Electrochemical Oxidation of Formate on Palladium

In situ mechanistic study of formate bonding and reaction pathways

Background. Interest in formate has grown over the past decade, both due to it being a product of the popular electrochemical CO_2 reduction reaction and as a candidate hydrogen/energy carrier. The formate–bicarbonate/CO_2 couple can be charged and discharged under comparatively mild conditions, and has been proposed as a safe, carbon-neutral route to store and release hydrogen [1, 2]. Discharging this carrier requires an active and durable oxidation catalyst. The oxidation of formate itself, however, remains fairly unstudied.

Formic acid/formate oxidation is generally described by a dual-pathway mechanism, established on platinum [3]:

$$\textit{direct:} \quad HCOO^- \longrightarrow CO_2 + H^+ + 2e^-$$
$$\textit{indirect (poisoning):} \quad HCOO^- \longrightarrow CO(ads) + OH^- \longrightarrow CO_2 + H^+ + 2e^-$$

Both routes lead to CO_2, but the indirect route passes through adsorbed CO, which binds strongly and is only oxidised onward to CO_2 at higher potentials, therefore blocking active sites and making it rate-limiting on platinum. Palladium resists this poisoning entirely (during oxidation), but the mechanism at which it does this isn't settled. Chen et al. attribute the difference to competition: a high coverage of inactive adsorbed formate protects the palladium from the CO-forming step, so the indirect pathway is suppressed rather than absent [4]. An alternative explanation is that the indirect pathway does not run at all on palladium: several in situ infrared studies, including surface-enhanced IR work on Pd films, report no measurable CO signature during formic acid oxidation under conditions where it is clearly seen on platinum [5]. The work of Chen et.al[**?**] of the inactive formate however is not proven by spectroscopy, and doubt exist if a layer such as this would truly be innert. Either way, the bonding geometry of adsorbed formate on palladium either bridging bidentate or monodentate remains unresolved: first-principles studies on related transition metals favour a bidentate configuration [6], but palladium-specific experimental evidence is lacking.

This gap exists largely for practical reasons: identifying a short-lived, weakly scattering adsorbate under an applied potential and Faradaic current is difficult. A recent development within the PCF group is a combined electrochemical quartz crystal microbalance (EQCM) and Raman spectroscopy set-up, operated in tandem, with possibilties to add atomic force microscopy (AFM) at the same electrode (Figure 1). EQCM and Raman spectroscopy give simultaneous, time-resolved access to interfacial mass change and vibrational fingerprints at the same electrode, offering a realistic route to test both the coverage and the absent-CO hypotheses directly.

A second point of interest is the pair of oxidation peaks that formate and formic acid voltammograms characteristically show on the forward and reverse potential scans, with the reverse peak often the more intense of the two. The working hypothesis to be tested is that formate accumulates as a reservoir either at or near the surface during the forward scan. And that this reservoir is responsible for the enhanced reactivity seen on the reverse scan, rather than a mechanism based on surface reactivation alone. This is not settled on palladium and will be examined alongside the bonding question, with EQCM well placed to track any mass build-up through the forward scan and its subsequent release, and Raman able to identify the origin of the mass increase.

A related reaction runs in the opposite direction: the catalytic hydrogenation of bicarbonate to formate on palladium, using H_2 rather than an applied potential. Whether this pathway is a genuine contributor, rather than a minor side process, is unconfirmed; if it is significant,

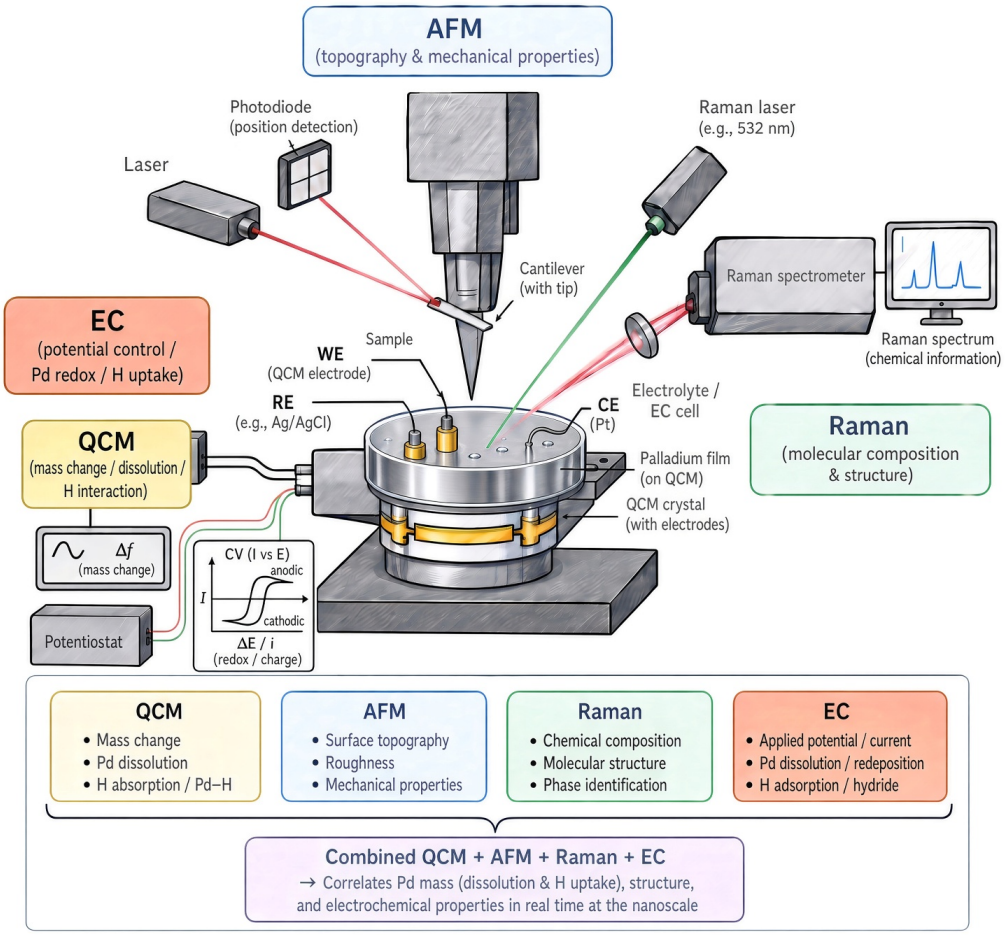

Figure 1. *Schematic of the combined electrochemical set-up. A quartz crystal microbalance (QCM) tracks mass change and viscoelastic properties at the working electrode (WE) via the potentiostat-controlled resonance frequency; a Raman laser probes the same electrode for chemical composition and molecular structure; and an atomic force microscope (AFM) cantilever, positioned above the electrochemical cell, provides surface topography and mechanical properties. The potentiostat (EC) sets the applied potential and records the resulting current/charge. Combining QCM, AFM, Raman and EC correlates mass, structure, chemistry and electrochemical response at the same interface in real time.*

it would in principle allow reduction of CO_2/bicarbonate at a considerably lower overpotential than direct electroreduction [7].

Research questions. Using the tandem EQCM–Raman platform (Figure 1), this project addresses the following questions:

- Can a bidentate or monodentate formate adlayer be identified spectroscopically on palladium during formate oxidation, and does its presence correlate with suppressed CO accumulation?
- Does a near-surface formate reservoir, built up during the forward potential scan, account for the enhanced reactivity observed on the reverse scan, rather than a mechanism based on surface reactivation alone?
- To what extent does catalytic hydrogenation of bicarbonate to formate contribute under the same electrode and electrolyte conditions, and could this pathway offer a lower-

overpotential route to CO_2/bicarbonate reduction?

These questions will be addressed by combining tandem EQCM and Raman results into a coherent mechanistic picture. The set-up, although shown to work, is still in the early stages of implementation, and further optimisation will likely be required. If time allows, coupling atomic force microscopy (AFM) to the same electrode may also be explored, to give complementary topographic and nanomechanical evidence for the mass and film-rigidity changes tracked by EQCM. This project is a collaboration between the PCS group and the PCF group.

Learning objectives. In addition to the standard learning objectives for a Master's project (research planning, academic writing, data presentation, working in a laboratory environment, etc.), you will:

- Learn to operate a combined electrochemical quartz crystal microbalance (EQCM)–Raman spectro-electrochemical set-up, and, time permitting, in situ AFM.
- Gain experience with cyclic voltammetry and the mechanistic interpretation of electrocatalytic reaction pathways.
- Acquire skills in the acquisition and analysis of in situ Raman spectra of adsorbed reaction intermediates.
- Learn to correlate mass-based (QCM), spectroscopic (Raman) and electrochemical data into a coherent mechanistic picture.
- Learn to set hypothesis and using multiple analysies to piece together proof.

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