Challenges of Modelling Real Nanoparticles: Ni@Pt Electrocatalysts for the Oxygen Reduction Reaction

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Supplementary Information

Table S1. Spectral fitting parameters from Ni $2p_{3/2}$ and Pt 4f of Ni-Core and $Ni_x@Pt_{1-x}$ catalysts.

Sample	Binding Energy (eV)				
	Ni-Met	**NiO**	**$Ni(OH)_2$**	**Pt-Met**	**PtO**
Ni-Core	852.49	853.85	-	-	-
$Ni_{82}@Pt_{18}$	852.50	853.78	855.47	71.05	72.25
$Ni_{62}@Pt_{38}$	852.44	853.88	855.70	71.07	72.25
$Ni_{56}@Pt_{44}$	852.50	853.90	855.70	71.04	72.25
$Ni_{30}@Pt_{70}$	852.40	853.76	855.45	71.10	72.25

†Average binding energy for metallic Pt-$4f_{7/2}$ (71.05 ± 0.17 eV) considering values reported in http://srdata.nist.gov/xps/.

Table S2. XRD parameters calculated by Rietveld analysis for the Ni-core and $Ni_x@Pt_{100-x}$ catalysts.

Parameters	**Ni-Core**	**$Ni_{82}@Pt_{18}$**	**$Ni_{62}@Pt_{38}$**	**$Ni_{30}@Pt_{70}$**
Lattice Parameter (Å) [Ni/Pt]	3.524/-	3.5256/3.7980	3.5295/3.9167	3.5210/3.8448
Crystal Size (nm) [Pt]	-	10	-	9.3
Phase (%) [Ni/Pt]	100/-	82.9/17.1	61.8/38.2	34.3/65.7
2 theta (111) [Ni/Pt]	44.26/-	44.3/40.92	44.38/39.86	44.26/39.68
Rwp	1.11	1.25	1.74	1.7

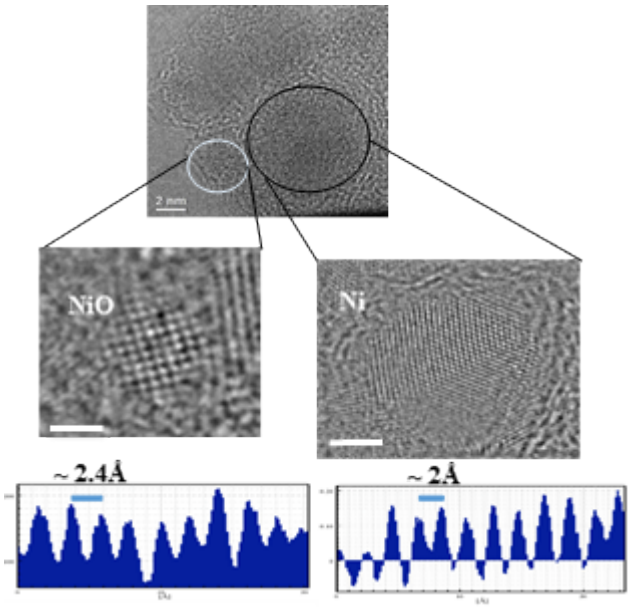

Figure S1. Set of experimental atomic resolution transmission electron microscopy (ARTEM) images of Ni-core at different defocus settings using 60 $e^{-}Å^{2}s$ (above) together with phase images calculated from the exit wave reconstruction procedure (middle). Intensity profile from the phase image on the larger Ni and smaller NiO nanoparticles

Figure S1 depicts a set of core-nanoparticles obtained by using low dose-rate electron microscopy in order to assure the structural integrity. A bimodal size distribution with small (~ 1 nm) and big nanoparticles (~ 9 nm) were characterized. According to the intensity profile from the phase image, the structure was different in both nanoparticles. The small were more likely correlated with NiOx while the big nanoparticles present a structure related to metallic Ni. This observation agree with that observed by XPS were both phases were detected.

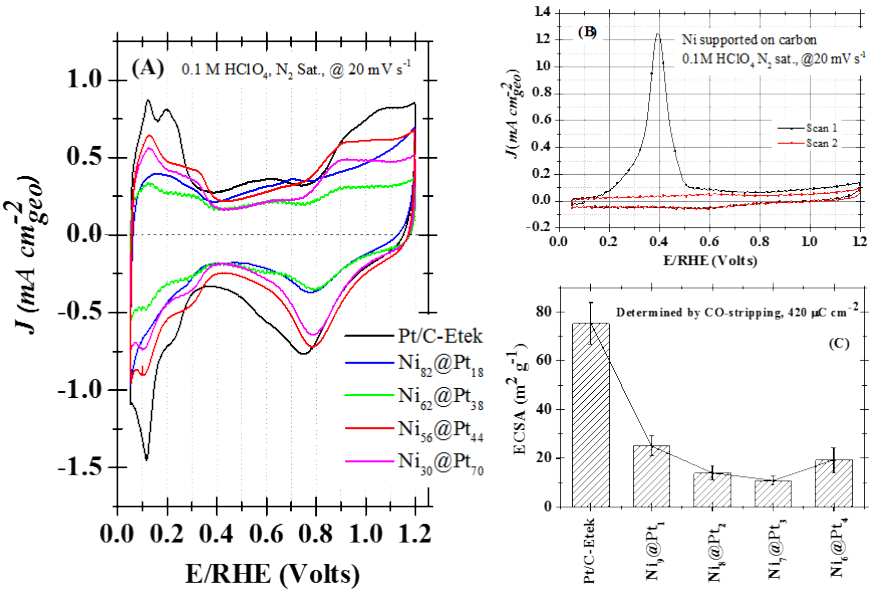

Figure S2. A) Set of potentiodynamic curves of Pt/C-Etek and $Ni_x@Pt_{100-x}$/C catalysts in N_2 purged electrolyte 0.1 M $HClO_4$. B) Potentiodynamic curve of carbon supported Ni-core in 0.1 M $HClO_4$ saturated with N_2. C) Electrochemical surface area (ECSA) determined by CO-stripping.

As a systematic procedure, the immersion potential of working electrode was controlled at 0.1 V/RHE, then cycled several times to attained a stable curve (Figure S2A). The control of plunging potential was carried out in order to monitoring likely leaking of Ni from the catalysts. The presence of unstable nickel species were characterized through an oxidation process around 0.4 V as exemplified in the Figure XB, where Ni nanoparticles used as core without Pt on surface were swiped in similar condition. The CV curves for $Ni_x@Pt_{100-x}$ catalysts (Figure S2A), resembled the characteristic profiles for typical high-surface-area polycrystalline Pt used as reference (Pt/C-Etek). The three different potential zones ascribed to hydrogen UPD (0.05-0.4 V), double layer capacitance (04-0.8 V) and oxide formation/reduction (E > 0.8 V) were distinguished. Only $Ni_{82}@Pt_{18}$ displayed a very little peak related with Ni-leaking during the first scan (not show), accordingly with partial coverage of Pt on the surface of Ni-core

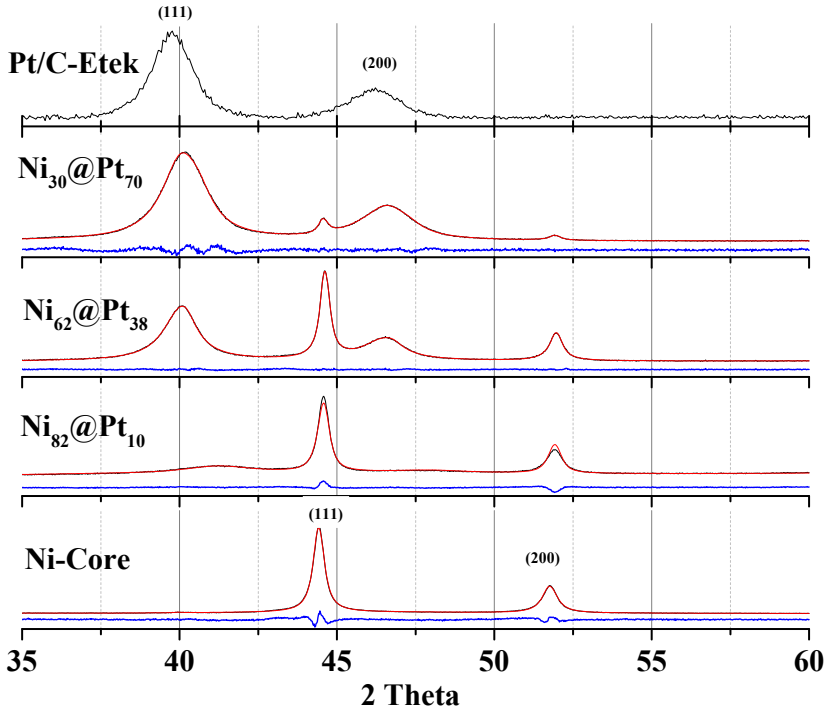

Figure S3. Rietveld refinement XRD patterns for samples Pt/C-Etek, Ni-core and $Ni_x@Pt_{100-x}$ core-shell electrocatalysts. The experimental data are shown as Black line. The calculated data and the differences between experimental and fitted parameters are represented as Red and Blue line respectively.