

Supporting information for

Effect of interfacial water structure on the Hydrogen Evolution Reaction on Pt(111) modified with different Nickel Hydroxide coverages in alkaline media.

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Spectroscopic analysis by FTIR

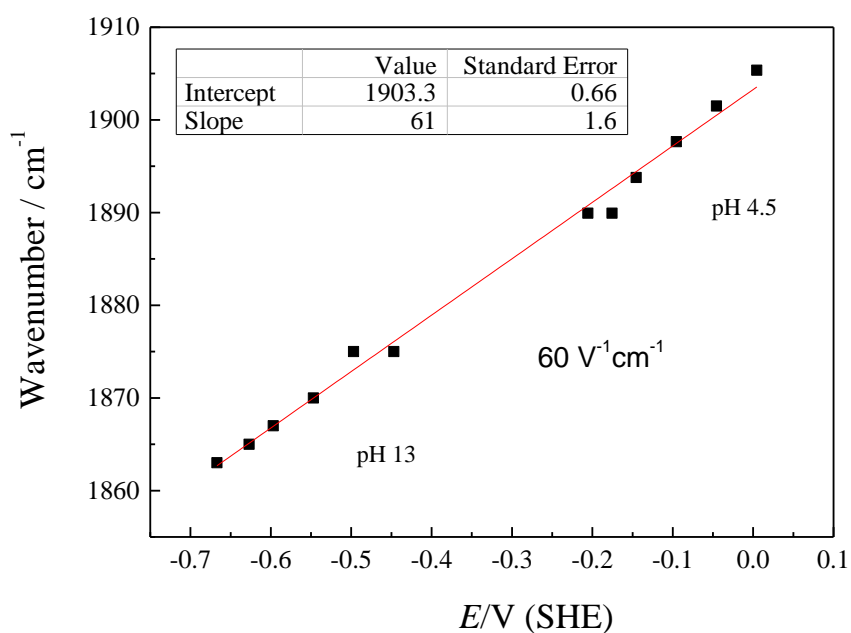


Figure S1. Plot of the wavenumber corresponding to CO adsorbed on nickel versus the potential (SHE) for alkaline and acid media.

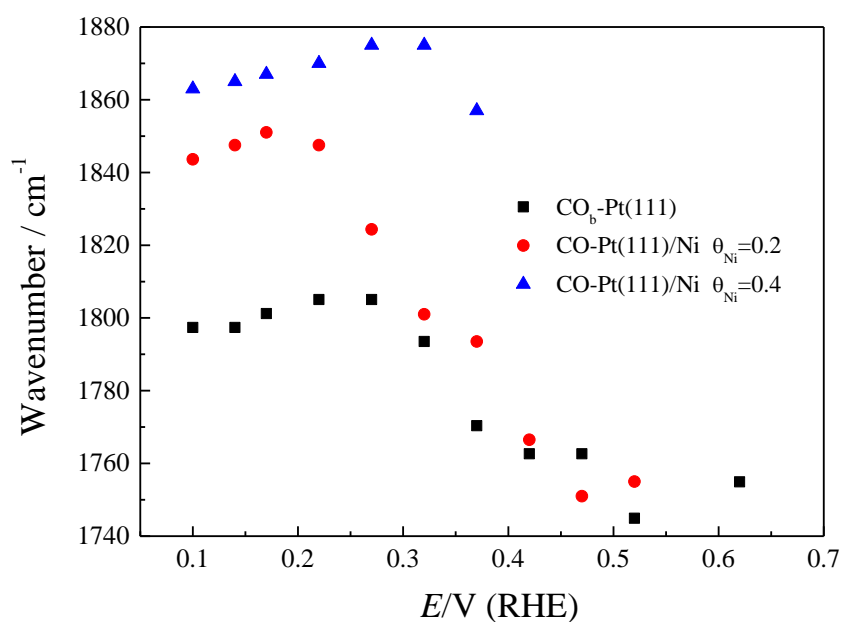


Figure S2. Plot of the wavenumber corresponding to CO adsorbed on Pt(111) (black) and Pt(111)-Ni(OH)₂ at 0.2 and 0.4 nickel coverages (red and blue respectively) versus the potential (RHE) for alkaline media.

Contribution to the total displaced charge from the residual charge on the CO covered surface, q_{CO}

$\theta_{Ni(OH)_2}$	q_{CO} ($\mu C/cm^2$)
0	-41.7
0.046	-45
0.07	-47
0.1	-47
0.22	-51
0.37	-57

Table S1. Contribution to the total displaced charge from the residual charge on the CO covered surface, q_{CO} , at 0.1 V (RHE) at pH 13 for each nickel coverage, calculated from the double layer capacitance and the estimated value of the potential of zero charge for the CO covered surface.

Determination of thermal coefficients from ΔE vs t laser transients.

In the absence of specific adsorption phenomena, or when adsorption phenomena responses are negligible in the microsecond scale, the potential change in the electrode after the laser perturbation follows the relaxation of the temperature in the interfacial region. By applying a simple thermal model, the temperature change with time can be estimated assuming that the only effect is the heating of the interfacial region, i.e., the non-reflected part of the laser is suddenly converted into heat. Then, linearization of potential electrode change with temperature allows calculating thermal coefficients, which are extracted from ΔE vs $t^{1/2}$ slopes, by using the next equation:

$$\Delta E = \frac{1}{2} \frac{\partial E}{\partial T} \Delta T_0 \sqrt{\frac{t_0}{t}} \quad (1)$$

where t_0 equals to 5 ns and ΔT_0 is the maximum temperature change achieved (25-30°C) which is obtained using a simple thermal model of heat diffusion including parameters such as the thermal conductivity, the thermal diffusivity of the metal and the solution, the laser intensity and the reflectivity of the surface.¹

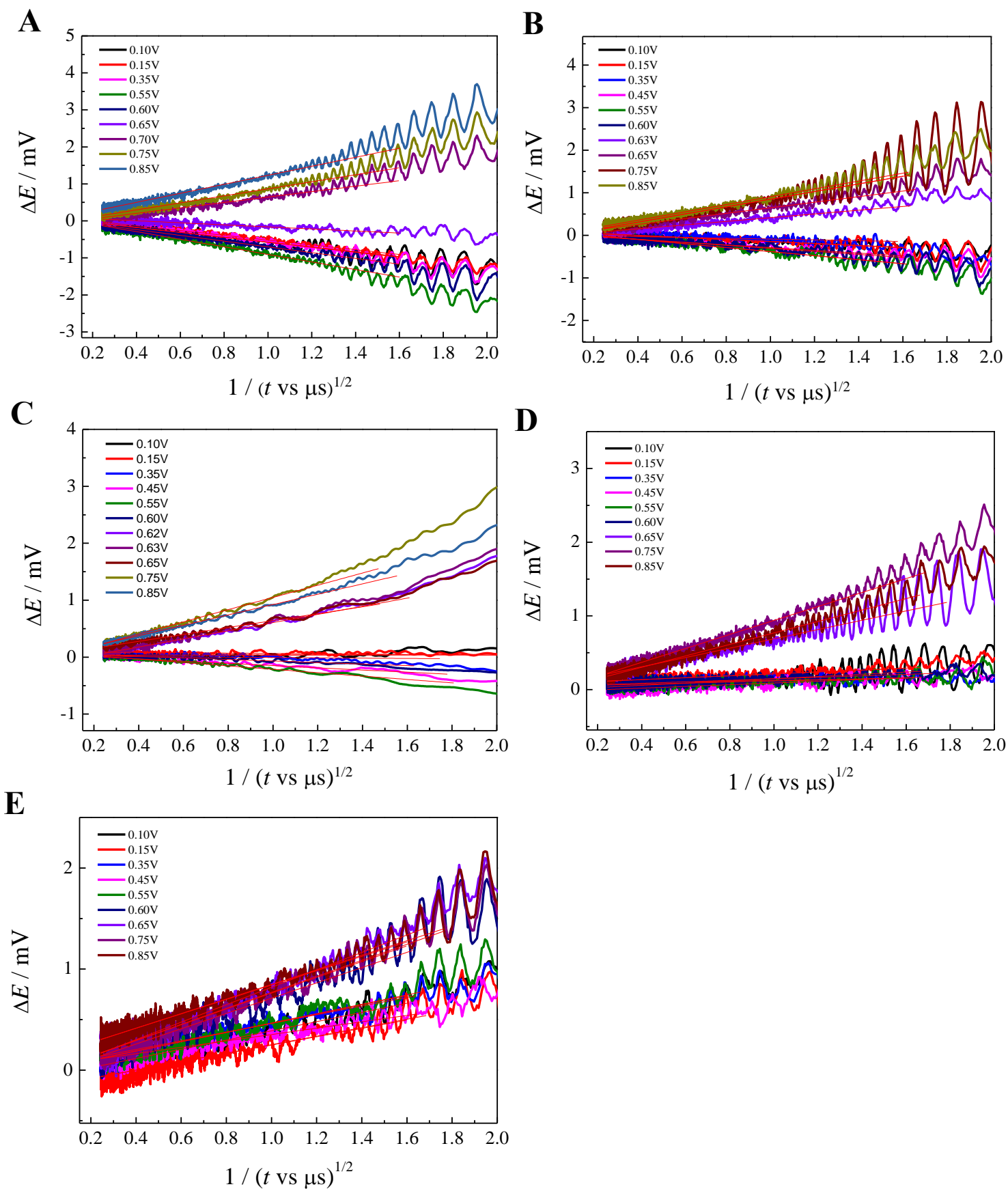


Figure S3: ΔE vs $t^{-1/2}$ for the $\theta_{\text{Ni(OH)}_2}$ recoveries: A) bare Pt(111), B) $\theta=0.07$, C) $\theta=0.15$, D) $\theta=0.22$, E) $\theta=0.37$.

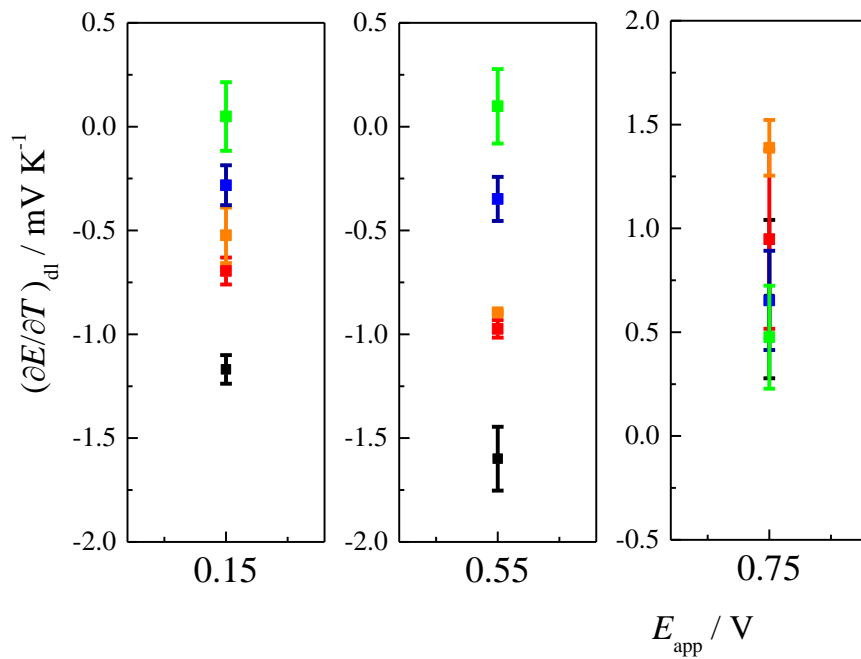


Figure S4: Thermal coefficients of double layer formation for the different $\theta_{\text{Ni(OH)}_2}$ at three applied potentials. $\theta_{\text{Ni(OH)}_2}$ equals to: black) Bare Pt(111), red) 0.07, orange) 0.15, blue) 0.22 and green) 0.37.

Thermal coefficients

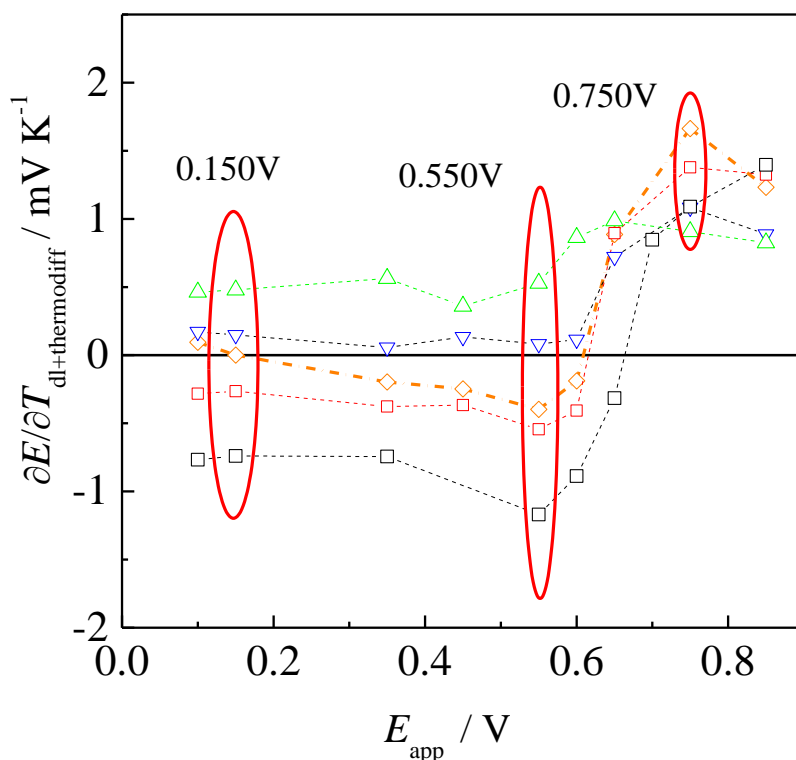


Figure S5. Thermal coefficients without thermodiffusion correction. Color legend: Black) Pt(111), and $\theta_{\text{Ni(OH)}_2}$ = red) 0.1, orange) 0.15, blue) 0.22 , green) 0.37.

The thermal coefficients are slightly overestimated since they contain a thermodiffusion potential. The thermodiffusion potential has its origin in the temperature difference between reference and working electrode, and causes a potential drop due to the motion of ions generated by this thermal gradient. Although in most cases this contribution was demonstrated to be negligible, the abnormal high mobility of OH^- increases the thermodiffusion potential, and makes necessary to correct it in order to provide more accurate results. A way to roughly calculate the thermodiffusion potential is from the Eastman entropies of transport and mobilities of the ions. It must be mentioned that ion mobilities available are those calculated for infinite dilution and then the thermodiffusion potential calculated is approximated, but gives an idea of how temperature gradients affect the measure of the electrode potential.²

References

- (1) Garcia-Araez, N.; Climent, V.; Feliu, J. 1 Temperature Effects on Platinum Single-Crystal/Aqueous Solution Interphases. Combining Gibbs Thermodynamics with Laser-Pulsed Experiments. In *Mod Asp Electrochem*, Vayenas, C. G., Ed. Springer New York: 2011; Vol. 51, pp 1-105.
- (2) Agar, J. N. Thermogalvanic Cells. Wiley-Interscience: New York, 1963; Vol. 3, pp 31-121.