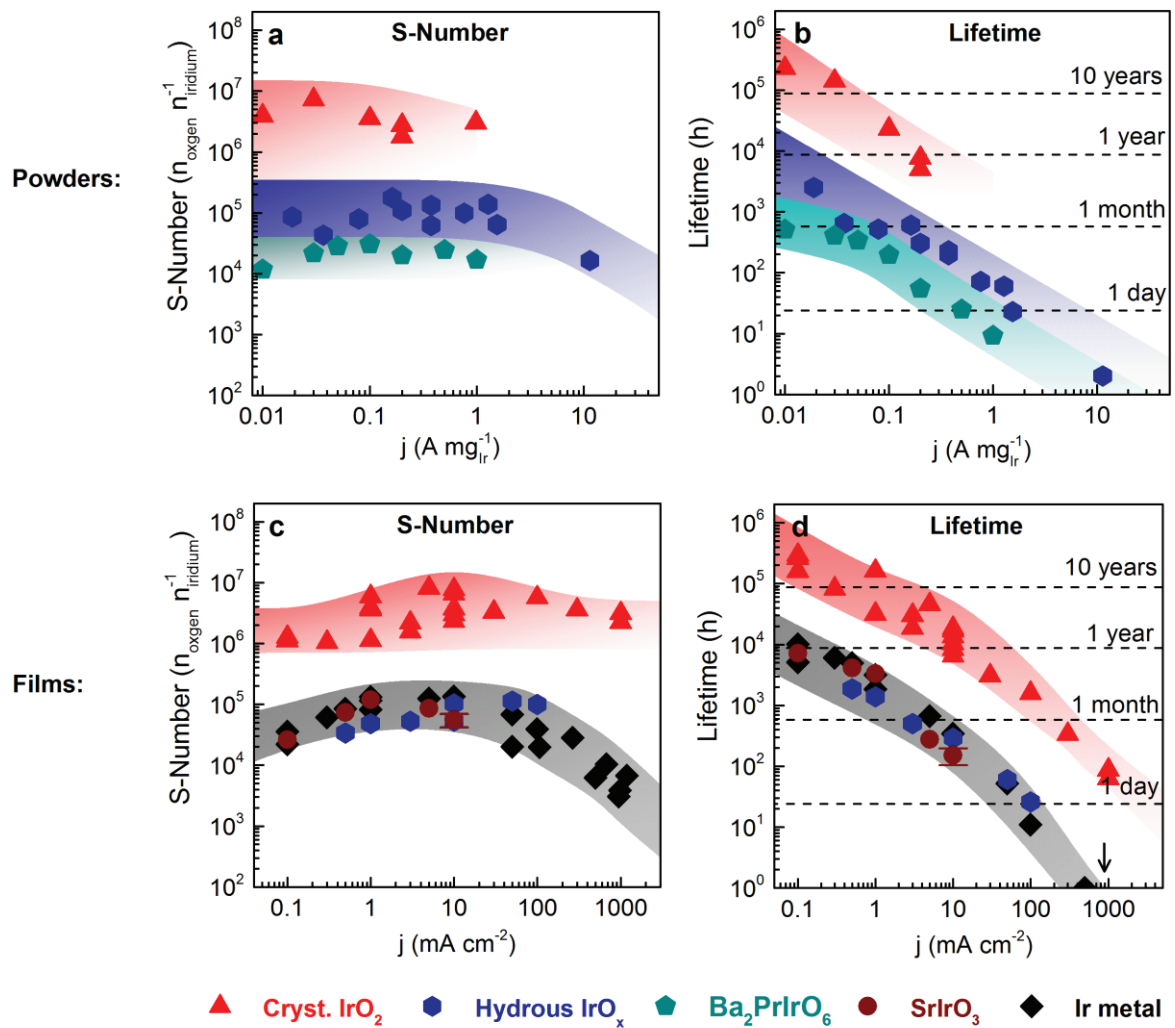
408 Hereby, lifetimes of a few days (Ba₂PrIrO₆), one month (IrO_x) and one year (IrO₂) were
409 obtained when considering a constant current density of 0.2 A mg_{Ir}⁻¹. Note these findings are

410 specific for the electrochemical cell used. Lifetimes in a PEM system can deviate, which is
411 discussed in more detail in the supporting information (see Fig. S12 and related text).

412 In order to widen our scope, also sputtered films were investigated using the same
413 procedure (Fig. 7c). The trends resemble the ones observed for powders. Additionally, S-
414 numbers for sputtered metallic iridium are presented, which drop at current densities above 50
415 mA cm⁻². A similar trend was observed for IrO_x in Fig. 7a. The reason is the onset of a second
416 dissolution pathway forming IrO₄²⁻, which is expected to occur at potentials > 1.8 V vs. RHE⁹
417 (see Fig. S13). Through kinetic stabilization, the latter pathway is successfully suppressed for
418 rutile IrO₂ at even higher potentials (reported as well for the hydrogen region³⁹). For metallic
419 iridium and amorphous iridium oxide, a self-accelerating degradation process can be observed
420 when a critical current density is reached by insufficient loading or degraded catalyst. The
421 degradation of IrO₂, however, is exclusively linked to the amount of oxygen evolved and not
422 to the applied potential.

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Figure 7. Investigation of S-Number and lifetime depending on the current load. (a, c) Stability-number (S-Number) plotted versus mass specific current density for powders (a) and geometric current density for sputtered films (c). $\text{Ba}_2\text{PrIrO}_6$ was leached for 5 days in advance. (b, d) Calculation of the catalyst's lifetime, based on equation 1 for powders (b) and films (d). This approach assumes “steady state” dissolution and neglects increased dissolution towards the end of life due to loss of surface area. In case of powder materials m equals the mass of loaded iridium. In case of films m was set to $50 \mu\text{g}_{\text{Ir}} \text{cm}^{-2}$ which equals film thicknesses of about 100 nm SrIrO_3 , 50 nm IrO_2 , and 20 nm iridium metal. Measurements were carried out in 0.1 M HClO_4 .

440 3. Conclusion

441 In this work, a new metric for stability benchmarking of electrocatalysts, the so called S-
442 number is introduced, enabling direct evaluation of lifetimes, illustrative comparison of
443 stability properties, and insights into degradation mechanisms. This concept can be adapted to
444 a wide range of electrochemical reactions and can be understood as an electrochemical turn
445 over number (TON) known from the field of heterogeneous catalysis.

446 Moreover, for the first time the in situ dissolution of various iridium-based oxides
447 including highly crystalline, perovskite-based, and amorphous structures over a wide range of
448 current densities is presented. The measurements were carried out in acidic electrolyte with
449 iridium-based perovskites undergoing severe leaching. Hence, in acidic conditions,
450 explanations for the enhanced activity based on electronic interactions with rare earth or alkali
451 elements are debatable. The resulting amorphous iridium oxide, which is part of several
452 studies on innovative OER materials,¹⁻⁵ shows exceptional high activity accompanied by high
453 iridium dissolution. We demonstrate the participation of activated lattice oxygen atoms as
454 trigger for the boost in activity and the high dissolution rate due to arising oxygen vacancies.

455 Based on our findings, future research in this field should be devoted to formation of
456 ultrathin films of crystalline iridium oxide on stable and conductive substrates with high
457 surface area, such as fluorine doped tin oxide (FTO), antimony doped tin oxide (ATO) or
458 similar materials.⁶³ By doing so the lower intrinsic activity and the fact that exclusively the
459 surface of the material is participating in the reaction could be compensated. In case the
460 superior activity of amorphous iridium oxides is utilized, stabilization of the weak iridium
461 intermediate caused by oxygen vacancies will be of great importance. Further fundamental
462 research in understanding dissolution processes of amorphous iridium oxides will be essential
463 to reach this goal.

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470 **Methods**

471 **Powder materials.** $A_2B\text{IrO}_6$ (A= Pr, Nd or Y; B = Ba or Sr) double perovskites were
472 synthesized in alumina crucibles using BaCO_3 , SrCO_3 , Pr_6O_{11} , Nd_2O_3 , Y_2O_3 and metallic
473 iridium powder, respectively. The standard solid-state reactions are described in the
474 literature.³⁵ All reactions were carried out in air and the products were furnace-cooled to room
475 temperature. The powders were intermittently reground during the synthesis. Amorphous
476 iridium oxide (iridium (IV) oxide dihydrate) and crystalline iridium oxide (iridium (IV)
477 oxide) were purchased from Alfa Aesar. To ensure complete crystallisation, iridium (IV)
478 oxide was additionally calcined at 600°C for 48 h in air.

479 For powder samples the electrodes were prepared by dropcasting 0.3 μL suspension on a
480 glassy carbon plate. All suspensions contained the same amount of iridium (0.27 mg mL^{-1}).
481 For some measurements of crystalline IrO_2 , however, the concentration was enhanced to 4.5
482 mg mL^{-1} in order to exceed the detection limit of the ICP-MS and measure reasonable
483 currents in the cyclic voltammograms. To avoid detachment 20 μL of Nafion solution (5 w%,
484 Sigma-Aldrich) was added to 5 mL of suspension. The dried spots ($\text{Ø} \sim 1 \text{ mm}$) were rinsed
485 with water and located with the help of a vertical camera attached to the SFC. The
486 measurements were carried out by placing the spot in the centre of the SFC's opening area
487 ($A = 0.035 \text{ cm}^2$).

488
489 **Film materials.** Ir metal films were deposited by physical vapour deposition in a magnetron
490 sputter system (AJA ATC 2200-V) with a confocal target setup. The 100 nm thick Ir film was
491 deposited on a thermally oxidized ($1.5 \mu\text{m SiO}_2$) 4-inch diameter Si (100) wafer with an
492 intermediate, 10 nm thick, Ti adhesion layer. Sputter targets were pre-cleaned at 150 W direct
493 current (DC), 4 Pa, 300 s for Ti and 100 W DC, 4 Pa, 30 s for Ir. The deposition was
494 performed at 150 W DC, 1.3 Pa, 150 s for Ti and 60 W DC, 0.66 Pa, 1200 s for Ir. Both layers
495 were deposited with substrate rotation. The sputter system was operated with a base pressure
496 $<2.6 \times 10^{-5} \text{ Pa}$ and an Ar plasma.

497 For high current density measurements on iridium metal, lift-off photolithography was used to
498 structure the thin film and create small catalyst dots (see Fig. S14). By doing so the bubble
499 detachment in the SFC was facilitated significantly. For the lift-off a bilayer photoresist
500 system consisting of an LOR 20 B (MicroChem) bottom and an AZ 1518 (MicroChemicals)
501 top layer was utilized. After deposition the photoresist was removed in a cleaning cascade of
502 acetone and isopropanol under ultrasonic agitation.

503 Hydrous IrO_x films were grown on the sputtered iridium spots by 300 square wave pulses of
504 0.5 s between 0.05 V and 1.4 V vs. RHE.

505 Crystalline IrO₂ films were produced on Si/SiO₂ wafers via reactive sputtering in the presence
506 of O₂ using a DC magnetron sputtering machine (BesTech GmbH, Berlin) followed by
507 additional thermal treatment at 600°C for 48 h in air.

508 SrIrO₃ film samples were epitaxially grown using on-axis, RF magnetron sputtering of a
509 Sr₄IrO₆ target on (001) SrTiO₃. Due to two-dimensional growth, the surface of the samples
510 was atomically flat, with 0.4 nm steps corresponding to the pseudo-cubic cell parameter. X-
511 ray diffraction showed that the films were single crystals, oriented [110] perpendicular to the
512 substrate⁶⁴.

513 **Labelled samples.** Thin films of isotope labelled reactively sputtered Ir¹⁸O₂ were deposited
514 by magnetron sputtering (BesTech GmbH, Berlin) at 100 W in a mixture of ¹⁸O₂ (99.00 at.%,
515 Sigma Aldrich) and Ar as the sputter gas and the chamber pressure was regulated to 0.5 Pa at
516 room temperature. The base vacuum before deposition was 2.0x10⁻⁶ Pa. The Ø3 inch target of
517 Ir (99.9%, Evochem) was pre-cleaned by sputtering against closed shutters prior to
518 deposition. To prepare films with a minimal surface roughness, on the smooth substrates of
519 single crystalline Si(100) wafers with a 1.5 µm thermal SiO₂ diffusion and reaction barrier
520 layer were used. The resulting thickness of the obtained coating was approximately 80 nm.
521 After the deposition films were annealed in vacuum at 500°C during 2 hours. Unlabelled
522 reactively sputtered Ir¹⁶O₂ were deposited using a mixture of ¹⁶O₂ and Ar. All other
523 conditions were kept as described before.

524 The ¹⁸O-labelled samples of hydrous Ir¹⁸O_x were prepared using a solution of 0.1 M HClO₄ in
525 H₂¹⁸O (97.76 at.%, Campro Scientific GmbH) applying a square wave potential program with
526 upper and lower potential limits of 1.4 and 0.04 V vs. RHE, respectively (600 cycles at 0.5
527 Hz) to a sputtered Ir film (see description above). Afterwards the electrodes were carefully
528 rinsed with ultrapure H₂¹⁶O water and threated in the vacuum at 80°C during 2 hours.
529 Unlabelled samples were prepared using electrolyte containing 0.1 M HClO₄ (Suprapur[®] 70%
530 HClO₄, Merck) in ultrapure H₂¹⁶O water (PureLab Plus system, Elga, 18 MΩcm, TOC < 3
531 ppb), using the same electrochemical program.

532 All ¹⁸O-labelled samples were prepared right before the OLEMS measurements and
533 transferred in a desiccator to avoid exchange of lattice oxygen in topmost layers with air.

534

535 **Electrochemical measurements.** Dissolution measurements were performed in argon purged
536 0.1 M HClO₄ using a scanning flow cell (SFC) connected to an inductively coupled plasma
537 mass spectrometer (ICP-MS)⁶⁵. A graphite rod and an Ag/AgCl electrode (Metrohm,
538 Germany) were used as counter and reference electrode, respectively. The electrolyte was
539 prepared by dilution of concentrated acid (Suprapur[®] 70% HClO₄, Merck) in ultrapure water
540 (PureLab Plus system, Elga, 18 MΩ cm, TOC < 3 ppb). Flow rate through the cell was 352
541 μL min⁻¹. Steady performance of the ICP-MS (NexION 300X, Perkin Elmer) was ensured by
542 addition of internal standard solution (¹⁸⁷Re, ¹³⁰In) downstream to the flow cell and daily
543 calibration. A scheme of the SFC is presented in the supporting information (Fig. S14).
544 OLEMS (online electrochemical mass spectrometer) measurements were carried out using a
545 SFC – set up, previously described elsewhere.⁶⁶ In contrast to the SFC connected to ICP-MS,
546 here the surface area of the working electrode was 0.125 cm² and a PTFE tip from the top of
547 the cell through an extra vertical channel was introduced. A 50 μm thick PTFE Gore-Tex
548 membrane with a pore size of 20 nm, through which products can evaporate into the vacuum
549 system of the mass spectrometer (Max 300 LG, Extrel) was mounted onto the very end of the
550 tip. The approximate distance from the tip to the electrode was about 50 μm, which is
551 determined by the thickness of the silicon ring sealing around the cell opening and the applied
552 contact force. These parameters were kept constant during the whole set of measurements.
553 A potentiostat (Reference 600, Gamry) was used for the electrochemical measurements with
554 both setups.

555
556 **Materials characterisation.** Scanning electron microscopy (SEM) measurements were
557 performed in secondary electron mode using a Leo 1550 VP (Zeiss) operated at 15 kV and 6
558 mm sample distance. For energy-dispersive X-ray spectroscopy (EDS) the acceleration
559 voltage was increased to 30 kV.

560 Measurements of x-ray photoelectron spectra were performed applying a monochromatic Al
561 Kα X-ray source (1486.6 eV) operating at 15 kV and 25 W (Quantero II, Physical Electronics,
562 Chanhassen, MN, USA). The binding energy scale was referenced to the C 1s signal at 285.0
563 eV.

564 TEM and SAED analysis were performed with a CM20 FEG electron microscope (from
565 Philips) operated at 200 kV. The samples were prepared by dropcasting about 5 μl of catalyst
566 suspension onto a gold TEM grid coated with a Lacey carbon film (NH7, Plano GmbH).

567

568 **Data availability**

569 The authors declare that the main data supporting the findings of this study are available
570 within the article and its Supplementary Information file. Extra data are available from the
571 corresponding authors upon request.

572

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581

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