nature portfolio

Peer Review File

Disentangling Heterogeneous Thermocatalytic Formic Acid Dehydrogenation from an Electrochemical Perspective

Reviewer #1 (Remarks to the Author):

Thank you for addressing the previous concerns and providing a clear summary of the core findings of your work. The manuscript has significantly improved, and it highlights the importance of applying interfacial electrochemistry theories and methodologies to study thermocatalytic kinetics at the metal-solution interface.
However, before the manuscript can be accepted for publication, I recommend making the following minor revisions:

Provide basic catalyst characterization: please include some basic characterization techniques used to confirm the state of the catalyst used in the study. This could include techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), or any other relevant techniques that can provide information about the catalyst's structure, morphology, and composition.

Analyze the catalyst state before and after electrochemical reactions: discuss the catalyst's state before and after the electrochemical reactions. It is essential to assess the possibility of any changes or degradation of the catalyst during the electrochemical process. This analysis will help to evaluate the potential impact of catalyst transformations on the observed electrochemical behavior and overall reaction kinetics.

Consistency in figure symbols: It has come to my attention that the symbol used in Figure 3 is noticeably different from the symbols used in the other figures. Please ensure that the symbol used in Figure 3 is consistent with the symbols used in the rest of the figures to maintain uniformity

Once these minor revisions are made, the manuscript will be ready for publication. Thank you for your hard work and attention to detail. I look forward to reviewing the revised manuscript.

Reviewer #2 (Remarks to the Author):

The authors improved the manuscript considerably and try to sketch the overall scheme connecting thermo and electro-catalysis, seeing the thermocatalytic part basically as a short circuited electrocatalyst. This is quite similar to studies by Flaherty et al for the thermo and electrocatalytic reduction of O2 to H2O2. This would be the second study showing such connections which should be interesting for this high ranking journal.
I am therefore inclined to recommend to accept this manuscript for publication. There are still two issues that the authors should address.
(1) the Figure R1. flow char to show the logic chain if this work: This is very hard to follow. Since this is an integral part, I recommend to revise this to a more understandable figure.
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Reviewer #3 (Remarks to the Author):

The authors combine thermocatalytic, electrocatalytic, and surface spectroscopy methods to examine the mechanism of formic acid dehydrogenation on Pd catalysts. The methods include careful use of isotope labels to test the kinetic relevance of C-H and O-H rupture events. In a later section, the authors report the effects of cation identity on rates and activation energies. As an earlier reviewer mentioned, the catalytic dehydrogenation of formic acid has been examined by numerous groups. Many of these utilized kinetic isotope effects as the authors did to propose the rate determining steps for the reaction under the conditions selected. The authors examined a wider range of conditions than most, which adds some novelty to their findings. In addition, the illustration of the role of cation identity on rates of thermocatalysis is somewhat novel but covers discussions in prior articles.

The promise of the paper brought from the title, however, is that the electrochemistry provides a unique insight to the reaction and helps to resolve the mechanistic questions. This is a topic of growing interest but also a very challenging prospect for most research groups due to the need to seamlessly integrate rigorous electrochemical and thermocatalytic measurements with quantitative models.

Based upon the methods used by groups cited in the references, I had hoped to see a model based prediction for open circuit potentials under set conditions (derived from measured kinetics of half reactions) and a direct quantitative comparison to these data collected. The manuscript does not do this clearly – the article is full of schemes but seems to have few corresponding depictions of data. For example, Figure 3d-f are described as schematic polarization curves of HER and FAOR and are later described as model plots. The supplementary material (Fig. 1) shows that HER kinetics depend strongly on rotational velocity of the RDE system. No Koutecky Levich plot or analysis is given to separate intrinsic kinetics from the mass transport issues evident here. Therefore, I cannot determine how the authors measure kinetics of separate half-reactions to model the OCP and validate their hypotheses from mixed potential theory. Since this is the aspect of the article described as being novel, the lack of clarity here is concerning. Ideally, the authors would demonstrate correlations between model predicted quantities and measured values across a range of conditions that include differences in the isotopolog, the cation, and the temperature. Perhaps it is a matter of presentation and writing but that does not seem evident in the current manuscript.

Response Letter to Referees

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However, before the manuscript can be accepted for publication, I recommend making the following minor revisions:

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Response 1.1:

Per your suggestion, TEM, SEM and XRD characterizations on the as-prepared Pd/C are now added in the Supplementary Information (see Supplementary Fig. 9). The following figures and relevant statement have been added in the supplementary information.
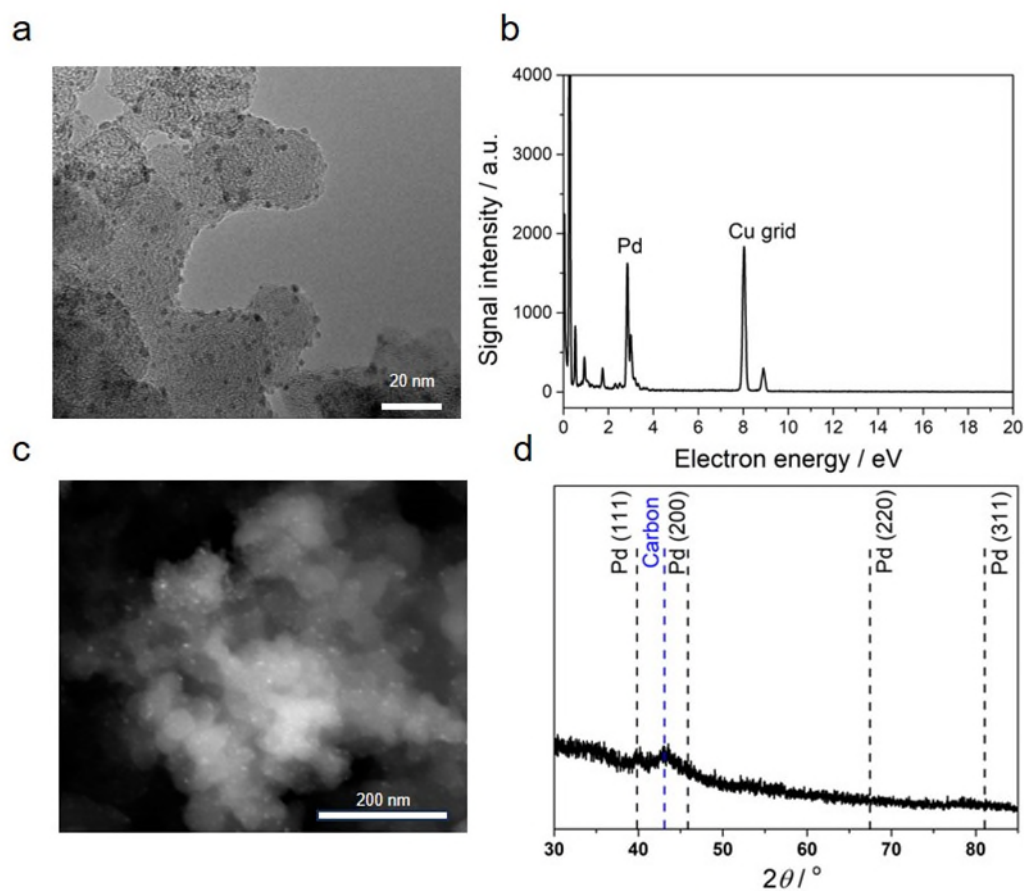
Supplementary Fig. 9 | Physical Characterizations of the as-prepared 5 wt.% Pd/C catalyst. (a) HR-TEM characterization of the as-prepared Pd/C catalyst. (b) EDS spectrum of the as-prepared Pd/C catalyst. (c) HR-SEM characterization of the as-prepared Pd/C catalyst. (d) XRD characterization of the as-prepared Pd/C catalyst.

The TEM, SEM and XRD characterizations of the 5 wt.% Pd/C catalyst used in this work show Pd nanoparticles with an average size of 2.3 nm are well dispersed on Vulcan XC72 carbon black support.

Analyze the catalyst state before and after electrochemical reactions: discuss the catalyst's state before and after the electrochemical reactions. It is essential to assess the possibility of any changes or degradation of the catalyst during the electrochemical process. This analysis will help to evaluate the potential impact of catalyst transformations on the observed electrochemical behavior and overall reaction kinetics.

Response 1.2：

TEM characterizations of the Pd/C catalyst after FAOR and HER tests are provided in the supplementary information of this manuscript as requested. The figure shows that the average Pd particle size increased from ~2.3 nm to ~2.6 nm after the electrochemical tests as described in Fig. 7c, which indicates that (electro)chemical aging of Pd particles may slightly increase the mean particle size.

In addition to aging of Pd particles, gradual accumulation of CO is another issue leading to the activity loss for FAD and FAOR. Having this in mind, in this work, we measured the reaction rate of FAD, FAOR and HER at the initial stage of the reactions to minimize the measurement errors or deviations introduced by catalyst degradation and CO accumulation.

The following two Figures and the relevant statement have been added in Supplementary Information:
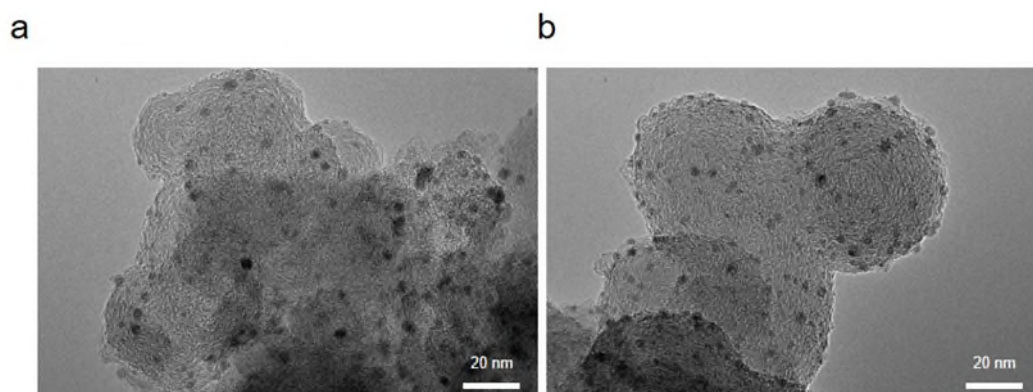
Supplementary Fig. 10 | Physical Characterizations of the used Pd/C catalyst after electrochemical reactions. (a) HR-TEM image of the Pd/C catalyst after FAOR test, or (b) after HER test at 323 K. Relevant electrochemical results are shown in Fig. 7c.

After electrochemical measurements as described in Fig. 7c, the mean particle size of Pd nanoparticles on carbon black grows slightly from ~2.3 nm to ~2.6 nm as statistically estimated by TEM images in **supplementary Figs. 10a** and **10b.**

Consistency in figure symbols: It has come to my attention that the symbol used in Figure 3 is noticeably different from the symbols used in the other figures. Please ensure that the symbol used in Figure 3 is consistent with the symbols used in the rest of the figures to maintain uniformity Once these minor revisions are made, the manuscript will be ready for publication. Thank you for your hard work and attention to detail. I look forward to reviewing the revised manuscript.

Response 1.3：

Thank you for the notice, we have replotted all the figures to meet the standards for publication in Nature Portfolio.

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I am therefore inclined to recommend to accept this manuscript for publication. There are still two issues that the authors should address.

Response 2.1：

Thank you for directing us to the relevant report, which has been cited as a reference in the revised manuscript, see: 28. Wilson, N.M. & Flaherty, D.W. Mechanism for the Direct Synthesis of H_2O_2 on Pd Clusters: Heterolytic Reaction Pathways at the Liquid–Solid Interface. *J Am Chem Soc* 138, 574-586 (2016).

(1) the Figure R1. flow char to show the logic chain if this work: This is very hard to follow. Since this is an integral part, I recommend to revise this to a more understandable figure.

Response 2.2：

Thanks for your inspiring question on how to link electrochemical to chemical reaction. We replot the schematic flow chart to show the logic chain as follows,
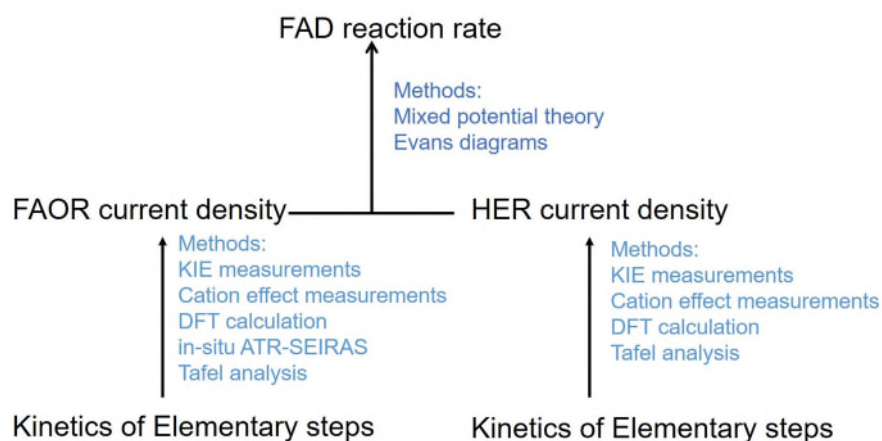

Fig. R1 Schematic flow chart to show the methods used in this article to link electrochemical to chemical reaction.

(2) The calculations are very intriguing, but a part linking the electro- and thermocatalytic routes is the solid-liquid interface. While I do not suggest that the authors reconsider everything with a full explicit liquid layer, they need at least discuss this in depth, as interactions of e.g. formate intermediates with surrounding water might have a drastic effect of barriers and stability.

Response 2.3：

Thank you for the insightful suggestions. We agree that "a part linking the electro- and thermocatalytic routes is the solid-liquid interface". Two main roles of the local water are generally considered during catalytic processes. The first one is simply the solvation effect, which suggests that local water can help stabilize hydrogen ion, formic acid and formate intermediate with hydrogen bonding. Here, we involved implicit solvation model throughout the simulations, which can provide relatively accurate elaboration for solvent-species interactions. For the solvation effect of hydrogen ion, explicit water molecules were also included in the models.

The other effect is that the local water may participate in chemical reactions and affect the reaction barriers.

According to the work of Qi et al. (*Catal. Sci. Technol.*, 5, 3322-3332 (2015)), the local water dramatically accelerates the O-H dissociation in formic acid decomposition over Pt(111), but the C-H dissociation barrier is less sensitive as the local water only show stabilization effects. Without considering the presence of water, the C-H dissociation barrier is 0.50 eV, but the addition of explicit water molecules only reduces the barrier to 0.26 eV. Although the results were obtained over Pt(111), we believe the trend is also valid over Pd(111). Given that the implicit solvation model was considered in our work, the difference between the barriers determined in our model and those in the presence of explicit water molecules should be even smaller, which would not alter our conclusions regarding the identification of rate determining step between FAOR / HER. We have revised the manuscript according to your helpful comment.

In Page 10 of the revised manuscript:
Noteworthy, implicit solvation model was involved throughout all the simulations, a discussion on the effectiveness of the model can be found in the paragraphs related to **Supplementary Fig. 4**.

In Page 7 of Supplementary Information:
Two main roles of the local water are generally considered during catalytic processes. The first one is simply the solvation effect, which suggests that local water can help stabilize hydrogen ion, formic acid and formate intermediate with hydrogen bonding. Here, we involved implicit solvation model throughout the simulations, which can provide relatively accurate elaboration for solvent-species interactions. For the solvation effect of hydrogen ion, explicit water molecules were also included in the models.

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As an earlier reviewer mentioned, the catalytic dehydrogenation of formic acid has been examined by numerous groups. Many of these utilized kinetic isotope effects as the authors did to propose the rate determining steps for the reaction under the conditions selected. The authors examined a wider range of conditions than most, which adds some novelty to their findings. In addition, the illustration of the role of cation identity on rates of thermocatalysis is somewhat novel but covers discussions in prior articles.

Response 3.1:

Thank you for the generally positive comments on our work. With respect to the role of cation identity on thermocatalytic FAD rates, we have recently obtained direct and tenable evidence to reveal how cation entities in the interfacial EDL alter the rates of thermocatalysis of FAD at molecular level by in situ ATR-SEIRAS. We found that the IR peaks of adsorbed HCOO* get redshifted from 1338 to 1320 cm^{-1} as the hydrated cation entities changed from H^+ to Cs^+, indicating that cation-induced EDL field strength tuned the adsorption configuration and adsorption energies of HCOO* and finally changed FAD reaction rates. The new data can effectively improve the novelty and solidity of this work.

The experiment data and discussion are added in the revised manuscript, and copied as follows (see Fig. 6e):
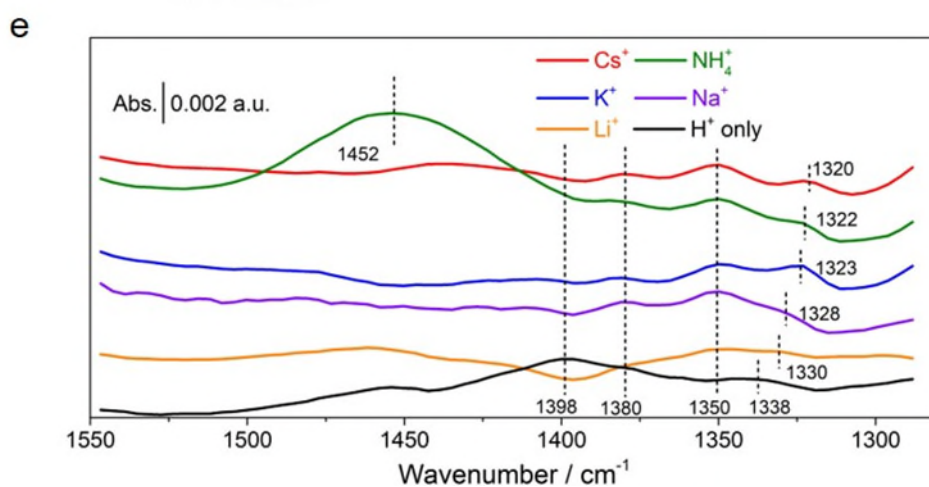
Fig. 6 | Cation effect measurements for FAD on Pd/C catalyst. (e) *in situ* ATR-SEIRA spectra at the Pd/C-solution interface during FAD in solutions containing different cations: 0.2 M HCOOH + 0.2 M $HCOO^-$ (colored lines) and 2 M HCOOH (the black line). The reference spectra were taken before the injection of solutions.

To further verify the origin of this cation effect on FAD at the molecular level, *in situ* ATR-SEIRA spectra were obtained on Pd/C in different cation-contained 0.2 M HCOOH + 0.2 M $HCOO^-$ solutions (colored lines) and neat 2 M HCOOH solution (without any alkali-cations, black line) at 298 K. The peaks at 1350 cm^{-1} and 1380 cm^{-1} can be attributed to aqueous $HCOO^-$, the 1398-cm^{-1} peak to aqueous HCOOH, and the 1452-cm^{-1} peak to aqueous NH_4^+. The peaks ranging from 1320 - 1340 cm^{-1} were assigned to adsorbed HCOO*, showing the cation-dependent frequency. Specifically, in 2.0 M FA solution (pH ~1.7) without any alkali cations, the 1338-cm^{-1} peak was assigned to bidentate formate $HCOO_B$ on Pd. In 0.2 M HCOOH + 0.2 M $HCOO^-$ solutions with varying cations (pH 3.7), the peaks centered at 1320 – 1330 cm^{-1} to monodentate formate $HCOO_M$ on Pd. Interestingly, as the hydrated cation

radius decreases from Li^+ to Cs^+, the peak is redshifted from 1330 cm^{-1} to 1320 cm^{-1}. In one word, the spectral observation indicates that HCOO* adsorption configuration and energy indeed can be tuned by the structure and strength of the EDL, a stronger electric field in the EDL favors the adsorption of reactive $HCOO_M$* species for FAD.

The promise of the paper brought from the title, however, is that the electrochemistry provides a unique insight to the reaction and helps to resolve the mechanistic questions. This is a topic of growing interest but also a very challenging prospect for most research groups due to the need to seamlessly integrate rigorous electrochemical and thermocatalytic measurements with quantitative models. Based upon the methods used by groups cited in the references, I had hoped to see a model based prediction for open circuit potentials under set conditions (derived from measured kinetics of half reactions) and a direct quantitative comparison to these data collected.

Response 3.2：

Thank you for the constructive comment, we agree that a model-based prediction for FAD OCPs and reaction rates can help to improve the quality of this work. A new section is added in the revised manuscript accordingly where we used the Evans diagram to successfully predict the FAD reaction rates across a range of conditions that include differences in the isotopolog, the cation, and the temperature as exemplified in solutions of pH3.7 (a typical pH with the most active FAD) (see Figs.1c, 3d, 6c and 7c).

We suppose that the method you mentioned here refers to the one recently presented by Yogesh's group (*Nat Catal* 4, 742-752 (2021)). In that work, the thermocatalytic oxidation of formic acid ($2HCOOH + O_2 = 2CO_2 + 2H_2O$) was regarded as the coupling of FAOR and oxygen reduction reaction (ORR: $O_2 + 4e^- + 4H^+ = 2H_2O$), the FAOR current j_{FAOR} was measured without O_2, and the ORR current j_{ORR} measured without HCOOH as a function of potential E. In a j-E diagram involving the two half reactions, the potential at which $j_{FAOR} = -j_{ORR}$ is the mixed potential for the overall oxidation of formic acid while the current density $j_{FAOR} = -j_{ORR}$ corresponds to the reaction rate of oxidation of formic acid in consideration of Faraday's Law on electrolysis. This diagram is also known as the Wagner-Traud diagram in classic electrochemistry, which is often used to quantify the kinetics of electroless metal plating.

As for the heterogeneous FAD in solutions, the overall reaction can be deemed as the combination of two half cell reactions: FAOR and HER. The standard electrode potential for the redox couple of H^+(aq.)/H_2(g) is 0 V vs RHE while that of CO_2(g) /HCOOH(aq.) is around -0.11 V vs RHE. Therefore, HER and FAOR reactions may take place spontaneously to form a short circuit galvanic cell on a metal catalyst to yield the mixed potential, which is equivalent to the stabilized open circuit potential (OCP) for FAD in a deaerated solution. However, since the reactant for kinetically facile HER is proton or water which is a ubiquitous species in aqueous solution, one cannot directly measure with confidence the net FAOR current density in isolation of HER around the OCP. Thus, the Wagner-Traud diagram based method is no longer suited for predicting the reaction rate of FAD. In fact, in a latest report (*J Am Chem Soc* 146, 9191-9204 (2024)), Takanabe's group tried to directly apply Wagner-Traud diagram to predict FAD reaction rates but ultimately failed during the revision of this work. In their work, the estimated FAD rate is one order of magnitude smaller than the measured one (18.2 h^{-1} vs. 117.5 h^{-1}).

To address this issue, a method based on the Evans diagram which is widely used in corrosion electrochemistry is invoked in this work. The key point of such a method involves the Tafel straight line extrapolation on the polarization curves of the two half reactions, where the crossing point yields the mixed potential (OCP) and the short-circuit current. A representative Evans diagram for FAD in a FA/SF mixed solution (pH3.7) is shown in **Fig. 1b**, in which 0.2 M $NaClO_4$ was added as a supporting electrolyte to minimize the solution resistance without a significant effect on the reaction kinetics. Ideally, both FAOR and HER currents on the Tafel extrapolation lines would yield the FAD reaction rate at the mixed potential. Practically, as we found, the Tafel equation fits well for

the current density of FAOR between 0.15 and 0.3 V, while the Tafel equation deviates significantly from the current density of HER in the whole potential range, given the fact that the HER current density is drastically influenced by the reoxidation of H_2 at low overpotentials and the slow diffusion of H_2 in the supported catalyst layer at high overpotentials. (*ACS Central Sci* 10, 658-665 (2024)) Therefore, we used the Tafel extrapolation line of FAOR rather than that of HER at OCP in the Evans diagram to derive the FAD reaction rate in **Fig. 1b.** Indeed, the FAD reaction rate was satisfactorily predicted by this method, as shown **Fig. 1c**. In other words, we have demonstrated for the first time that the mixed potential theory in electrochemistry can be applied in dealing with thermocatalytic FAD kinetics.

Furthermore, per your suggestion, we demonstrated correlations between model predicted FAD reaction rates and measured ones in different isotopolog, cation and temperature conditions (see Fig. 3d, 3e, 6c, 6d, 7c and 7d).
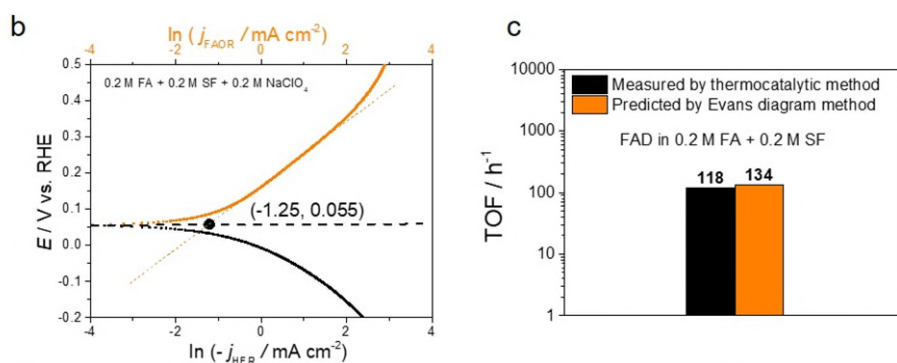

Fig. 1 | FAD mechanism at metal-gas and metal-solution interfaces. (b) Evans diagram for FAD in 0.2 M FA + 0.2 M NaHCOO (SF) + 0.2 M $NaClO_4$ at pH3.7. (c) The measured value of FAD reaction rate as compared to the value predicted in the Evans diagram in **Fig. 1b.**
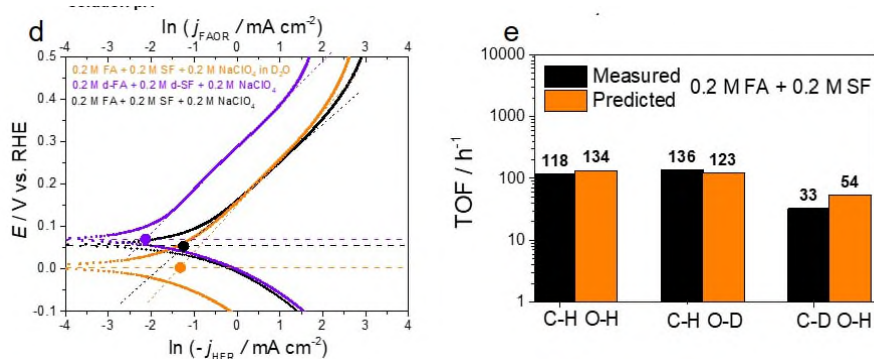
Fig. 3 | Determination of RDS of FAD on Pd/C catalysts. (d) Evans diagrams for KIE measurements of FAD in solutions of pH3.7. (e) Comparisons between measured FAD reaction rates (adapted from data in **Fig. 3a**) and predicted FAD reaction rates in Evans diagrams (adapted from data in **Fig. 3d**)
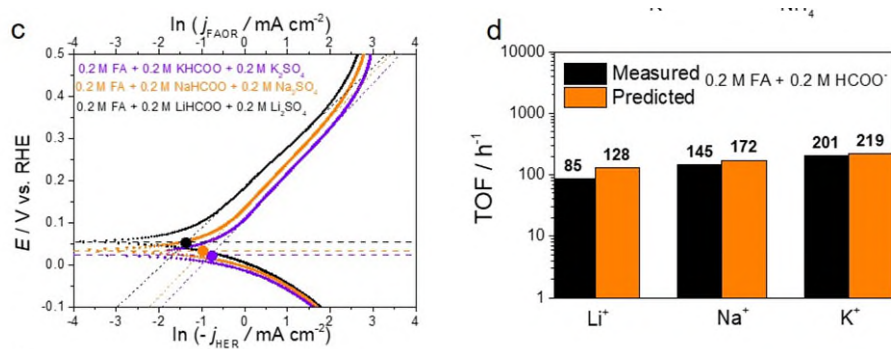
Fig. 6 | Cation effect measurements for FAD on Pd/C catalyst. (c) Evans diagrams for cation effects on FAD in solutions of pH3.7. (d) Comparisons between measured FAD reaction rates (adapted from data in **Fig. 6a**) and predicted FAD reaction rates in Evans diagrams (adapted from data in **Fig. 6c**).
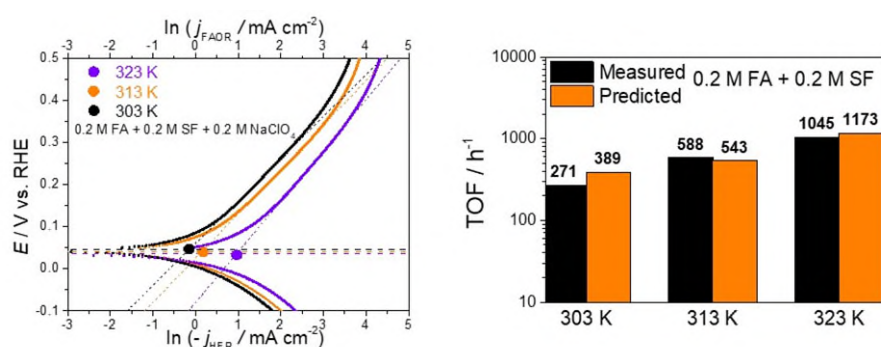
Fig. 7 | Temperature dependent FAD reaction rates. (c) Evans diagrams for temperature effects on FAD in solutions of pH3.7. (d) Comparisons between measured FAD reaction rates (adapted from data in **Fig. 7a**) and predicted FAD reaction rates in Evans diagrams (adapted from data in **Fig. 7c**).

The experiment procedure is also added onto Page 16 of revised manuscript:

Evans diagrams of FAD reactions. To generate the Evans diagrams for FAD, we measured the currents of the apparent FAOR and HER current densities by electrochemical measurements carried out on a Pd/C catalyst layer-coated RDE. For FAOR, the linear sweep voltammetry was started from the OCP to 0.6 V; For HER, the linear sweep voltammetry was started from the OCP to -0.2 V. Tafel fitting was performed on a polarization curve of FAOR to estimate the net FAOR current at sufficiently high overpotentials. The current densities on the extrapolated Tafel straight line at the mixed potential yielded the overall FAD reaction rate. Test conditions: scan rate of 10 mV/s and rotation rate of 1600 rpm in an Ar-sparged solution. Ar stream kept flowing vigorously through the headspace of the electrolytic cell chamber during the measurements. The current density was converted to the overall FAD reaction rate by using

$$\text{TOF}_{\text{FAD}} = \frac{j_{mix}A}{2Fn_{\text{Pd}}}$$

where j_{mix} is the above-mentioned current density at the mixed potential in the Evans diagrams, A is the electrode area, F is the Faraday constant and n_{Pd} is the mole number of Pd used in the Evans diagram measurement.

The manuscript does not do this clearly – the article is full of schemes but seems to have few corresponding depictions of data. For example, Figure 3d-f are described as schematic polarization curves of HER and FAOR and are later described as model plots.

Response 3.3：

Thank you for your comment. We replotted the schematic plots in **Fig. 1d** and **1e** to show that OCP is an indicator to tell the rate-limiting half reaction and explained it in detail. The other schematic plots (e.g., the former Fig. 3d-f) were removed from the article now as we have Evans diagrams based on experiment data.
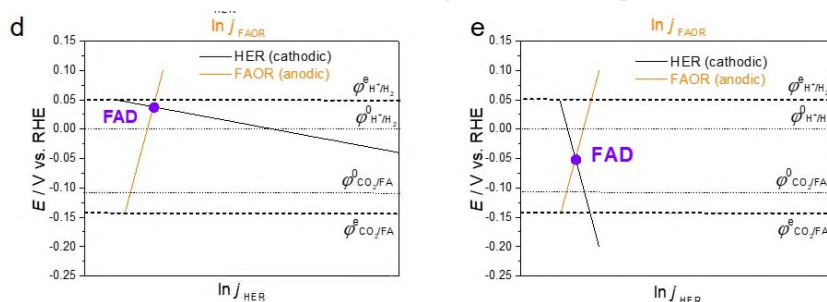
Fig. 1 | FAD mechanism at metal-gas and metal-solution interfaces. (d) A typical schematic plot of the Evans diagram where FAOR is relatively sluggish. (e) A typical schematic plot of the Evans diagram on FAD with similar reaction rate of FAOR and HER.

In addition, the relative biases of the mixed potential (or OCP) from the equilibrium potentials of the two redox couples can be used to gauge the kinetically sluggish half reaction. For instance, **Fig.1d** is a schematic of that the FAD rate is mainly determined by the FAOR rate as judged by the more proximity of the OCP to the equilibrium potential $\varphi^e(H^+/H_2)$. And if the OCP locates around the middle of $\varphi^e(H^+/H_2)$ and $\varphi^e(CO_2/HCOOH)$, the FAOR and HER half reactions are expected to exhibit comparable kinetics (see **Fig.1e**). Note that

$$\varphi_{H^+/H_2}^e \approx 0 \text{ V} + \frac{RT}{2F} \times \ln\left(\frac{1}{p_{H_2}}\right) \qquad \text{(vs. RHE)}$$

$$\varphi_{CO_2/FA}^e \approx -0.11 \text{ V} + \frac{RT}{2F} \times \ln\left(\frac{p_{CO_2}}{c_{HCOOH}}\right) \quad \text{(vs. RHE)}$$

where p_{H_2} and p_{CO_2} are the partial pressures of product gases in the catalyst layer, and c_{HCOOH} is the concentration of formic acid；R, T and F are gas constant, Kelvin temperature and Faraday constant, respectively.

The supplementary material (Fig. 1) shows that HER kinetics depend strongly on rotational velocity of the RDE system. No Koutecky Levich plot or analysis is given to separate intrinsic kinetics from the mass transport issues evident here.

Response 3.4：

Koutecky Levich plot was performed to analyze the intrinsic HER/HOR exchange current densities on Pd/C. At pH1, the exchange current density of HER/HOR on Pd/C electrode is fitted to be as high as 0.84 mA cm^{-2}, which is in line with the data reported in a published work (*Science Advances* **2**, e1501602 (2016)). The slight deviation in the HER branch can be attributed to slow diffusion of H$_2$ in the supported catalyst layer (*ACS Central Sci* **10**, 658-665 (2024)).
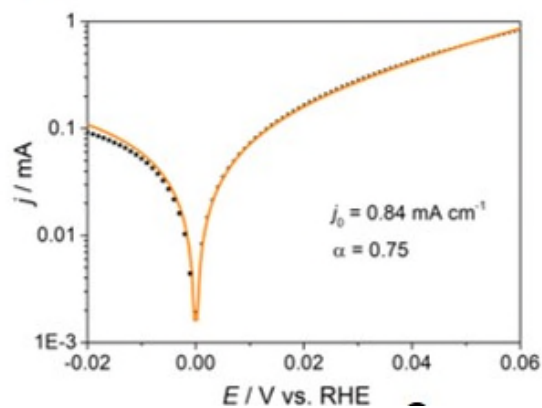
Supplementary Fig. 1 | Determination of RDS for HER on Pd/C. (b) Butler-Volmer equation fitting plot of HER/HOR kinetics on Pd/C-covered RDE in a H_2-saturated 0.1 M $HClO_4$ solution (pH1) at 1600 rpm. Black dots correspond to the experimentally determined by Koutecky Levich plot, and orange line corresponds to the Butler-Volmer equation fit line.

Therefore, I cannot determine how the authors measure kinetics of separate half-reactions to model the OCP and validate their hypotheses from mixed potential theory. Since this is the aspect of the article described as being novel, the lack of clarity here is concerning. Ideally, the authors would demonstrate correlations between model predicted quantities and measured values across a range of conditions that include differences in the isotopolog, the cation, and the temperature. Perhaps it is a matter of presentation and writing but that does not seem evident in the current manuscript.

Response 3.5:

Thank you for the inspiring comment. Comparisons between model predicted FAD reaction rates and measured values with different isotopologs, different cations, and different temperatures are given in the revised manuscript as requested. For more detailed explanation, please see Response 3.2.

Reviewer #2 (Remarks to the Author):

The reviewers addressed my concerns satisfactorily. I would therefore recommend to accept to manuscript for publication.

Reviewer #4 (Remarks to the Author):

The authors have adequately addressed the technical issues raised by reviewers. The quality of the work has been enhanced. Nonetheless, the paper needs to provide a more comprehensive background introduction on two aspects to make it clear what has been already done, and what is new in this current study.
First, adequate discussion on the current developments of thermal catalysis for formic acid decomposition, in particular those based on Pd catalysts, should be included. Clearly mention the current proposal of reaction mechanisms (rate determing step, active sites, ect).
Second, using electro-chemical perspective to understand thermal catalysis is a relatively emerging area but it is not totally new. Apart from Flaherty's work on H_2O_2 formation as mentioned by one reviewer, electro-pathway for hydrogenation reactions has also been proposed (ACS Catal., 2022, 12, 15021-15027). This work, together with related other ones, should be introduced in the introduction to give a complete context.

Response Letter to Referees

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Response 2.1:

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Response 4.1:
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First, adequate discussion on the current developments of thermal catalysis for formic acid decomposition, in particular those based on Pd catalysts, should be included. Clearly mention the current proposal of reaction mechanisms (rate determing step, active sites, ect).

Response 4.2:
Thank you for the comment. In this work, we focus on revealing the mechanism of FAD from the perspective of electrochemistry with a focus on electric double layer effect at the metal-solution interface by tuning the solution side on a given catalyst, so we prefer not to give a more detailed introduction on the relation of catalyst surface structure and its catalytic activity from the metal side to avoid distracting the readers. Nevertheless, in response to the reviewer's comment, we have newly added a brief description introducing the development of Pd catalysts for FAD by taking advantage of more active sites and facile deprotonation of FA (see below).
Line 42-43, Introduction:
Among them, decreasing the Pd particle size to enrich the active sites (e.g., the Pd(0)-Pd(II) interface) and modifying the support with alkaline groups (e.g., amines) to facilitate the deprotonation of FA are two effective tactics for developing FAD catalysts.

As for the current proposal of rate determining step (which is more relevant to our work), detailed description was actually presented in the Introduction section in the last version of our manuscript (copied below).
Line 44-48, Introduction:
Virtually no attention has been paid to the metal-solution interface for FAD. Therefore, the mechanism of thermocatalytic FAD is far from clear in terms of the rate determining step (RDS) and its deciding interfacial factors. Among others, the combinative desorption of hydrogen ($2H^* \rightarrow H_2 + 2*$) has been suggested as the RDS of FAD based on apparent activation energy determination and DFT calculations on neat Pd(111), whereas, the C-H bond cleavage step as the RDS based on kinetic isotopic effect (KIE) and reaction order of formate.

Second, using electro-chemical perspective to understand thermal catalysis is a relatively emerging area but it is not totally new. Apart from Flaherty's work on H_2O_2 formation as mentioned by one reviewer, electro-pathway for hydrogenation reactions has also been proposed (ACS Catal., 2022, 12, 15021-15027). This work, together with related other ones, should be introduced in the introduction to give a complete context.
Response 4.3:
Thank you for the comment. It should be emphasized that in this work the mixed potential theory combined with interfacial electrochemistry theory and method is applied for the first time to unraveling the formic acid dehydrogenation reaction mechanism. The previous works are introduced in the first paragraph of the Results and Discussion section as a transitional paragraph following the Introduction section. The suggested paper (*ACS Catal.*, 2022, 12, 15021-15027) about nitrophenol hydrogenation is now cited as an example of the mixed potential theory

application. Please see below.

A mixed potential theory originating from classical corrosion electrochemistry has been put forward to address the thermochemical catalytic reaction at metal/solution interfaces, including small organic molecules oxidation, hydrogen peroxide production and nitrophenol hydrogenation.