Na-doped ruthenium perovskite electrocatalysts with improved oxygen evolution activity and durability in acidic media

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The design of active and durable catalysts for the H2O/O2 interconversion is one of the major challenges of electrocatalysis for renewable energy. The oxygen evolution reaction (OER) is catalyzed by SrRuO3 with low potentials (ca. 1.35 V_{RHE}), but the catalyst’s durability is insufficient. Here we show that Na doping enhances both activity and durability in acid media. DFT reveals that whereas SrRuO3 binds reaction intermediates too strongly, Na doping of ~0.125 leads to nearly optimal OER activity. Na doping increases the oxidation state of Ru, thereby displacing positively O p-band and Ru d-band centers, weakening Ru-adsorbate bonds. The enhanced durability of Na-doped perovskites is concomitant with the stabilization of Ru centers with slightly higher oxidation states, higher dissolution potentials, lower surface energy and less distorted RuO6 octahedra. These results illustrate how high OER activity and durability can be simultaneously engineered by chemical doping of perovskites.
Electrochemical technologies promise the efficient and versatile storage and use of renewable energy in cycles that do not generate harmful by-products. Therefore, they are expected to become major players in the shift towards circular economy and energy systems, once their present problems are solved. For instance, the oxygen evolution reaction (OER) in which \( \text{H}_2\text{O} \) is oxidized to \( \text{O}_2 \) is crucial in electrolyzers and in the charging of metal-air batteries. To compensate the sluggish kinetics of the OER, high overpotentials are needed in practical applications, causing severe energy losses. Ir-based materials are the state-of-the-art OER catalysts, which, owing to their high price and scarcity must be replaced to facilitate wider implementation of electrolyzers. Functional oxides such as perovskites are promising OER electrocatalysts, especially in alkaline media.

Recently, high OER activities in alkaline electrolyte have been reported for thin films of SrRuO\(_3\) (0.1 mA cm\(^{-2}\) at 1.33 V vs. RHE). However, this material loses its activity after only two cycles. The lack of stability of Ru-based oxides appears to be related to the transformation of Ru\(^{4+}\) into Ru\(^{2+}\) at high voltages, leading to the decompositions of the perovskite, which starts with Sr dissolution followed by the collapse of the mixed-oxide structure. Very few examples of perovskites with high OER activity in acid exist. For instance, SrRuO\(_3\) nanoparticles and Sr\(_{0.95}\)Na\(_{0.05}\)RuO\(_3\) thin films show high OER activity, Ru-based compounds present regular and not distorted as in SrRuO\(_3\), perovskites adopt an orthorhombic perovskite structure with space group \( \text{Pbnm} \), with Sr\(^{2+}/\text{Na}^+\) located randomly at A sites and Ru\(^{3+}/\text{Ru}^2+\) at B sites, as previously reported. Fig. 1a shows good agreement between calculated and experimental PND data. The structural results obtained from PND Rietveld refinements are shown in Supplementary Table 4. First, we verified the lack of vacancies in A-sites and then we refined the Na occupancy into Sr-sites. The refined Na contents are close to the nominal values, in agreement with the values obtained by ICP-OES and the cell volume observed with XRD (Supplementary Note 1, Supplementary Table 5). Figure 1b and Supplementary Fig. 3 show the Ru-O distances on the RuO\(_6\) octahedra. Ru\(_3\) octahedra in SrRuO\(_3\) are more distorted than in Sr\(_{0.95}\)Na\(_{0.05}\)RuO\(_3\) and Sr\(_{0.90}\)Na\(_{0.10}\)RuO\(_3\), with large \( \text{ab} \) in-plane deformation, shortened Ru-O1 distances (1.950(2) Å) and elongated Ru-O1 distances (2.006(2) Å). Note that this deformation has been previously reported for SrRuO\(_3\). Conversely, Na-doped samples show very similar Ru-O distances (of ca. 1.98 Å) on the RuO\(_3\) octahedra, indicating that the octahedra are regular and not distorted as in SrRuO\(_3\) (Fig. 1c). The different octahedra distortion of SrRuO\(_3\) and Na-doped samples could be a consequence of the slight change of Ru oxidation states in Na-doped perovskites, as confirmed from XAS (see below). SrRuO\(_3\) contains Ru\(^{4+}\) cations (4d\(^4\)) with relatively extended d orbitals. Ru\(^{4+}\) adopts a low spin configuration (\( t_2g^3e_g^0 \))\(^\circ\), favouring Jahn–Teller distortions that split the threefold \( \text{t}_2g \) into one lower \( \text{d}_{\text{ez}} \) orbital and two higher \( \text{d}_{\text{xy}} \) and \( \text{d}_{\text{yz}} \) orbitals. Such Jahn–Teller distortion causes the aforementioned elongated and shortened Ru–O distances. However, upon Na doping, a slight oxidation to Ru\(^{2+}\) occurs resulting in the partial elimination of the fourth spin of the \( \text{t}_2g \) which could prevent the Jahn–Teller effect (or produce a switch to a high spin configuration) resulting in more regular octahedra. In addition, the higher temperatures used for the synthesis of the Na-doped perovskites could affect the different distortions. The implications of the actual structure of the perovskite for the OER performance are discussed below.

PND results also show that, within the error, the perovskites lack cationic and oxygen vacancies (Supplementary Table 4). Further experimental evidences of the absence of short- or long-range ordered oxygen vacancies were attained from HRTEM and selected area electron diffraction (SAED) patterns (Supplementary Fig. 4) in which diffraction spots for stoichiometric perovskites are the only ones observed. Moreover, DFT reveals large energies of formation of oxygen vacancies (bulk and surface), confirming the unlikely formation of such vacancies (Supplementary Note 3, Supplementary Fig. 5, and Supplementary Table 6). The lack of oxygen vacancies implies that Na incorporation is compensated by partial oxidation of Ru atoms. The effect of Na doping in the structure and oxidation state of Ru was analyzed by x-ray absorption spectroscopy (XAS). We performed XAS in different energy ranges, soft and hard x-rays, to study the K-edge of Na, and the K-edges and M\(_{2,3}\)-edges of Ru. The spectra of the Na K-edge confirm the presence of Na in the Na-doped perovskites (Supplementary Fig. 6). The strong overlap with the Sr L-edge background signal prevents an accurate estimation of the actual Na-content in each perovskite by this technique. In addition, the analysis of the Ru K-edge further confirms the incorporation of Na into the perovskites.

### Results and discussion

**Composition, structure, and oxidation state.** SrRuO\(_3\), Sr\(_{0.95}\)Na\(_{0.05}\)RuO\(_3\), and Sr\(_{0.90}\)Na\(_{0.10}\)RuO\(_3\) were prepared by sol–gel chemistry followed by thermal treatment in air, with an increase of the synthesis temperature as the content of Na increases (Methods section). The chemical composition of the samples was analyzed by PND, EDX, and ICP-OES (see Supplementary Note 1). Sr and Na contents of Sr\(_{0.936(7)}/\text{Na}0.064(7)\) for Sr\(_{0.936(7)}/\text{Na}0.064(7)\) and Sr\(_{0.906(1)/\text{Na}0.094(1)}\) for Sr\(_{0.906(1)/\text{Na}0.094(1)}\) can be enhanced by Na and long-lasting OER activities in acid media.

Here we show that the OER activity and durability in acid of bulk SrRuO\(_3\) can be enhanced by Na\(^+\) doping in the Sr\(^{2+}\) position. Thus, Sr\(_{0.95}\)Na\(_{0.05}\)RuO\(_3\) and Sr\(_{0.90}\)Na\(_{0.10}\)RuO\(_3\) exhibit very high specific OER activity, with a potential of \( \approx 1.35 \text{ V} \) (an overpotential of only 120 mV) at 0.5 mA cm\(^{-2}\) and 1.33 V vs. RHE. Thorough physical and chemical studies of fresh and used perovskites reveal that substituting Sr by Na increases the stability of the perovskite structure, thus preventing deactivation during repeated cycling. This result is also supported by DFT, demonstrating lower surface energy and higher dissolution potentials for Na-doped perovskites, which slows down the collapse of the perovskite structure.

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(Supplementary Note 4, and Supplementary Figs. 6b and 7). The Fourier transforms from the Ru K-edge EXAFS signals (phase non-corrected) shown in Supplementary Fig. 6b reveal that the signals for SrRuO₃ are less intense than the ones of the Na-doped samples, indicating a higher distortion of the RuO₆ octahedra in SrRuO₃, in agreement with PND data.

The oxidation state of Ru was determined by the analysis of the Ru M₂,₃-edge. This edge is associated with the promotion of 3p to 4d orbitals in Ru and is more sensitive to changes in the d-states than the K-edge. As observed in Fig. 1d, the XANES signals of SrRuO₃, Sr₀.₉₅Na₀.₀₅RuO₃ and Sr₀.₉₀Na₀.₁₀RuO₃ appear at higher energies than SrRuO₃. In addition, a slight broadening to the low energy region of the peaks of the Na-doped is observed. Both features are indicative of a higher oxidation state of Ru atoms in the Na-containing perovskites.

**Electrochemical performance.** The OER activity of SrRuO₃, Sr₀.₉₅Na₀.₀₅RuO₃, and Sr₀.₉₀Na₀.₁₀RuO₃ was evaluated in O₂-saturated 0.1 M HClO₄ at 1600 rpm. The catalysts were deposited onto a glassy carbon electrode using an ink (Methods section). High surface area carbon was mixed with the perovskites (1:5 in weight) to improve the conductivity.

Figure 2a shows the current densities (j) normalized by the geometric area (0.196 cm²). Na-doped samples present similar current densities than SrRuO₃ in the whole polarization range. The potential to reach a current density of j = 0.5 mA cm⁻²geo is ~1.35 V for the three samples, equivalent to an overpotential (η) of only 120 mV. In comparison, the potential to achieve j = 0.5 mA cm⁻²geo with RuO₂ is ~1.4 V. The low overpotentials of Sr₁₋ₓNaₓRuO₃ are in line with the potential reported to achieve the same current density for thin films of SrRuO₃ in alkaline media of 1.35–1.40 V (the actual value depending on the exposed plane) and Ru metal in acid media (~1.32 V). However, the latter catalysts transform into RuO₂ already in the first reaction cycle losing most of their initial activity.

As reported in Supplementary Table 7, the Na-containing perovskites have larger particle sizes than SrRuO₃. Although it is well accepted that the OER is a structure sensitive reaction, the actual effect of particle size is not clear. Krtíš et al. reported that the onset for the oxygen evolution current is particle-size independent for RuO₂ electrodes, but not for Ru₀.₈Co₀.₂O₂−ₓ. By contrast, Reier et al. reported that nanosized Pt, Ru, and Ir particles are more active than the corresponding bulk phases. Shao–Horn et al. found that the OER activity of Laₓ(Ba₀.₅Sr₀.₅)ₓCo₀.₈Fe₀.₂O₃−δ perovskites does not follow a linear relationship with particle size, and Schmidt et al. indicated that the OER activity of IrO₂ does not increase monotonically with the surface area and suggest that morphology can also play a key role. In this sense, Matsumoto et al. reported that OER activity of mixed oxides could be related to the exposed facets, but failed to identify the most active ones. Recently, by using thin films of SrRuO₃, Markovic et al. reported that the (111) face is more active for the OER than (001). Shao–Horn et al. reported that (100) facets of RuO₂ and IrO₂ are more active in alkaline media than the thermodynamically stable (110). We have found no evidences of preferential surface termination in our samples, but as shown in Supplementary Table 7, particle size increases with Na doping. Therefore, and in order to assess intrinsic catalytic activities (iₐ), the OER currents have been normalized to the oxide active area during the OER has been reported.

In Fig. 2b we report the OER intrinsic activities vs. Aₛ. Na-doped perovskites show higher current densities than SrRuO₃. For comparison, the potential to reach 10 mA cm⁻²oxide with Sr₀.₉₀Na₀.₁₀RuO₃ is 1.4 V, less positive than those reported for state-of-the-art perovskites of 1.5 V for SrIrO₃/IrOₓ or 1.5–1.6 V for Ir-based double perovskites. The actual production of O₂ during the OER has been confirmed by using a RRDE (rotating ring disk electrode, see Supplementary Note 6 and Supplementary Fig. 9) and by following O₂ evolution during the OER, using a mass spectrometer probe immersed in the electrolyte (Supplementary Note 7 and Supplementary Fig. 10).
Figure 2b compares the Tafel plots of the intrinsic activities of the catalysts under study with the best catalysts in acid electrolyte reported in the literature. The initial activities of Sr$_{1-x}$Na$_x$RuO$_3$ are higher than the ones reported for similar catalysts. Currents similar to Ir double perovskites or SrIrO$_3$/IrO$_2$ (~5–10 mA cm$^{-2}$ oxide) are achieved by Sr$_{1-x}$Na$_x$RuO$_3$ at significantly lower overpotentials.

The catalytic activity enhancement of SrRuO$_3$ upon Na doping is analyzed in Fig. 2c using a DFT-based screening study in which the OER mechanism on all materials is assumed to proceed as: H$_2$O $\rightarrow$ *OH $\rightarrow$ *O $\rightarrow$ *OOH $\rightarrow$ O$_2$. This analysis outlines clear activity trends, namely that progressive Na doping weakens the adsorption energies because the surface oxygen p-band center and the Ru d-band center are positively displaced (see Supplementary Note 8 and Supplementary Fig. 11). The combinatorial model in Supplementary Note 9 and Supplementary Fig. 12 shows that Sr$_{0.875}$Na$_{0.125}$RuO$_3$ at the top of the volcano and that its decomposition into RuO$_2$ decreases the activity. The activity of Na-doped perovskite decomposes (via Sr dissolution, Na dissociation or both, see Supplementary Note 10 and Supplementary Figs. 14b and 15), the activity decreases until it reaches that of RuO$_2$, in agreement with our durability experiments (see below).

Although there is no one-to-one connection between theoretical and experimental overpotentials (Fig. 2b, c); Jaramillo et al. noted that the two overpotentials agree well when the experimental ones are taken at a current density of 1 mA cm$^{-2}$ oxide. Thus, Fig. 2c contains suitable data from the literature showing good agreement between theory and experiments and confirms the high activity of Na-doped SrRuO$_3$. The differences between Fig. 2b, c are probably due to DFT-based errors, which in view of their intrinsic nature (because they are present in all data), translate into error bands around the volcano lines in Fig. 2c. In particular, the use of scaling relations (Supplementary Fig. 14a) and GGA exchange-correlation functionals set those errors at approximately ±0.2 eV for adsorption energies (±0.2 V for (over) potentials). See Supplementary Notes 11 and 12.

We stress here that screening analyses are not intended to elucidate the exact OER mechanism, which is the subject of different types of studies, but rather to enable the simultaneous comparison of several different materials that clarify the role of Na incorporation and dissolution on the activity. Further discussion on this subject is provided in Supplementary Note 11.
Note in passing that Govindarajan et al.\textsuperscript{39} recently proposed a descriptor called electrochemical-step symmetry index (ESSI) for OER catalysts (see Supplementary Note 11 and Supplementary Fig. 14b). Although the descriptor is based on the departures of OER reaction energies from the ideal value of 1.23 V, it does not depend on scaling relations, unlike the volcano plot in Fig. 2c. The conclusions drawn using ESSI are analogous to those of Fig. 2c, which substantiates our analysis. Furthermore, the ESSI analysis in Supplementary Fig. 14b suggests that Sr\textsubscript{0.875}Na\textsubscript{0.125}RuO\textsubscript{3} could be further improved by strengthening its *OH adsorption energy by 0.16 eV.

**Stability during OER.** Durability is a major concern when considering the actual implementation of an active OER catalyst in an electrolyzer, especially in acid electrolyte. As observed in Fig. 2d, replacing Sr by Na significantly improves the catalyst’s stability. After 20 consecutive cycles of reaction, SrRuO\textsubscript{3} loses more than 85% of its initial activity. This is in line with the observation that SrRuO\textsubscript{3} loses its activity after few cycles\textsuperscript{11,13}. Remarkably, Na-doped perovskites only lose ca. 15% of their initial activity after 20 cycles. In other words, to lose 65% of initial activity, SrRuO\textsubscript{3} needs only ~7 cycles while Sr\textsubscript{0.90}Na\textsubscript{0.10}RuO\textsubscript{3} needs ~80 (Supplementary Note 13 and Supplementary Figs. 16 and 17). The voltammograms recorded during the OER (Supplementary Fig. 16) are in line with those of Ru-based perovskites\textsuperscript{15}. Contrary to what is observed for Ir-based perovskites\textsuperscript{40}, features due to the formation of oxides (RuO\textsubscript{x}) are not observed in the capacitive region of the voltammograms, probably because the expected features for the oxides overlap with the current due to the OER\textsuperscript{13}. We emphasize the durability obtained for Sr\textsubscript{0.95}Na\textsubscript{0.05}RuO\textsubscript{3} and Sr\textsubscript{0.90}Na\textsubscript{0.10}RuO\textsubscript{3}, first because most mixed oxides are not stable in acid, so finding a catalyst with such high activity, low overpotential, and durability over several cycles is already a noteworthy result. Second, because the high activities obtained are only met by Ru or Ir metals, which are rather unstable\textsuperscript{41}. For instance, Ru metal in acid media loses most of its activity after the first cycle of reaction and completely dissolves within the first 10 cycles, due to metal oxidation when the potential rises\textsuperscript{12}. RuO\textsubscript{x} also presents high OER activity but suffers from corrosion after the first cycle; it should be noted, however, that RuO\textsubscript{2}’s performance for the OER is influenced by its morphology\textsuperscript{42}. Finally, the number of perovskites reported as OER catalysts in acid is limited and those with high activity are SrIrO\textsubscript{3} and SrRuO\textsubscript{3}. In SrRuO\textsubscript{3}, Sr dissolves after the first cycles and it is suggested that IrO\textsubscript{2} oxides at the catalyst’s surface are responsible for the catalytic activity\textsuperscript{13}. In SrRuO\textsubscript{3}, Sr dissolves decreasing the activity dramatically\textsuperscript{11,13}. Durability studies of powder L\textsubscript{2}LiIrO\textsubscript{6} in acid and alkaline conditions concluded that during the OER, IrO\textsubscript{2} nanoparticles segregate to the perovskite surface, resulting in an oxidized surface with high OER activity\textsuperscript{43}. In summary, most reports indicate that metal oxides prone to severe degradation issues under oxygen evolution conditions\textsuperscript{31,44}.

**Evolution of structure and composition during OER.** Insights into deactivation of representative SrRuO\textsubscript{3} and Sr\textsubscript{0.90}Na\textsubscript{0.10}RuO\textsubscript{3} were obtained by analyzing fresh and used samples (after 20 OER cycles) and from the evolution of the composition of the electrolyte after 10, 40, and 80 OER cycles by ICP-OES (see also Supplementary Note 14).

As observed from the micrographs in Fig. 3a, SrRuO\textsubscript{3} consists of particles between ca. 200 and 800 nm with perovskite structure, see HRTEM/Digital Diffraction Pattern (DDP) in Fig. 3b and HRTEM/SAED in Supplementary Fig. 4. STEM-EDX mappings (Fig. 3c) reveal a homogeneous distribution of Sr and Ru along with segregated RuO\textsubscript{x} particles as shown in Fig. 3g. This observation is consistent with the analysis of the composition of the electrolyte during OER with SrRuO\textsubscript{3}. As shown in Supplementary Fig. 17, the concentration of Sr in the electrolyte during OER cycles increases faster than that of Ru. HRTEM images in Supplementary Fig. 18 reveal an evident loss of crystallinity of used SrRuO\textsubscript{3}.

Representative TEM and HRTEM/DDP images of Sr\textsubscript{0.90}Na\textsubscript{0.10}RuO\textsubscript{3} are shown in Fig. 4a, b, respectively. The sample consists of particles of ~2.8 (±0.5) μm with perovskite structure; see DDP (inset of Fig. 4b) and SAED in Supplementary Fig. 4). STEM-EDX mapping (Fig. 4c) reveals the homogeneous
distribution of Sr, Ru, and Na in the perovskite. Figure 4d shows a representative HRTEM/DDP image for used Sr0.90Na0.10RuO3. Contrary to SrRuO3, used Sr0.90Na0.10RuO3 still presents the perovskite structure (inset of Fig. 4d). As shown in Fig. 4e, the size and Sr/Ru atomic ratio (~0.95) of used Sr0.90Na0.10RuO3 is similar to that of the fresh one. STEM-EDX mapping in Fig. 4f shows a homogeneous distribution of Sr, Ru, and Na in the used sample. These observations clearly indicate that neither the composition nor the structure of Sr0.90Na0.10RuO3 are affected after 20 cycles in the OER. HRTEM/DDP images (Supplementary Fig. 19) also reveal the high crystallinity of used Sr0.90Na0.10RuO3. However, note that the incipient formation of RuO2 is evidenced in the FFT filtered image shown in Supplementary Fig. 19b. Again, this observation is in good agreement with the ICP results shown in Supplementary Fig. 17b revealing small concentrations of Sr and Ru in the electrolyte after the OER, significantly lower than those found for SrRuO3. In fact, Supplementary Fig. 17b confirms that the Na-doped perovskite is more stable than SrRuO3 during the OER in acid electrolyte.

The structure of the used samples (20 cycles in the OER) has also been studied by XRD and XAS. The x-ray diffractograms of the fresh and used samples are similar and only show diffraction lines for the perovskite phase (Supplementary Fig. 20). The analysis of the Ru K-edge of fresh and used SrRuO3 and Sr0.90Na0.10RuO3 are shown in Fig. 5 and Supplementary Fig. 21. The intensity of the FT-EXAFS signals of the used SrRuO3 sample is significantly lower than that of the fresh one, especially for the higher shells (Fig. 5a). This result reveals severe degradation (loss of crystallinity) of the SrRuO3 structure after the OER. Conversely, the FT-EXAFS signals of both fresh and used Sr0.90Na0.10RuO3 are similar (Fig. 5b), indicating that the perovskite structure remains stable during the OER. It is possible to estimate the composition of the used samples by a linear combination fit on the EXAFS signals of the fresh perovskites and RuO2. An approximate ratio of 20:80 SrRuO3:RuO2 is obtained for SrRuO3 (Supplementary Fig. 21c) being of 80:20 Sr0.90Na0.10RuO3:RuO2 for the Na-doped one (Supplementary Fig. 21d). These results are in excellent agreement with the microscopy results, and indicate that Na doping enhances the structural stability (and hence durability) of the perovskites during the OER. These conclusions also result from the evolution of the pre-edge features of the XANES Ru K-edge and the decrease in the white line (Supplementary Fig. 21a).

Finally, the surface composition of the fresh and used perovskites was analyzed by XPS. Figures 5c,d depict the spectra of the Sr 3d core-level regions of the fresh and used samples. The two Sr 3d doublets are associated to carbonate (high binding energy) and Sr–O–M (lower binding energy) moieties. According to Supplementary Table 8, the surface atomic Ru/Sr ratio of both SrRuO3 and Sr0.90Na0.10RuO3 increases after the OER. Nevertheless, Ru enrichment is more pronounced in SrRuO3 (2.7) than in Sr0.90Na0.10RuO3 (1.8) indicating a more severe decomposition of SrRuO3.

The results above clearly indicate that Sr dissolves from the perovskite structure during the OER, especially from SrRuO3. Upon Sr dissolution, the perovskite structure becomes ill-defined, as observed by TEM and XAS. At some point, Ru segregates from the perovskite and forms nanosized RuO2 phases, which in some cases are deposited at the surface of the perovskites, but are mostly found as isolated particles (Supplementary Fig. 18). As predicted by DFT (Fig. 2c), the collapse of the perovskite and the formation of RuO2 lead to a significant loss in OER activity. The higher durability of Na-doped samples is due to their higher structural stability and lower dissolution rates of Sr and Ru compared with SrRuO3. Na incorporation enhances the formation of different phases during the OER. Several features can explain the enhanced durability of Na-doped perovskites. On the one hand, it is known that Ru centers oxidize to Ru4+ during potential excursions above ~1.4 V incest. These highly oxidized Ru atoms are not stable within undoped SrRuO3. Na incorporation permits the stabilization of Ru4+ ions within the lattice, resulting in versatile Ru catalytic centers that can easily increase or decrease their charge depending on the adsorbates, which is advantageous for the OER. Our results show that Na incorporation results in less distorted RuO6 octahedra and higher durability. This observation is in line with previous reports indicating that less distorted structures are more susceptible to suffer structural variations without being destroyed when subjected to voltage changes. Finally, DFT calculations indicate that (i) the surface energetics of Sr1−xNa2xRuO3 are considerably lower compared with SrRuO3; (ii) the dissolution potentials of the cations in the A site of the perovskites are shifted toward more positive values in presence of Na; and (iii) the stability at low pH is also enhanced upon Na doping. Such observations, described in detail in the Supplementary Note 10, attest to more stable perovskite structures upon doping.

To summarize and conclude, we have synthesized a series of active catalysts (Sr1−xNa2xRuO3) for the OER in acid media with extraordinary features. The measured activities are comparable to or surpass those of other remarkable OER catalysts in the literature. Na incorporation in the lattice also grants these compounds high electrochemical and structural stability, so as to
Sr0.90Na0.10RuO3.

normalized to the intensity of Sr in the fresh samples

convenient weakening of the adsorption energies of the OER

(a) other monovalent cations such as Li

conclusions could help in guiding future research in several ways:

(b) If Ru\(^{5+}\) sites are instrumental for the enhancement of SrRuO\(_3\), then B-site doping with e.g., trivalent cations might as well enhance the activity and/or the stability. (b) If Ru\(^{5+}\) sites are instrumental for the enhancement of SrRuO\(_3\), then B-site doping with e.g., trivalent cations might as well enhance the activity and/or the stability. (c) Since Sr\(_{0.875}\)Na\(_{0.125}\)RuO\(_3\) is the most active compound in Fig. 2c, we
can be further optimized if the *OH binding energy is strengthened by 

−0.16 eV. This is an interesting hypothesis to be verified experimentally in subsequent studies.

Methods

Synthesis. Sr\(_x\)Na\(_{2-x}\)RuO\(_3\) \((x = 0.00, 0.05, 0.10)\) perovskites were synthesized in polycrystalline form by a wet-chemistry procedure to obtain very reactive precursors and reduce the final synthesis temperature. Stoichiometric amounts of Sr (NO\(_3\))\(_2\) (Sigma Aldrich 99.99% trace metals basis), Na\(_2\)CO\(_3\) anhydrous (Sigma Aldrich 99.9% trace metals basis) were dissolved in 150 mL of 0.1 M citric acid (Sigma Aldrich assay ≥ 99.5%) and 20 mL of nitric acid (Panreac 65%), to ensure complete dissolution of the starting materials. We added 5% excess of Na\(_2\)CO\(_3\) to compensate the possible volume of gas adsorbed on the surface is measured at −196 °C (nitrogen boiling point). The samples are finally degassed at 140 °C under vacuum for 24 h. Specific areas were calculated by applying the BET method.

Inductively coupled plasma optical emission spectrometry (ICP-OES). An ICP-OES Analytik Jena PQ 9000 spectrometer was used for the analyses.

Specimens for analysis were subjected to acid digestion in a mixture of 3 mL of HNO\(_3\), 2 mL HCl, 3 mL HF, and 3 mL H\(_2\)PO\(_4\), in a pressurized microwave.

Powder X-ray diffraction (XRD). The phases and their purity were determined by XRD in Bragg-Brentano reflection geometry with CuK\(_\alpha\) radiation (\(\lambda = 1.5418 \) Å).

Powder neutron diffraction (PND). PND was carried out in the high-resolution powder diffractometer D2B at ILL (Grenoble, France). The data were collected at room temperature and \(\lambda = 1.594 \) Å. For the refinement of the crystal structures, we used the Rietveld method and the Fullprof crystallographic program. The function selected to generate the diffraction peaks shape was pseudo-Voigt. The parameters refined in the final run were the scale factor, linear interpolation between a set of background points, zero-point error, pseudo-Voigt parameters, positional coordinates, isotropic thermal factors an occupancy factors.

Transmission electron microscopy (TEM). TEM data was recorded on a JEOL 2100 field emission gun transmission electron microscope operating at 200 kV and equipped with an EDX spectrometer Oxford INCA Energy 2000 system. Specimens were prepared by depositing small portions of the samples on top of a Cu grid supporting a lacey carbon film. Deposition was achieved by preparing a suspension of the material in ethanol.

BET method. The measurements were performed in a Micromeritics ASAP 2000 apparatus. Surface areas were evaluated by purging with nitrogen the samples within the relative pressure range \(P/P_0 = 0.05−0.30\). The amount of adsorbed nitrogen is related to the total surface area of the samples. The volume of gas adsorbed on the surface is measured at −196 °C (nitrogen boiling point). The samples are finally degassed at 140 °C under vacuum for 24 h. Specific areas were calculated by applying the BET method.

X-ray absorption spectroscopy (XAS). XAS measurements were performed at room temperature at Diamond Light Source (UK) on the B18 and I10 beamlines. In the case of I10 measurements, data were collected at Na K-edge (\(E = 1070.8 \) eV) and Ru M\(_{4,5}\)-edge (\(E = 461 \) and 483 eV) in fluorescence mode with a photodiode sited to measure by back-scattering geometry. The Sr L\(_3\) and L\(_2\) edges appear at the half energy (1940 eV and 2007 eV, respectively) as the undulator second harmonic is mostly absorbed but it partially passes through the monochromator at the energy of the first harmonic as a contamination. On the B18 beamline, data were collected...
X-Ray photoemission spectroscopy (XPS). X-ray photoelectron spectra (XPS) were acquired with a VG ESCALAB 200 R at a pass energy of 50 eV using a Mg Kα X-ray source. The kinetic energies of the photoelectrons were measured using a hemispherical electron analyzer working in the constant-pass energy mode. The background pressure in the analysis chamber was kept below 3 x 10⁻⁸ mbar during data acquisition. At least 200 scans were collected in increments of 0.1 eV with dwell times of 50 ms in order to increase the signal-to-noise ratio. The binding energies (0.2 eV) were determined by setting the C 1s peak at 284.8 eV.

Electrochemical characterization. The electrochemical performance was tested in a computer-controlled Autolab PGStat 302 N potentiostat/galvanostat. A standard three-compartment glass cell and a rotating disk electrode (RDE) (Pine Research Instruments) were used. A graphite rod and a homemade Reversible Hydrogen Electrode (RHE) were used as counter and reference electrodes, respectively. Sr0.875Na0.125RuO3 samples were deposited on the electrode as inks. The powdered samples were mixed in a 5:1 mass ratio with carbon black (Vulcan-XC-72R) to improve the electrical conductivity. Then the solvents were added. Tetrahydrofuran (THF) and Naimprove the electrical conductivity. The samples were mixed in a 5:1 mass ratio with carbon black (Vulcan-XC-72R) to improve the electrical conductivity. Then the solvents were added. Tetrahydrofuran (THF) and Na.

The procedure for estimating the free energies of adsorption of the oxygen evolution intermediates, and details of the construction of the vol
cano plots making use of the scaling relations between the adsorption energies of the adsorbates (see Supplementary Note 11) appear elsewhere. We included total adsorbate coverages of 0.5 ML in all cases, so that °O, °OH, and °OOH were co-adsorbed with °O. Such co-adsorption accounts for the fact that OER potential at least part of the active Ru sites are likely covered with °O. The assessment of the ESSI is described in the Supplementary Note 11 and elsewhere.

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