In-Situ Liquid Phase Transmission Electron Microscopy and Electron Diffraction Provides Mechanistic Insight into Electrochemical CO₂ Reduction on Palladium/Palladium Hydride Catalysts

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Abstract

Electrochemical conversion of CO_2 (CO_2R) offers a sustainable route for producing fuels and chemicals. Pd-based catalysts are effective for selective conversion of CO_2 into formate at low overpotentials and CO/H2 at high overpotentials. Furthermore, Pd catalysts undergo morphology and phase structure transformations under reaction conditions that are not well understood. Herein, *in-situ* liquid phase transmission electron microscopy (LP-TEM) and select area diffraction (SAD) measurements under CO₂R conditions is applied to track the morphology and Pd/PdH_x phase interconversion as a function of electrode potential, respectively. Correlating in-situ characterization with electrochemical CO_2R activity/selectivity measurements, density functional theory and micro-kinetic analyses, the change in Pd/PdH_x catalyst selectivity from formate at low overpotentials towards CO/H₂ at higher overpotentials is found to result from electrode potential-dependent thermodynamic changes in the reaction energetics and not morphological or phase structure changes, providing insight that can guide advanced understanding and design of improved performance catalysts.

Introduction

Electrochemical conversion of CO₂ using renewable electricity is envisaged as an integral component of a future sustainable energy economy by providing an avenue for producing carbonbased fuels and chemicals from non-fossil fuel feedstocks. Nevertheless, electrochemical CO₂ conversion technologies require efficient, selective, and stable electrocatalysts for CO₂ reduction (CO₂R) reactions. The activity and selectivity of catalysts for CO₂R and the competing hydrogen evolution reaction (HER) are known to depend on the binding energies of adsorbed reaction intermediates, for example, *CO or *H, respectively, where * denotes an adsorbed species.¹ The binding energies between adsorbed species and the catalyst surface are dictated by the nature of the catalytically active site structure(s) present in the catalyst and can be modulated by tuning the catalyst properties by strategies such as alloying,²⁻⁵ surface modification or the exposure to different surface facets.⁶⁻⁸

Palladium-based electrocatalysts provide the lowest known overpotential for the CO₂R among all reported catalysts.^{9,10} Particularly, Pd exhibits high selectively (> 90%) for reducing CO₂ into formate at low overpotentials (< 200 mV).⁹ At higher overpotentials, Pd catalysts become selective towards the formation of H₂ and CO, including Faradaic efficiencies towards CO above 90% recorded at overpotentials of ca. 500 mV.¹¹ Under electrochemical CO₂R conditions, Pd undergoes transformation into Pd-hydride (PdH_x) phases.¹²⁻²⁵ Based on the stoichiometric ratio of hydrogen (x) in PdH_x, α - and β -phase PdH_x are formed in the range of 0 < x ≤ 0.03 and x ≥ 0.58, respectively, while α - and β -phase PdH_x coexist in the 0.03 < x < 0.58 region.^{14,26} These phase transformations cause the surface structure, electronic properties and lattice spacing of the PdH_x catalyst to vary, thus affecting catalytic activity and selectivity.^{24,25,27-29} Furthermore, the

(electro)chemical environment experienced under CO₂R conditions cause changes to the structure and properties of the electrocatalyst.^{7,9,30,31} Observing these changes under reaction conditions and correlating the results with measured catalytic properties can provide crucial mechanistic insight into catalytic activity and stability.

Various techniques have been developed to investigate Pd/PdH_x phase transformations and/or quantify the resulting H:Pd ratios. Using deuterium (D) instead of hydrogen, D:Pd ratios have been quantified by electrolytically forming PdD_x structures and then liberating D_2 by heating and measuring the amount of gas released.^{32,33} Such techniques are not amenable to Pd/PdH_x catalysts under CO₂ reduction conditions, which require applying external electrochemical potentials in the presence of liquid electrolytes. In-situ (operando) measurements including X-ray diffraction (XRD) and extended X-ray absorption fine structure (EXAFS) have been employed to identify the lattice parameters and interatomic distances of Pd/PdH_x phases, respectively.³⁴⁻³⁸ Landers et al.³⁹ utilized *in-situ* synchrotron XRD and coulometry measurements to understand intercalation/ deintercalation processes for hydrogen in palladium, enabling determination of the electrode potentials where α - and β -PdH_x phases were formed.³⁹ Gao et al.¹⁰ utilized *in-situ* XAS to demonstrate the coexistence of α - and β -phases at potentials above -0.2 V (vs. the reversible hydrogen electrode, RHE), which promoted electrochemical CO₂R into formate via a HCOO* intermediate. At potentials below -0.5 V vs. RHE, the formation of β -PdH_x was observed and claimed to promote formation of CO via a COO*H intermediate.¹⁰ While these in-situ synchrotronbased techniques provide in-situmonitoring of phase structure transformations, they do not provide opportunity to simultaneously observe morphological changes in Pd-based catalyst particles under CO₂ reduction conditions that have necessary implications on overall catalytic activity.

In-situ liquid-phase (scanning) transmission electron microscopy (LP-(S)TEM) provided opportunity to observe morphological/compositional changes of catalysts under electrochemical conditions.^{7,40,41} With appropriate instrumentation these measurements can be conducted at electron microscopy facilities, which for many researchers are more readily available and accessible than specialized research facilities, such as synchrotrons. Using *in-situ* LP-(S)TEM, advanced insight into catalyst properties with spatial resolution under reaction conditions can be achieved by correlating morphological imaging with analytical techniques such as select area diffraction (SAD) and energy dispersive X-ray (EDX) analysis. A previously *in-situ* LP-(S)TEM

study monitored the morphological evolution of Pd particles under electrochemical conditions, including during the electrodeposition of Pd particles⁴² or their morphological evolution under potential cycling,⁴³ but this work was not done in the context of electrocatalysis and the formation of PdH_x phases was not probed. The formation of PdH_x phases has been imaged previously by insitu TEM, however these studies were conducted using either an *in-situ* environmental gas cell⁴⁴ or via LP-(S)TEM electron energy loss spectroscopy (EELS) measurements⁴⁵. These measurements were done in the absence of electrode potential and are therefore not pertinent to electrochemical CO₂R investigations.

Despite advancements in *in-situ* LP-(S)TEM capabilities, detailed investigations of morphological changes in Pd-based catalysts under CO₂R conditions have not been investigated. Furthermore, implementation of *in-situ* SAD measurements under electrochemical conditions during LP-(S)TEM workflows has never been reported, yet provides opportunity to simultaneously measure and track phase structure transformations in catalysts under reaction conditions. Herein, in-situ LP-(S)TEM measurements on electro-deposited Pd/PdHx catalysts were employed to track morphological changes under electrochemical CO₂R conditions alongside LP-TEM/SAD patterns collected to probe the interconversion between metallic Pd and PdH_x phases. Distinct morphological changes occurring in the catalyst structures under electrochemical CO₂R conditions were observed alongside a phase transformation from metallic Pd to PdH_x at electrochemical CO₂R relevant potentials. Increasing lattice expansion due to increased absorption of H atoms occurred at more negative electrode potentials, seemingly giving rise to dramatic CO₂R selectivity changes from nearly exclusive production of formate at -0.2 V vs RHE towards the production of CO and H₂ at -0.5 V vs RHE. However, density functional theory (DFT) calculations complemented by micro-kinetic analyses ascribed the CO₂R selectivity shift to changes in reaction energetics resulting from the applied electrode potential and not due to the phase structure transformations. Ultimately, in-situ LP-(S)TEM imaging coupled with SAD analysis under electrochemical CO₂R conditions has been demonstrated for simultaneously observing morphology and phase structure changes, and has been coupled with electro-catalytic activity/selectivity measurements and computational analysis to provide new mechanistic insight into Pd-based catalysts for the electrochemical CO₂R.

Results and discussion:

Electrode preparation:

Figure 1 shows schematics of the two CO_2 electrolysis configurations used in this work. The first is the Protochips Poseidon Select in-situ LP-TEM electrochemical liquid cell microchip reactor (Figure 1a) employing a glassy carbon working electrode decorated with Pd particles for *in-situ* characterization under CO₂R conditions. The second is a two-compartment cell consisting of a large-format working electrode (Figure 1b) decorated with Pd particles to measure catalytic activity and selectivity towards CO₂R. Pd particles were deposited on the microchip glassy carbon working electrode (Figure 1c, and Figure S1) by electrodeposition after assembling the *in-situ* electrochemical TEM liquid reactor, and the same electrodeposition procedure was used for preparing large-format electrodes (Figure 1d). Electro-deposition of Pd particles on both the microchip (Figure 1c) and the large format electrode (Figure 1d) was observed by SEM imaging. Cyclic voltammetry measurements were collected in N₂ saturated 0.1 M KHCO₃ for the Pd particle decorated microchip glassy carbon working electrode (Figure 1e) and the Pd decorated largeformat electrodes (Figure 1f), demonstrating similar features that suggest similar local chemical environments at the Pd-decorated working electrode in the two different electrochemical reactors. The redox characteristics observed via cyclic voltammetry were characteristic of Pd-based catalysts.⁹ By comparing the cyclic voltammetry features of Pd, the Pt reference electrode employed in the microchip reactor was calibrated to the RHE scale, whereby 0.76 V vs. Pt corresponds to 0 V vs. RHE (Figure S2), in close agreement with previously reported values.^{46,47} All subsequent potentials will be reported versus RHE.



Figure 1. Schematics of the two CO₂ electrolysis cells utilized in this work: **a**, Protochips Poseidon *in-situ* LP-(S)TEM holder consisting of a Pd decorated glassy carbon working electrode within a microchip electrochemical cell. **b**, Two-compartment electrochemical cell

consisting of a large-format Pd decorated glassy carbon working electrode for electrochemical CO₂R activity and selectivity measurements. **c**, SEM images of the *in-situ* TEM microchip

working electrode coated with electrodeposited Pd particles. **d**, Micrograph of the large-format glassy carbon electrode and SEM image of the electrodeposited Pd particles. **e**, Cyclic voltammetry measurements of electrodeposited Pd particles measured in the *in-situ* TEM microchip electrochemical cell. **f**, Cyclic voltammetry measurements of electrodeposited Pd particles measured in the two-compartment cell using the large-format electrode. Note that all cyclic voltammetry measurements were collected in N₂ saturated 0.1M KHCO₃ at a scan rate of 50 mV/s.

SEM was employed to probe the morphology of electrodeposited Pd within the *in-situ* electrochemical TEM microchip reactor (**Figure 2a-c**), revealing semi-spherical particles covering the electrode surface and dendrimer-type structures at the electrode edges. **Figure 2d** and **e** show *in-situ* liquid phase high-angle annular dark-field scanning transmission electron microscopy (LP HAADF-STEM) images at various magnification and **Figure2f** shows *in-situ* LP-HAADF-STEM/EDX mapping of the deposited Pd . A similar morphology was observed for the Pd electrodeposited on the large-format glassy carbon electrodes prepared for CO_2R activity and selectivity measurements (**Figure S3**).



Figure 2. Structural characterization of Pd catalysts deposited on the electrochemical in-situ LP-(S)TEM microchip. a, SEM image of the three electrode-configuration of the *in-situ* LP-(S)TEM microchip cell. b-c, SEM of the working electrode showing electro-deposited Pd particles. d-e, *In-situ* LP-HAADF-STEM images of the working electrode at various magnification. f, *In-situ* LP-HAADF-STEM-EDX mapping of the electrodeposited Pd particles on the working electrode. g, *In-situ* LP-TEM imaging of Pd particles indicating the region where SAD patterns were measured. h, *In-situ* LP-TEM/SAD pattern of Pd particles at open circuit potential and radial intensity profiles of the diffraction patterns using the *in-situ* electrochemical TEM liquid reactor. i, Radial intensity profiles of the diffraction patterns at different beam irradiation times at a flow rate of 5 μL/min and a beam dose of 37 e⁻/nm².s. The acquisition time for the SAD patterns was

set to be 1sec.

In-situ (S)TEM/SAD:

In-situ LP-TEM and SAD (LP-TEM/SAD) characterization was conducted to investigate the morphology and phase structures of Pd particles under electrochemical CO₂R conditions. Prior to the measurements, in-situ LP-TEM images (Figure 2g) and in-situ LP-TEM/SAD patterns with radial intensity profiles (Figure 2i) were collected at open circuit potential. To ensure the diffraction patterns observed were from the Pd particles, *in-situ* LP-TEM/SAD patterns were also collected from an area of the electrode that did not contain any Pd particles (Figure S4a). No diffraction rings or spots were observed (Figure S4b), indicating that the glassy carbon working electrode, the SiN_x windows, and the electrolyte did not contribute to the measurements. Repeated in-situ LP-TEM/SAD measurements were conducted on the Pd particles at open circuit potential to evaluate if the electron beam dose applied (39.7 electron/nm².frame, whereby each frame = 1 second) had any impact on the phase of the Pd particles. No phase transformations as a function of beam dose were observed, in agreement with a recent report investigating the impact of beam dose on Pd/PdH_x interconversion, indicating no Pd to PdH_x transformations occurred at beam doses as high as ca. 3,900 electron/nm².sec.⁴⁵ In the present work no morphology changes in Pd were observed during LP-TEM measurements at open circuit potential, indicating the electron beam dose employed in does not induce morphology or phase structure changes.

In-situ LP-(S)TEM imaging of Pd particles in CO₂ saturated 0.1M KHCO₃ as a function of electrode potential was conducted, with results illustrated in **Figure 3**. HAADF-STEM images at 1.2 V vs RHE and after 27s of applying an electrode potential of -0.2 V vs. RHE (extracted from **Video S1**) are shown in **Figures 3a** and **b**, respectively. The corresponding *in-situ* LP-TEM/SAD patterns of the Pd particles are also shown for an electrode potential of 1.2 V vs RHE (**Figure 3c**) and -0.2 V vs RHE (**Figure 3d**). Going from 1.2 to -0.2 V vs RHE, the size of the Pd particles increased (**Figure 3b**, with images from additional locations shown in **Figure S5**) and the radial distance of the SAD patterns noticeably decreased, suggesting an expansion of the Pd crystal lattice (**Video S1**). To analyze collected *in-situ* LP-TEM/SAD patterns, radial intensity profiles were extracted using the CrysTBox-ringGUI⁴⁸ and the crystallographic information file (cif) acquired from the crystal structure database was used to index the patterns. Examples are shown in **Figures 3c**, **3d**, **S6 and S7**. This method was used to calculate the d-spacing of the Pd-based particles from *in-situ* LP-TEM/SAD patterns, which increased upon applying an electrode potential of -0.2 V vs

RHE (**Video S2**). The observed lattice expansion is likely attributed to hydrogen absorption and intercalation into Pd, resulting in the formation of different PdH_x phases.

To more closely probe the phase transformations occurring under electrochemical CO₂R conditions, *in-situ* LP-TEM/SAD patterns of Pd-based catalysts were collected at several CO₂R relevant electrode potentials. Before applying CO₂R relevant potentials, a potential of 1.2 V vs. RHE (significantly more anodic than CO₂R conditions) was applied for 60 s to ensure the Pd catalyst was in the same starting state before all *in* measurements as hysteresis in the Pd/PdH_x conversion is a known phenomenon.³⁹ After 60sec at .2 V vs. RHE, the Pd particles were in their metallic state (**Figure S6**) and the electrode potential was stepped to progressively more negative values (although always returning back to 1.2 V vs. RHE between each potential). The electrode potential profiles used in this work are depicted in **Figure S8**, and *in-situ* LP-TEM/SAD patterns collected at each measurement potential are shown in **Figure 3e**. Peak locations from the *in-situ* LP-TEM/SAD patterns were used to calculate crystal lattice spacing values which are shown in **Figure 3f** for the (111) diffraction plane.

In-situ LP-TEM/SAD measurements indicated crystal lattice expansion and compression based on the applied electrode potential. At 0.6, 0.8 and 1.2 V vs. RHE, Pd is in the metallic fcc form with Pd(111) d-spacings of 2.27 Å, 2.26 Å and 2.25 Å, respectively, in alignment with the theoretical value of 2.25 Å obtained from the cif database using CrysTBox-ringGUI (Figure S6 and Table $(S1)^{48}$ shown as the dashed blue line in Figure 3f. At 0.3 V vs. RHE, an increase in the d-spacing value to 2.31 Å was observed, likely due to the formation of the α -PdH_x phase and consistent with the recent study *in-situ* XRD study by Landers et al.³⁹ In the present work, as the electrode potential was stepped more negatively to -0.1 V vs. RHE, a further lattice expansion to 2.34 Å was calculated from the diffraction pattern, likely attributed to the formation of a mixture of the α - and β -PdH_x phases in agreement with previously reported DFT calculation.¹⁰ The dashed red line in **Figure 3f** represents the theoretical value for β -phase PdH_x, obtained from the cif database using CrysTBox-ringGUI; whereas Figure S7 and Table S2 demonstrate the comparison of the theoretical and experimental values of PdH_x . At electrode potnetials below -0.2 V vs. RHE, β -PdH_x was found to be the predominant phase with further lattice expansion. Noted that all the experimental d-spacing calculations were estimated using the Crystal Box software with an accuracy ± 0.02 Å.



Figure 3. In-situ LP-HAADF-STEM imaging and SAD patterns that illustrate lattice expansion due to the phase transformation of metallic Pd to PdH_x under electrochemical CO₂ reduction conditions. a and b, In-situ LP-HAADF-STEM snapshots extracted from Video S1 (Supporting information) revealing lattice expansion under applied potential (1.2 V and -0.2 V vs. RHE, respectively) in CO₂ saturated 0.1 M KHCO₃ electrolyte. c and d, In-situ LP-TEM-SAD patterns and corresponding radial intensity profiles revealing lattice expansion under applied electrode potentials of 1.2 V and -0.2 V vs RHE, respectively. e, Radial intensity profiles as a function of

applied electrode potential. **f**, Plot of average d-space values determined from the Pd/PdH_x(111) diffraction peak fitting as a function of electrode potential, with the dashed **blue** and **red** lines representing the theoretical values for the metallic Pd and β -phase PdH_x, respectively, obtained from crystallographic information file (cif) databases. The d-space values were calculated based on the center of the electron diffraction peak using the Crystal Box software with an accuracy of ± 0.02 Å.

Morphology Changes During CO₂R Imaged by In-situ LP-TEM:

Under electrochemical CO₂R conditions, the morphology and behaviour of Pd particles evolve over time.^{10,49} To investigate this phenomena, in-situ LP-(S)TEM measurements were condcuted on the PdH_x particles at -0.2 V vs. RHE (Figure 4, Video S3). At an applied potential of -0.2 V vs. RHE, some PdH_x particles were detached from the electrode surface after 5s and found to migrate to another region of the electrode (Figure 4a). For example, the particles in the region labelled P1 at t=5s migrated to the position labelled P2 after 16s and beyond, demonstrating that detachment and aggregation of Pd-based particles occurs under CO₂R conditions. The average PdH_x particle size was monitored in real time by *in-situ* LP-TEM (Figure 4a and S9) at -0.2 V vs RHE and after all in-situ LP-(S)TEM measurements were conducted, ex-situ TEM (Figure 4b and S10), HAADF-STEM (Figure 4c and S11), SEM (Figure 4d) and optical images (Figure S12) were conducted. Overall, an increase in Pd-based particle size from 80 ± 30 nm to 130 ± 30 nm was observed, indicating particle growth and agglomeration during electrochemical CO_2R . Additionally, the morphology of the Pd-based particles evolved into hollowed out sponge-like porous structures that are most clearly depicted in the HAADF-STEM images in Figure S11 that provide contrast between the Pd atoms and void spaces. Post CO₂R ex-situ characterization additionally revealed that Pd/PdH_x particles detached from the electrode surface in various locations across the electrode (Figure S10, S11, S12). This detachment could possibly be linked to mechanical stresses arising from the phase transitions between PdH_x and Pd, which are accompanied by particle volume expansion/contraction and can induce deformation mechanisms.⁵⁰ This could also be impacted by changes to the surface chemistry of the carbon electrode under electrochemically reducing conditions, which may weaken the interactions between the Pd/PdH_x particles and the carbon electrode, rendering the particles more prone to detachment. A similar observation was previously shown for carbon supported Pt and Pd catalysts

investigated using identical location TEM.^{51,52} **Figure 4e** provides a schematic depiction of the Pd/PdH_x transformations and particle degradation processes observed by LP-(S)TEM imaging under CO₂R conditions. To confirm the changes observed in the Pd/PdH_x particles were not influenced by contamination of the working electrode from the Pt-based counter electrode,⁵³ EDX mapping of the working electrode was conducted (**Figure S13**) and indicated the particles consisted of only pure Pd/PdH_x.



Figure 4. Morphological changes occurring in Pd/PdH_x particles under electrochemical CO_2 conditions. **a**, *In-situ* LP-HAADF-STEM snapshots extracted from Video 3 illustrating Pd/PdH_x particle migration, agglomeration, and detachment from the glassy carbon working electrode at different electrolysis times under an applied potential of -0.2 V vs. RHE (yellow circles indicate some areas where the agglomeration and detachment are more obvious). **b**, TEM **c**, HADDAF-

STEM, and d, SEM images of the Pd particle morphology on the *in-situ* glassy carbon electrode after in-situ imaging under CO₂ electrolysis conditions. e, Schematic depiction of the morphological evolution of Pd/PdH_x catalysts revealed by *in-situ* LP-TEM measurements.

Electrochemical CO₂R Activity and Selectivity:

The electrochemical CO₂R performance of Pd particles prepared by the same technique (electrodeposition) and with similar structural properties to those characterized by *in-situ* LP-(S)TEM/SAD was evaluated using large-format electrodes which enabled quantification of CO_2R activity and selectivity metrics. Figure 5a shows the Faradaic efficiency (selectivity) and current density (activity) of the Pd/PdH_x particles towards electrochemical CO₂R tested by 1-hour chronoamperometry measurements at electrode potentials between -0.1 to -0.5 V vs. RHE. The Pd/PdH_x particles showed the highest selectivity towards formate at -0.2 V vs RHE, with a Faradaic efficiency of 94%. At more negative applied potentials (-0.3 to -0.5 V vs. RHE), the selectivity of the Pd/PdH_x particles towards formate was reduced significantly, showing a Faradaic efficiency of only 6% at -0.5 V vs. RHE. The major products formed at this potential were H_2 (FE of 60 %) and CO (FE of 30%). Tafel plots of the partial current densities for H_2 , CO and formate versus potential are shown in Figure S14. An increase in partial current density towards formate is observed from -0.1 to -0.2 V vs RHE, as would be expected for a reaction following Tafel behaviour. However, at potentials more negative than -0.2 V vs RHE, the partial current density towards formate plateaus and then decreases substantially, indicating catalyst surface poisoning or a shift in the electrochemical CO_2R mechanisms that results in modulated product selectivity. This dramatic shift in CO₂R selectivity coincides with the increased intercalation of protons into the PdH_x structure, with more insight into these phenomena analyzed by DFT and discussed in more detail in the proceeding sections.

Pd Surface Recovery After CO₂R:

The presence of *CO and **H species (* indicates adsorbed species) on the surface of Pd/PdH_x under CO_2R conditions has been shown to influence the activity, selectivity and structural evolution of the catalyst.^{9,54,55} To investigate the presence of these species, CO_2 electrolysis was carried out on the Pd-decorated large-format electrode followed by cyclic voltammetry

measurements to determine the subsequent electrochemical responses of the particles. Initially, the electrodes were held for varying amounts of time at different electrochemical CO₂R relevant potentials in CO₂ saturated 0.1M KHCO₃. Without relaxing to open circuit potential, the electrode potential was then swept by linear sweep voltammetry up to 1.2 V vs RHE. Following this sweep, cyclic voltammetry was conducted until a steady state profile was collected, denoted as the "baseline CV" measurement. The results of these measurements are shown in **Figure 5b.** For each linear sweep voltammetry measurement that followed the chronoamperometric hold under CO₂R conditions (3 min hold at potentials from -0.1 to -0.5 V vs RHE), two oxidation peaks were observed and likely attributed to the oxidation of adsorbed surface *CO species or the desorption of H species.⁵⁶⁻⁶¹ As could be observed in **Figure 5b**, holding the potential at -0.1 V vs. RHE contributed to buildup of a *CO covered surface, as indicated by the oxidation peak observed at ca. 0.9 V vs RHE in the subsequent linear sweep voltammetry (inset of Figure 5b). The oxidation features observed at lower potentials (< 0.5 V vs RHE) are attributed to desorption of H species. When applying more negative electrode potentials during chronoamperometry, the subsequent linear sweep voltammetry measurements showed that the H desorption peaks shifted to higher potentials. This is likely due to the higher concentration of adsorbed *CO species accumulated at these more negative electrode potentials as claimed previously,⁶² as well as an increased amount of H absorbed into the PdH_x lattice as demonstrated by *in-situ* LP-TEM/SAD measurements. To investigate further, the same measurements were carried out in N₂ saturated 0.1 M KHCO₃ to gain insights into the electrochemical response of the Pd/PdH_x particles in the absence of significant concentrations of CO₂ (and subsequent buildup of adsorbed *CO species), with results shown in Figure S15. After a 3-min electrolysis hold at potentials ranging from -0.1 to -0.5 V vs RHE, only one oxidation peak at ≤ 0.5 V vs RHE was observed in the subsequent linear sweep voltammetry measurement, attributed to desorption of H from PdH_x. Substantial shifts in the electrode potential of these oxidation features were not observed when more negative chronoamperometry potentials were applied, providing evidence that the shifts in the H-desorption peaks observed in the case of CO₂ saturated 0.1 M KHCO₃ were largely due to the presence of the adsorbed *CO species and to a lesser extent from the increased concentration of absorbed H in the PdH_x structure.

For electrochemical CO_2R measurements, an increased current density was observed at more negative electrode potentials (**Figure 5a**). Over the course of the electrolysis holds, a decrease in the current density for CO_2R was observed with time (**Figure S16**), potentially due to gradual

poisoning of the Pd/PdH_x surface with *CO. In addition to surface poisoning by *CO, detachment and agglomeration of Pd/PdH_x particles shown by in-situ (S)TEM measurements (Figure 4) represents another mechanism by which the active surface available for the electrochemical CO₂R can become diminished To gain insight into these simultaneous processes, electrochemically active surface area (ECSA) values were estimated using double layer capacitance at various stages throughout the chronoamperometry holds and subsequent linear sweep voltammetry measurements detailed in the previous paragraph. Figure S17 and Supplementary Note 5 in the supporting information provide more details of these measurements. The ECSA for the electrodeposited Pd/PdH_x particles was calculated through double layer capacitance measurements before (ECSAt=0) and after chronoamperometry electrolysis holds at -0.1 V vs RHE in CO₂-saturated 0.1 M KHCO₃ for durations ranging from 3 to 45 mins (ECSA_{t=3 to t=45}). Following ECSA measurements, cyclic voltammetry scans from -0.1 to 1.3 V vs RHE were applied to remove adsorbed *CO species and restore the "clean" Pd surface. The cyclic voltammetry measurement immediately following the electrolysis holds are shown in **Figures 5c**, and the subsequent cyclic voltammetry measurement (2nd cycle) are shown in **Figure 5d.** It is worthwhile to note than subsequent cyclic voltammetry cycles showed negligible differences compared to the 2nd cycle, indicating the electrode had reached steady state. The first cyclic voltammetry cycle following the electrolysis hold (Figure 5c) showed the appearance of a *CO stripping peak between ca. 0.9 and 1.1 V vs RHE, with the magnitude of the peak increasing with increasing electrolysis hold times. This peak was not present in subsequent cyclic voltammetry measurements (Figure 5d), indicating that all adsorbed *CO species were successfully removed and a pristine Pd surface was recovered.

To track the impact of *CO* poising on the ECSA of the Pd/PdH_x particles during the CO₂R, the ECSA_{t=x}/ECSA_{t=0} was estimated (**Figure 5e**), where time (t) indicates the duration of the electrolysis hold at -0.1 V vs RHE. When the electrolysis period was prolonged from 3 min to 45 mins, the ECSA_{t=x}/ECSA_{t=0} ratio was reduced from 1.01 to 0.8, demonstrating an approximately 20% loss in surface area. This reduction in the ECSA could be recovered after the subsequent cyclic voltammetry cycle to restore the pristine Pd surface, indicating the loss in ECSA following electrolysis hold likely arose due to *CO poisoning. It was then desirable to identify ECSA changes following longer electrolysis holds under CO₂R conditions. 1hr electrolysis holds were conducted sequentially at increasingly more negative electrode potentials, starting at -0.1 V vs RHE and

proceeding in increments of 100 mV down to -0.5 V vs RHE. Between each 1hr electrolysis hold, repeated cyclic voltammetry measurements were conducted to clean the Pd surface and ECSA values were measured by double layer capacitance to calculate the ECSA/ECSA_{t=0} ratios shown in Figure 5f. The electrolyte was also replaced with fresh electrolyte to remove possible contaminants or liquid phase CO₂R products that could impact subsequent measurements before subquent electrolysis holds and electrochemical measurements were applied. The calculated ECSA/ECSA_{t=0} after a 1hr electrolysis hold at -0.2 V vs RHE and cyclic voltammetry cleaning showed the highest value of 1.5. This increase was attributed to the introduction of porosity into the Pd/PdH_x particles revealed by ex-situ HAADF-STEM imaging of the electrodes after CO_2R (Figure S11) as discussed previously. ex-situ. At more negative electrode potential holds (electrolysis) from -0.3 to -0.5 V vs. RHE, the calculated ECSA /ECSA_{t=0} decreased from 1.3 to 0.9, respectively. This subsequent decrease in ECSA is likely due to detachment of the Pd/PdH_x particles from the electrode surface, also as discussed previously ex-situ. Similar particle detachment morphological changes were also observed on the large-format electrodes after one hour of electrolysis at -0.5 V vs RHE (Figures S18 and S19), reinforcing the fact that Pd/PdH_x particle detachment was prevalent at these conditions and responsible for the observed ECSA decrease.



Figure 5. Electrochemical CO₂R selectivity and surface recovery of Pd particles after poisoning by adsorbed *CO species: a, Faradaic efficiencies (left y-axis) and partial current densities (right y-axis) for the production of formate, H₂ and CO. b, Positive linear sweep voltammetry following a 3min electrolysis hold at various CO₂R electrode potentials, along with baseline cyclic voltammetry curves collected in CO₂ saturated 0.1 M KHCO₃ electrolyte with a scan rate of 20mV/s. c and d, Cyclic voltammetry measurements including the 1st and 2nd cycle following

varying durations of an electrolysis hold at -0.1 V vs. RHE. **e**, ECSA estimations using electrochemical double layer capacitance measurements immediately following an electrolysis hold at -0.1 V vs RHE for varying time durations (x) normalized by the original ECSA of the catalyst particles (i.e., ECSA_{t=x}/ECSA_{t=0}), demonstrating the effect of *CO poisoning on the ECSA. **f**, ECSA estimations following a 1hr electrolysis hold at various electrode potentials and subsequent cyclic voltammetry sweeps to strip *CO species and recover a clean Pd surface.

ECSA values are normalized by the original ECSA of the catalyst particles (i.e.,

 $ECSA/ECSA_{t=0}$).

Mechanistic Insight into CO₂R Activity and Selectivity Through Density Functional Theory:

DFT calculations were performed to provide understanding of the structure-property-performance trends observed via *in-situ* LP-(S)TEM correlated with CO₂R activity/selectivity measurements on electro-deposited Pd/PdH_x particles. The constant potential methodology implemented in the Solvated Jellium Method (SJM)⁶³ was applied, enabling the simulation of adsorbed *CO₂, which is only possible when including explicit charging of the electrode. The (111) and (100) facets of the fully hydrogenated β -phase PdH_x were studied in accordance with the identification of this phase at potentials below -0.2 V vs RHE. Hydrogen atoms were located in the octahedral sites of bulk Pd, corresponding to hollow sites on the surface of Pd. The lattice parameters of the β -PdH_x bulk structure were optimized, leading to a 0.12 Å increase in the d-spacing compared to metallic Pd, in line with the experimental observations presented in **Figure 3f. Figure S20** shows the calculated adsorption free energies of H⁺ from solution on a PdH_x(111) surface at varying **H coverages. The calculated binding energies suggest an incomplete monolayer of **H is present at 0 V vs. RHE, with nearly thermoneutral binding energies up to a coverage of ¾ at -0.3 V vs. RHE a complete monolayer is present.

Figure 6a shows the calculated free energy pathways for electrochemical CO₂R towards formate and CO occurring on the PdH_x(111) facet, while results for the PdH_x(100) facet are shown in **Figure S21**. Particularly, the PdH_x(100) facet is found to be poisoned with *CO adsorbates under reaction conditions and hence not active to produce CO or formate. All subsequent calculations discussed were therefore performed on the PdH_x (111) facet. The mechanism of CO₂R to produce CO was found to pass through a (bent) *CO₂ intermediate bound to PdH_x on a Pd top-site via the

carbon atom, as shown in the atomic scale schematic at the top of **Figure 6a**. On the other hand, the mechanism of CO₂R toward formate does not proceed through a stable *CO₂ intermediate. Rather, CO₂ is found to react with a surface bound hydrogen in a Heyrovsky-like mechanism⁶⁴ after being activated close to the PdH_x surface (Figure S22). This mechanism towards producing formate on PdH_x (and possibly other metal hydrides) is in stark contrast to proposed mechanisms of formate production on oxophilic post-transition metals (such as Pb⁶⁵ and Sn⁶⁶) that have been proposed as capable of stabilizing CO₂ binding via the oxygen atoms (*OCO) followed by protonation to produce formate.⁶⁶⁻⁶⁸ Conversely, stabilizing the *OCO intermediate on PdH_x in the simulations was not successful, even upon rigorous sampling of various binding motifs. The fact that the key intermediate in formate production, *OCO, does not bind strongly on PdH_x suggests that the hydrogenation of the central carbon atom occurs via the weakly bound (sub-)surface hydrogen atoms. The reaction mechanism involving CO_2 hydrogenation towards producing formate was identified as an outcome of the transition state searches starting from both solvated (planar) and adsorbed (bent) CO_2 . Both starting states for the reaction (i.e., solvated or adsorbed CO₂) led to the same transition state, where partially activated CO₂ reacts with a (sub)surface *H (*H-CO₂). The potential response at the transition state was calculated to be 0.2 eV/V, while the majority of the charge injection leading to the formate occurred after the transition state (Figure S22b).

The formation of *COOH was identified as the bottleneck towards producing CO with the formation calculated to exhibit a potential response of 1.13 eV/V (**Figure 6a**). As the energetics for forming *COOH are more strongly dependent on potential that the formation of *H-CO₂, CO production becomes energetically favored at increasingly negative electrode potentials. At 0V vs. RHE, however, *H-CO₂ is 0.30 eV more stable than *COOH, rendering formate the preferentially formed product at this electrode potential. It should been noted that the reaction rate of *CO₂ to *COOH is only limited by the thermodynamic barrier, as the negative partial charge on the O-end of *CO₂ to *COOH would not change the qualitative behavior of a larger stabilization of the CO-path with more negative potentials. The 0.36 eV/V potential response of *CO₂ is still larger than the 0.2 eV/V of *H-CO₂, and the barrier from *CO₂ to *COOH cannot exhibit a lower potential response than either of the end states.

Based on the described reaction energetics, a microkinetic model was constructed (Figure 6b). The calculated turnover frequencies (TOF) towards formate outweighs the TOF towards CO at electrode potentials between -0.2 and -0.35 V vs RHE. At more negative potentials, the TOF towards both CO and HCOO- increases, although the increase in TOF for CO is much more drastic ⁻. The selectivity for CO (TOF towards CO divided by the sum of the TOFs towards both CO and HCOO⁻) increases as a result of the strong potential response calculated for *COOH as described above. Therefore, this analysis indicates the CO₂R selectivity towards CO should increase at more negative potentials owing to the electrode potential dependent energetics of the reaction relevant species. The results of this microkinetic modelling are in agreement with experimental CO_2R measurements that indicate a shift in selectivity from formate towards CO at increasingly negative potentials (Figure 5a). A quantitative agreement between experiment and theory is not always expected,⁷⁰ thus calculations were performed to understand the sensitivity the calculated microkinetic models have on the calculated free energy values of *H-CO. Figure 6b shows blue shaded areas that represent the variation in TOF and selectivity that would be expected with a difference in the calculated *H-CO free energy of ± 0.1 eV. This range in the energetic uncertainty leads to a ca. 0.2 V difference in the electrode potential at which a CO₂R selectivity change from producing HCOO- to producing CO would be expected. However, as discussed above, this uncertainty does not alter the qualitative finding that PdH_x produces formate almost exclusively at low overpotentials, followed by a sharp change in selectivity towards CO production at more negative potentials.

Discussion

The morphological and phase structure conversions occurring in Pd/PdH_x catalyst under electrochemical CO₂R conditions was revealed by *in-situ* LP-(S)TEM characterization and supplemented by *ex-situ* post-CO₂R characterization of the electrodes. As shown in **Figure 4e**, three primary changes to the Pd/PdH_x were observed under CO₂R conditions: (1) Particle agglomeration; (2) Particle detachment from the electrode surface; and (3) Hollowing out of the particles to form a sponge-like porous morphology.

To an extent, the particle agglomeration observed could follow Ostwald ripening or other sintering mechanisms. Localized *in-situ* particle tracking measurements could be applied to understand this process of particle sintering as well as the underlying kinetics,⁹ which is outside the scope of the

present work. The particle agglomeration observed in the *in-situ* LP-(S)TEM measurements was found to occur by particle detachment from the electrode surface and subsequent deposition on another region of the electrode (**Figure 4a**) that was most prevalent at more negative electrochemical CO_2R conditions. It is speculated that particle detachment was largely induced by mechanical forces that arose due to the absorption of increased amounts of H into the PdH_x lattice at increasingly negative electrode potentials, which led to significant volume expansion (and contraction upon conversion back to metallic Pd). This could lead to mechanical instabilities at the catalyst/electrode interface, causing the detachment of catalyst particles.⁵⁰ It should also be noted that mechanical agitation from the formation of bubbles (H₂ and/or CO) at increasingly negative potentials could also influence particle detachment; however, there was no direct observation of this by *in-situ* LP-(S)TEM measurements.

The hollowing of Pd/PdH_x to form porous sponge-like particles also occurred under CO_2R conditions, likely due to thermodynamic driving forces.⁷¹ Additionally, the evolution of porosity through morphological changes could arise due to adsorbate (i.e., *CO) induced restructuring.^{72,73} The presence of *CO species on the surface of Pd/PdH_x under CO₂R conditions was demonstrated in this work (**Figure 5b**), with DFT calculations suggested *CO poisoning to be a facet dependent occurrence on Pd/PdH_x.

The phase structure of Pd/PdH_x was observed as a function of electrode potential under CO₂R conditions by *in-situ* LP-TEM/SAD. At potentials between -0.1 and -0.2 V vs RHE, the particles were in a mixed α/β -phase PdH_x, with complete formation of the β -PdH_x phase observed at more negative potentials. Interestingly, this conversion of mixed phase α/β -PdH_x to β -phase PdH_x coincided with a CO₂R selectivity shift from formate (at lower overpotentials) towards CO (at higher overpotentials), suggesting that the phase transformation may be underlying the catalytic trends. However, DFT calculations coupled with micro-kinetic modelling indicated the primary reason for the CO₂R selectivity change was due to the electrode potential dependent thermodynamic energetics of adsorbed reactive intermediate — *COOH in the case of CO or *H-CO₂ in the case of formate. For the production of formate, the hydrogenation of the C atom in CO₂ by (sub)surface *H was identified as a key step, in contrast to the formate production mechanism suggested previously for oxo-philic metals such as Sn and Bi, whereby the CO₂ molecules were found to adsorb on the catalyst surface via the O atoms.⁶⁶⁻⁶⁸ Previous calculations also suggested

that Pd catalysts can produce formate through the mechanism where CO₂ is adsorbed via the Oatom, but this configuration was not found to be energetically possible on β -PdH_x. Formate production through the reaction of CO₂ with *H has been suggested in the past,⁹ but has not been rigorously explored through the combination of *in-situ* catalyst characterization alongside DFT and micro-kinetic modelling. A The direct participation of (sub)surface *H in CO₂R towards formate suggests that PdH_x catalysts with a increased *H availability as a reactant (and a reduction in the binding strength of *H) is a desirable catalyst design principle . However, at -0.2 V vs RHE where the highest selectivity towards formate is observed, the catalyst is in a mixed $\alpha/\beta PdH_x$ phase. At lower electrode potentials complete conversion to the β -PdH_x phase and increased saturation of the lattice with hydrogen does not coincide with an increase in activity/selectivity towards formate. Instead, the opposite trend is observed. and DFT alongside micro-kinetic calculations show that at more negative electrode potentials, the formation of *COOH intermediate (for producing *CO) becomes energetically more favourable than the formation of the *H-CO₂ intermediate for producing formate. Therefore, the selectivity change of the CO_2R from producing formate toward CO at more negative electrode potentials is attributed to thermodynamic changes to the energetics of the reaction and not due to the phase transformation of increased content of absorbed H in the PdH_x structures present under reaction conditions.



Figure 6. Density functional theory and micro-kinetic modelling analyses. **a**, Calculated DFT (constant potential) free energy diagram of the reaction pathways for CO_2R towards formate and CO, including the calculated reaction barrier of CO_2 hydrogenation (*H-CO₂) plotted at 0 and -

0.5 V vs. RHE (solid lines and dashed lines, respectively). The optimized geometries of the associated reaction steps are shown explicitly next to the labels. **b**, Turnover frequency and selectivity results obtained from micro-kinetic modelling using the results from DFT analyses as inputs. The shaded blue region indicates the uncertainty in TOF and selectivity calculations that

arise if the barrier for CO_2 surface hydrogenation varies by +/- 0.1eV.

Conclusion:

In-situ LP-(S)TEM and SAD measurements were conducted on electro-deposited Pd/PdH_x catalysts for the electrochemical CO_2R to identify morphological and phase structure changes. Under electrochemical CO2R conditions, the Pd/PdH_x catalysts underwent morphological changes, including: (i) particle agglomeration; and (ii) formation of a porous sponge-like morphology likely arising from adsorbate (i.e., *CO) induced restructuring. Additionally, particle detachment from the electrode surface was observed, likely due to mechanical agitation induced by the process of interconversion between the metallic Pd and PdH_x phase(s). Electrochemical CO₂R activity and selectivity measurements revealed that formate was produced almost exclusively at -0.2 V vs RHE, whereby the production of H2 and CO became prominent at more negative potentials. Correlation with LP-TEM-SAD measurements showed this selectivity shift coincided with increased H absorption into the PdH_x , forming a β -PdH_x phase. By coupling *in*situ structural analysis and electrochemical evaluation of the Pd/PdH_x catalysts with DFT calculations and micro-kinetic modelling, it was demonstrated the CO₂R selectivity from formate to CO/H₂ changes occurred due to potential-dependent reaction energetic changes and not due to the observed PdH_x lattice expansion. DFT calculations on revealed the reaction mechanism towards formate on β -PdH_x involved hydrogenation of the C atom in the CO₂ molecule by (sub)surface *H present in PdH_x. This contrasts the formate production mechanism suggested previously for oxo-philic metals where the CO_2 molecule adsorbs on the catalyst surface via the oxygen atom and is subsequently protonated. At more negative electrode potentials, the *COOH intermediate for producing CO was stabilized in comparison to the *H-CO₂ intermediate for producing formate, explaining the dramatic shift in selectivity from nearly-exclusive production of formate at -0.2 V vs RHE to the production of CO/H₂ at -0.5 V vs RHE. This work therefore provides mechanistic insight into the electro-catalytic mechanisms of CO₂R occurring on Pd-based catalysts that can be applied to understand and guide future catalyst designs. Furthermore *in-situ* LP-(S)TEM including SAD has been demonstrated as a powerful technique for gaining unprecedented insight into the morphological and phase structure changes occurring in catalysts under electrochemical CO₂R conditions.

Materials and Methods:

Materials:

Potassium bicarbonate (ACS reagent, 99.7%), palladium (II) chloride (99.9%), and hydrochloric acid (ACS reagent, 37%), were purchased from Sigma Aldrich and used without any further purification.

Methods:

Pd particle electrodeposition using *in-situ* LP-TEM electrochemical reactor:

The electrochemical setup for Pd electrodeposition onto the *in-situ* electrochemical TEM sample holder is shown in **Figure S1**. The Poseidon Select (Protochips) *in-situ* TEM sample holder was utilized, whereby the micro-chip electrochemical cell mounted in the tip of the TEM holder consists of a Pt reference and counter electrode, and a glassy carbon working electrode (**Figure S1**). The micro-chip reactor consists of a top and bottom chip that are sealed together with a gasket and fastened with screws. Both the bottom and top chips contain a thin silicon nitride (SiN_x) membrane viewing window that enables electron transmission for *in-situ* TEM measurements. As received, both the top and bottom chips are coated with a protective photoresist layer to prevent SiN_x membrane damage. The protective photoresist layer was removed prior to the two-step rinse process, whereby chips were submerged first in acetone and then methanol, each for 2 minutes. To enhance the hydrophilicity of the chips, a plasma cleaning (Gatan plasma system model 950 advanced plasma, with Ne/H₂/Ar gas mixture and operating at 15 W) was used. The process was performed for 2 minutes for the small E-chip and 30 seconds or less for the large E-chip as the excessive plasma cleaning could damage the glassy carbon electrode. Following assembly of the micro-chip electrochemical cell, a liquid solution of 5 mM H₂ PdCl₄ with 0.015 M HCl was introduced at a flow rate of 5 μ L/min through the microfluidic channels of the sample Poseidon Select holder using an external syringe pump. Once the solution was introduced, electrochemical chronoamperometry was carried out at 0.2 V vs. RHE using a floating potentiostat (Gamry Reference 600+) for 120 seconds to ensure the electrodeposition of a sufficient amount of Pd particles on the working electrode. Following electrodeposition, the *in-situ* TEM holder was purged with Millipore water to remove the electrodeposition solution.

In-situ (S)TEM measurements under electrochemical CO₂R conditions:

In-situ electrochemical (S)TEM liquid cell measurements were conducted to investigate the phase and structural transformations of electrodeposited Pd particle catalysts under CO₂R conditions. For all *in-situ* TEM experiments, to avoid SiN_x window bulging due to the pressure difference between the electrochemical micro-chip cell and the vacuum in the TEM column, a perpendicular (crossed configuration) window strategy was utilized as recommended by previous studies.⁷⁴ After electrodeposition of Pd and purging of the Pd salt solution by Millipore water, the Millipore water was replaced by flushing the electrochemical cell TEM holder with freshly prepared CO₂ saturated 0.1 M KHCO₃ solution at a flow rate of 5 µL/min. Confirmation that the 0.1 M KHCO₃ had entered the sample holder was indicated when the open circuit potential was stabilized. Leak checking of the in-situ TEM sample holder was performed before insertion into the microscope using a customdesigned vacuum pump station. To establish a baseline, *in-situ* LP-TEM imaging and select area electron diffraction (in-situ LP-TEM/SAD) measurements were performed at different times: 1, 5,7, and 10 minutes before applying any electrode potential. After these measurements, chronoamperometry at different applied potentials in the range of 1.3 to -0.2 V vs. RHE was applied for 60 seconds at each potential, during which time in-situ LP TEM imaging and in-situ LP-TEM/SAD patterns were collected. Between each chronoamperometry experiment, a potential of 1.2 V vs. RHE was applied for 60 sec to recondition the particles to be in metallic Pd form, thereby avoiding any issues pertaining to Pd/PdH_x transformation hysteresis.⁷⁵ Detailed information about in-situ LP-TEM/SAD analysis and beam dose calculations are included in the Supporting Information.

Pd electrodeposition on large-format glassy carbon electrodes for CO₂R:

Electrodes to test the electrochemical CO₂R activity and selectivity of electro-deposited Pd were prepared using a large-format glassy carbon electrode with dimensions of 2cm by 5cm. Electrodeposition of Pd particles was performed by chronoamperometry at 0.2 V vs. RHE for 120 seconds in 5 mM H₂PdCl₄ mixed with 0.015 M HCl. A Pt foil counter electrode and Ag/AgCl reference electrode that was calibrated and converted to the RHE scale were used. After electrodeposition, the electrode was rinsed carefully with Millipore water and dried at room temperature under N₂ gas flow.

Electrochemical CO₂R activity/selectivity measurements:

Electrochemical CO₂R activity and selectivity of the electrodeposited Pd catalyst were investigated using a custom-built electrochemical cell (**Figure S2**) reported on previously,⁷⁶ which was designed and improved upon to provide high sensitivity for CO₂R product detection and quantification. On-line gas chromatography (SRI Multigas #5) was used to detect/quantify gas products while liquid products were quantified using the Bruker AVIII 700 NMR available at McMaster University's Nuclear Magnetic Resonance Facility. A mass flow control unit (pMFC, MKS Instrument) was used to maintain a CO₂ flow rate of 20 sccm through the catholyte chamber throughout the entire course of the reaction. A Pt foil was used as the counter electrode and Ag/AgCl as the reference electrode, which was calibrated and converted to the RHE scale by measuring the open circuit potential of the Ag/AgCl versus an in-house designed RHE. CO₂R electrolysis measurements were conducted by chronoamperometry at a potential between -0.1 V to -0.5 V vs. RHE for one hour each, while cyclic voltammetry measurements were conducted at 50mV/s before and after chronoamperometry. The geometric surface area of the large format electrode exposed to the electrolyte was 5.6 cm².

Materials Characterization:

To investigate the morphology and composition of Pd electrocatalysts immediately after electrodeposition and after CO₂R testing, optical microscopy (CLEMEX, Axioplan 2 imaging), scanning electron microscopy (JEOL JSM-7000F SEM), high-resolution transmission electron microscopy (HRTEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging, along with energy dispersive X-ray (EDX) mapping were carried out. All TEM and HAADF-STEM imaging were performed using an image-corrected FEI Titan 80-

300LB operating at 300kV and a Thermo Scientific Talos 200X operate at 200kV available at the Canada Center for Electron Microscopy (CCEM) at McMaster University.

Computational details:

The reported DFT-based (constant potential) energies were calculated using the constant-potential mode of SJM ⁶³ implemented in GPAW ^{77,78}. A real-space grid basis set was applied with a grid-spacing of 0.18 Å. The BEEF-vdW functional⁷⁹ was applied for approximating the XC contributions. All slab calculations were conducted with periodic boundary conditions parallel to the slab surface and a dipole correction in the-direction perpendicular to the surface was applied. 3x4x4 supercells were used, with the bottom two layer being constrained to the bulk lattice constants of Pt and PtH, respectively. Monkhorst–Pack *k*-point grids of 4 x 4 x 1 and 4 x 3 x 1 were applied for palladium and palladium hydride structures, respectively. The setup used a Fermi smearing of 0.1 eV / k_B. Forces were converged to 0.03 eV / Å and 0.05 eV / Å for stable intermediates and transition states, respectively.

SJM uses an effective potential cavity solvation model implemented into GPAW by Held and Walter ⁸⁰. The parameters used were: Bondi's van der Waals radii ⁸¹,Strength of the repulsion at the atomic radii controlling the cavity size, u0= 0.18eV, surface tension 0.001148 Pa*m (Both taken from ⁸⁰, (maximal) dielectric constant (ϵ)=78.36 and temperature=298.15K. The tolerance for the electrode potential deviation from the target potential was set to 10mV.

All possible adsorbate binding configurations were sampled using the CatKit Surface module⁸². For the palladium hydride structures, hydrogens were placed in all the octahedral holes of a palladium bulk structure, corresponding to a 1:1 Pd:H ratio, resembling a β -PdH structure. The most stable structures were determined with a d-spacing of 2.42 and 2.09 for the 111 and 100 facets, respectively. Activation energies were calculated using the Climbing Image Nudge Elastic Band (CI-NEB) method⁸³ within the dynamic NEB (DyNEB) implementation⁸⁴. Electronic energies are converted into free energies via a vibrational analysis within the harmonic approximation for adsorbates and an ideal gas approximation for gas phase species, as implemented in the Atomic Simulation environment (ASE)⁷⁵

The free energy of HCOO⁻_(aq) was calculated from its equilibrium with HCOOH at the pK_a (3.75), following the relationship $G_{\text{HCOO}_{\overline{aq}}} = G_{\text{HCOOH}_{(aq)}} - \ln(10)k_{\text{B}}T(pH - pK_{\text{a}}).^{85}\text{A}$ partial pressure of 5728.86Pa was applied for the calculation of $G_{\text{HCOOH}_{(aq)}}$ from its equilibrium with $G_{\text{HCOOH}_{(q)}}$.

A free energy correction of +0.33eV was added for all molecules including an OCO-backbone, i.e. $CO_{2(g)}$,*H-CO₂,*COOH,HCOO⁻ in order to correct systematic errors of DFT when applying the BEEF-vdW XC functional.^{86,87}

Noted that, while in the transition state search of *H-CO₂, the unit cell explicitly contained CO₂ and HCOO⁻ hovering in the implicit solvent above the electrode surface. However, **in Figure 6**, the states $CO_{2(g)}$ and $HCOO^{-}_{(aq)}$ represent the species in gas phase and bulk solution, respectively.

Data availability

The data that support the experimental findings of this study are available from the corresponding author upon request. The theoretical data and analysis routines will be made publicly available on https://github.com/CatTheoryDTU upon acceptance of the article.

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