Dynamic observation of manganese adatom mobility at perovskite oxide catalyst interfaces with water

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Real time in-situ microscopy imaging of surface structure and atom dynamics of heterogeneous catalysts is an important step for understanding reaction mechanisms. Here, using in-situ environmental transmission electron microscopy (ETEM), we directly visualize surface atom dynamics at manganite perovskite catalyst surfaces for oxygen evolution reaction (OER), which are ≥20 times faster in water than in other ambients. Comparing (001) surfaces of La0.6Sr0.4MnO3 and Pr0.67Ca0.33MnO3 with similar initial manganese valence state and OER activity, but very different OER stability, allows us to distinguish between reversible surface adatom dynamics and irreversible surface defect chemical reactions. We observe enhanced reversible manganese adatom dynamics due to partial solvation in adsorbed water for the highly active and stable La0.6Sr0.4MnO3 system, suggesting that aspects of homogeneous catalysis must be included for understanding the OER mechanism in heterogeneous catalysis.
The efficiency of electrochemical water splitting for the sustainable production of clean fuels from renewable energy sources is limited by a large overpotential of the anodic oxygen evolution reaction (OER)\textsuperscript{20,21}. Understanding of its origin requires knowledge about the pathway of the formation of di-oxygen O\textsubscript{2} out of 2 H\textsubscript{2}O molecules by a proton-coupled electron transfer. Even for the best electrocatalysts, i.e., transition metal (M) oxides (O), the reaction path for O–O formation is not well understood. For heterogeneous systems, the reaction is catalyzed at active surface sites, where different sites and mechanisms are suggested. This includes single\textsuperscript{6} or dual\textsuperscript{7,8} transition metal (M) sites with flexible valence states, concerted proton–electron transfer\textsuperscript{9,10} as well as redox active lattice O\textsuperscript{11–13}, including oxygen vacancy formation and annihilation\textsuperscript{14}. Despite remarkable progress in application of density functional theory (DFT) to the oxide-water interface, the theoretical understanding of the dynamic interface structure during OER is still limited since it requires serious approximations\textsuperscript{15}. Among of the far-reaching are the frozen surface approximation and that solvation effects are, if at all, only considered as a static average. This underestimates the flexibility of M surface coordination\textsuperscript{16} due to interface solvent effects that is on the other hand known to be crucial in homogeneous catalysis for the formation of high- or hetero-valent M–O moieties that precede O–O bond formation\textsuperscript{17}. There are controversial conclusions whether the predicted unsuitable scaling relation between metal M–OH and M–O adsorption energies\textsuperscript{16,17} as the origin of large overpotentials for single surface sites can be broken by bifunctional mechanism at two distinct M and M\textsuperscript{+} sites\textsuperscript{18} or is restored by surface solvation\textsuperscript{19}. Recent experiments show that tertiary alloying of two different transition metals with a highly flexible coordination metals indeed lead to a remarkable reduction of OER overpotential in gelled oxyhydroxides\textsuperscript{20}. An improved theoretical understanding thus requires a comprehensive atomic scale understanding of the dynamic electrolyte-catalyst interface structure under OER conditions as an essential ingredient for the knowledge driven further improvement of electrocatalysts by material design.

In addition to OER activity, the stability is strongly affected by the interfacial electrolyte interactions. A distinction between reversible dynamics that emerges in a stationary state and irreversible processes that change the activity is essential. Such insights are promoted by the progress of in situ studies that can address different types of dynamical changes. A first type of rather slow dynamics is the change of electrode surface during potential cycling. The important role of solvate interactions has been e.g., established for the noble metal Pt, where Pt surface oxide that is formed under anodic polarization adsorbs water that dissociates and forms hydrated Pt\textsuperscript{21}. Metal oxides such as CoO\textsubscript{x} can form a disordered surface during OER\textsuperscript{22,23}. A second type of rather fast dynamics is due to thermally activated mobility of surface atoms\textsuperscript{24} or adatoms\textsuperscript{25} that is hardly accessible in operando experiments. Clearly, surface adatom dynamics depends on temperature and surface barriers that can be modified due to H\textsubscript{2}O solvation or dissociation\textsuperscript{26} and is always present, even in thermal equilibrium. Driving the OER, the emerging non-equilibrium surface should show a reversible dynamics in a stationary state that depends on the formed atomic and chemical surface structure. Non-equilibrium dynamics of catalyst atoms may be even involved in OER mechanism\textsuperscript{27}. A third type of surface dynamics is irreversible defect reactions, typically the formation of oxygen vacancies\textsuperscript{13,28} or the dissolution of metallic species\textsuperscript{29}. Such processes are even gradually present at the highest performance system RuO\textsubscript{2}\textsuperscript{30}. Metal dissolution can depend on overpotential\textsuperscript{31,32} surface symmetry\textsuperscript{33}, pH value and particle size\textsuperscript{34}. In order to avoid such corrosive processes, approaches for self-repair have been pursued\textsuperscript{35}. Despite a huge progress in application of different in situ techniques\textsuperscript{36}, comprehensive atomic scale understanding of all three classes of surface dynamics are far of reach at present, but are urgently required to establish the intimate connections between surface stability, the nature of the active sites and reaction pathways\textsuperscript{37}.

In situ environmental transmission electron microscopy (ETEM) in combination with aberration correction and image simulation has developed to a level where it can provide atomic resolution real space information about the equilibrium surface reconstruction in various ambient conditions\textsuperscript{38–40} including strategies for controlling the impact of electron beam\textsuperscript{41,42}. The recent development of atomic scale dynamic studies show surface mobility of Ce atoms on CeO\textsubscript{2} facets in high vacuum\textsuperscript{43} and a transition of a TiO\textsubscript{2} surface reconstruction in H\textsubscript{2}O from static to dynamic after adding CO\textsubscript{44}. Steps towards the control of electron beam-induced and applied electric potentials at TEM samples enable in situ studies of electrode surfaces in ETEM under anodic polarization, approaching OER relevant potentials\textsuperscript{39,45}. In this study, two perovskite manganites AMnO\textsubscript{3} were selected, where the Mn valence state can be controlled by A-site doping without changing the crystal symmetry. Specifically, La\textsubscript{1–x}Sr\textsubscript{x}MnO\textsubscript{3} at x = 0.4 (LSMO) is a metal-like electrode with high and stable oxygen evolution activity that is close to IrO\textsubscript{2}\textsuperscript{29}. Moreover, Pr\textsubscript{1–x}Ca\textsubscript{x}MnO\textsubscript{3} at x = 0.33 (PCMO) is a semi-conducting small polaron material with high initial OER activity, yet less stability, due to oxygen vacancy formation and fast leaching of the resulting reduced Mn species. Thus LSMO is suitable for the study of reversible surface dynamics, whereas PCMO shows a pronounced irreversible defect reaction. Both systems have almost the same initial Mn valence but differ in Mn–O covalency and charge localization. This differences allows us to correlate in situ ETEM studies of surface structure and dynamics with ex situ analysis of electrochemical OER. We find that the (001) surfaces of both manganites show an at least 20 times higher Mn-adatom mobility in an adsorbed water layer compared to other ambients.

**Results and discussion**

**Structure, activity, and stability of LSMO and PCMO (001).** Rotating ring disk electrode (RRDE) cyclovoltammetry (CV) was carried out at epitaxial (001) oriented thin film electrodes in 0.1 M aqueous KOH solution (Fig. 1). Both materials initially show good electrocatalytic oxygen evolution performance (for oxygen detection and Tafel analysis see Supplementary Figs. 1–3). Most striking is the different behavior just below the onset of the OER, where a redox wave is visible in PCMO as a negative current peak at E = 1.3 V versus reversible hydrogen electrode (RHE), complemented by a positive shoulder at the onset of OER. This feature is absent in LSMO. The redox couple is related to reversible formation and annihilation of oxygen vacancies, which are electron donors and thus induce a surface reduction of the transition metal\textsuperscript{13}. The defect reaction is given by

\[
\text{Pr}_{1–x}\text{Ca}_x\text{Mn}^{2+\text{x}}\text{O}_{2+x} + V_0 + 1/2\text{O}_2 \geq \text{Pr}_{1–x}\text{Ca}_x\text{Mn}^{2+\text{x}}\text{O}_x + 2\text{e}^–
\]

For neutral pH values in an unbuffered solution, which is more relevant for the comparison to in situ XANES and ETEM studies, a similar behavior of the CV is observed\textsuperscript{13}. The easy formation of V\textsubscript{0} in PCMO indicates that lattice oxygen is redox active, such that transfer of holes between Mn3d and O2p states can oxidize O\textsuperscript{2–} to form O\textsuperscript{−} and O\textsubscript{2}(g); see e.g., refs. 46,47. For LSMO such a surface redox process is only observed when the cycling is extended to more negative potentials below E = 0.6 V versus RHE\textsuperscript{48}.

Comparing the cycle dependence of the OER activity for LSMO and PCMO in Fig. 1b, there is a strong difference in...
Environmental high-resolution transmission electron microscopy (HRTEM) combined with electron energy loss spectroscopy (EELS) of LSMO and PCMO after 50 electrochemical cycles (Supplementary Figs. 13–15). Based on contrast simulations, the interpretation of dynamic adatom contrast other than Mn on a static A-layer is unlikely: O and OH species are below the contrast detection limit. La/Sr occupancy on B-terminated layers can be excluded from contrast. Fast La/Sr adatom dynamics on a stable A-terminated layer can be not entirely excluded from contrast. However, this would lead to an A-enriched surface with a Mn depleted layer, which is contrary to our observations for LSMO but in agreement to Mn surface leaching in PCMO reported below. Since all experiments in different environments.

Fig. 1 Electrocatalytic characterization. a Cyclovoltammetry of (001) oriented epitaxial thin film manganese electrodes in 0.1 M aqueous KOH solution at 10 mV/s and rotated at 1600 rpm for cycles #2/#50 (PCMO) and #3/#100 (LSMO), respectively. In addition to the OER, PCMO shows a pronounced surface redox couple. b Temporal stability of the electrode current density at $E = 1.75 \text{ V } \text{vers}$. RHE for cycling from $E = 1.1$–1.75 V vers. RHE and 7 min chronoamperometric OER between cycle 3 and 4 (see method section).

Surface termination of the manganite films in $\text{H}_2\text{O}$. The study of surface termination of epitaxial perovskite films using environmental high-resolution transmission electron microscopy (ETEM) was demonstrated by Roodt et al. and requires careful TEM lamella preparation, as documented in the Supplementary Figs. 8–11 and the associated text. The changes of surface termination of the LSMO and PCMO (001) oriented thin film electrodes in high vacuum (HV), $\text{O}_2$ and $\text{H}_2\text{O}$ are shown in Fig. 2. For LSMO predominant A-terminated surfaces (La–Sr–O) are observed in $\text{O}_2$, whereas in high vacuum (HV), a mixed surface termination with disorder at the B-terminated (Mn–O) areas is developed. This is observed even after saturation of the surface in 1 mbar $\text{O}_2$. In $\text{H}_2\text{O}$ vapor, the LSMO surface appears to be dominated by an A-site layer; however, Mn is still present as dynamic surface adatoms. For PCMO, a disordered surface develops in HV following the ordering of the surface in 1 mbar of $\text{O}_2$ where a mixed termination of an ordered surface is observed. In $\text{H}_2\text{O}$, a mixed surface termination emerges, where the A-terminated areas (Pr–Ca–O) show higher ordering compared to the B-terminated areas. Surface Mn adatoms as well as subsurface lattice Mn is highly mobile.

The determination of surface termination requires the comparison of the HRTEM images with simulated images (Fig. 2d, h). In these simulations, the lamella thickness $t$ at the surface is estimated from measurement of the inelastic scattering intensity by EELS and fine-tuned by a fit of contrast of simulated to experimental images using a Monte–Carlo-based simulated least-squares optimization, yielding $t = 4.2$ (4.3) nm for LSMO (PCMO). The obtained electron optical parameters, such as defocus, spherical aberration, astigmatism, and axial coma, fit reasonably well to those estimated from tilt-tableau measurements via the Cs-corrector software. The different surface terminations can be clearly distinguished by the weaker contrast of the MnO columns. In the subsurface, A-site and B-site columns are separable from contrast due to different atomic numbers and octahedral tilt patterns of MnO$_6$ octahedra. Details of the image fitting and parameters used can be found in the Supplementary Fig. 12 and Supplementary Table 1.

Reversible Mn-adatom dynamics at the LSMO–$\text{H}_2\text{O}$ interface. Figure 3 shows a time sequence of HRTEM images for the LSMO $x = 0.4$ (001) surface in 0.5 Pa of $\text{H}_2\text{O}$. The full image series is compiled in Movie M01. The surface is well ordered and shows stable A-termination over more than 30 min. However, mobile Mn is, in fact, present on the surface. This is indicated by the sudden appearance and disappearance of atom contrast at B-layer surface positions on flat stable A layers (Fig. 3a). We define the detection limit of Mn atoms by the amplitude of the signal above the noise level 3, where $\sigma$ is the standard deviation of the background fluctuations of the CCD signal at an area above the surface in the presence of the experimental gas. Image simulation and contrast quantification show that signal to noise ratio at the used frame rate of 4.4 fps does allow for detection of triple or higher occupancy of B-columns by Mn at a 4.2-nm thick lamella surface (Fig. 3b, c).

Closer inspection of image contrast in Fig. 3a reveal adatom contrast mainly appears at interstitial surface positions and rarely at the nominal octahedral positions of an ideal non-reconstructed surface. Contrast quantification of the columns of Mn adatoms is obtained by calibration of the experimental A-site contrast at the lamella surface to the simulated contrast, as shown in the Supplementary Figs. 13–15. Based on contrast simulations, the interpretation of dynamic adatom contrast other than Mn on a static A-layer is unlikely: O and OH species are below the contrast detection limit. La/Sr occupancy on B-terminated layers can be excluded from contrast. Fast La/Sr adatom dynamics on a stable A-terminated layer can be not entirely excluded from contrast. However, this would lead to an A-enriched surface with a Mn depleted layer, which is contrary to our observations for LSMO but in agreement to Mn surface leaching in PCMO reported below. Since all experiments in different environments...
reveal that surface Mn is more mobile than A-type cations, our overall conclusion from image contrast and electrochemical behavior is that Mn adatoms are the highly mobile species on stable LSMO surfaces in H2O.

The camera frame rate of around 4 fps is selected as a compromise between achieving sufficient signal to noise ratio and capturing some of the surface dynamics. Double Mn B-layer occupancy corresponds to the detection limit at 3σ of the noise level. Both triple Mn as well as higher Mn B-layer occupancy contrast appears and disappears with the frame rate used. We can thus only determine a lower limit of the surface hopping rate of \( r \geq 4 \text{ s}^{-1} \).

**Fig. 2** HRTEM cross plane images of LSMO and PCMO (001) surfaces in different ambients. All images are taken at negative defocus, i.e., atomic columns appear as dark contrast, and with objective lens aberrations corrected up to 5th order. a–d LSMO is imaged in the pseudocubic [110] zone axis. a Mixed B- and A- termination in high vacuum (HV). b Dominant A-termination in 1 mbar O2. c In 0.5 Pa H2O, the surface consists of a stable A-layer with highly mobile Mn on top (see Fig. 3). d Simulated image with A-termination and surface step. e–h PCMO is imaged in the orthorhombic [110] zone axis. e Disordered surface structure in HV. f Highly ordered surface in 1 mbar of O2 with a mixed termination. g In 0.5 Pa of H2O, the B-terminated areas of PCMO exhibit pronounced disorder with mobile Mn. h Simulated image for PCMO with different surface terminations.

**Fig. 3** Observation of dynamic Mn adatoms on a LSMO (001) surface in 0.5 Pa of H2O at [110] zone axis. a Time sequence of HRTEM images taken at 4.4 fps at negative defocus. Mn-adatom contrast appears and disappears on a stable La(Sr)O surface layer as indicated by white arrows. b Simulated HRTEM image with Mn-adatom column occupation of 3, 4, and 5. The Mn columns are located at interstitial surface positions on an A-terminated sample. Lamella thickness is 4.2 nm. c Line profiles of simulated (red) and experimental (black with symbols) images of B-columns with 3, 4, and 5 Mn atom occupation. The 3σ threshold indicates the detection limit of Mn columns above noise level, i.e., triple Mn occupation at a B-layer column. The time sequence gives a lower limit of the Mn-adatom hopping rate of \( r \geq 4 \text{ s}^{-1} \).
ionization of H$_2$O. Despite the high mobility, the Mn leaching is rather slow, as confirmed by the post-ETEM stoichiometry analysis (Supplementary Fig. 20). Furthermore, the Mn valence state remains quite stable, indicating only a slight Mn reduction in increasing H$_2$O pressure and ruling out pronounced formation of oxygen vacancies.

**Irreversible Mn-adatom dynamics at the PCMO–H$_2$O interface.** Figure 5 shows a time series of HRTEM images of the (001) PCMO surface in 0.5 Pa H$_2$O, taken from Movie M06. After fully ordering in O$_2$ (Fig. 2f), the addition of H$_2$O causes the surface to form a disordered layer of highly mobile Mn atoms, visible as rapid fluctuation of B-site contrast. Similar to LSMO, the hopping rate of Mn atoms is above the frame rate of the camera, i.e., $r \lesssim 4$ s$^{-1}$. In contrast to the disordered B-terminated surface, the A-subsurface layer remains highly ordered and static on the timescale of several seconds (Movie M06). In addition, an increase of contrast dynamics is observed at the B-site columns at the subsurface. Figure 5b, c shows the later stages of the PCMO (001) surface in 0.5 Pa H$_2$O. Three min after initiation, the fast Mn leaching has led to the formation of a Pr-rich surface bilayer (Movie M06) which further grows up to a thickness of 3–4 monolayers over the course of the in situ experiment (11 min). The growth of a cubic phase due to Mn leaching is directly visible in the surface structure. Postmortem EELS analysis of the surface area in Fig. 5f reveals Pr and O, whereas the Mn L-edge at 346 eV (not shown) are below the noise level. We thus associate the cubic oxide visible in HRTEM with PrO$_x$, with x close to 2. The growth speed of the PrO$_x$ slows down over time, indicating self-passivation of the surface by the formed PrO$_x$ layer. Post-ETEM EELS of the Mn L and O K edges at the PCMO surface region reveals a pronounced Mn depletion (Supplementary Fig. 20), which is accompanied by Mn reduction. Leaching out of subsurface Mn in PCMO (001) is only observed in H$_2$O and is absent in HV (Movie M07) and O$_2$ (Movie M08).

In contrast, the Mn concentration at LSMO surfaces remains unmodified. This is fully consistent with the observation of different electrode behavior in electrochemical experiments described above.

**Enhanced Mn mobility at (001) surface due to presence of adsorbed H$_2$O layer.** The formation of a few monolayer thick water layer on oxide surfaces down to pressures of ~10$^{-5}$ Pa much below the equilibrium vapor pressure of water of p$^{\text{eq}}$ = 3.17 kPa at T = 25 °C has been previously demonstrated$^{49,50}$. It is driven by the large adsorption enthalpy of H$_2$O on oxide surfaces of the order of $\Delta H^{\text{ads}}$ = −160 kJ/mol$^{51,53}$. Although this value might vary between different oxides, $\Delta H^{\text{ads}} < \Delta H^{\text{evap}}$ = −44 kJ/mol for H$_2$O on bulk water reflects exothermic water adsorption on oxide surface at much reduced pressures. In the HV of the ETEM (p $\gtrsim$ 10$^{-5}$ Pa), the effect of H$_2$O condensation on manganite surfaces can be only avoided by using a cold trap that is reducing the partial pressure of H$_2$O in HV by one order of magnitude$^{48}$. The thickness of the adsorbed water layer in the ETEM experiments as a function of $p_{\text{H}_2\text{O}}$ is calculated by using the energy balance between surface energy $\gamma_s$ of the oxide in HV, the surface energy $\gamma_{\text{H}_2\text{O}}$ of liquid H$_2$O to vapor and $\Delta H^{\text{ads}}$ (see Supplementary Fig. 22 and associated text). The liquid state of 2–4 monolayer H$_2$O is consistent with our observation of enhanced mobility of Mn on manganite (001) surfaces in a pressure range between 0.01 and 5 Pa of H$_2$O compared to HV.

**Thermally induced versus electron beam-induced hopping.** In order to separate out the effect of the electron beam on adatom motion from the thermally induced motion, the momentum...
transfer from scattering of the high energy primary electron beam on the adatoms is calculated. As pointed out by Egerton\textsuperscript{54}, for energies of primary electrons $E_0 \geq 10$ keV, the interaction is dominated by elastic scattering of the incident electrons at the atomic nuclei, and momentum transfer due to inelastic scattering at the electron shell can be disregarded. This allows calculation of the momentum transfer using the Rutherford scattering equation. We consider the maximum momentum transfer perpendicular to the primary electron beam, which gives rise to transversal movement of adatoms on a surface parallel to the electron beam.

Figure 6 compares the beam-induced hopping rates for O, Mn, Sr and La adatoms to the thermally activated hopping rate as a function of the surface activation energy $E_a$ for an upper limit of used dose rates of $12,000$ e$^{-}$/Å$^2$s (see method section). For $E_a \geq 0.2$ eV, the calculated beam-induced hopping rate for Mn adatoms is below the experimentally observed hopping rate in HV, indicating that the slow Mn motion is thermally activated. The comparison of the calculated thermally activated hopping with the experimentally observed hopping rate in HV, indicating that the slow Mn motion is thermally activated. The comparison of the calculated thermally activated hopping with the experimentally observed hopping rate in HV, indicating that the slow Mn motion is thermally activated. The comparison of the calculated thermally activated hopping with the experimentally observed hopping rate in HV, indicating that the slow Mn motion is thermally activated.

Parallel trends in electrolysis and ETEM studies with respect to reversible and irreversible dynamics. For LSMO $x = 0.4$, the (001) interface to liquid H$_2$O is quite stable both in in situ ETEM experiments as well as in cyclovoltammetry in alkaline conditions between $+1.1$ and $1.75$ V vers. RHE. Only slow Mn leaching is observed in previous studies by postmortem XPS after 1 h of electrochemical OER, which can be further slowed down by choosing a Mn/A ratio $\geq 1$ ref.\textsuperscript{55}. In contrast to LSMO, the in situ ETEM study of PCMO shows pronounced irreversible surface dynamics of Mn, leaching into the liquid H$_2$O layer in parallel to fast drop of OER activity in electrolysis and observation of a Pr-rich surface layer in postmortem studies. The huge difference in reversibility of Mn-adatom motion at the interface between the more or less static A-site terminated layer and liquid H$_2$O must therefore be attributed to the different materials properties of LSMO and PCMO. Post-ETEM electron energy loss spectroscopy (EELS) of the Mn L edge at a $= 1$-nm thick surface layer on PCMO demonstrates a change of Mn valence from $3.5 \pm 0.1$ after oxidation in O$_2$ to $3.2 \pm 0.1$ after ETEM study in 0.5 Pa and $3.1 \pm 0.1$ in 5 Pa of H$_2$O (Supplementary Fig. 21). Thus, Mn is reduced although the experiments are performed under anodic polarization. In contrast, for LSMO the pristine Mn valence of $3.5 \pm 0.1$ after oxidation in O$_2$ and $3.4 \pm 0.1$ after ETEM study in 0.5 Pa H$_2$O is preserved within the error of measurements (Supplementary Fig. 20). Previous post electrochemical XPS studies of
Additionally, the experimentally observed Mn-adatom hopping rates in high doped LMO grain boundaries from ref.66. For the activation energy of Mn adatom hopping rate in liquid H2O is connected to the absence of defect reactions and preservation of Mn oxidation state.

For LSMO, the observed reversible Mn-adatom dynamics in liquid H2O is connected to the absence of defect reactions and preservation of Mn oxidation state. In contrast, PCMO shows a broad range of values, depending on the La-off-stochiometry of the sample67. See method section for details of the calculations.

In Fig. 6, calculated beam-induced and thermally activated adatom hopping rate \( r \) at \( T = 22 \, ^\circ C \) as a function of the surface activation energy \( E_a \). Additionally, the experimentally observed Mn-adatom hopping rates in high vacuum \( r(HV) \) and \( r(H_2O) \) in 0.5 Pa H2O are indicated. Colored areas mark the regimes for thermally and beam-induced hopping for Mn. The activation energy of O diffusion in bulk LMO is from ref.65 and for O in Sr-doped LMO grain boundaries from ref.66. For the activation energy of Mn the lower and upper limit of Mn diffusion in LMO are indicated, since it shows a broad range of values, depending on the La-off-stochiometry of the sample67. See method section for details of the calculations.

Solvated dynamic Mn adatoms and impact on reaction mechanisms of oxygen evolution. The demonstrated parallel trends in in situ ETEM and electrolysis studies underpins that the observation of enhanced surface dynamics of Mn adatoms in H2O is highly relevant for the real-world electrochemical behavior of the manganite electrodes. Clearly, there are differences in the properties of a Helmholtz layer in a liquid electrolyte with ion concentration of \( 10^{-4} \) M and the thin water layer adsorbed on top of oxide materials in ETEM. In particular, the ion concentration is much lower, with typically \( 10^{-6} - 10^{-7} \) M in the vapor45 that is close to the ion concentration at neutral pH. However, the composition of ions generated by electron impact is different since positively charged ions such as H2O2+ dominate over anions such as OH−. Our ETEM studies are performed under positive electric potentials of \( U = +2 \, V \) with respect to ground and thus under anodic polarization. Due to the high electric conductivity of the manganite lamella on highly conductive Nb-doped SrTiO3, beam-induced potentials can be disregarded45. The comparison of hopping rates in different ambients clearly demonstrate that the observed \( \geq 20 \times \) increased Mn-adatom mobility in H2O while other conditions of the experiment remain the same is not due to the electron beam. This is fully understandable from the calculation of beam-induced momentum transfer in Fig. 6. Therefore, the enhancement of thermally activated adatom motion in water is fully relevant for OER catalysis in ex situ electrochemical conditions. It can be attributed to a partial solvation of surface Mn in liquid H2O. Such solvation effects thus do not only affect the adsorption energies of the reactants but also strongly modify the coordination and electronic properties of active sites.

The formation of a partial solvation shell of H2O around chemisorbed Mn adatoms in OER thus has far-reaching consequences for understanding of the reaction pathways. First
of all, Mn can develop other, more flexible coordination to OH2 and OH compared to a static octahedral Mn–O coordination of a frozen surface (Fig. 7). This would allow new configuration for the formation of the O–O double bond. Furthermore, the question is raised whether the Mn dynamics affect the OER. The electron transfer rate per surface Mn atom derived from RRDE measurements is between 0.2 s−1 (1.6 V) and 10 s−1 (1.74 V vrs RHE), assuming a Faraday efficiency of 1 and a complete Mn surface coverage. Due to partial coverage, these numbers represent a lower limit of the electron transfer rate per Mn. Comparing these numbers with the observed lower limit of Mn-adatom hopping \( r = 4 s^{-1} \), shows that both are of the same order of magnitude or even higher. Consequently, Mn can move over several surface sites during a full \( O_2 \) evolution cycle.

In summary, our study reveals unexpectedly high Mn-adatom hopping rates implying that the understanding of OER mechanisms requires theoretical treatment beyond the frozen surface approximation. There is strong experimental evidence from ref. 71 that surface Mn species represent the catalytically active sites for LSMO. Fast Mn leaching at PCMO surfaces dramatically decreases OER activity. Although hopping rates and contrast of single Mn atoms are beyond the resolution of our experiments, the observation of dynamic multiple occupancy of surface sites by Mn moieties establishes a pronounced dynamical surface reconstruction of the catalyst-water interface with partial solvation of surface Mn atoms in \( H_2O \). Mn-adatom contrast dominantly appears at interstitial surface sites rather than the nominal octahedral B sites of an unreconstructed ideal surface, suggesting a modified surface coordination. The implications of these findings are quite far-reaching. First of all, leaching of reduced transition metal species is observed for many transition metal oxides.\(^{61,62}\) Our results imply that the underlying transition from reversible dynamics of surface atoms to irreversible leaching of surface and subsurface metal species is controlled by charge localization and a related shift of the Fermi energy. Indeed, the recent results on self-gating of electrocatalysts evidence a modification of the Fermi level at the onset of an electrochemical reaction\(^{63}\). The finding of pronounced reversible dynamics of partially solvated adatoms in the stationary state of OER implies that for the theoretical understanding of heterogenous catalysis some aspects of homogeneous catalysis must be taken into account, such as modified metal coordination, different valence states, solvation shell reorganization during electron transfer, solvent thermal fluctuations and possibly Mn displacements during intermediate formation. Incorporating these effects into theoretical analysis will open new strategies of breaking scaling relations between adsorption energies and thus new perspectives in atomic scale design of efficient and stable electrode surfaces for OER.

**Methods**

**Film fabrication and structure.** \( La_{0.8}Sr_{0.2}MnO_3 \) and \( Pr_{0.5}Ca_{0.5}MnO_3 \) (001) films were prepared by ion-beam sputtering (IBS) on 0.5 wt% Nb-doped \( SrTiO_3 \) (STNO) substrates with (100)-orientation (CrysTec GmbH, Berlin, Germany). The \( La_{0.8}Sr_{0.2}MnO_3 \) \( (Dr=0.8\%\, M_{Antim}) \) with thickness of 80 nm were grown at 800 °C (630 °C) in an oxygen atmosphere of 1.7 \( \times 10^{-4} \) mbar. In order to avoidrectifying junction properties for PCMO, a 20-nm thick \( La_{0.8}Sr_{0.2}MnO_3 \) (LSMO) buffer layer was deposited without vacuum breaking. LSMO has a rhombohedral lattice, space group \( R \bar{3}c \) with a small rhombohedral tilt angle of 90.37°, lattice parameter \( a = 5.47 \text{ Å} \), which converts in a pseudocubic lattice constant \( a = 3.87 \text{ Å} \). PCMO is orthorhombic, space group \( Pbnm \), with ideal lattice parameters \( a = 5.42 \text{ Å}, b = 5.45 \text{ Å}, c = 7.67 \text{ Å} \). Due to the larger lattice constant of STNO \( (a = 3.92) \), the films have in-plane tensile and out-of-plane compressive strain leading to \( a = 3.85 \text{ Å} \) (LSMO) and \( c = 7.62 \text{ Å} \) (PCMO). For LSMO, we use pseudocubic notation to facilitate the comparison of the (001) surface with the equivalent (001) surface of PCMO. The films show atomically flat surfaces with unit cell high steps. The temperature dependent electric resistivity of the films shows the expected metal–like (LSMO) and small polaron hopping like (PCMO) characteristics. See Supplementary Figs. 4–7 and 24 for more details.

Backside contacts for the STNO substrate consisted of 5 nm Ti and 100 nm Pt layers prepared by IBS at room temperature to ensure an ohmic contact. Carbon tape and conductive Sigma–Aldrich (Sigma–Aldrich, Munich, Germany) served as the top contact and a conductive silver paste was used to make contact to the Pt backside and a conductive silver paste was used to make contact to the Pt backside. The electrochemical experiments were carried out during intermediate formation. Incorporating these effects into theoretical analysis will open new strategies of breaking scaling relations between adsorption energies and thus new perspectives in atomic scale design of efficient and stable electrode surfaces for OER.

**Electrochemistry.** The electrochemical measurements were carried out with two Intertech 1000E potentiostats (Garny Instruments Inc., Warminster, PA, USA) in a bipotentiostat setup and an RRDE-3A rotator (AIS Co. Ltd., Tokyo, Japan). The rotating ring electrode consists of a disk electrode of the assembled PCMO/LSMO/NSTO electrode with a diameter of 4 mm and a Pt ring electrode with an inner diameter of 5 mm and an outer diameter of 7 mm. All electrochemical measurements were performed in 0.1 M KOH electrolyte prepared by diluting KOH stock solution (Sigma–Aldrich, Munich, Germany) with deionized water. Mn4+ (>16.5 M) stock solution was saturated with Ar gas at least 30 min before measurements and continuously purged with Ar throughout the measurement. Electrode potentials were converted to the reversible hydrogen electrode (RHE) scale using ERHE = Eapp + E0H2O + E0H2O + E0O2

**Environmental TEM experiments.** Transmission Electron Microscopy (TEM) experiments were carried out using a FEI Titan TEM G2 80–300, operated at 300 kV. The microscope is equipped with a Cs-corrector of the image forming lens for enhanced high-resolution TEM (HRTEM) imaging, and a Gatan Image Filter (GIF) Quantum 965ER. A Gatan UltraScan 1000XP CCD was used to collect all movies with rate of about 4 frames per second (fps) in 512 x 512 pixels. The microscope was used in the high vacuum (HV) mode (\( \sim 10^{-5} \text{ Pa} \)) with cold trap to reduce \( H_2O \) partial pressure, as well as in environmental mode using \( H_2O \) and \( He \) in a pressure range between 0.01 and 100 Pa. The following movies are provided: M01 LSMO 0.5 Pa \( H_2O \) flat facet, M02 LSMO 0.5 Pa \( H_2O \) Schwoebel Barrier, M03 LSMO HV, M04 LSMO 0.5 Pa \( O_2 \), M05 LSMO 0.5 Pa \( N_2 \), M06 PCMO 0.5 Pa \( H_2O \), M07 PCMO 0.5 Pa \( O_2 \), M08 PCMO 0.5 Pa \( O_2 \), M09 LSMO 10 Pa \( O_2 \) re-crystallization early state and M10 LSMO 10 Pa \( O_2 \) re-crystallization late state. All time resolved HRTEM experiments were performed at a beam current of 4 nA and beam radius between 80 and 100 nm, resulting in a spatially in homogene I electron dose rate of 8000–12,000 e/Å²/s. Local electron dose rates at the location of TEM lamellae surface are measured by calibrated CCD contrast with <0.136 electrons/counts, yielding <10,000 e/Å²/s for the adatom hopping studies. This dose rate is two orders of magnitude below the damage threshold in HV. Imaging over a time of 10 min keeps the total electron dose <6 \( 10^6 \) As/cm², where no changes by electron irradiation are observed in HV, in good agreement with the studies of the intrinsic surface in ref. 41.

**Electron energy loss spectroscopy (EELS).** Was performed using Gatan Quantum 965ER post-column energy filter in the same FEI Titan TEM. Spectra of the Mn L, O K, and Pr M edges were acquired. For analysis of the Mn L edge spectra, Hartree–Slater (HS) type cross-section functions from Gatan’s Digital Micrograph are used. The Mn valence state has been acquired from a C++ based LabTalk script using OriginLab software. EEL spectra are extracted from spectrum images at an area of vacuum and at different \( H_2O \) vapor pressure for postmortem analysis. Power-law background functions are fitted to a 50 e/ eV wide window before each Mn L-edge and 25 e/ eV for O K-edge for background subtraction. Using dual EELS acquisition, the ZLP is used to correct the drift of the energy shift.

**TEM lamella preparation.** TEM lamellae were prepared from epitaxially grown (001) oriented thin films by Focused Ion Beam lift-out technique using a noble metal free protection layer and careful low energy ion milling for the preparation of ultrathin lamella with a thickness close to the surface between 4 and 10 nm. The loss of oxygen by Ar milling is compensated by a treatment in pure oxygen. Further details are described in the Supplementary information and Movies M09–M10.

**Image simulations.** Atomic models and the high-resolution TEM simulated images were calculated using the multisite method as established in the QSTEM package\(^{64}\), where electron optical parameters were optimized by using a metropolis algorithm implementation to fit simulated to experimental images. Structure models for the image simulations are based on the Pbnm space group for PCMO with lattice parameters \( a = 5.42 \text{ Å}, b = 5.45 \text{ Å}, c = 7.67 \text{ Å} \) and R3c for LSMO using \( a = 3.87 \text{ Å} \). Details and parameters used for image simulation are given in the SI.
Calculation of electron beam-induced and thermally activated hopping. Using the analytical solution given in ref. 32, the adatom hopping rate is

\[ R = \frac{1}{4} \frac{\sqrt{2}}{\sin^2(\theta_{\text{min}}/2)} \int \left( 1 - \frac{1}{\sin^2(\theta_{\text{max}}/2)} \right) \]

where \( \theta \) is the scattering angle of the electrons. The limits

\[ \theta_{\text{min}} = \arcsin \left( \frac{2}{E_{\text{max}}} \right)^{1/2} \]

and \( \theta_{\text{max}} = \pi - \arcsin \left( \frac{2}{E_{\text{max}}} \right)^{1/2} \)

are given by the ratio of the captured surface energy \( E_s \) of the adatom to the maximum possible energy transfer \( E_{\text{max}} \), which would correspond to a 180° scattering, i.e.,

\[ E_{\text{max}}(E) = \frac{1}{2} \rho \frac{V^2}{F} \]

and

\[ F = (1 - v^2/c^2)^{1/2} \]

A is the atomic mass, \( Z \) the nuclear charge, \( e \) the elementary charge, \( J \) is the current density of the primary electron beam, \( \rho = 1 \text{ barn} = 10^{-28} \text{ m}^2 \) and \( F \) is the velocity of light and \( v \) the velocity of the primary electrons. In order to calculate the hopping rate of an adatom on a surface, it is assumed that the kinetic energy transfer to the surface is equal to the surface activation energy \( E_A \).i.e., \( E_s = E_A \). In the Mn-adatom hopping studies, \( E_s = 300 \text{ keV} \) and for the current density an upper limit of the experimental values of \( J = 2 \cdot 10^4 \text{ A/m}^2 \) is chosen, corresponding to 12,000 eA/\( \mu \text{m}^2 \).

The thermally activated hopping rate is given by

\[ R_{\text{th}} = \frac{v_0}{e^{E_0/k_B T}} \]

with adatom vibration frequency \( v_0 \) and Boltzmann constant \( k_B \). We have chosen \( v_0 = 10^{12} \text{ s}^{-1} \), which for \( E_0 = 0 \text{ eV} \) results in a thermal velocity for Mn atoms matching the maximum of the Maxwell–Boltzmann distribution.

Data availability
All relevant data are available from the corresponding authors on request.

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Author contributions

G.L. and V.R. carried out the ETEM experiments. T.M. and U.R contributed to image analysis. J.G. and G.W. did manganite epitaxy and structural analysis as well as electrochemical measurements. M.R. contributed to analysis of electrochemical data. L.R. provided software for image simulation. P.B. contributed to theoretical analysis of the results. C.J. did calculations on beam effects and water adsorption and wrote the manuscript. All authors commented on, discussed and edited the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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