The role of water in hydrogen electrocatalysis

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Appendix A: Supplementary Material for Chapter 2

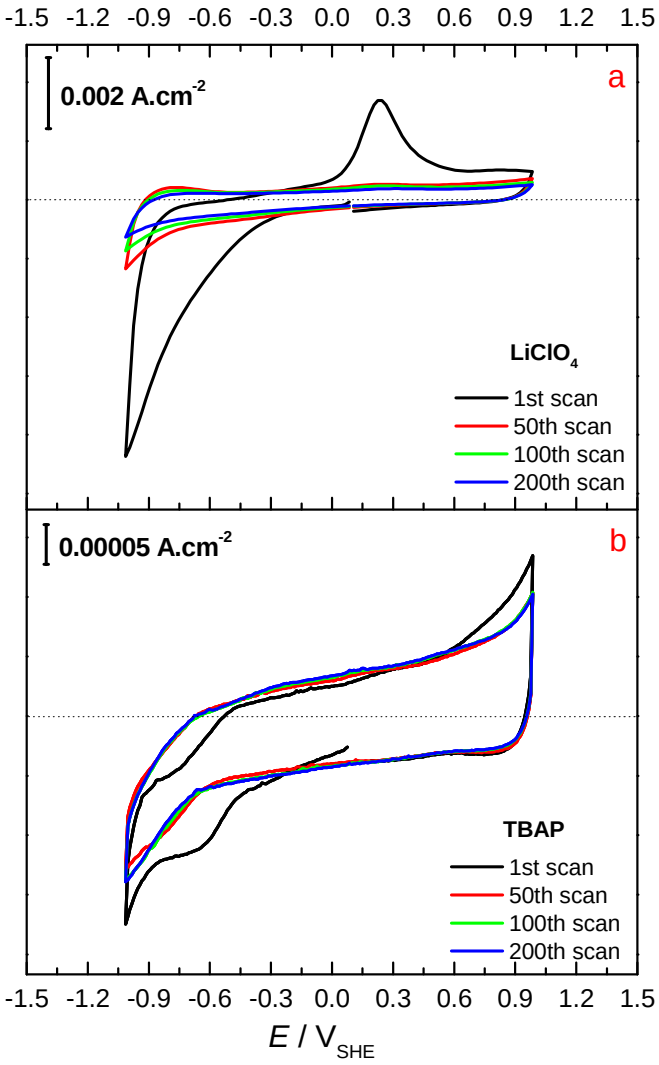

Figure A1. Cyclic voltammetries for a polycrystalline platinum wire in acetonitrile, containing: a) 100 mM $LiClO_4$ or b) 100 mM TBAP, as supporting electrolytes, under argon atmosphere. Scan rate: 500 mV/s. The horizontal dotted lines mark zero current.

Figure A1 shows the evolution in time of the blank voltammetries for polycrystalline platinum in acetonitrile, using $LiClO_4$ (Figure A1a) or TBAP (Figure A1b) as supporting electrolytes, in presence of argon. The scans were taken from 0.1 V_{SHE} towards cathodic potentials and back towards the anodic end potential. The background current for the solution with $LiClO_4$ is two orders of magnitude larger compared with the solution containing TBAP. For the $LiClO_4$ electrolyte, the interfacial water reduction starts at ca. -0.350 V_{SHE}, and in the anodic sweep shows a corresponding oxidation peak at ca. 0.050 V_{SHE}. It is noteworthy mentioning that the peaks observed in the first scan disappear from the second scan on (not shown), and that the system shows a similar double layer from the second till the last scan registered. For the TBAP electrolyte, we observe a redox couple at ca. -0.450 $V_{SHE,}$ assigned to the water reduction and oxidation, and the shape of the first scan disappears from the second scan on, adopting the shape shown in the consecutive scans.

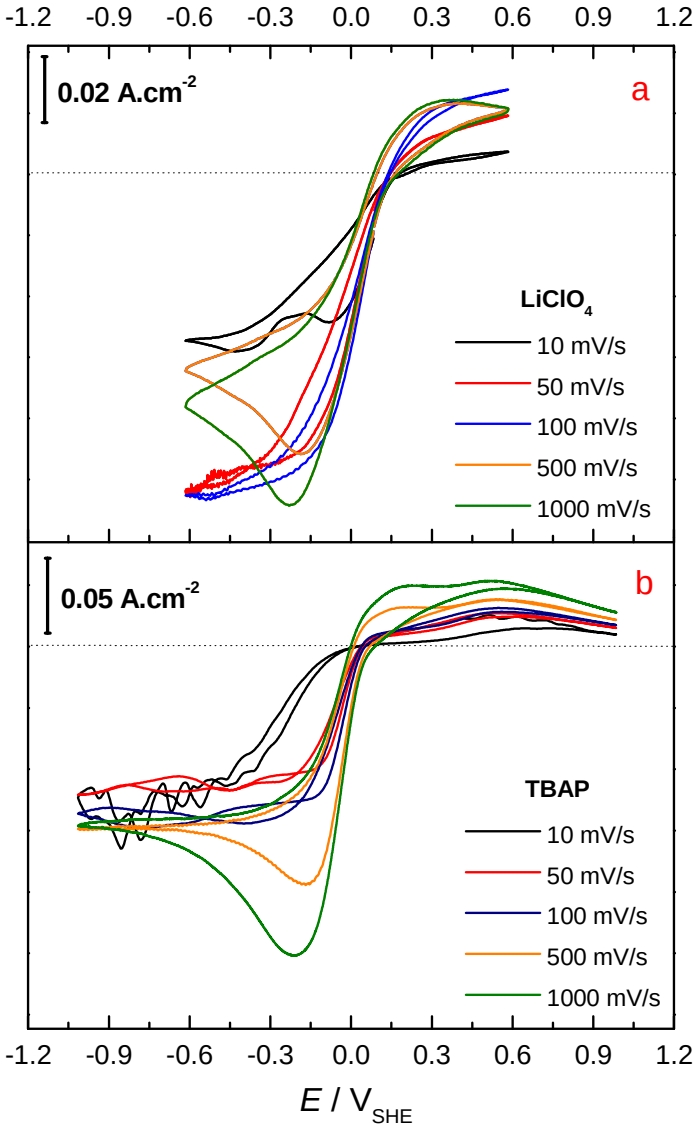

Figure A2. Cyclic voltammetries for a polycrystalline platinum wire in acetonitrile, in presence of 10 mM $HClO_4$, under hydrogen atmosphere. The second cycle is shown for each scan rate. a) 100 mM $LiClO_4$ or b) 100 mM TBAP, as supporting electrolytes. The horizontal dotted lines mark zero current.

Figure A2 shows the voltammetric response towards scan rate variations for polycrystalline platinum in acetonitrile, containing 10 mM $HClO_4$ and saturated with hydrogen, using $LiClO_4$ (Figure A2a) or TBAP (Figure A2b) as supporting electrolytes. The potential window for the measurements in Figure A2a was shortened to avoid formation and adsorption of lithium hydroxide on the electrode surface at low scan rates. The scans were taken from 0.1 V_{SHE} towards cathodic potentials and back towards the anodic end potential. Subfigures A2a and A2b depict an increase in current as a function of scan rate. As a general remark, we point out the fact that the voltammetries tend to get steeper with the increase in scan rate.

Figures A3 and A4 depict the SER spectra for the acetonitrile-$LiClO_4$ and acetonitrile-TBAP respective characteristic bands, under argon atmosphere, hydrogen atmosphere and after the addition of 10 mM of acid, under hydrogen atmosphere. From left to right, all three figures show the δ-C-CN, the v-C-C, the δ-C-H and the v-CN modes from the solvent as main features.

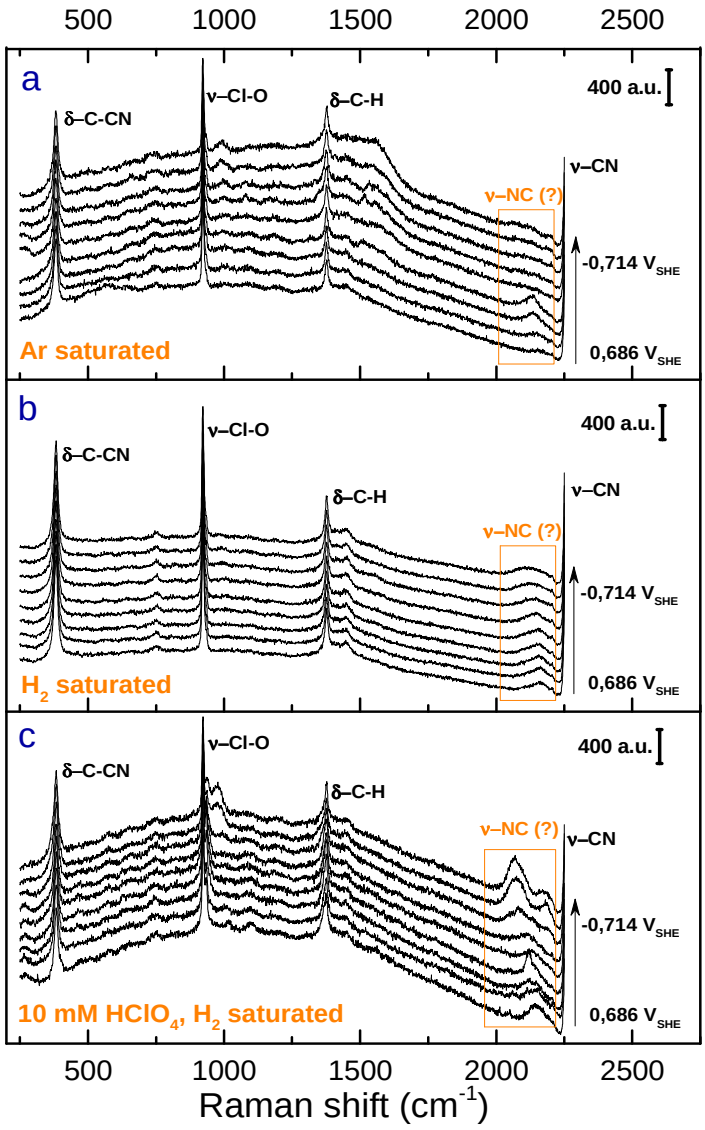

Figure A3. SERS spectra for acetonitrile, containing 100 mM $LiClO_4$ as supporting electrolyte.

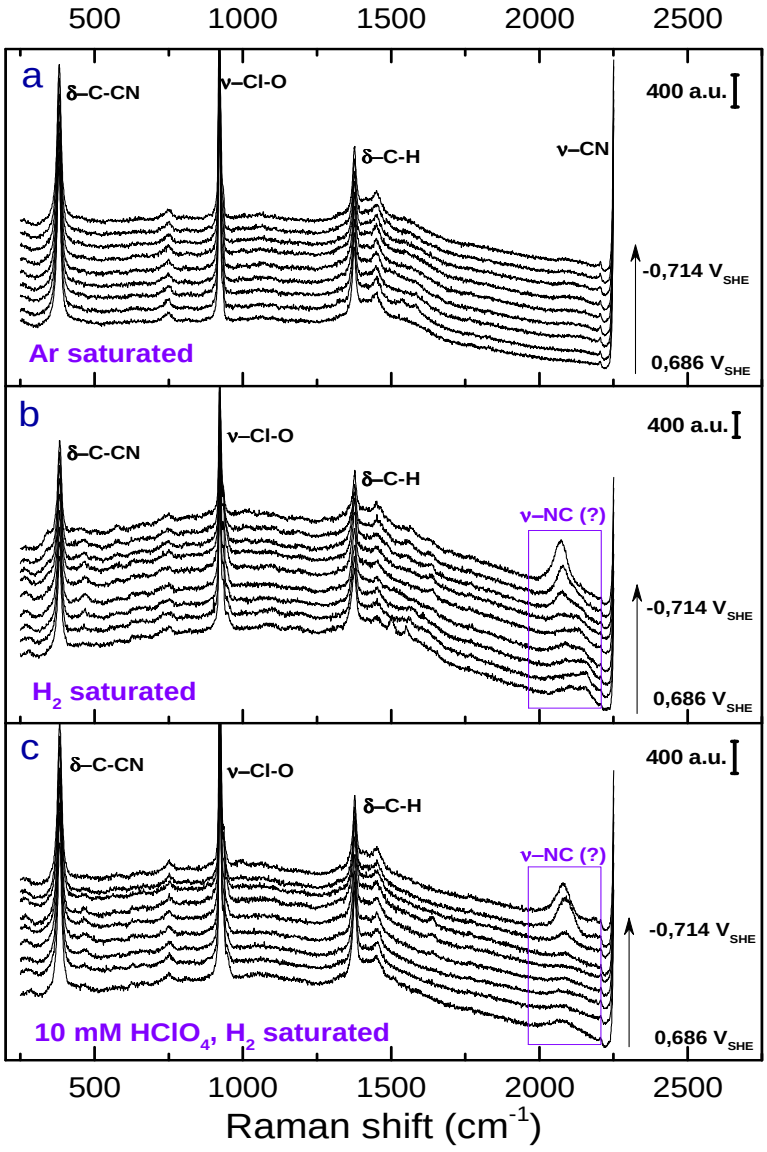

Figure A4. SERS spectra for acetonitrile, containing 100 mM TBAP as supporting electrolyte.

Figure A5 shows the SER spectra for 100 mM of TBAP in presence of acetonitrile and 50 mM of water, under argon atmosphere. We observe the characteristic bands for acetonitrile, and the ν-Cl-O mode for the perchlorate anion from the electrolyte. The spectra were collected from cathodic towards anodic potentials, starting at -1.014 V_{SHE} till 0.896 V_{SHE}, every 0.2 V. As a remarkable feature, we point out the formation of Pt-O around 0.496 V_{SHE}, at 520 cm^{-1}. Interestingly, the band from the ν-NC mode is weak and present only at positive potentials.

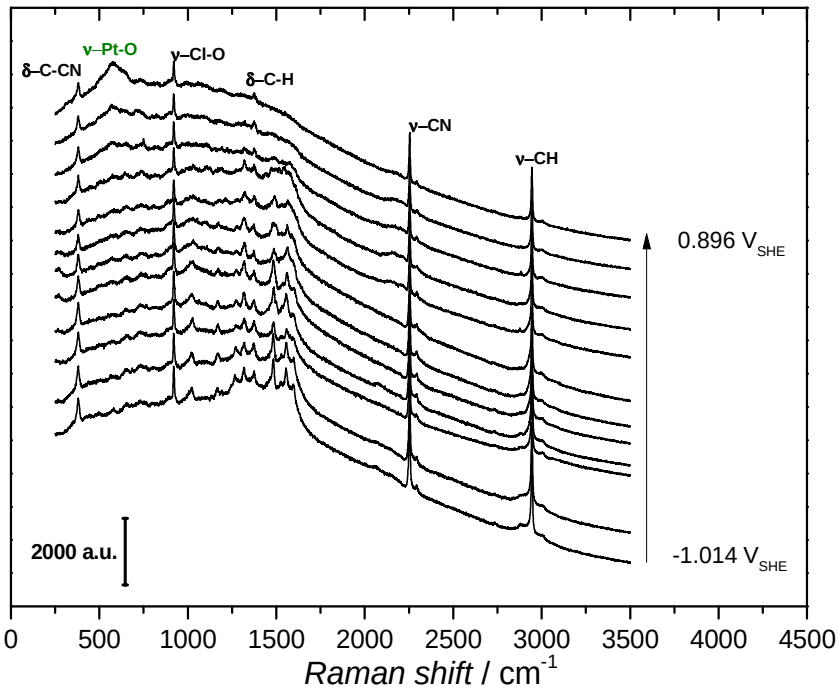

Figure A5. SERS spectra for acetonitrile, containing 100 mM TBAP as supporting electrolyte, after adding 50 mM H_2O. Argon atmosphere.

Figure A6 shows the SER spectra for 100 mM of TBAP in presence of acetonitrile and 50 mM of water, saturated with molecular hydrogen. This spectra also shows the characteristic bands for acetonitrile, and the ν-Cl-O mode for the perchlorate anion from the electrolyte. The spectra were collected using the same procedure as described for Figure A5. However, there is no evidence for the formation of Pt-O in presence of hydrogen, and the band corresponding to the ν-NC mode is present in the whole potential range studied.

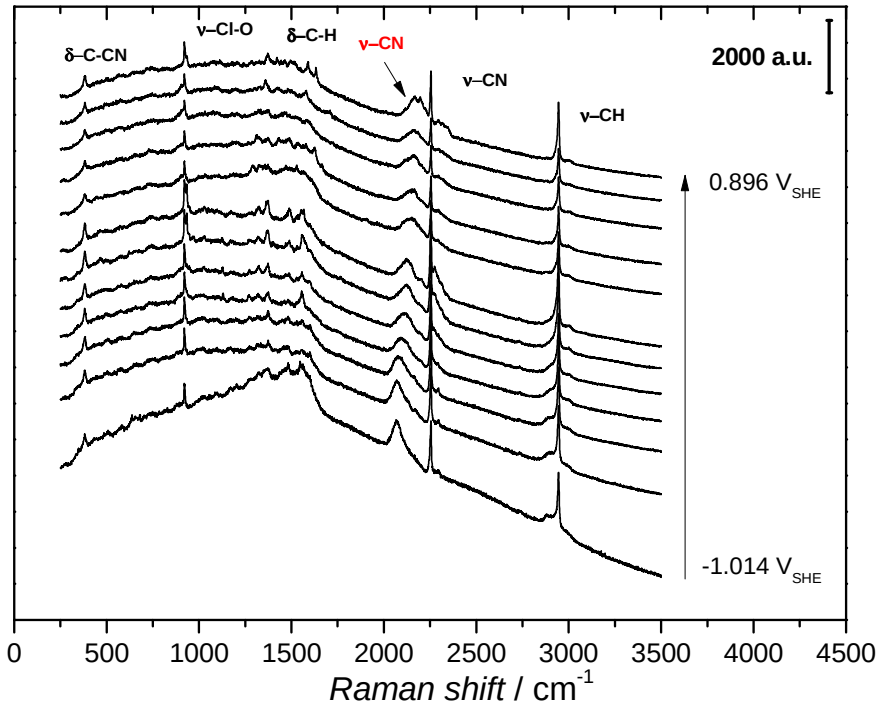

Figure A6. SERS spectra for acetonitrile, containing 100 mM TBAP as supporting electrolyte, after adding 50 mM H_2O. Hydrogen atmosphere.

Appendix B: Supplementary Material for Chapter 4

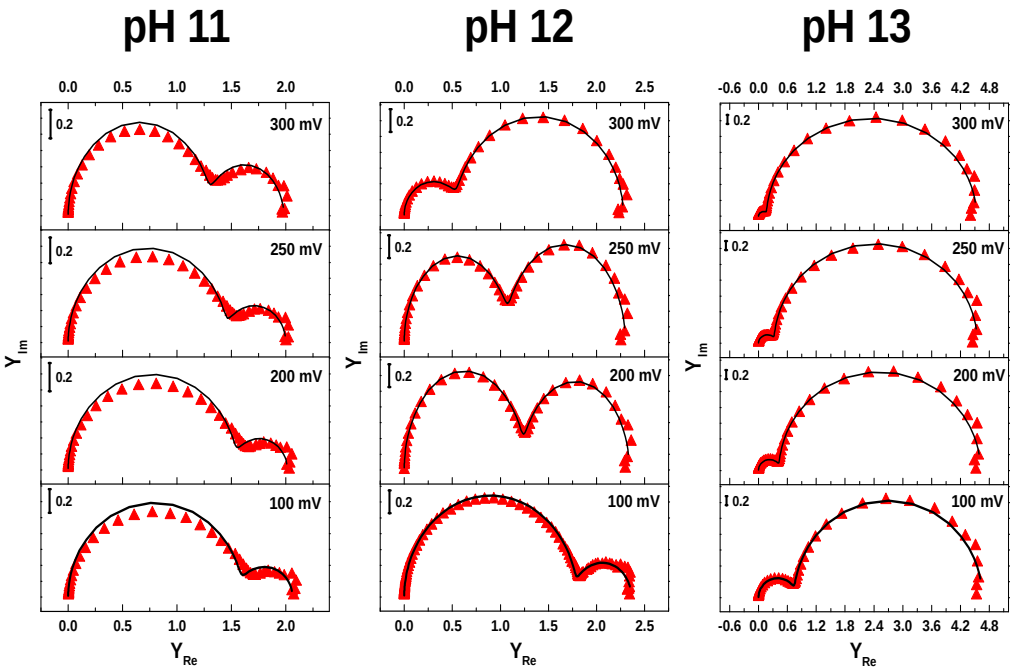

Figure B1. Admittance Nyquist plots for Pt(111) in 0.1 M solutions for different pH values, measured with frequencies ranging from 10 kHz to 0.1 Hz and an amplitude of 5 mV, at 0.1, 0.2, 0.25 and 0.3 V_{RHE}: the dots represent the experimental data points collected, while the solid lines correspond to the fit obtained using the EEC.

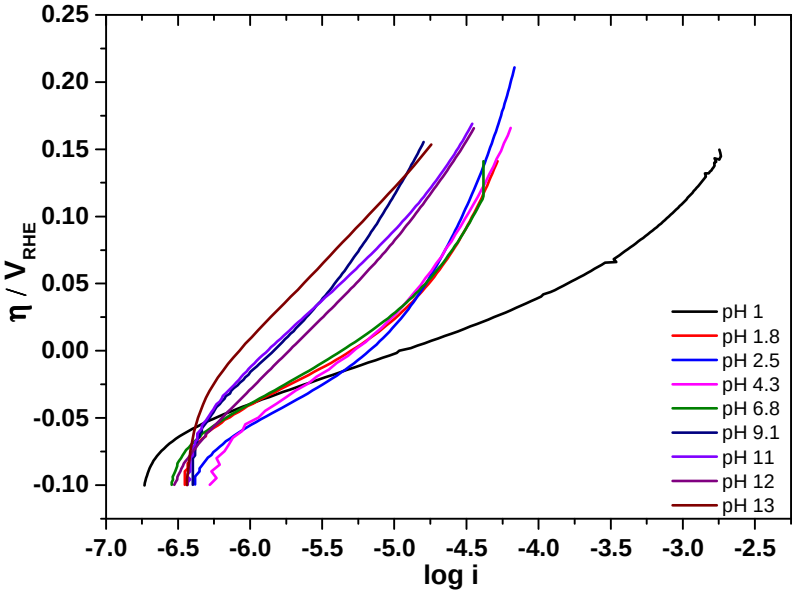

Figure B2. Tafel plots for Pt(111) in solutions with 0.1 M ionic strength and different pH values (see legend). Scan rate: 10 $mV.s^{-1}$.

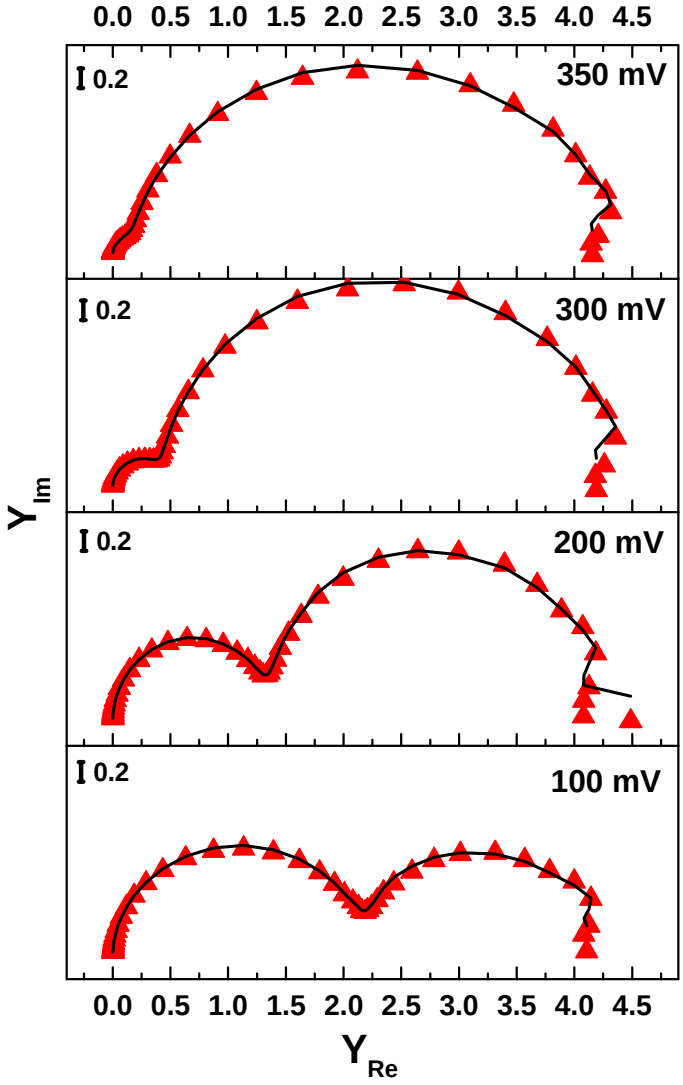

Figure B3. Admittance Nyquist plots for Pt(111) decorated with 0.14 ML of $Ni(OH)_2$ in 0.1 M NaOH (pH 13), measured with frequencies ranging from 10 kHz to 0.1 Hz and an amplitude of 5 mV, at 0.1 V_{RHE}: the dots represent the experimental data points collected, while the solid lines correspond to the fit obtained using the EEC.