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S. Dessources, C. Morais, C. Canaff, Teko Napporn, K.B. Kokoh. Ensemble effects of nickel in surfactant-less prepared Pt-Ni materials on the carbon monoxide oxidative removal. *Journal of Solid State Electrochemistry*, 2020, 25 (1), pp.219-223. <10.1007/s10008-020-04817-6>. <hal-03055005>

HAL Id: hal-03055005

<https://hal.science/hal-03055005v1>

Submitted on 11 Dec 2020

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Ensemble Effects of Nickel in Surfactant-less Prepared Pt-Ni Materials on the Carbon Monoxide Oxidative Removal

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Abstract

This work reports the effect of the Ni content in a Pt_xNi_y/C electrode on the CO oxidation reaction. A series of complementary and physicochemical techniques reveal the surface modification by the formation of Pt and Ni hydroxides which contribute to the removal of such model poisoning molecule in the utilization of organics as fuel in fuel cell applications. This cooperative activation of bimetallic materials, prepared without any organic surfactant, occurs at lower and lower potentials. As a result, a large 270 mV cathodic shift is observed when increasing the Ni amount up to 80% in the Pt_xNi_y composition. XPS measurements are correlated with the electrochemical characterization of the Pt_xNi_y/C electrodes surface through CO stripping investigations. Although there is a low shift of the Pt 4f_{7/2} peak, the presence of Ni-OH species in the close environment of Pt-CO_{ads} mainly contributes to change the Langmuir-Hinshelwood mechanism into a bifunctional one which takes place at *ca.* 0.40 V vs. RHE

Keywords: Pt_xNi_y electrocatalyst; CO-to-CO₂ mechanisms; CO-stripping; BAE synthesis method

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This paper is dedicated to Professor José H. Zagal on the occasion of his 70th birthday and in recognition of his outstanding contribution to electrocatalysis.

Introduction

In the Direct Alcohol Fuel Cells (DAFCs) investigations, carbon monoxide (CO) is pointed out as the main poisoning intermediate through its strong adsorption at the Pt-based electrode surface [1-4]. The development of such solid polymer electrolyte (SPE) systems involves the design of materials capable of releasing the electrode surface at lower potentials, which prolongs the durability of the catalytic process [5, 6]. Amongst the main alcohols commonly studied as promising fuels for sustainable applications such as SPE fuel cells, our research group contributed during these last decades to the possible development of DMFC (methanol) [7, 8], DEFC (ethanol) [9-11] and DGFC (glucose) [12, 13]. As can be evidenced through this literature, the breakthrough consists in adding a co-catalyst (Sn, Co, Ru, Ni,...) in the electrode composition to remove from the anodic surface at low potential values the remaining adsorbed CO formed during the alcohol oxidative conversion at the Pt-based material. This activity promoting element which is often a transition metal (TM) is considered to modify chemically, geometrically or electronically the properties of platinum. Consequently, the reaction can be controlled by the so-called bifunctional mechanism. If Sn and Ru were considered to contribute, respectively, to electronic and geometric effects in the enhancement of Pt electroactivity towards alcohol oxidation, Ni is a thermodynamically stable TM in alkaline medium and can play a co-catalyst role in the Pt-M anode towards alcohol oxidation. We synthesized by a surfactant-less method, *e.g.* a bromide anion exchange approach, Pt-based catalysts for which the precious metal loading was “diluted” by adding various nickel amounts in order to investigate the effect towards the removal of CO from the electrode surface. This synergistic contribution of Ni observed by combining XPS and electrochemical methods (CO stripping/voltammetry) results in “ensemble effects” [14, 15], hard to discriminate and mainly

composed of chemical (early formation of hydroxyl species at the electrode surface), electronic (shift in Pt4f) and geometric properties in the Pt_xNi_y electrode materials.

Experimental

The “Bromide Anion Exchange” (BAE) method, recently reported in ref. [16] was adapted to synthesize a large range of Pt_xNi_y/C nanoparticles (x and y being the molar ratios of Pt and Ni, respectively) [17]. The carbon substrate (Vulcan XC-72R, Cabot), used as matrix for preparing Pt_xNi_y/C materials with 20 wt.% metal loading, was previously heat-treated at 400 °C under N₂ atmosphere for 4 h. XPS was also used to probe and characterize the surface and oxidation states of the obtained Pt-based materials. Analysis was performed in a high vacuum chamber on a Kratos Axis Ultra DLD spectrometer at pressure $\leq 9 \cdot 10^{-8}$ Pa, with a monochromatic radiation source (Al_{K α} : 1486.6 eV) operating at 150 W (15 kV and 10 mA). Survey spectra were recorded with a step of 1 eV (transition energy: 160 eV), which permits to check after the cleaning step whether the as-prepared materials do not contain any impurities (boron and bromide species from NaBH₄ and KBr). Based on the collected basic information, high-resolution XPS spectra were collected at a step of 0.1 eV (transition energy: 20 eV). XPS peaks were fitted using Gaussian–Lorentzian profile function and asymmetry determined from an etched bulk Pt metal. The cross-section Tougaard background has been chosen. It should be noted that a systematic subtraction of the background noise preceded the normalization of the spectra and the measurement of binding energies (BE) was corrected based on the energy of C1s at 284.4 eV (Vulcan XC 72R carbon). Quantifications were done from the corresponding XPS peak area after correction with suitable sensitivity factors and the CASA XPS software was used for peak fitting. The electrochemical measurements were conducted in a three-electrode Pyrex cell using a potentiostat EG&G PARC Model 362 (Princeton Applied Research). The current densities were normalized with the constant metal loading (79.3 μ g

cm⁻²) deposited onto a glassy carbon disc (0.071 cm² geometric surface area). This avoids expressing the activity of the Pt-based catalysts as function of the electrochemical active surface area, dependent of the Pt content, which decreases with the Ni addition. The CO stripping measurement consists of adsorbing during 5 min CO at constant potential of 0.1 V vs. RHE until the current decreases down to the capacitive one. Subsequently and at the same applied potential, nitrogen was bubbled in the solution during 25 min in order to remove remaining free CO. Afterwards, cyclic voltammetry (CV) was performed for recording 2 consecutive cycles: the first one permitted to oxidize adsorbed CO, while the second CV permits to confirm the complete oxidation of adsorbed CO since the first run. The shift of the main oxidative peak position, known to be at ca. 0.7 V vs. RHE at the Pt surface, allows appreciating how active the Pt_xNi_y catalyst as ensemble effects.

Results and discussion

The Pt_xNi_y/C materials were successfully prepared by the BAE method [17]. From our previous paper [17], data from different physicochemical characterizations were summarized in Table 1. XRD analysis revealed that the increase of Ni content in Pt_xNi_y/C materials, leads to the formation of Ni(OH)₂ species which presence was observed at 33.5 and 59.3° 2θ values, respectively [17]. Consequently, samples with a high Ni content (y_{Ni} > 0.5) lead to a wide range of particles size (2 to 30 nm) due to the presence of these species, which are amorphous-like and not well crystallized. Therefore particles and crystallite size were not assessed for pure Ni/C to avoid any error of estimation.

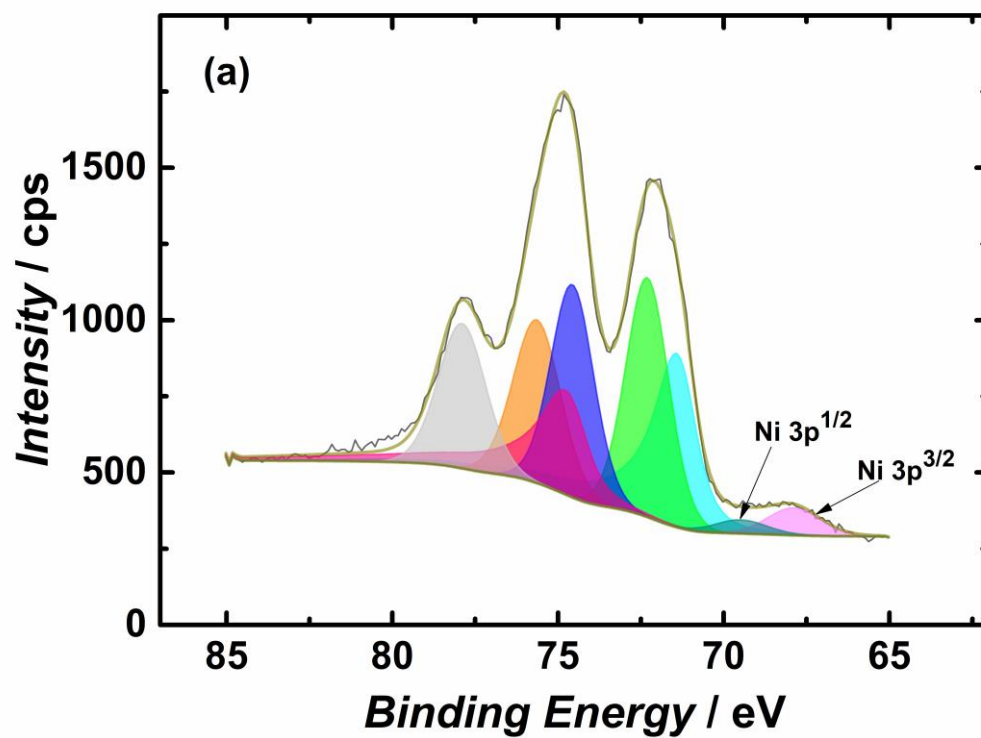
Table 1. Physical properties of Pt_xNi_y materials obtained from TGA/DTA, XRD and TEM measurements

	Pt _x Ni _y					
	1:0	0.7:0.3	0.5:0.5	0.3:0.7	0.2:0.8	0:1
Molar ratio	1:0	0.7:0.3	0.5:0.5	0.3:0.7	0.2:0.8	0:1
Metal loading (%)	20.6	19.3	22.0	23.2	22.8	21.3
<i>L</i> _v /nm (XRD)	4.9	4.5	3.5	3.2	3.5	-
<i>D</i> _m /nm (TEM)	2 to 11	2 to 9.5	1.5 to 7	2 to 20	3 to 35	-

Further to these results, we scrutinized herein XPS measurements and the correlation with releasing the electrode surface from CO poisoning.

To provide relevant additional insights on the ensemble effects responsible for the CO-to-CO₂ oxidative removal at lower potentials, the material surface state was investigated through XPS analysis (**Fig. 1**). Therefore, observations are focused on the modifications of the Pt4f regions in the different prepared Pt_xNi_y materials. As can be seen in **Fig. 1a**, the 4f_{7/2} and 4f_{5/2} peaks are centered respectively at 71.2 eV and 74.5 eV in Pt/C, as reported [18]. The decomposition of these peaks suggests that the Pt material is mainly composed of Pt⁰ (peaks at 71.1 and 74.5 eV), but it also contains two Pt oxide/hydroxide including Pt²⁺ (peaks at 72.1 and 75.5 eV) and Pt⁴⁺ (peaks at 74.6 and 77.7 eV). This speciation analysis reveals that the increase of the nickel content enhances the oxide/hydroxide species in the Pt_xNi_y/C samples, which reaches *ca.* 25% (for Pt²⁺) and 22% (for Pt⁴⁺) (**Fig. 1a**). Even if the Pt4f_{7/2} peak is partially in the PtNi-based materials, **Fig. 1b** shows a slight shift in binding energy which can be associated with an electronic change in the precious element when increasing the nickel content as the ligand effect associated with the nickel amount stops having effect. From the physicochemical characterizations, it can be pointed out that introduction of the Ni element in the Pt structure leads to the formation of nickel hydroxide and Pt oxide/hydroxide species in the prepared Pt_xNi_y/C catalysts. In addition to this chemical effect, the ligand one was evidenced by XPS

measurements. Indeed, we are wondering how the ensemble effects match for releasing the electrode surface in the CO-to-CO₂ removal at lower electrode potentials.



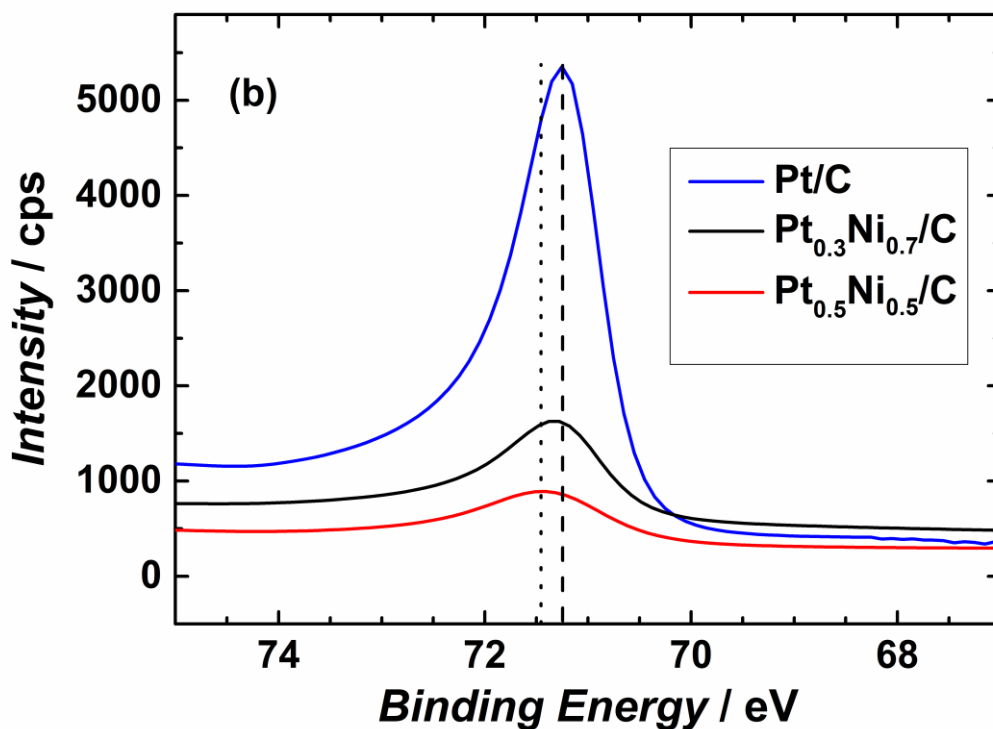
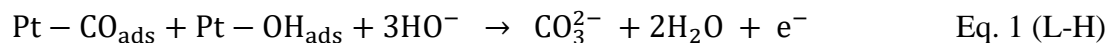


Fig. 1. High resolution XPS spectra of the $\text{Pt}_x\text{Ni}_y/\text{C}$ materials prepared from the BAE method. a) $\text{Pt}4f$ and $\text{Ni}3p$ in the $\text{Pt}_{0.5}\text{Ni}_{0.5}/\text{C}$ material; b) $\text{Pt} 4f_{7/2}$ peak shift of Pt-based materials.

As shown in **Fig. 2**, the electrochemical characterization of the electrode materials was performed through the CO stripping technique described above in the experimental section. A voltammogram of a Pt/C electrode in the absence and presence of CO (**Fig. 2a**) was first recorded to optimize the operating conditions of the electrochemical investigations. Therefore, the three main regions of the signature of a Pt electrode (reversible hydrogen adsorption/desorption, Pt double layer and irreversible Pt hydroxide/oxide) in alkaline medium can be well observed in this voltammogram in the second cycle. It is worthy of noting herein that the upper potential limit was set at the common one in Pt (*i.e.*, we do not consider a higher potential of the NiOOH formation (*ca.* 1.32 V vs. RHE), which is convenient for comparing all the as-prepared $\text{Pt}_x\text{Ni}_y/\text{C}$ materials including Pt/C with the same upper potential limit). Actually, if CO is the main intermediate compound which prevents advanced oxidation of carbonaceous

fuels, the strategy that consists in removing it by bifunctional mechanism deserves to be more investigated. CO-stripping was performed onto Pt_xNi_y/C catalyst prepared by bromide anion exchange method. One of the various advantages of the surfactant-less BAE method is that no pre-treatment is required before electrochemical experiments [19, 20]. This means that the electrocatalysts keep for sure the as-prepared aspects and structure at the beginning of the CO-stripping which is a sensitive electrochemical surface probing technique to evaluate the activity of an electrode. Before each CO-stripping the background cyclic voltammogram (CV) of the catalyst in the supporting electrolyte was recorded. One observes in **Fig. 2a** a main CO oxidation peak (A) at 0.67 V vs. RHE. It is commonly assigned to the CO-to-CO₂ oxidative removal following the Langmuir-Hinshelwood (L-H) mechanism [21, 22], which proceeds by a concerted desorption of Pt-CO_{ads} and Pt-OH_{ads}, the latter adsorbate being the result of the dissociative adsorption of H₂O molecules (or HO⁻ adsorption in alkaline medium).



Peak A is preceded by two shoulders (B and C) that are located at 0.58 and 0.40 V vs. RHE, respectively. It was reported that CO oxidation at 0.58 V vs. RHE occurs on terrace sites with (110) orientation, while that at 0.40 V vs. RHE is taking place on kink-type defects [19, 23].

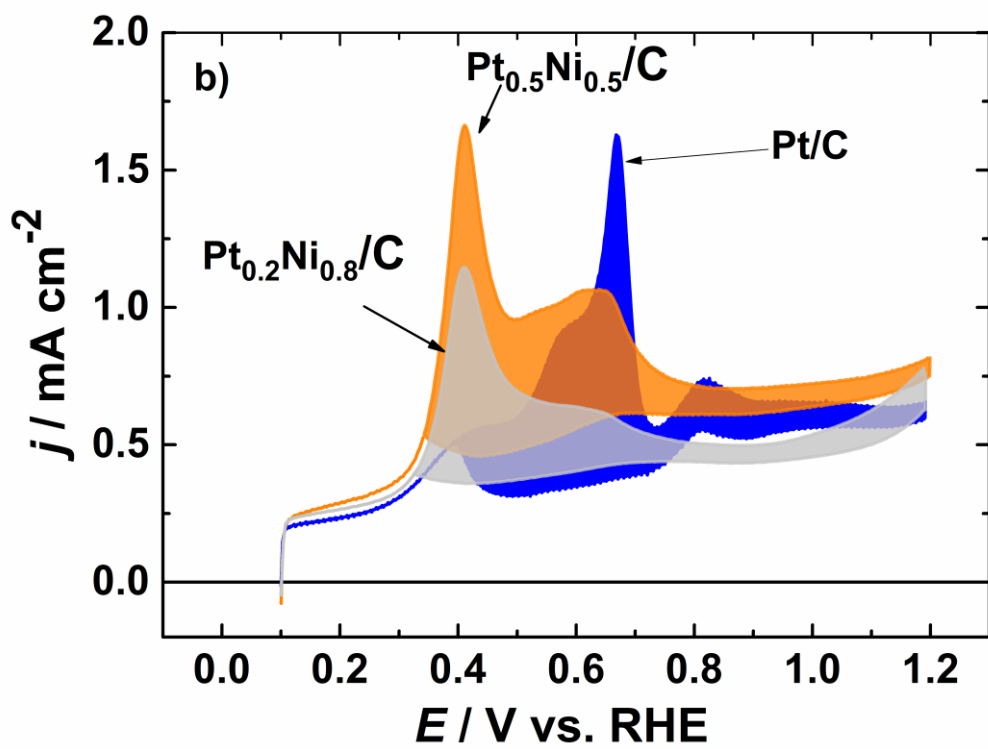
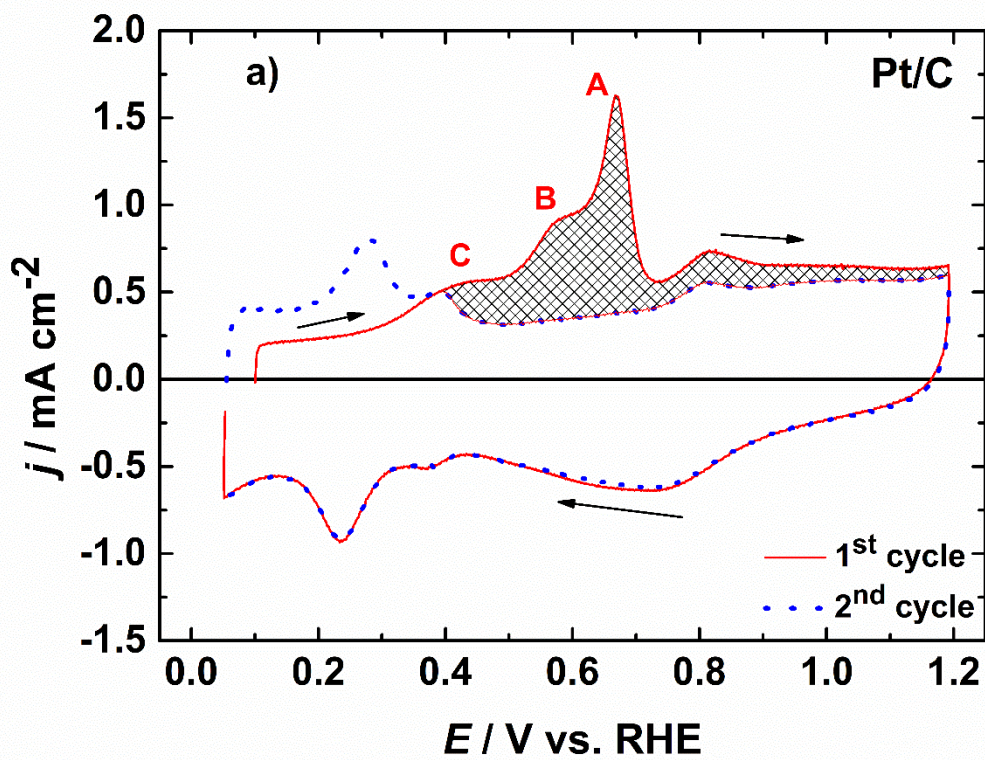


Figure 2. CO-stripping of different molar ratio Pt_xNi_y/C catalysts in a CO-saturated solution containing 0.1 mol L⁻¹ NaOH recorded at 20 mV s⁻¹ and at 21 °C; a) 1st cycle (red line, presence of CO) and second one (blue dot, absence of CO) at the Pt electrode surface; b) CO stripping curves on two Pt_xNi_y/C bimetallics compared with Pt/C electrode.

Addition of nickel in the Pt-based material composition increases the peak current at 0.4 V vs. RHE, synonymous of the electronic transfer of element which downshifts the center of the d-band with respect to the Fermi level of Pt 4f (**Figure 1**). This enhancement of the activity of the electrode at lower potentials is undoubtedly due to the increasing formation of Ni(OH)₂ species up to a molar ratio of $y_{Ni} = 0.8$ (**Figure 2b**). As at this electrode potential it is considered theoretically that no oxygenated species are present at the Pt surface, the increase in the peak current densities is certainly due to either Eley-Rideal (E-R) mechanism (with the interaction between HO⁻ species from electrolyte and Pt-CO_{ads}) [22, 24, 25] or a bifunctional catalysis (BC) mechanism that consists in the interaction between Ni hydroxyl and Pt-CO_{ads} [26], as assumed below:



As result, for $y_{Ni} = 0.5$ peak C has a current density value equal to that of peak A at Pt/C, i.e an impressive 270 mV shift towards the lower potentials. For $y_{Ni} > 0.5$, peak A is disappearing, while peak C starts decreasing. This double phenomenon can be explained by the conjugation of repulsive adsorption of CO towards the HO species and the lowering Pt content, which inhibits the surface structure, *i.e* prevents the L-H mechanism at the Pt surface. Table 2 gives the coulombic charges associated with the CO oxidation on the different catalysts. As the Ni content increases in the bimetallic composition up to 50%, the coulombic charge associated with the CO oxidation to carbonate increases from 0.69 to 0.79 mC. If on Pt/C this charge is only associated with the above-mentioned L-H mechanism, its increase to 0.79 mC could result

from the co-existence of the two mechanisms (L-H and BC) on Pt_{0.5}Ni_{0.5}/C, as can be seen through the two oxidation peaks at 0.4 and 0.6-0.7 V/RHE (Figure 2b). Then the coulombic charge decreases to 0.54 mC when the Ni content is higher in the bimetallic anode composition (Pt_{0.2}Ni_{0.8}/C). This corresponds to the progressive setting up of the BC and E-R mechanisms to that of L-H as a result of the marked decrease in the Pt content, which is responsible for and where CO adsorption phenomena take place.

Table 2. Charge associated with the CO stripping on different Pt_xNi_y/C nanocatalysts.

Nanomaterials	Charge related to CO oxidation peak/ mC
Pt/C	0.69
Pt _{0.5} Ni _{0.5} /C	0.79
Pt _{0.2} Ni _{0.8} /C	0.54

The excellent catalytic ability of the prepared Pt_xNi_y/C materials towards the CO oxidation at lower potential values, as the common and major poisoning intermediate in the organics electrooxidation, provides sound evidences to the utilization of this type of catalyst either as CO tolerant cathode or anode in the alcohol fuel cells.

Conclusion

As CO is the main poison species that is responsible for the deactivation of the anode catalyst in the direct alcohol fuel cells, its oxidation reaction was investigated on Pt_xNi_y/C synthesized from a surfactant-less simple reduction approach. XPS measurements revealed to be herein complementary techniques that provided evidences on the ensemble effects allowing to appreciate the excellent ability of Pt_xNi_y/C anodes towards the CO oxidation reaction. Indeed, the physicochemical analyses of the materials correlated with the electrochemical characterization allowed to show that the increase of the Ni content in the Pt structure does modify the initial L-H mechanism towards E-R and finally BC ones. The 270 mV negative shift of the CO oxidative removal cannot be explained as the sole effect of the low Pt 4f_{7/2} peak shift,

but also by the contribution of the Ni-OH species in the close environment of Pt-CO_{ads}, which mainly leads to a bifunctional mechanism. This trend, emphasized by the increase of the Ni content up to $y_{Ni} = 0.8$, makes these bimetallics, either a CO tolerant cathode or promising active anode material in a direct alcohol fuel cell. Importantly, this work shows Ni as low-cost and earth-abundant element that allows to decrease the amount of the precious metal in a catalyst composition, not only without decreasing the electroactivity, but with improving its ability towards organics oxidation.

Acknowledgements

The authors thank the European Union (ERDF) and “Région Nouvelle-Aquitaine for their support.

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Graphical Abstract

