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Decision letter and referee reports: first round

27th Apr 20

Dear Prof Jooss,

Thank you for submitting your manuscript, "Dynamic observation of Mn-atom mobility at perovskite oxide catalyst interfaces to water", to Communications Materials. It has now been seen by 3 referees. You will see from their comments below that while they find your work of interest, some important points are raised. In particular, Reviewer 1 has some concerns regarding identification of surface Mn atoms.

We are interested in the possibility of publishing your study in Communications Materials, but would like to consider your response to these concerns in the form of a revised manuscript, followed by further review, before we make a decision on publication. We therefore invite you to revise and resubmit your manuscript, taking into account the points raised.

We are committed to providing a fair and constructive peer-review process. Please don't hesitate to contact us if you wish to discuss the revision in more detail.

When submitting your revised manuscript, please include the following:

-A rebuttal letter with a point-by-point response to each of the referee comments and a description of changes made. Please include the complete referee report in the rebuttal letter. Please note that the rebuttal letter must be separate to the cover letter to the editors.

-A marked-up version of the manuscript with all changes to the text in red colored font. Please do not include tracked changes or comments. Please select the file type 'Revised Manuscript - Marked Up' when uploading the manuscript file to our online system.

-A clean version of the manuscript. Please select the file type 'Article File'.

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We hope to receive your revised paper within three months; please let us know if you aren't able to submit it within this time so that we can discuss how best to proceed. If we don't hear from you, and the revision process takes significantly longer, we will close your file. In this event, we will still be happy to reconsider your paper at a later date, as long as nothing similar has been accepted for publication at Communications Materials or published elsewhere in the meantime.

We understand that due to the current global situation, the time required for revision may be longer than usual. We would appreciate it if you could keep us informed about an estimated timescale for resubmission, to facilitate our planning. Of course, if you are unable to estimate, we are happy to accommodate necessary extensions nevertheless.

Please do not hesitate to contact me if you have any questions or would like to discuss these revisions further. We look forward to seeing the revised manuscript and thank you for the opportunity to review your work.

Best regards,

John Plummer, PhD
Chief Editor
orcid.org/0000-0003-4824-8497
Communications Materials

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

In this manuscript, the authors directly visualized the surface atom dynamics at manganite perovskite catalysts for oxygen evolution reaction (OER) via in-situ environmental transmission electron microscopy (ETEM). Comparing the (001) surfaces of LSMO and PCMO, the reversible and irreversible surface processes and their dependence on electronic structure and correlations can be distinguished.

This is a systematic and interesting study, which shows detailed analysis on the dynamic surface structure of complex oxides in different gas environments. However, there are some important issues need to be addressed before considering publication.

1. The main concern is the identification of Mn adatoms, which mainly relied on the simulations. The surface adatoms involve many elements, such as Mn, O, La, Sr and H₂O, which are very complicated and could result in many combinations although the authors considered Mn and La/Sr, respectively. Furthermore, it is hard to derive reliable information of hopping rate based on these simulations and the TEM data from a normal CCD. In addition, the gas environment would have some impacts on the simulations, which need to be considered.

2. What did the reversible mean? It can be seen that the surface adatoms sitting randomly on the surface of LSMO. One cannot see a particular situation is coming back when changing environment.

3. The beam damage is an important issue although the beam dose is relatively low in this study. The authors should find the intrinsic surface as reported in a previous literature (Angew. Chem. Int. Ed. 51(2012) 7729), which is an important step before doing detailed analysis. It is obvious that beam damage can be seen in Figure 5.

4. In Figure 3, one can see the surface adatoms (dark spots) in the top of white spots (rows) in Figure 3a. However, the surface adatoms in the simulated image are on the top of dark spots (rows) in Figure 3b. Why is different?

5. The introduction part needs to be re-organized/re-written. It should be condensed and more focused. In addition, some important works in ETM should be cited when they talk about the

powerful ability of ETEM, such as, Science 335 (2012) 317 & Science 367 (2020) 428, especially, the latter is related to water environment.

6. The scale bar is missing in Figure 2(g).

7. Please indicate which line is experimental and which line is simulated in Figure 3(c).

8. There are some writing problems at the figure legends in Figures S5 and S6.

9. It's better to provide some HADDF-STEM images of LSMO and PCMO surfaces, which show more precise atomic positions.

Reviewer #2 (Remarks to the Author):

The paper by Lole et al. reports the dynamic observation of Mn-atom mobility of perovskite oxides in an environment simulating electrochemical water oxidation. Using TEM spectroscopy in a quasi in-situ environment, they found that the stability of perovskite oxides (La and Pr-based ones) for electrochemical water oxidation at alkaline pH correlated with the mobility of Mn-atom monitored under low-pressure H₂O gas conditions. I fully agree with the author's assertion that real-world electrochemical catalysis is dynamic, and there is a need for the mechanistic studies that take into account such dynamic surface processes. To the best of my knowledge of electrocatalysis, this paper is one of the few important studies that allows us to see the real-world chemistry that is happening on the surface of Mn oxides during water oxidation. Therefore, I recommend that this paper be published in Material Communication.

One weak point of this study is the insufficient discussion which is needed to narrow the gap between environmental TEM experiments and electrochemical experiments. Environmental TEM experiments were performed under low-pressure H₂O gas conditions, which to some extent, replicates electrochemical systems. However, physicochemical parameters, such as ionic concentration, electrochemical potential, solvation energy, and etc., are different from electrochemical interfaces. I recommend the authors to have more detailed discussion on the differences between ETEM and electrochemical conditions. Related to this comment, did the authors confirm that perovskite oxides indeed split water to oxygen and proton during ETEM experiments? What is the actual electrochemical potential of materials during ETEM experiments?

Reviewer #3 (Remarks to the Author):

This manuscript reports dynamic observation of Mn-atom mobility at perovskite oxide catalyst interfaces in OER using in-situ ETEM. The use of such a high resolution technique to probe catalysts is promising and novel. Authors took efforts to present the data well. The reviewer suggests some minor revisions.

Data on perovskite oxide (LMSO and PMCO) are presented in the paper. How can the insight here be applied to other OER catalysts with different structures like rutile, spinel, rock salt, and bixbyite oxides?

Recently, self-gating has been proposed in semiconductor electrocatalysis: Nat. Mater. 2019, 18, 1098-1104. Some discussion should be added with respect to perovskite catalysts in this paper.

In Fig 1a, is the current density normalized by geometric area? Normalization by electrochemical surface area should be provided as well.

In Fig 2g, scale bar is missing.

Fig 4c is unclear and of low resolution.

Relevant review papers related to in-situ catalyst studies and electrocatalysis should be cited in the introduction: Science 2017, 355, eaad4998, Nanoscale Horiz. 2019, 4, 809-827 and Nat. Catal. 2018, 1, 922-934

Point-to-Point Responses to Reviewers' Comments and Suggestions

First of all, we thank the referees for reviewing our manuscript and giving valuable comments and suggestions, which have resulted in modifications that have improved the quality and clarity of the paper. We address each point specifically.

Reviewer #1:

1. The main concern is the identification of Mn adatoms, which mainly relied on the simulations. The surface adatoms involve many elements, such as Mn, O, La, Sr and H₂O, which are very complicated and could result in many combinations although the authors considered Mn and La/Sr, respectively. Furthermore, it is hard to derive reliable information of hopping rate based on these simulations and the TEM data from a normal CCD. In addition, the gas environment would have some impacts on the simulations, which need to be considered.

We thank the reviewer for this critical comment. To clarify, this is indeed essential for main conclusions of the manuscript. We do not consider surface oxygen or H₂O, since we want to study the metal centers that represent active sites for catalysis. Furthermore, light elements in a disordered dynamic state cause insufficient contrast to be studied with the methods available at present. Only from contrast simulations alone, a complete proof that the mobile atomic species on top of the LSMO surface are Mn adatoms and not La/Sr atoms is not possible. Our statement of highly mobile Mn-adatoms on a more or less static A-site terminated surface is based on the following arguments combining contrast analysis, and correlating the different behaviour of PCMO /LSMO to real world catalysis:

- Image simulation in Fig S15 rules out the following configurations of the LSMO (001) surface in H₂O: B-site terminated surface with static Mn atoms as the surface layer with either La/Sr adatoms on top (that would be the natural stacking sequence) or Mn adatoms on top (that would occur for a loss of A site atoms in H₂O).
- For all ambients (HV Fig. S 17 and O₂ Fig S18) , the B site terminated areas are always more disordered than the A site terminated areas and more dynamic. Even for the B-site terminated surface in N₂ in Fig. S 19 (Movie M05) the ordered B site structure is much more dynamic than any A site terminated layer. This all shows that Mn has a lower surface activation barrier of thermally activated hopping than A site atoms.
- Ex situ electrochemical experiments show that there is a leaching process of Mn (slow for LSMO, fast for PCMO) and no leaching process of the A site cations. This also indicates that Mn is more susceptible in H₂O and thus the more mobile species.
- A surface where A site adatoms are present on top of a A site terminated layer is indeed visible for the PCMO after some Mn has leached out in Fig. 5 (a, 0.69s) and Fig. 5b,c. The resulting surface layer is however stable and more or less immobile on the time scale of our experiments.

These arguments leave no other conclusion than Mn adatoms being the mobile surface contrast visible in H₂O experiments.

We have clarified the arguments in our article by adding the following paragraph:

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.

2. What did the reversible mean? It can be seen that the surface adatoms sitting randomly on the surface of LSMO. One cannot see a particular situation is coming back when changing environment.

Reversible adatom hopping does not mean that atoms necessarily need to come back into exactly the same surface configurations. There are many equivalent surface Mn configurations that belong to a fixed surface concentration of Mn. Reversible means that the surface concentration of Mn is preserved, at least on the time scale of our experiments.

3. The beam damage is an important issue although the beam dose is relatively low in this study. The authors should find the intrinsic surface as reported in a previous literature (Angew. Chem. Int. Ed. 51(2012) 7729), which is an import step before doing detailed analysis. It is obvious that beam damage can be seen in Figure 5.

We thank the reviewer to bring this article to our attention and we cite it in the revised version of our paper. Indeed, it is one important approach to study the materials under different beam dose rates and doses in order to separate out beam effects from the effect of the ambients on the structure. An alternative approach is to study dose rate and total dose in HV and determine the HV thresholds for beam damage and then stay at least one order of magnitude below these thresholds.

In our experiments at LSMO and PCMO, HV thresholds for dose rate are with 10^6 e/Å²s (from STEM) two orders of magnitude above the used values for the in situ HRTEM of 10^4 e/Å²s. The total dose for oxygen vacancy related sample reduction in HV is with 6×10^3 As/cm² quite comparable to the values in the reference. We have included the thresholds in the method section of our manuscript.

We disagree that Figure 5 is showing beam damage. If the effect of formation of a cubic Pr-O phase in Figure 5 was beam damage, it would be also observed in HV or in O₂. This is not the case. We have added these two additional experiments in the new movies M07 PCMO HV and M08 PCMO O₂. Furthermore, as shown in Figure S6 c and d, strong Mn leaching and transformation to a Pr rich phase is observed in post electrochemical studies and thus is an intrinsic material property of PCMO.

4. In Figure 3, one can see the surface adatoms (dark spots) in the top of white spots (rows) in Figure 3a. However, the surface adatoms in the simulated image are on the top of dark spots (rows) in Figure 3b. Why is different?

We thank the reviewer for this comment. Indeed, the experimental images suggest that the adatoms are rather placed on interstitial surface sites than on the B-sites of a nominally unreconstructed surface. We have thus performed additional images simulations with the same electron optical parameters but displaced Mn adatoms. This fits better to the experimental observations and supports our main conclusion of occurring changes in surface coordination of partially solvated Mn adatoms.

Consequently, we have exchanged the simulated image Figure 3b and have included the comparison of the two surface sites in Figure S15 in the Supplemental Material.

Furthermore, we have included a new Figure S12 in the supplement in order to clarify the exact position and procedure of fitting of simulated to experimental image. Please note that TEM lamella has wedge shape structure and due to the thickness gradient from bulk to surface the contrast is changing in the experimental image, whereas the thickness of the simulated image is taken at the first subsurface A layer.

5. The introduction part needs to be re-organized/re-written. It should be condensed and more focused. In addition, some important works in ETEM should be cited when they talk about the powerful ability of ETEM, such as, Science 335 (2012) 317 & Science 367 (2020) 428, especially, the latter is related to water environment.

We thank the reviewer for the critical comment and have rewritten the introduction with the focus on solvation effects on the dynamic state of an electrode water interfaces. In addition, we included more reference on previous ETEM work. In particular the very recent work on dynamic surface reconstruction of TiO₂ is very important and is specifically addressed.

6. The scale bar is missing in Figure 2(g).

The scale bar is added

7. Please indicate which line is experimental and which line is simulated in Figure 3(c).

Experimental - black line and simulated – red line. We thank the reviewer and have improved the description of Figure 3.

8. There are some writing problems at the figure legends in Figures S5 and S6.

We have corrected the figure captions and thank the reviewer for the remark.

9. It's better to provide some HAADF-STEM images of LSMO and PCMO surfaces, which show more precise atomic positions.

Since the study of surface adatom dynamics requires image acquisition at a frame rate of > 1 fps, only HRTEM is suitable for these in situ studies. They require to understand the HRTEM image contrast for different surface terminations as provided in Figure 3.

In order to take up the suggestion of the reviewer, we have added HAADF-STEM images of LSMO and PCMO surfaces in high vacuum in a new figure in the SI (Fig. S11) where the order A site terminated surface of LSMO and the disordered surface of PCMO in high vacuum is shown after same treatment in oxygen.

Reviewer #2:

One weak point of this study is the insufficient discussion which is needed to narrow the gap between environmental TEM experiments and electrochemical experiments. Environmental TEM experiments were performed under low-pressure H₂O gas conditions, which to some extent, replicates electrochemical systems. However, physicochemical parameters, such as ionic concentration, electrochemical potential, solvation energy, and etc., are different from electrochemical interfaces. I

recommend the authors to have more detailed discussion on the differences between ETEM and electrochemical conditions. Related to this comment, did the authors confirm that perovskite oxides indeed split water to oxygen and proton during ETEM experiments? What is the actual electrochemical potential of materials during ETEM experiments?

We thank the reviewer for these comments. Indeed, the development of the connection between ETEM studies in H₂O vapour and real world electrochemical studies in aqueous electrolytes is one of the big challenges of ETEM. We have worked quite a lot on understanding the exact electrochemical conditions of the sample in the ETEM.

The electric field at the TEM lamella is not only dependent on the applied voltage between TEM lamella and ground (stainless steel frame of the TEM holder) but also on the beam induced electric potential due to secondary electron emission.

In S. Raabe, et al *Advanced Functional Materials*, 22 (2012) 3378 we have shown that beam induced potentials are relevant for the OER and the H₂O splitting and formation of oxygen was proven by a sacrificial reaction, i.e. SiH₄(g) → SiO₂ (solid). This reaction only takes place in the presence of H₂O and an OER catalyst, and is absent for TEM lamella without catalytic activity for OER. In S. Mildner et al *J. Phys. Chem. C*, 119 (2015) 5301, we have quantified the beam induced potential as a function of the beam dose rate and electric resistance of the TEM lamella by means of off-axis electron holography.

However in the study presented in the actual paper, electric resistance of the samples is minimized in order to keep the beam induced potential small (a few 10 mV) compared to the applied potential (+2V).

Another important topic is the concentration of ions that influence the structure of the electric double layer. Whereas in electrochemistry, we measured at pH 13 ($c(\text{OH}^-) = 0.1 \text{ M}$) and pH7 ($c(\text{OH}^-) = c(\text{H}^+) = 10^{-7} \text{ M}$), in the ETEM at 5 μbar of H₂O at the ion concentration at the used beam current density it is of the order of 10^{-6} - 10^{-7} , based on known ionization cross sections of water at 300 keV and a balance equation, where the loss of ions due to surface attachment is taken into account.

Based on the cross sections, the electron impact ionisation results mostly in positively charged ions, such as H₂O⁺ (65%), H⁺ (15%) and OH⁺ (15%). Cross section for dissociative electron capture are quite low and mainly lead to H⁻. OH⁻ can be only formed from the neutral OH peroxy radical which has a high electron affinity. If we assume that it is formed from OH⁺ by a two electron capture process its upper limit is of the order of the initial OH⁺ ratio.

Altogether, this implies low ion concentrations close to neutral pH, however, the composition is different compared to an aqueous electrolyte. Since the detailed analysis of the H₂O state under electron impact is subject of a forthcoming paper, we only give some brief insights in the discussion section and have improved the text:

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^{-1} 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} to 10^{-7} M in the vapor³⁶ that is close to ion concentration at neutral pH. However, the composition of ions generated by electron impact is different since positively charged ions such as H₂O⁺ dominate. Our ETEM studies are performed under positive electric potentials of $U=+2\text{V}$ 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 disregarded³⁶. The comparison of hopping rates in different ambients clearly

demonstrate that the observed $\geq 20x$ increased Mn-adatom mobility in H_2O 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 H_2O . 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.

In this study two important new steps for ETEM studies are performed:

- We compare two different perovskite manganite systems which show different electrochemical behaviour in cyclovoltammetry (stability) and find the same trends in the ETEM experiments, i.e. fast Mn leaching for PCMO and very slow (and on the time scale of the experiments invisible) Mn leaching for LSMO.
- We give strong evidence that the H_2O absorbed on the oxide lamella is in a condensed, liquid H_2O state.

Reviewer #3

1. *Data on perovskite oxide (LMSO and PMCO) are presented in the paper. How can the insight here be applied to other OER catalysts with different structures like rutile, spinel, rock salt, and bixbyite oxides?*

Adatom dynamics due to partial solvation does not depend very much on the crystal structure but rather on the formation of a solvation shell at surface species. For a polar solvent such as H_2O , the attraction of negatively charged dipole of the H_2O to positively charged metal ions is generally observed. Furthermore, solvation effects are nowadays studied in advanced DFT studies of the electrocatalysts but only taking the effect on the adsorption energy of reaction intermediates into account. The effect of partial solvation on the surface structure and active sites is, however, ignored.

In order to make this point clear, we have rewritten the introduction of the paper, where the significance of the dynamic surface studies for the fundamental understanding of electrocatalysts, in particular the breaking of scaling laws is reviewed.

To distinguish between enhanced reversible surface dynamics due to partial solvation of metal surface species in H_2O and irreversible leaching of fully solvated metal species is highly relevant for many different transition metal oxides, where leaching of reduced metal species is experimentally observed e.g. by Najafpour et al *New J. Chem.*, 2013, 37, 2448 for Mn-O compounds, and by J. Chivot et al *Corros. Sci.* 2008, 50, 62–69 for Co-O systems. For binary Mn-O compounds leaching of reduced Mn species is theoretically supported by the Pourbaix diagram, see Izgorodin et al, *Aust. J. Chem.* 2012, 65, 638–642.

We have modified the summary of the paper accordingly:

Although hopping rates and contrast of single Mn atoms are beyond the resolution of our experiments, the observation of dynamic multiple occupancy of B sites by Mn moieties establishes a pronounced dynamical structure of the catalyst-water interface with partial solvation of surface Mn atoms in H_2O . 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 (Najafpour et al, J. Chivot et al). 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 related shift of Fermi energy.

2. *Recently, self-gating has been proposed in semiconductor electrocatalysis: Nat. Mater. 2019, 18, 1098-1104. Some discussion should be added with respect to perovskite catalysts in this paper.*

The observation of an increase of the electronic conduction in correlation to the onset of the electrochemical reaction at semiconductor electrode surfaces due to an induced tuning of the Fermi level (called self-gating) is a very interesting phenomenon. It is consistent to our statement about the limitations of frozen surface approximations in theoretical understanding of the reaction mechanisms, since this also involves changes of electronic properties. Maybe the reported changes of the Fermi level in the paper Nat. Mater. 2019, 18, 1098-1104 reflect some kind of surface reconstruction in contact to an electrolyte under electric polarisation. We included a citation of the work into the revised manuscript and discussed the effect in the summary:

Indeed, the recent results on self-gating of electrocatalysts evidences a modification of the Fermi level at the onset of an electrochemical reaction (He et al). The presence of pronounced reversible dynamics of partially solvated adatoms in the stationary state of OER requires that for the theoretical understanding of heterogeneous catalysis some aspects of homogeneous catalysis, i.e. modified metal coordination, valences, solvation shell reorganization during electron transfer, solvent thermal fluctuations and possibly Mn displacements during intermediate formation must be taken into account. Incorporating these effects into theoretical analysis will open new perspectives in atomic scale design of efficient and stable electrode surfaces for OER.

3. *In Fig 1a, is the current density normalized by geometric area? Normalization by electrochemical surface area should be provided as well.*

Since the epitaxial films are atomically flat, as visible the Figure S. 5, the geometric and the electrochemical surface area coincidence.

4. *In Fig 2g, scale bar is missing.*

The scale bar is added

5. *Fig 4c is unclear and of low resolution.*

The image is replaced

6. *Relevant review papers related to in-situ catalyst studies and electrocatalysis should be cited in the introduction: Science 2017, 355, eaad4998, Nanoscale Horiz. 2019, 4, 809-827 and Nat. Catal. 2018, 1, 922-934*

We have added the relevant references in the introduction and thank the reviewer to bring them to our attention.

Decision letter and referee reports: second round

1st Jul 20

Dear Prof Jooss,

Your manuscript titled "Dynamic observation of Mn-adatom mobility at perovskite oxide catalyst interfaces to water" has now been seen again by the three referees, whose comments appear below. In light of their advice I am delighted to say that we are happy, in principle, to publish a suitably revised version in Communications Materials under the open access CC BY license (Creative Commons Attribution v4.0 International License).

We therefore invite you to edit your manuscript to comply with our format requirements and to maximise the accessibility and therefore the impact of your work.

EDITORIAL REQUESTS:

* Your manuscript should comply with our policies and format requirements, detailed in our checklist for authors at:

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* I suggest a few small modifications to the title and abstract as follows, to meet our house style:

Title: "Dynamic observation of Manganese adatom mobility at perovskite oxide catalyst interfaces with water" or "Dynamic observation of Manganese adatom mobility at perovskite oxide catalyst/water interfaces"

Abstract: 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, we directly visualize surface atom dynamics at manganite perovskite catalysts surfaces for oxygen evolution reaction (OER), which are ≥ 20 times faster in water than in other ambients. Comparing (001) surfaces of $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ and $\text{Pr}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ 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 $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ system, suggesting that aspects of homogeneous catalysis must be included for understanding the OER mechanism in heterogeneous catalysis.

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* Please title the Results section as 'Results and Discussion'. Please do not use bold font for "In summary" in the final paragraph.

* In the Competing Interests please also mention any non-financial competing interests.

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- Other unique identifiers (such as DOIs and hyperlinks for any other datasets)
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- If applicable, a statement regarding data available with restrictions
- If a dataset has a Digital Object Identifier (DOI) as its unique identifier, we strongly encourage including this in the Reference list and citing the dataset in the Data Availability Statement.

DATA SOURCES: We strongly encourage authors to deposit all new data associated with the paper in a persistent repository where they can be freely and enduringly accessed. We recommend submitting the data to discipline-specific, community-recognized repositories, where possible and a list of recommended repositories is provided at http://www.nature.com/sdata/policies/repositories.

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"Atomic processes on the surface of a catalyst control reaction mechanisms. Here, in-situ imaging of manganese adatom dynamics for La_{0.6}Sr_{0.4}MnO₃ and Pr_{0.67}Ca_{0.33}MnO₃ surfaces used in the oxygen evolution reaction reveals the importance of homogeneous catalysis on reaction mechanism."

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The authors have reasonably addressed all of my comments and therefore, I recommend the publication of the revised manuscript.

Reviewer #2 (Remarks to the Author):

The authors have responded appropriately to my comments. Therefore, I recommend its publication.

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