The use of renewable electricity to prepare materials and fuels from abundant molecules offers a tantalizing opportunity to address concerns over energy and materials sustainability. The oxygen evolution reaction (OER) is integral to nearly all material and fuel electrolysises. However, very little is known about the structural evolution of the OER electrocatalyst, especially the amorphous layer that forms from the crystalline structure. Here, we investigate the interfacial transformation of the SrIrO$_3$ OER electrocatalyst. The SrIrO$_3$ amorphization is initiated by the lattice oxygen redox, a step that allows Sr$^{2+}$ to diffuse and O$^{2-}$ to reorganize the SrIrO$_3$ structure. This activation turns SrIrO$_3$ into a highly disordered Ir octahedral network with Ir square-planar motif. The final Sr$_x$IrO$_y$ exhibits a greater degree of disorder than IrO$_x$ made from other processing methods. Our results demonstrate that the structural reorganization facilitated by coupled ionic diffusions is essential to the disordered structure of the SrIrO$_3$ electrocatalyst.

**INTRODUCTION**

The production of materials and fuels from widely available molecules is one of the most important challenges facing 21st-century society (1–3). Electrocatalysts function by providing environments conducive to the fuel and material electrosynthesis (4, 5). However, developing high-performance electrocatalysts is far from straightforward. One of the major hurdles is the lack of information regarding the evolving structure of the electrocatalysts during the electrochemical operations. This knowledge gap is particularly problematic for the oxygen evolution reaction (OER), where the reaction environment is highly oxidizing and can rearrange the structure of the electrocatalyst (6–8). Given that the OER, the key electro-oxidation reaction, is one of the major causes of inefficiency in the fuel and material electrosynthesis (1, 2), understanding the structural and chemical evolution of the electrocatalyst during the OER is essential to the development of active future electrocatalyst materials and, more broadly, to the prospect of materials and energy sustainability.

The search for more active and stable OER electrocatalysts has motivated several investigations into the structure-activity relationship of perovskite-based oxides (9, 10). Aside from studying how surfaces stabilize adsorbates, a number of theoretical and experimental studies have indicated that high-performance electrocatalysts can undergo interfacial transformations during the OER, in particular, from the crystalline to amorphous structure (11–14). For instance, Ba$_{0.5}$Sr$_{0.5}$CoO$_3$ and Fe$_{0.2}$O$_{3.8}$ (BSCF) particles have been reported to undergo surface morphology and local structure change during the OER in alkaline media. This transformation is accompanied by metal dissolution and increased capacitive and OER current (7, 8, 15). Similar phenomena have been observed for active Ir-based complex oxides (16, 17), a finding that led to a suggested relationship between structural transformation and OER (6, 18–20). The current picture is that the transformation process involves the collapse of the pristine structure and the reformation of Ir compounds, for example, segregated Ir oxides/hydroxides (16, 21) associated with higher degrees of disorder (6). This amorphization could originate from a direct metal dissolution or electrochemically from the close proximity of the O p-band to the Fermi level (16, 22). In the latter mechanism, the lattice oxygen redox can be activated, leading to the lattice oxygen activation, a process that allows the lattice oxygen to directly participate in the electrochemical reaction. This participation of lattice oxygen in the OER has also been suggested to be a source of surface restructuring in BSCF, which has caused a cycle of dissolution/deposition during the OER (7). However, there remain many critical questions, for example, how the lattice oxygen activation is connected to metal dissolution, and whether lattice oxygen activation occurs simultaneously or sequentially with metal dissolution. It is unclear how the lattice oxygen activation leads to surface transformation and why the resulting amorphous structure is distinct from other amorphous oxides made electrochemically or thermally.

In this work, we provide atomic-level insight into the crystalline-to-amorphous transformation and describe a mechanism that holistically
connects the lattice oxygen activation, metal dissolution, and amorphization in SrIrO$_3$. We focus on SrIrO$_3$, the state-of-the-art OER electrocatalyst in acid (21), to understand the origin of its high activity and track its interfacial evolution during the OER, providing the knowledge essential to the future electrocatalyst development. Our experiment begins with an atomically smooth, single-crystalline film of SrIrO$_3$ grown by molecular beam epitaxy (MBE). The use of an epitaxial film allows us to track the structural evolution without concerns over sample heterogeneity such as surface terminations, structural defects, and phases (23, 24). In conjunction with theoretical modeling, we use a suite of synchrotron-based surface-sensitive x-ray techniques and electron microscopy to understand the surface transformation process: surface x-ray diffraction (XRD) and x-ray reflectivity (XRR) to track the crystalline-to-amorphous transformation at the oxide surface and grazing incidence x-ray absorption near-edge spectroscopy (XANES), extended x-ray absorption fine structure (EXAFS), and soft x-ray absorption spectroscopy (XAS) to identify the local geometry/coordination and electronic structure in the amorphous and crystalline layers of SrIrO$_3$.

Our results show that the OER leads to the formation of an active ~2.4-nm-thick amorphous Sr$_x$IrO$_{3-x}$ film atop crystalline, highly defective “SrIrO$_3$.” This amorphous structure results from the lattice oxygen activation, which initiates coupled Sr$^{2+}$ and O$^{2-}$ diffusion at the oxide-electrolyte interface. The amorphous Sr$_x$IrO$_{3-x}$ layer protects the underlying SrIrO$_3$ from further amorphization but is ionically conductive, i.e., supports the passage of Sr$^{2+}$ and O$^{2-}$ ions. These ionic movements cause both the amorphous and crystalline layers to undergo additional transformations even after the amorphous Sr$_x$IrO$_{3-x}$ layer has reached a steady-state thickness. We probe the structural and chemical evolution and the atomic details of the active amorphous material, which we find to be a highly disordered, amorphous structure of Ir$^{4+}$O$_6$ octahedra with Sr$^{2+}$-Ir$^{3+}$ residue.

Despite the amorphous layer appearing to reach a steady-state thickness at 0.25 hours, we observe a continual increase in the CV current upon cycling for up to 4 hours (Fig. S1). After this point, the current stayed approximately at the same value. While this electrochemical behavior is consistent with what has been reported (21), it is interesting that the OER current continued to increase after the amorphous layer had stopped growing, indicating that the amorphous oxide went through additional reorganization after it has finished growing. We will later discuss the mechanism behind this reorganization. First, we show that the OER is necessary to start amorphization. When cycled between 0.8 and 1.0 V versus RHE, which is below the potential required for the OER, both XRR and XRD show that the SrIrO$_3$ film showed no amorphous layer in this pre-OER potential window (Fig. 1). This finding suggests that the transformation from crystalline SrIrO$_3$ to iridate is driven by the oxidative potential in the range of the OER. This observation is consistent with the recent suggestion that the amorphization is connected to the OER (6, 7, 16).

Local structure and compositions of the amorphous layer

We probed the structural evolution of the amorphous layer during the first 4 hours of potential cycling using XANES and EXAFS. While care has been made to minimize the time between electrochemistry and x-ray experiments, air exposure could affect surface chemistry. We have, therefore, restricted our analysis to the amorphous layer, which spanned the first nanometers, instead of the topmost surface. To minimize the sample variability, we tracked the progression of the same SrIrO$_3$ sample, starting with Sr$_3$L$_3$-edge. To distinguish the Sr signals from the amorphous layer and the overall film, we performed Sr$_3$L$_3$-edge XANES in both the total electron yield (TEY; which has a probing depth of few nanometers, which is about the thickness of the amorphous layer) and total fluorescence yield (TFY; which has a probing depth that exceeds the total film thickness) modes. We compare the XANES intensities to assess the evolution of the Sr concentration. The Sr$_3$L$_3$-edge XANES reveals that the Sr content decreased in both the amorphous and crystalline layers (Fig. 2) with respect to the initial Sr composition, with the loss being more pronounced in the amorphous layer. After 0.25, 1, and 4 hours, the amorphous layer loses ~27% (“Sr$_{0.72}$IrO$_x$”), ~65% (“Sr$_{0.35}$IrO$_x$”), and ~80% (“Sr$_{0.2}$IrO$_x$”) of Sr, while the overall film loses ~0%, ~20%, and ~45% over the same time span. With x-ray photoelectron spectroscopy (XPS), we verified that ~20% of Sr remained in the surface layer after 4 hours (table S2). We note that a previous study of SrIrO$_3$/SrTiO$_3$ showed that ~20% of Sr remained in the surface layer after 24 hours (21), suggesting that ~20% is likely the steady-state Sr concentration.

The observed Sr loss is not surprising given the strong thermodynamic driving force for the Sr dissolution in SrIrO$_3$ (section S7.1). However, it is not understood how the catalyst achieves charge neutrality upon dissolution, i.e., whether the charge compensation occurs via the change in the Ir formal oxidation state or the loss of lattice oxygen. To address this question, we tracked the evolution of the Ir formal oxidation state and local coordination via XANES and EXAFS measurements at the Ir L$_{III}$-edge. The grazing incidence configuration (GI-XANES and GI-EXAFS) was used to limit the probing depth (~2.2 nm) to the surface amorphous layer (~2.4 to 2.6 nm thick). The Ir L$_{III}$-edge (Fig. 3) shows a decrease in the white-line intensity at 0.25 hours, indicating that the near-surface Ir formal oxidation state decreases after 0.25 hours. From reference Ir

RESULTS

Formation of the amorphous layer

An SrIrO$_3$ film was grown on a DyScO$_3$ (110) orthorhombic substrate along the (001)$_{pc}$ orientation (subscript pc denotes a pseudocubic orientation) (25). The well-defined oscillations in both XRR and XRD (Fig. 1) indicate a high-quality film-substrate interface and that SrIrO$_3$ is atomically smooth with a starting thickness of 16.0 ± 0.1 nm. To monitor the evolution of the thickness upon OER cycling, we take advantage of the differential sensitivities of XRR and XRD. Specifically, XRR is sensitive to the total film thickness (both crystalline and amorphous layers), while XRD is only sensitive to the crystalline part. After 0.25 hours of cyclic voltammetry (CV) between 1.05 and 1.75 V versus reversible hydrogen electrode (RHE) in 0.1 M HClO$_4$ negligible change to the overall film thickness was observed (15.8 ± 0.4 nm). In this same period, the thickness of the Ir formal oxidation state and local coordination via XANES and EXAFS measurements at the Ir L$_{III}$-edge. The grazing incidence configuration (GI-XANES and GI-EXAFS) was used to limit the probing depth (~2.2 nm) to the surface amorphous layer (~2.4 to 2.6 nm thick). The Ir L$_{III}$-edge (Fig. 3) shows a decrease in the white-line intensity at 0.25 hours, indicating that the near-surface Ir formal oxidation state decreases after 0.25 hours. From reference Ir
compound measurements, we estimate the Ir formal oxidation state to be 3.1 (± 0.1) at 0.25 hours (fig. S4) and the Ir-O coordination number to be 4.5 (Fig. 3). The drop in the Ir-O coordination to 4.5 (±0.4) from 6 (±0.6) in pristine SrIrO₃ at 0.25 hours implies the loss of the lattice oxygen. This finding is consistent with the observed reduction of the Ir formal oxidation state and Sr stoichiometry. Together, our result suggests that the lattice oxygen left the amorphous layer in a greater quantity than Sr. We note that this conclusion was derived from the transient averages in the Ir oxidation state and Sr composition. While we cannot rule out the possible heterogeneity issue within the amorphous layer, the observed drop in the Ir-O coordination and Sr composition is consistent with the idea that the loss of lattice oxygen plays an essential role in the early stage of the SrIrO₃ amorphization. We present the exact values in each transformation stage with error bars. We use these results to assign the nominal composition of the amorphous layer at 0.25 hours as “Sr₀.₇₃ Ir₃.₁₊O₂.₂₈”. Density functional theory (DFT) calculations show that Sr has higher migration (3.1 eV) barrier than O (1.9 eV) in SrIrO₃, suggesting that Sr loss is kinetically inhibited compared to O loss (see fig. S11 and section S7.1 for calculation details).

We propose the mechanism underlying the SrIrO₃ transformation based on these observations. First, the high oxidation potential activates the lattice oxygen (Oₗattice), leading to the lattice oxygen loss and the creation of oxygen vacancy (Voxxygen). This increase in the oxygen vacancy concentration consequently affects the oxygen diffusion coefficient. The connection between the oxygen vacancy formation and lattice oxygen activation has been discussed (7, 11, 16). During the lattice oxygen activation (Oₗattice + H₂O → O₂ + 2H⁺ + 2e⁻ + Voxxygen), the buildup of excess electronic charge reduces the Ir oxidation state, in agreement with the Ir L₃-edge XANES. After the lattice oxygen activation step, the lattice oxygen regeneration (i.e., filling of the vacancies, Voxxygen + H₂O → Oₗattice + 2H⁺ + 2e⁻) is kinetically sluggish, e.g., slower than the lattice oxygen activation process. In this scenario, oxygen vacancies accumulate to the point where crystalline SrIrO₃ experiences structural instability and collapses into Sr-doped amorphous IrOₓ. Note that the accumulation of the oxygen vacancy can also enable Sr to migrate. Our DFT calculations demonstrate that removing one or two of the oxygen atoms along its migration pathway can decrease the activation energy of Sr migration from 3.1 to 2.7 and 2.25 eV (see fig. S11 and section S7.1). The beneficial effect of the oxygen vacancy on the Sr migration provides a channel for Sr to migrate away from the crystalline subsurface SrIrO₃ layer during electrochemistry. The underlying SrIrO₃ layer maintains its crystallinity even after ~40% Sr is lost (according to the TFY Sr L₃-edge measurement at 4 hours; Fig. 2). This finding suggests that the Sr loss alone cannot cause amorphization. We thus postulate that it is the coupled O-Sr out-diffusion that caused the amorphization of SrIrO₃. Geiger et al. (6) and Grimaud et al. (16) have suggested that the Ir formal oxidation state may decrease as the oxygen vacancies form. Our work supports their views and further shows that the metal (Sr) dissolution and the
The process of amorphization are coupled through the lattice oxygen activation and that one cannot happen without the other.

**Subsequent diffusional reorganization**

Having identified how the crystalline-to-amorphous transformation starts at 0.25 hours, we next examine the subsequent reorganization at 1 and 4 hours using Ir L\textsubscript{III}-edge GI-XANES and GI-EXAFS. The Ir oxidation state and coordination number increase from 3.1 (±0.1) and 4.5 (±0.4) (0.25 hours), respectively, to 3.6 (±0.1) and 5.3 (±0.7) (1 hour), and then to ~3.7 (±0.1) and 5.8 (±0.6) (4 hours) (Fig. 3). Because the Sr composition also decreases during this period, we propose that the Ir oxidation state increases after 0.25 hours to offset the Sr loss and maintain charge neutrality, effectively oxidizing Ir\textsuperscript{3+} to Ir\textsuperscript{4+}. Simultaneously, the oxide regains the lattice oxygen (via the oxygen vacancy filling), gradually restoring the Ir-O coordination. The dynamic behaviors on the oxidation states of surface Ir are confirmed by the Ir M\textsubscript{III}-edge near-edge XAFS (NEXAFS) detected in TEY mode (fig. S5). During this period, the amorphous oxide also becomes more active for the OER.

We summarize our observations thus far with the following mechanism. The transformation starts with the lattice oxygen activation at high oxidation potential. This lattice oxygen activation leads to the lattice oxygen loss and increased oxygen vacancy concentration. The newly formed oxygen vacancies facilitate the oxygen diffusion and transform the surface SrIrO\textsubscript{3} layer into an amorphous Ir\textsuperscript{3+} oxide. At 0.25 hours, the Ir-O coordination number is 4.5 (±0.4), which suggests that the local structure of the amorphous layer at the early stage could have a square-planar structure that is derived from the apical oxygen removal and is stabilized by Sr\textsuperscript{2+}. To assess the energetics of the square-planar geometry, we calculated the energy of the Sr\textsubscript{0.5}Ir\textsubscript{0.5}O\textsubscript{2} structure created by removing O and Sr from perovskite SrIrO\textsubscript{3} as a model for Sr-/O-deficient SrIrO\textsubscript{3}. Our DFT calculations reveal a strong preference for Ir\textsuperscript{3+} to be in a square-planar environment when both Sr and O are removed (fig. S12). This calculation also shows that the Sr diffusion is faster in the presence of the oxygen vacancy, supporting our hypothesis of an open square-planar network that facilitates the Sr loss. We propose that this open square-planar structure facilitates the Sr\textsuperscript{2+} diffusion out of the film. This leads to a strong leaching of Sr\textsuperscript{2+} at 1 and 4 hours. This Sr loss destabilizes the defect-rich structure and causes Ir to reoxidize and form a mixture of Ir\textsuperscript{3+}/Ir\textsuperscript{4+} octahedral clusters (Fig. 4). The final structure is thus a disordered mixture of Ir\textsuperscript{3+}/Ir\textsuperscript{4+} octahedra, which is the result of the coupled diffusion between the anions (O) and cations (Sr) during the amorphization.

**Signature of the active moiety**

We now discuss what makes the amorphous, disordered iridate structure obtained from SrIrO\textsubscript{3} different from the chemically and thermally grown amorphous iridates. We performed NEXAFS at the O K-edge in the TEY mode (with a probing depth of few nanometers) to probe the local Ir-O bonding properties in the amorphous layer. The pristine SrIrO\textsubscript{3} (Fig. 4A) shows two peaks at ~529 and ~532 eV, which we assign to the t\textsubscript{2g} and e\textsubscript{g} parentage states based on the similar assignments in rutile IrO\textsubscript{2} (26). After 0.25 hours,
the intensity of the $t_{2g}$ peak at $\sim 529$ eV drops, while the $e_g$ peak at $\sim 532.5$ eV moves to higher energy. The weakening of the first peak intensity is consistent with the decrease in the Ir formal oxidation state, i.e., decreasing amount of empty Ir $t_{2g}$ peak state. The shift in the second peak is attributed to the changing crystal field of the square-planar structure, which changes the energy levels of the O 2p–Ir 5d states ($27$). After 1 hour of cycling, the first peak (nominally $t_{2g}$) regains intensity. This observation is consistent with the Ir L 3-edge result, which shows that the Ir formal oxidation state recovers at the 1-hour point.

After 4 hours, the O K-edge spectrum shows substantially decreased intensity in the low-energy region and a broader peak at higher energy. These observed features are markedly different from those for conventional amorphous IrO$_x$ ($28$, $29$), which exhibits two sharp features corresponding to the nominally $t_{2g}$ and $e_g$ excitations. Only a highly disordered amorphous model of IrO$_2$ derived from the reported amorphous TiO$_2$ structure ($30$) leads to O K-edge spectra, consistent with the experiment (Fig. 4). Thus, we conclude that Sr$_y$IrO$_x$ is highly disordered. This structural heterogeneity broadens the energy distribution of the $t_{2g}$ and $e_g$ excitations, causing nominally sharp $t_{2g}$ and $e_g$ peaks to blur. The outcome is one broad excitation feature, although the structure contains predominantly the Ir octahedra that should normally exhibit two distinct ($t_{2g}$ and $e_g$) excitations (figs. S11 and S12). Amorphization leading to the disappearance of the $t_{2g}$ and $e_g$ peaks at the O K-edge has been observed in TiO$_2$ ($31$). We expect this effect to be even stronger in IrO$_2$ in view of the smaller crystal field splitting. While we cannot extract the exact iridate structure within the amorphous layer, this observation of the loss of distinctive $t_{2g}$ and $e_g$ excitations in amorphous iridates suggests a high degree of disorder within the amorphous iridate layer atop SrIrO$_3$.

An interesting observation can be made given the energetics regarding different polymorphs. All stable iridate polymorph structures present octahedral environments. Among the five lowest energy structures, we find not only the previously considered brookite and anatase but also the more open hollandite and romanechite structures. The hollandite structure has the lowest energy among the nonrutile polymorphs, indicating that structural reorganizations could favor hollandite-like motifs in the amorphous layer (figs. S13 and S14). The hollandite structure presents open cavities that could accommodate the remaining Sr in the iridate and may explain why Sr diffuses faster after the amorphization. We hypothesize

**DISCUSSION**

Our computational results indicate that none of the known iridate polymorphs can replicate the observed, broad O K-edge peak, as all iridate polymorphs exhibit sharp peaks corresponding to the $t_{2g}$ and $e_g$ excitations. Only a highly disordered amorphous model of IrO$_2$ derived from the reported amorphous TiO$_2$ structure ($30$) leads to O K-edge spectra, consistent with the experiment (Fig. 4). Thus, we conclude that Sr$_y$IrO$_x$ is highly disordered. This structural heterogeneity broadens the energy distribution of the $t_{2g}$ and $e_g$ excitations, causing nominally sharp $t_{2g}$ and $e_g$ peaks to blur. The outcome is one broad excitation feature, although the structure contains predominantly the Ir octahedra that should normally exhibit two distinct ($t_{2g}$ and $e_g$) excitations (figs. S11 and S12). Amorphization leading to the disappearance of the $t_{2g}$ and $e_g$ peaks at the O K-edge has been observed in TiO$_2$ ($31$). We expect this effect to be even stronger in IrO$_2$ in view of the smaller crystal field splitting. While we cannot extract the exact iridate structure within the amorphous layer, this observation of the loss of distinctive $t_{2g}$ and $e_g$ excitations in amorphous iridates suggests a high degree of disorder within the amorphous iridate layer atop SrIrO$_3$.

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that the amorphization of SrIrO$_3$ results primarily in this structure, which we propose is the active moiety of Sr$_y$IrO$_x$/SrIrO$_3$: A hollandite-like (or romanechite-like) structure with Sr$^{2+}$ stationed in the cavity helps to stabilize Ir$^{3+}$. Sun et al. (32) have demonstrated high OER activity on K$_x$IrO$_2$ hollandite, and Willinger et al. (33) have proposed that amorphous iridates have hollandite-like structural motifs and stressed the importance of Ir$^{3+}$ on the OER catalysis. Our analysis agrees with the hypotheses of these early works.

The difference between the O K-edge of Sr$_y$IrO$_x$/SrIrO$_3$ after 4 hours and conventional amorphous IrO$_x$ provides insights into how Sr$_y$IrO$_x$/SrIrO$_3$ is different from conventional amorphous IrO$_x$ structure. In thermally or chemically grown amorphous IrO$_x$, the $t_{2g}$ and $e_g$ peaks are observable at the O K-edge (26), similar to crystalline rutile. In contrast, the O K-edge of Sr$_y$IrO$_x$/SrIrO$_3$ has a broad feature, indicating a more diverse oxygen environment—a sign of a greater extent of disorder. This greater extent of disorder, in combination with the presence of romanechite/hollandite moieties, differentiates Sr$_y$IrO$_x$/SrIrO$_3$ from conventional amorphous IrO$_x$, which is more ordered based on their sharp $t_{2g}$ and $e_g$ features. From the comparison between TEY (probing the amorphous layer) and TFY (probing the whole SrIrO$_3$ film, both amorphous and crystalline parts) O K-edge NEXAFS (figs. S8 and S9), this unique structure is specific to the top Sr$_y$IrO$_x$/SrIrO$_3$ layer and does not exist in bulk Sr-deficient SrIrO$_3$, although it has lost more than 40% of Sr. Increased proportion of defects generated from the destabilization of the active site/structure and the octahedral distortion has been suggested by several authors as means of increasing activity (28, 29, 34). We hypothesize that the unique structure of SrIrO$_3$ originates from its topochemical transformation, where the lattice oxygen activation serves as the “seed” for the structural transformation. This activation step turns crystalline SrIrO$_3$ to Sr-doped amorphous IrO$_x$ with a suggested square-planar motif. This square-planar structure has loose network, which allows Sr to dissolve further. After more Sr has dissolved, the square-planar structure collapses into a disordered mixture of Ir(III)/Ir(IV).

![Fig. 4. Local structure of the SrIrO$_3$ film undergoing the OER.](http://advances.sciencemag.org/) Start (A) O K-edge NEXAFS of SrIrO$_3$ in TEY mode. The pre-peaks correspond to the O 2p–Ir 5d excitation ($\pi$ and $\sigma$ interactions, i.e., the $t_{2g}$ and $e_g$ parentage states). At 0.25 hours, the intensity of the first pre-peak decreases, corresponding to the reduced Ir formal oxidation. At 1 hour, the pre-peak regains the intensity, corresponding to the Ir reoxidation. At 4 hours, the pre-edge features transform into a broad peak. We ascribe this result to the heterogeneous broadening of the final amorphous IrO$_x$ structure. (B) Simulated O K-edge of rutile, anatase, brookite, and amorphous IrO$_2$, demonstrating the high degree of structural disorders in the Sr-doped amorphous IrO$_x$ layer. Despite having well-defined local octahedral environment, the structural heterogeneity broadens the O 1s to O 2p–Ir 5d excitation into one single distribution. The simulated O K-edges were shifted to match the experimental O K-edge result at 4 hours. (C) Our proposed crystalline-to-amorphous transformation pathway in SrIrO$_3$. The oxygen loss from the lattice oxygen activation serves as the “seed” for the structural transformation. This activation step turns crystalline SrIrO$_3$ to Sr-doped amorphous IrO$_x$ with a suggested square-planar motif. This square-planar structure has loose network, which allows Sr to dissolve further. After more Sr has dissolved, the square-planar structure collapses into a disordered mixture of Ir(III)/Ir(IV).
the OER potential (36) and how these molecular transformations affect long-term stability.

In conclusion, we report the atomic details behind the crystalline-to-amorphous transformation of SrIrO$_3$ as a model system for the OER electrocatalysts. The surface structural transformation is triggered by the lattice oxygen activation. This step increases the oxygen vacancy concentration to destabilize the SrIrO$_3$ structure. This initial process transforms SrIrO$_3$ into amorphous Sr$_2$IrO$_5$ with predominantly Ir square-planar motifs. The amorphous oxide then undergoes a second-stage transformation as more Sr$^{2+}$ leaves the oxide. This final transformation creates a highly disordered structure containing Ir$^{4+}$ octahedra with some remaining Sr$^{2+}$, which are likely accommodated in the cavities within the open romanechite- or hollandite-like structures. Our work explains how the active Sr$^{2+}$ units transform to amorphous SrIrO$_3$ and points to the critical role of the lattice oxygen activation and coupled ion diffusion on the formation of the active OER units. In the case of SrIrO$_3$, the coupled Sr$^{2+}$ and O$^{2-}$ diffusion allow the structure to evolve into the final Sr$_2$IrO$_5$ form that is more disordered than the electrochemically or thermally grown amorphous IrO$_2$. Our work provides insight into how applied potential facilitates the formation of the functional amorphous layers at the electrochemical interface and demonstrates how coupled ion diffusions activate the crystalline-to-amorphous transformation to form a highly disordered, amorphous oxide with high OER activity.

**MATERIALS AND METHODS**

**MBE growth of SrIrO$_3$ thin films**

The SrIrO$_3$ films were grown by MBE on single-crystal DyScO$_3$ (110) substrates (CrysTec GmbH) using a distilled ozone (O$_3$) oxidant at a background pressure of $10^{-6}$ torr and a growth temperature of 700°C. In bulk, both SrIrO$_3$ and DyScO$_3$ are orthorhombic, but they are only slightly distorted compared to cubic perovskite. The (110) orientation of DyScO$_3$ provides a surface facet similar to the (001) plane in the pseudo-cubic (pc) system. The resulting (001)$_{pc}$ SrIrO$_3$ film grown on DyScO$_3$ is under 0.05% biaxial compression at room temperature. Detailed growth parameters can be found in a previous publication (25).

**Electrochemical characterization**

Electrical contacts were made using the same protocol as reported previously (21). The nonreactive parts of the oxide were sealed using a chemically inert sample holder (made of Kel-F, polychlorotrifluoroethylene) to ensure that only the active surface was exposed to the electrolyte. All electrochemical characterization was conducted in a compact three-electrode cell (containing <10 ml of electrolyte volume) designed for rapid transfer to x-ray stations. We used a Biologic potentiostat. The reference was a Ag/AgCl redox couple in a saturated KCl solution, and the counter electrode was a Pt wire. The experiment was performed without an ohmic compensation; thus, the data presented in fig. S1 contain a resistance artifact that results in a relatively high Tafel slope (>300 mV/decade). All electrochemical measurements were performed in an Ar-saturated 0.1 M HClO$_4$ (99.999% trace metals basis, Sigma-Aldrich). All synchrotron x-ray characterizations were conducted within 1 hour from the electrochemical experiment, with the exception of XPS, which was done within 48 hours.

**Synchrotron x-ray scattering**

Synchrotron x-ray scattering of the SrIrO$_3$ films was conducted at undulator beamlines, 12ID-D and 33-ID-D, at the Advanced Photon Source (APS) on a six-circle Huber goniometer with an x-ray energy of 20 keV using a pixel array area detector (Dectris Pilatus 100K). The incoming x-ray beam had a flux of $10^{12}$ photons per second. The Q$_y$ scans (L scans) were obtained after removing background contributions in the two-dimensional images. Our ex situ synchrotron-based surface x-ray scattering experiments of thin-film samples in the He environment excluded any beam damage effects on the amorphization of SrIrO$_3$.

**Synchrotron XAS**

The Sr L$_{III}$-edge, Ir M$_{III}$-edge, and O K-edge XAS detected in either TEY and TFY modes were carried out at the 4-ID-C beamline of the APS. The x-ray energy was calibrated using a reference measured simultaneously with the samples. Sr L$_{III}$-edge, Ir M$_{III}$-edge, and O K-edge XAS spectra normalization was performed by setting the intensity of the baseline before the absorption edge as zero. The Ir L$_{III}$-edge XANES and EXAFS measurements were conducted at beamline 20-ID-B of the APS in grazing incidence geometry and fluorescence mode after different cycling times with a polarization-dependent measurement (out-of-plane polarization). In the grazing incidence XAS measurement, the samples were aligned using x-ray, with controlled incidence angles. In this experimental configuration, the x-ray penetration thickness is directly related to the photon energy. The estimated penetration depth at the Ir L$_{III}$-edge x-ray energy is ~2.2 nm based on the calculation of the attenuation length using the SrIrO$_3$ mass density and the angle of incidence (https://henke.lbl.gov/optical CONSTANTS), which has an error bar of 0.1 nm. Bulk-sensitive Ir L$_{III}$-edge XANES of the pristine and cycled SrIrO$_3$ (SIO) films were also detected in fluorescence mode with an incidence angle of 45° at beamline 5-BM-D of the APS. The XANES data of references IrO$_2$ and IrCl$_3$ were collected at beamlines 20-ID-B and 5-BM-D in transmission mode. Ir L$_{III}$-edge XAS spectra including XANES and EXAFS were processed and analyzed using the Athena and Artemis programs (https://bruceralv.github.io/demeter).

**Transmission electron microscopy**

The TEM experiment was carried out using an FEI Titan microscope operated at 200 kV, which is equipped with an image corrector to correct both spherical and chromatic aberrations. The TEM specimen was prepared by mechanically grinding the substrate side down to about 100 μm thick, followed by cleaving the thinned sample into small pieces. Small pieces with sharp tips were chosen to glue on a copper oval grid with silver epoxy. These small pieces were oriented edge-on such that TEM specimen was along the cross-sectional view with respect to electron beam. This TEM specimen preparation method avoids any TEM specimen preparation artifacts such as ion beam damage and yields thin areas suitable for cross-sectional high-resolution TEM observations. Because of the arbitrary cleaving directions, different pieces may have different crystallographic orientations. As shown in Fig. 1D, the zone axis of the pristine and cycled pieces of SrIrO$_3$/DyScO$_3$ thin-film samples shows different crystallographic orientations.

**X-ray photoelectron spectroscopy**

XPS measurements were conducted using a PHI 5600 system with a base pressure of $1 \times 10^{-10}$ torr. Monochromatized Al K$_{α}$ radiation
structures were relaxed to reach forces lower than 0.01 eV/Å.

The peak fits and positions agree well with previous literature. The screened component of the Ir oxide peak had binding energies of 62.3 ± 0.2 eV for Ir 4f7/2 and 66.6 ± 0.2 eV for Ir 4f5/2, while the screened component of the Ir oxide peak had binding energies of 131.9 ± 0.1 and 133.7 ± 0.1 eV, respectively, for the first doublet. The second doublet represents another Sr compound, where the Sr 3d5/2 is found at 123.9 ± 0.2 eV and Sr 3d3/2 at 134.7 ± 0.2 eV for pristine SrIrO3 and SrIrO3 after 0.25 and 0.4 hours of cycling. All Sr 3d peaks were constrained to maintain a 3:2 ratio between the 5/2 and 3/2 peak intensities. The Sr 3d5/2 and Sr 3d3/2 peak were found to be 131.9 ± 0.1 and 133.7 ± 0.1 eV, respectively, for the first doublet.

The electron attenuation lengths for each core level were estimated considering a depth that contains 95% of the detected signal (38). Using this calculation, this results in sampling depths of 3.7, 3.6, and 2.7 nm for the Ir 4f, Sr 3d, and O 1s core levels, respectively.

### DFT calculations
All energy computations were performed using VASP (Vienna Ab initio Simulation Package) with a k-point sampling of 1000 per atoms (39). The inputs were generated using pymatgen (40). The plane-wave energy cutoff was set to 400 eV. The exchange correlation functional used was Generalized Gradient Approximation-Revised Perdew-Burke-Ernzerhof (GGA-RPBE) unless specified otherwise. All structures were relaxed to reach forces lower than 0.01 eV/A. The ion energies have been extracted from experimental data using the approach of Persson et al. (41). The K-edge XANES spectra were computed using the FEFF9 code, which uses the Green’s formulation of the multiple scattering theory to compute the spectra (42). The x-ray absorption μ is computed in a manner similar to Fermi’s golden rule when written in terms of the projected photoelectron density of final states or the imaginary part of the one-particle Green’s function. We used the set of optimized FEFF parameters, which were benchmarked in (43) and determined to achieve the best balance between the computational cost and convergence performance.

### SUPPLEMENTARY MATERIALS
Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/7/2/eabc7323/DC1

### REFERENCES AND NOTES
1. T. R. Cook, D. K. Dogutan, S. Y. Reece, Y. Surendranath, T. S. Teets, D. G. Nocera, Solar energy supply and storage for the legacy and non legacy worlds. Chem. Rev. 110, 6474-6502 (2010).
2. M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori, N. S. Lewis, Solar water splitting cells. Chem. Rev. 110, 6464-6473 (2010).
3. J. W. Ager, A. A. Lakpin, Chemical storage of renewable energy. Science 360, 707-708 (2018).
4. Z. W. Seh, J. Kibsgaard, C. F. Dickens, I. Chorkendorff, J. K. Norskov, T. F. Jaramillo, Combining theory and experiment in electrocatalysis: Insights into materials design. Science 355, eaad4998 (2017).
5. V. R. Stamenkovic, D. Strmciñik, P. P. Loepes, N. M. Markovic, Energy and fuels from electrochemical interfaces. Nat. Mater. 16, 57-69 (2017).
6. S. Geiger, O. Kasan, M. Ledendecker, E. Pizzuto, A. M. Mingers, W. T. Fu, O. Diaz-Moraes, Z. Li, T. Dellers, L. Fruchter, A. Ludwig, K. J. I. Mayrhofer, M. T. M. Koper, S. Cherevko, The stability number as a metric for electrocatalyst stability benchmarking. Nat. Catal. 1, 508-515 (2018).
7. E. Fabbi, M. Nachtegaal, T. Binninger, X. Cheng, B.-J. Kim, J. Durst, F. Bozza, T. Graule, R. Schaublin, L. Wiles, M. Persiano, N. Danilovic, K. E. E. Ayers, T. J. Schmidt, Dynamic surface self-reconstruction is the key of highly active perovskite nano-electrocatalysts for water splitting. Nat. Mater. 16, 925–931 (2017).
8. K. J. May, C. E. Carlton, K. A. Storzeringer, M. Risch, J. Suntivich, Y.-L. Lee, A. Girmaud, Y. Shao-Horn, Influence of oxygen evolution during water oxidation on the surface of perovskite oxide catalysts. J. Phys. Chem. Lett. 3, 3264-3270 (2012).
9. S. Samra, X.-K. Gu, E. Nikolka, Design strategies for efficient nonstoichiometric mixed metal oxide electrocatalysts: Correlating measurable oxide properties to electrocatalytic performance. ACS Catal. 9, 10575–10586 (2019).
10. J. T. Mefford, X. Rong, A. M. Abakumov, W. G. Hardin, S. Dai, A. M. Kolpak, K. P. Johnston, K. J. Stevenson, Water electrolysis on La1-xSrxCO3 perovskite electrocatalysts. Nat. Commun. 7, 11053 (2016).
11. T. Binninger, R. Mohamed, K. Watter, E. Fabbri, P. L. Leveque, R. Kötz, T. J. Schmidt, Thermodynamic explanation of the universal correlation between oxygen evolution activity and corrosion of oxide catalysts. Sci. Rep. 5, 12167 (2015).
12. A. Girmaud, O. Diaz-Moraes, B. Han, W. T. Hong, Y.-L. Lee, L. Giordano, K. A. Storzeringer, M. T. M. Koper, Y. Shao-Horn, Activating lattice oxygen redox reactions in metal oxides to catalyse oxygen evolution. Nat. Chem. 9, 457–465 (2017).
13. A. Bergmann, E. Martínez-Moreno, D. Teschner, P. Cherniev, M. Gilech, F. J. de Araújo, T. Reier, H. Dau, P. Strasser, Reversible amorphization and the catalytically active state of crystalline Co3O4 during oxygen evolution. Nat. Commun. 6, 8625 (2015).
14. A. Indra, P. W. Menezes, N. R. Sahraie, A. Bergmann, C. Das, M. Tallarida, D. Schmieder, P. Strasser, M. Dries, Unification of catalytic water oxidation and oxygen reduction reactions: Amorphous base crystalline cobalt iron oxides. J. Am. Chem. Soc. 136, 17530–17536 (2014).
15. G. Chen, W. Zhou, D. Guan, J. Sunarso, Y. Zhu, X. Hu, W. Zhang, Z. Shao, Two orders of magnitude enhancement in oxygen evolution reactivity on amorphous Ba0.5Sr1.5Co3O7-δ nanofilms with tunable oxidation state. Sci. Adv. 3, e1603206 (2017).
16. A. Girmaud, A. Demortière, M. Saubanère, W. Dachraoui, M. Duchamp, M.-L. Doublot, J.-M. Tarascon, Activation of surface oxygen sites on an iridium-based model catalyst for the oxygen evolution reaction. Nat. Energy 2, 16189 (2017).
17. O. Diaz-Moraes, S. Raaajman, R. Kortlever, P. J. Kooyman, T. Wezenendonk, J. Gascon, W. T. Fu, M. T. M. Koper, Iridium-based double perovskites for efficient water oxidation in acid media. Nat. Commun. 7, 12363 (2016).
18. N. Danilovic, R. Subbaraman, K.-C. Chang, S. H. Chang, Y. Kang, J. Snyder, A. P. Paulikas, D. Strmciñik, Y.-T. Kim, D. Myers, V. R. Stamenkovic, N. M. Markovic, Activity-stability trends for the oxygen evolution reaction on monometallic oxides in acidic environments. J. Phys. Chem. Lett. 5, 2474–2478 (2014).
19. O. Kasan, S. Geiger, T. Li, J.-P. Grote, K. Schweinar, S. Zhang, C. Schue, D. Raabe, S. Cherevko, B. Gault, K. J. I. Mayrhofer, Degradation of iridium oxides via oxygen evolution from the lattice: Corroding atomic scale structure with reaction mechanisms. Energ. Environ. Sci. 12, 3548–3555 (2019).
20. G. C. da Silva, N. Perini, E. A. Ticianelli, Effect of temperature on the activities and stabilities of hydrothermally prepared IrO2 nanocatalyst layers for the oxygen evolution reaction. Appl. Catal. B-Environ. 218, 287–297 (2017).
21. L. C. Seitz, C. F. Dickens, K. Nishio, T. Hikita, J. Montoya, A. Doyle, C. Kirk, A. Vojvodic, H. Y. Hwang, J. K. Norskov, T. F. Jaramillo, A highly active and stable IrO2/SrIrO3 catalyst for the oxygen evolution reaction. Science 353, 1011–1014 (2016).
22. R. H. Zhang, N. Dubouis, M. B. Osman, W. Yin, M. T. Sougrati, D. A. D. Corte, D. Gaume, A. Girmaud, A dissolution/precipitation equilibrium on the surface of iridium-based perovskites controls their activity as oxygen evolution reaction catalysts in acidic media. Angew. Chem. Int. Ed. 58, 4571–4575 (2019).
23. A. R. Akbashev, L. Zhang, J. T. Mefford, J. Park, B. Bus, H. Luftman, W. C. Chueh, A. Vojvodic, Activation of ultrathin SrIrO3 with subsurface SrRuO3 for the oxygen evolution reaction. Energ. Environ. Sci. 11, 1762–1769 (2018).
T. Reier, Z. Kawashima, T. Jones, D. Teschner, S. Selve, A. Bergmann, H. N. Nong, R. Schläg, K. J. Mayhofer, P. Strasser, Molecular insight in structure and activity of highly efficient, Low-Ir In-Ni oxide catalysts for electrochemical water splitting (OER), J. Am. Chem. Soc. 137, 13031–13040 (2015).

J. J. Zhang, A. S. Botana, J. W. Freeland, D. Phelan, H. Zheng, V. Pardo, M. R. Norman, J. F. Mitchell, Large orbital polarization in a metallic square-planar nickelate. Nat. Phys. 13, 864–869 (2017).

V. Pfeffer, T. E. Jones, J. J. Vélez, C. Massué, M. T. Greiner, R. Arrigo, D. Teschner, F. Girsigdeis, M. Scherer, J. Allan, M. Hashagen, G. Weinberg, S. Piccinin, M. Hävecker, A. Knop-Gericke, R. Schläg, The electronic structure of iridium oxide oxides active in water splitting. Phys. Chem. Chem. Phys. 18, 2292–2296 (2016).

V. Pfeffer, T. E. Jones, S. Wrbetz, C. Massué, J. I. Velasco Vélez, R. Arrigo, M. Scherer, S. Piccinin, M. Hävecker, A. Knop-Gericke, R. Schläg, Reactive oxygen species in iridium-based OER catalysts. Chem. Sci. 7, 6791–6795 (2016).

B. Prasai, B. Cai, M. K. Underwood, J. P. Lewis, D. A. Drabold, Properties of amorphous and crystalline titanium dioxide from first principles. J. Mater. Sci. 47, 7515–7521 (2012).

S. K. Gautam, A. Das, S. Ojha, D. K. Shukla, D. M. Phase, F. Singh, Electronic structure modification and Fermi level shifting in niobium-doped anatase titanium dioxide thin films: A comparative study of NEXAFS, work function and stiffening of phonons. Phys. Chem. Chem. Phys. 18, 3618–3627 (2016).

W. Sun, Y. Song, X. Q. Gong, L.-M. Cao, J. Yang, Hollandite structure Sr0.29IrO2 catalyst with highly efficient oxygen evolution reaction. ACS Appl. Mater. Interfaces 8, 820–826 (2016).

E. Willinger, C. Massué, R. Schläg, M. G. Willinger, Identifying key structural features of IrO2 water splitting catalysts. J. Am. Chem. Soc. 139, 12093–12101 (2017).

Z. Xu, J. R. Kitchin, Tuning oxide activity through modification of the crystal and electronic structure: From strain to potential polymorphs. Phys. Chem. Chem. Phys. 17, 28943–28949 (2015).

R. D. L. Smith, M. S. Prévot, R. D. Fagan, Z. Zhang, P. A. Sedach, M. K. J. Siu, S. Trudel, C. P. Berlinguette, Photochemical route for accessing amorphous metal oxide materials for water oxidation catalysis. Science 340, 60–63 (2013).

H. G. S. Casalongue, M. L. Ng, S. Kaya, D. Friebl, H. Ogasawara, A. Nilsson, In situ observation of surface species on iridium oxide nanoparticles during the oxygen evolution reaction. Angew. Chem. Int. Ed. 53, 7169–7172 (2014).

P. J. Cumpson, M. P. Seah, Elastic scattering corrections in AES and XPS. II. Estimating attenuation lengths and conditions required for their valid use in overlay/substrate experiments. Surf. Interface Anal. 25, 430–446 (1997).

C. J. Powell, Practical guide for inelastic mean free paths, effective attenuation lengths, mean escape depths, and information depths in x-ray photoelectron spectroscopy. J. Vac. Sci. Technol. A 38, 023209 (2020).

G. Kresse, J. Furthmuller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. Comput. Mater. Sci. 6, 15–50 (1996).

S. P. Ong, W. D. Richards, A. Jain, G. Hautier, M. Kocher, S. Cholia, D. Gunter, V. L. Chevrier, K. A. Persson, G. Ceder, Python materials genomics (pymatgen): A robust, open-source python library for materials analysis. Comput. Mater. Sci. 68, 314–319 (2013).

K. A. Persson, B. Walldicz, P. Lazic, G. Ceder, Prediction of solid-liquid equilibria: Scheme to combine first-principles calculations of solids with experimental aqueous states. Phys. Rev. B 85, 235438 (2012).
Amorphization mechanism of SrIrO$_2$ electrocatalyst: How oxygen redox initiates ionic diffusion and structural reorganization

Gang Wan, John W. Freeland, Jan Kloppenburg, Guido Patretto, Jocienne N. Nelson, Ding-Yuan Kuo, Cheng-Jun Sun, Jianguo Wen, J. Trey Diulius, Gregory S. Herman, Yongqi Dong, Ronghui Kou, Jingying Sun, Shuo Chen, Kyle M. Shen, Darrell G. Schlom, Gian-Marco Rignanese, Geoffroy Hautier, Dillon D. Fong, Zhenxing Feng, Hua Zhou and Jin Suntivich

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