Supporting information for

A Study of the Mechanism of the Hydrogen Evolution Reaction on Nickel by Surface Interrogation Scanning Electrochemical Microscopy (SI-SECM)

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SI-SECM tip-substrate alignment and approach

The Pt tip and Ni substrate electrodes (ultramicroelectrodes (UMEs) of radius $a = 12.5$ µm), were initially placed at a close proximity in a SECM cell by visually alignment. The tip and the substrate electrodes are positioned such that the substrate UME is placed vertically pointing up and the tip UME points down. The substrate electrode is immobile during the experiments (only tilt correction available by a three-point stage positioner) and the tip electrode is motile by inchworm stepper motors and piezo controllers in all three dimensions. A biopotentiostat connects to the tip and substrate UMEs, rendering them as working electrodes. After positioning the two electrodes, the SECM cell was filled with the analyte solution (1.0 mM FcMeOH in 0.010 M KOH). The solution was purged thoroughly with argon before use, and was kept under a humid argon blanket throughout the experimental procedures. A voltage (-0.94 V) was applied on the substrate electrode to produce positive feedback as the tip electrode scanned across it. A current profile (2D slice, in X or Y direction at a constant Z position) representing the contour of the diffusion layer of the substrate UME was obtained as shown in Figure S1. The tip-substrate alignment was performed by repeatedly scanning the tip over the substrate (in X and Y), seeking for maximum positive feedback and centering the tip electrode where the pinnacle occurs. Stage tilt correction was done by observing current profiles such as that shown in Figure S1, and repeating the scans until a symmetrical current profile with respect to the vertex was obtained as the stage (where the substrate UME was mounted) was tilt corrected in X and Y. After tilt correction and tip-substrate alignment, the tip was slowly approached to the substrate in the Z direction. The tip electrode was positioned at 1.5 µm away from the substrate – close enough for 100 % generation-collection (see Figure S1b) – before the SI-SECM experiments began.
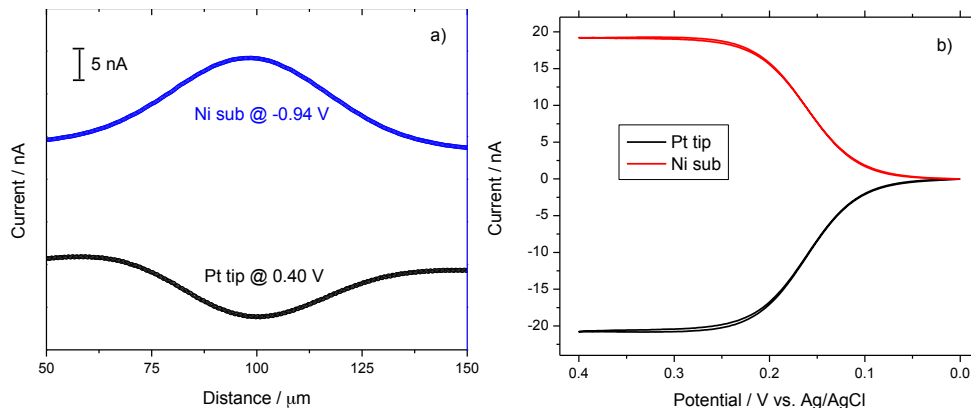

Figure S1. a) A scan in the X of the tip over the substrate. The alignment and tilt-correction process was repeated in the X and Y to obtain good approach for surface interrogation. b) Cyclic voltammograms of the Pt tip electrode at the approached distance of 1.5 µm. The potential of the Ni substrate is set at -0.94 V.

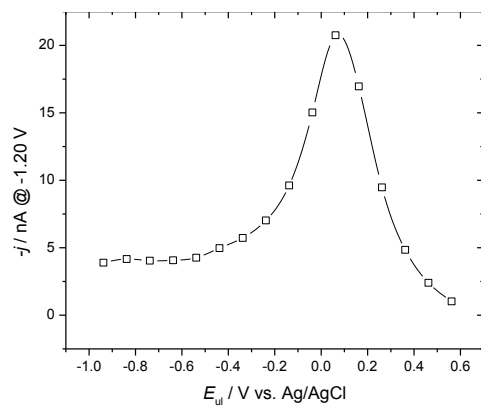# Relationship between HER current and upper limit potential

Figure S2. The change in the HER current (measured at -1.20 V in Figure 2) with respect to upper limit potentials.
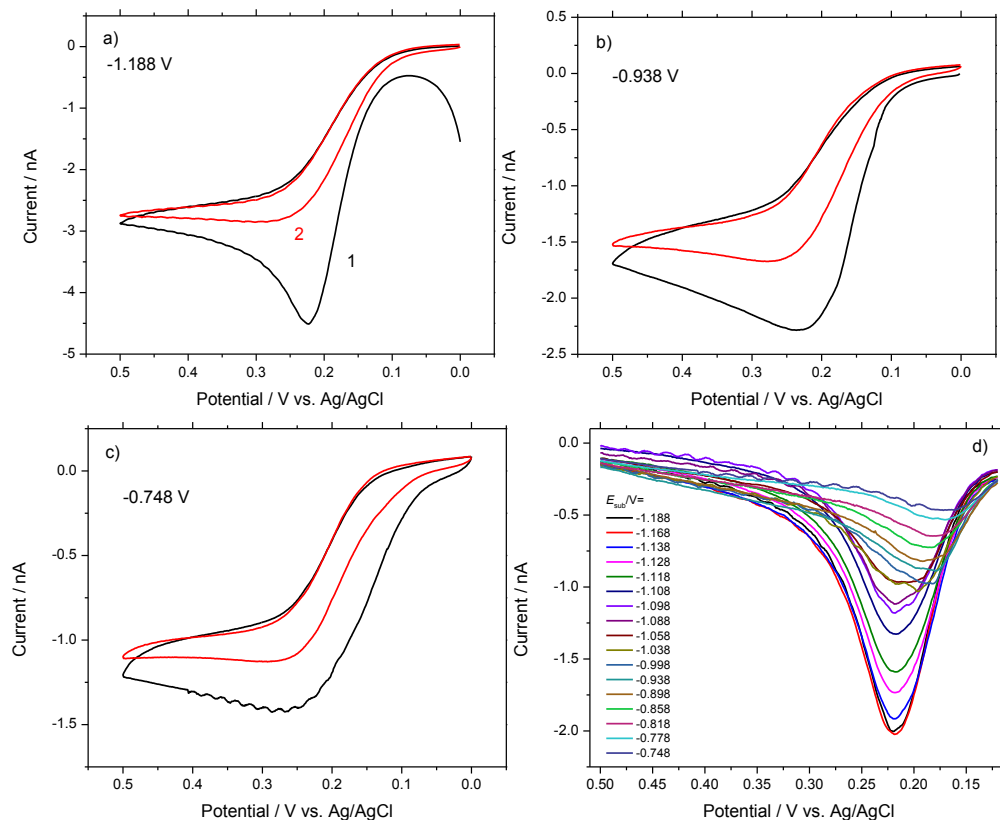
Titration curves

Figure S3. (a-c) Cyclic voltammograms (CVs) of the Pt tip electrode during titration at different potentials of the Ni substrate, v=50 mV s^{-1}; shown in red is the negative feedback CVs (2nd scan, after the full consumption of the surface analyte) in the absence of any surface analyte, therefore resembling that of a plain CV on a UME; the black traces are titration voltammograms that show a positive feedback response due to the interaction of the titrant (ferrocenemethanol^{+}) with the surface reduceable species, delivering positive feedback current to the tip electrode. The current diminishes quickly as the scan progresses, this phenomenon is due to the consumption of the surface analyte and that continuous generation of the surface species is blocked at open circuit (in absence of reducing potential) d) the curves obtained by subtracting curve 2 from curve 1. The integrated area is divided by the scan rate to obtain the charge of the active species.

Fitting the kinetics parameters

The exchange current density (j^0) in Table 1 is obtained by fitting the positive-going branch in Figure 2b in the potential range of -0.99 ~ -1.10 V. The standard reaction rate constant (k^0) is then calculated with Eq. S1.
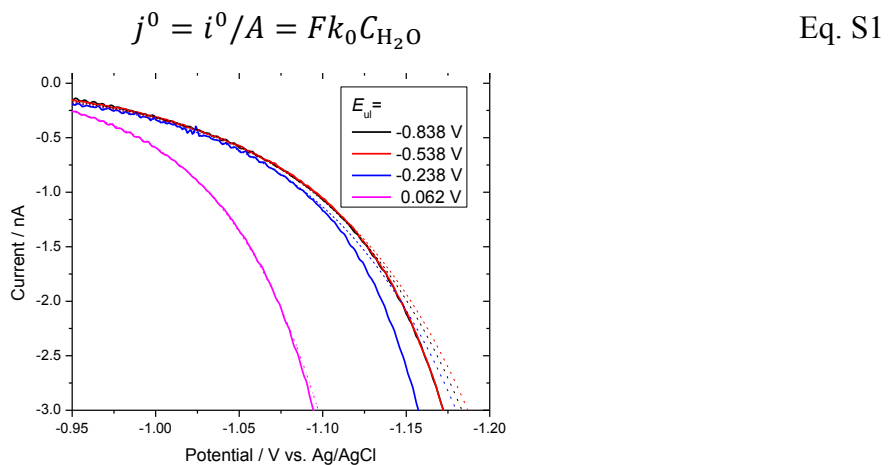
$$j^0 = i^0/A = Fk_0 C_{H_2O}$$
Eq. S1

Figure S4. The fitting results of the polarization curves.