Highly active and selective nickel molybdenum catalysts for direct hydrazine fuel cell.

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Abstract:

Carbon-supported NiMo catalysts (NiMo/C) were synthesized and investigated for the electrooxidation of hydrazine. Their morphology and composition were determined with physicochemical characterizations (TEM-EDS, XPS and XRD) and further bridged to their electrocatalytic activity. The electrochemical performances measured in rotating disk electrode ex-

periments reached $7.68 \pm 0.96 \text{ kA g}_{\text{metal}}^{-1}$ for hydrazine electrooxidation at $E = 0.4 \text{ V vs. RHE}$ for the carbon-supported NiMo (9:1)/C. This value is amongst the highest reported in the literature. The large activity of the carbon-supported NiMo (9:1) catalyst was ascribed to the effect of a low but non-negligible ($< 15 \text{ at. \%}$) molybdenum content, as molybdenum atoms stabilize the hydrazine N-N bond, thereby preventing the chemical decomposition of hydrazine into ammonia, and improving the catalyst selectivity towards the complete (and desired) hydrazine oxidation into N_2 gas.

Key Words: Direct Hydrazine Fuel Cell, Ni-based catalyst, Nickel, Molybdenum, Ammonia Generation.

1. Introduction

The interest for fuel cells has been growing over the past decades, as a response to the forecast depletion of fossil energies. Indeed, fuel cells enable a more efficient fuel-to-electricity conversion than internal combustion engines. In particular, low-temperature fuel cells are extremely promising technologies for a wide range of applications, such as portables electronic devices, electric vehicles, or stationary power supplies. However, they must overcome several challenges to become commercially viable. For example, the development of proton exchange membrane fuel cells (PEMFCs) and direct alcohol fuel cells (DAFCs) presents issues linked to the anodic and cathodic electrocatalysts. Their catalysts materials are typically based on Pd and Pt^{1,2}, which implies cost and availability issues. Reducing the noble metal content in fuel cells is mandatory, and this can be achieved by *(i)* using tailored nanostructured materials, such as core-shell or alloy solid/hollow nanoparticles³⁻⁸, or by *(ii)* focusing on non-noble materials. In that latter strategy, recent but nonetheless impressive progresses have been obtained

with catalysts of the carbon-nitrogen-iron family for the oxygen reduction reaction (both in alkaline and acidic conditions)^{9–12}.

On the anode side, the most studied fuels to feed these systems still present drawbacks: hydrogen gas is expensive to produce in a sufficiently clean manner, to store/transport, and there are still no active noble-free catalysts capable to oxidize hydrogen efficiently. Oxygenated organic molecules (alcohols, aldehydes, organic acids, *etc.*) are easily produced, stored and transported, but their oxidation proceeds with very sluggish kinetics even on noble catalysts, adversely affecting the DAFC performances-to-catalyst cost ratio^{1,2}. The choice of potential fuels is however wider in alkaline than in acidic medium, which enables to look at candidates beyond molecular hydrogen and the alcohols family. In particular, non-carbon fuels of the boron (*e.g.* NaBH₄, NH₃BH₃) and nitrogen-derived family (N₂H₄) are of interest, owing to their large theoretical energy density, ease of storage/transport and faster overall oxidation kinetics than for their carbon-containing competitors^{13–20}.

In particular, hydrazine oxidation as a replacement for alcohol or hydrogen oxidation was extensively studied from the sixties to nowadays^{21–34}.

The DHFC (direct hydrazine fuel cell), which completes the oxygen reduction reaction at the cathode, also presents a higher theoretical cell voltage than PEMFC fed with hydrogen: 1.56 V vs. 1.23 V, owing to the very strong reducing behaviour of its fuel (Eq. 1). Insuring DHFCs efficiency is essential to enable their commercialization; in that frame one should avoid the chemical decomposition of hydrazine into ammonia (NH₃, Eq. 2), since it leads to incomplete

fuel oxidation (lower faradic efficiency), poisoning of the anode catalyst by ammonia (and also of the cathode catalyst if ammonia cross-over proceeds through the membrane), all these phenomena decreasing the voltage and therefore the energy density of the DHFC¹⁸.

Sakamoto *et al.*^{24,25,27} observed that alloying nickel with another metal (*e.g.* cobalt, lanthanum or zinc) improves the catalysts performances toward hydrazine oxidation, both in the rotating disk electrode (RDE) and membrane electrode assembly (MEA) configurations. For example, unsupported nickel nanoparticles in DHFC anodes combined with a Co-polypyrrole-catalyzed carbon cathode (Co-PPY-C) for the oxygen reduction reaction (ORR) presented a lower maximum power density (389 mW cm^{-2})²⁴ than unsupported Ni_1Co_1 (423 mW cm^{-2}), unsupported Ni_9La_1 (453 mW cm^{-2}) and unsupported $\text{Ni}_{0.87}\text{Zn}_{0.13}$ (elaborated by spray pyrolysis²⁶, 486 mW cm^{-2}) in identical operating conditions ($T = 353 \text{ K}$, anolyte = $1 \text{ M KOH} + 20\% \text{ H}_2\text{O-N}_2\text{H}_4$). However, Daihatsu Motor Co. reported substantial ammonia production (from several hundred to several thousand ppm) on the catalysts listed above, which is unsuitable for widespread and durable DHFC applications³⁵. Consequently, a major challenge for DHFC commercialization is to avoid hydrazine chemical decomposition without reducing the catalyst electrochemical performances (*i.e.* enable the selective and complete hydrazine oxidation of Eq. 1). To this goal, one strategy is to investigate other elements that alloy with Ni. It has been shown that the presence of molybdenum in Ni-based catalyst influences their selectivity and efficiency toward several reactions^{36,37}. Based on this, the present study focuses on the synthesis of $\text{Ni}_x\text{Mo}_y/\text{C}$ catalysts and the analysis of the effect of molybdenum on the catalyst morphology and electrochemical performances.

2. Experimental

2. 1. *Ni-Mo catalysts elaboration*

The carbon-supported Ni-Mo catalysts were synthesized using a wet impregnation procedure. Firstly, calculated amounts of molybdenum precursor (Aldrich, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$), nickel precursor (Aldrich, $\text{Ni}_2\text{NiO}_6 \cdot 6\text{H}_2\text{O}$) and urea (Aldrich $\text{CN}_2\text{H}_4\text{O}$) were dissolved in ultrapure water, to obtain a specific nickel/molybdenum ratio. The theoretical ratios synthesized by the wet impregnation process were: NiMo (1:1); NiMo (2:1); NiMo (3:1); NiMo (4:1); NiMo (9:1) and Ni. Since urea was added to reduce the molybdenum precursor, no urea was added during the synthesis of the pure nickel catalyst. A calculated amount of carbon (Akzo Nobel Ketjen Black EC-600 JD) was dissolved in H_2O + IPA (isopropyl alcohol), to obtain 50 wt. % metallic loading. The metal precursors and the carbon powder were then mixed and dispersed using an ultrasonic probe during 5 min., before overnight drying at $T = 358$ K. This step was followed by 1 h heat-treatment at $T = 823$ K under 7 at. % H_2 atmosphere (balanced with Ar), with a 15 K min^{-1} heating ramp, to complete the metal precursors reduction and eliminate their ligands. After cooling, the catalyst was passivated by flowing argon in the tube for 15 min, followed by $t = 30$ min under 3% O_2 flow.

2. 2. *Physicochemical characterizations*

2. 2. 1. *X-ray diffraction*

Carbon-supported Ni and NiMo catalysts were analysed by X-ray diffraction (XRD) using a Scintag Pad V diffractometer (Bragg- Brentano geometry) with Data Scan 4 software (from MDI, Inc.) for system automation and data collection. $\text{Cu K}\alpha$ radiation (40 kV, 35 mA) was used with a Bicorn Scintillation detector (with a pyrolytic graphite curved crystal monochromator).

2. 2. 2. *Transmission electron microscopy*

Transmission electron microscopy (TEM) as well as energy dispersive spectrometry (X-EDS) were performed on a JEOL 2010 microscope, with a LaB₆ filament operated at 200 kV accelerating voltage (point-to-point resolution of 0.19 Å). The TEM micrographs were used to characterize the distribution of the metal nanoparticles on the carbon powder support and the particle sizes. The local or global Mo and Ni atomic percentages were determined by X-EDS using Oxford Inca control software. The acquisition was performed at the classical acceleration voltage of 200 kV on selected areas of the samples, over dozens (local analysis) to thousands (global analysis) of particles. The quantitative analyses were performed on Ni K α and Mo K α signal lines using the K factor provided by Oxford Inca software.

2. 2. 3. *X-ray photoelectron spectroscopy*

The X-ray photoelectron spectroscopy (XPS) analyses were performed using a Kratos AXIS-Ultra DLD photoelectron spectrometer using a monochromatic Al K α source operating at $P = 225$ W. No charge compensation was necessary. The survey of the sample was done first, followed by the recording of high-resolution spectra of C 1s, O 1s, Ni 2p and Mo 3d for three areas on the sample. All spectra processing was done in CasaXPS. Atomic % were calculated using sensitivity factors provided by the manufacturer. The inelastic mean free path for Ni 2p electrons with kinetic energy of ~ 600 eV is ~ 0.8 nm, while that for Mo 3d electrons with higher kinetic energy of ~ 1250 eV is ~ 1.6 nm. To calculate the atomic ratios for Mo and Ni coming from exactly the same depth, the relationship between the probability of a detected electron originating from a particular depth, d , and inelastic mean free path, λ has been used: $P(d) = \exp(-d/\lambda)$. Using this equation, the fractions of the total Ni 2p and Mo 3d signal at different depths were calculated. For example, at sampling depth of 1.6 nm, 95% of the Ni 2p electrons and 51% of Mo 3d electrons contribute to total signal. The atomic ratio of Ni/Mo at

1.6 nm is, thus, obtained by dividing the 0.95 Ni at. % by 0.51 Mo at%. The same was done for all other depths. Curve fitting was carried out using individual peaks of constrained width and shape. A 70% Gaussian / 30 % Lorentzian line shape was used for the curve-fits.

2. 3. *Density Functional Theory*

All the electronic structure calculations were performed using the generalized gradient approximation (GGA) in density functional theory (DFT) with the Perdew-Burke-Ernzerhof (PBE) functional^{38,39} and projector augmented-wave pseudopotentials^{40,41} as implemented in Vienna Ab initio Software Package (VASP)^{42–45}. Extended Ni (111), (Ni₉Mo)_{0.4} (111) and Ni_{0.16}Mo_{0.84} (111) surfaces were modeled using (4×4) unit cells with the dimensions of 0.996 nm × 0.996 nm (LP = 0.352 nm), 0.997 nm × 0.997 nm (LP = 0.352 nm) and 1.180 nm × 1.180 nm (LP = 0.417 nm), respectively. Specific compositions in the case of (Ni₉Mo)_{0.4} and Ni_{0.16}Mo_{0.84} were created by randomly replacing Mo/Ni atoms with Ni/Mo atoms. In all the cases the system was modeled using 4 layers of metal atoms and a vacuum region of 1.8 nm. To simulate the effect of the bulk, the two top layers and the adsorbed species were allowed to relax until the convergence in energy was 1 10⁻⁵ eV, while the two bottom layers with bulk parameters were held fixed. The electronic energies were calculated using 4×4×1 k-point Monkorts-Pack⁴⁶ mesh and Methfessel-Paxton smearing⁴⁷ of order 2 with a value of $\sigma = 0.2$ to aid convergence. In all the cases, plane-wave basis cutoff was set to 400 eV. Adsorption energies (ΔE_{ad}) were calculated using the formula of Eq. 3:

$$\Delta E_{ad} = E_{\text{surface+ad}} - (E_{\text{surface}} + E_{ad}) \quad \text{Eq. 3}$$

Where $E_{\text{surface+ad}}$ is the energy of N₂H₄ adsorbed on the surface, E_{surface} is the energy of the clean surface, and E_{ad} is the energy of N₂H₄ in the gas phase.

2. 4. Electrochemical characterization

2. 4. 1. Three electrode cell measurements

All the electrochemical experiments were carried out in a three-electrode cell, using a Hg/HgO with 1 M KOH (measured at $E_{\text{ref}} = 0.905 \text{ V vs. RHE}$) as reference, a platinum wire as counter-electrode and a Pine E5HT HotSpot glassy carbon rotating disk electrode as working electrode. The catalytic inks were prepared by mixing 10 mg of catalyst, 315 mg of ionomer solution (A3, Tokuyama corp.) and 1.595 mg of tetrahydrofuran (THF) solution. The thin-layer working electrodes were prepared by depositing 3 μL of this aqueous solution on the glassy carbon disk, yielding the desired thin-layer working electrode. All the catalysts were firstly activated in 1 M KOH by performing 50 cyclic voltammetry between $-0.5 < E < 0.7 \text{ V vs. RHE}$ at $\nu = 100 \text{ mV s}^{-1}$. The electrooxidation of hydrazine oxidation was performed in a 1 M KOH + 5 wt. % hydrazine electrolyte at $T = 333 \text{ K}$. Cyclic voltammograms were performed between $-0.5 < E < 0.7 \text{ V vs. RHE}$ at $\nu = 20 \text{ mV s}^{-1}$.

2. 4. 2. In situ Fourier-transform infrared spectroscopy

The *in situ* FTIR (Fourier-Transform Infrared Spectroscopy) experiments were performed at room temperature, after activation in 1 M KOH (50 cyclic voltammetry between $-0.5 < E < 0.7 \text{ V vs. RHE}$ at $\nu = 100 \text{ mV s}^{-1}$), using a Nicolet 6700 spectrometer, bearing a MCT (mercury cadmium telluride) detector cooled with liquid nitrogen. The background spectrum was collected at $E = -0.17 \text{ V vs. RHE}$. All the other spectra were taken during a 1 mV s^{-1} linear sweep voltammograms between $-0.17 < E < 0.73 \text{ V vs. RHE}$. The IR absorption spectra were calculated as $A = -\log(R/R_0)$ where R and R_0 represent the reflected intensity corresponding to the sample and the reference beam, respectively. A Teflon[®] cell was used for the *in situ* FTIR experiments, with a ZnSe hemisphere as the IR window, an Ag/AgCl in saturated KCl as the

reference electrode, a platinum wire as the counter-electrode and a glassy carbon disk coated with 3 μL of the aqueous suspension of catalyst described above as the working-electrode. Similarly to Ref. ^{26,48}, the working electrode was pressed against the IR window, to form an electrolyte – 0.1 M KOH + 0.5 wt. % hydrazine aqueous solution – layer of a few micrometres in thickness.

2. 4. 3. Ammonia Generation Experiments

The characterization of ammonia generation was performed by detection of NH_4^+ by ion chromatography (881 Compact IC pro, Metrohm) in a fuel cell. The fuel cell characteristics were the following one: Anode: 2.6 mg cm^{-2} of catalyst (Ni-Mo supported on carbon) - ink: 100 mg of catalyst; 0.96 mL of IPA ; 0.24 mL of THF ; 0.2 mL of 5 wt. % A3 ionomer - sprayed directly on the membrane. Cathode: 1 mg cm^{-2} - same ink process – Fe-AAPyr^{49–52}. The anodic fuel was supplied at a 2 mL min^{-1} - 1 M KOH + 5 wt. % Hydrazine Hydrate - whereas air gas, humidified at 323 K, was provided at the cathode at a 500 mL min^{-1} flow rate.

3. Results and Discussion

The NiMo/C catalysts were synthesized using a wet impregnation procedure with (i) urea as a reducing agent and (ii) a heat-treatment of $t = 1$ h under a 7 at. % H_2 atmosphere at $T = 823$ K (for the detailed process, see the Materials and Methods section). Here, it must be recalled that removing the metal oxides by increasing the temperature is impossible, owing to the thermodynamic affinity of molybdenum with carbon above $T = 741$ K⁵³, which yields hexagonal molybdenum carbide (Mo_2C). Besides, neither MoO_2 nor Mo_2C are stable in the electrochemical conditions of a DHFC anode. Preventing their presence is consequently essential. Luhrs *et al.*⁵⁴ observed that urea was able to directly reduce molybdenum oxides into metallic

molybdenum at high temperature under inert atmosphere, following a carbothermal reduction process (Eq. 4) on MoO_2 , where the CO group involved is provided by urea.

For this reason, urea was used to avoid the formation of crystalline molybdenum oxide (MoO_2). The duration of the heat-treatment was kept short ($t = 1$ h), assuming that molybdenum reduction presents faster kinetics than molybdenum carbide formation at $T = 823$ K or below. No crystalline molybdenum carbides and only residual levels of crystalline oxides were observed by X-ray diffraction (XRD) after the synthesis (Fig. 1), which supports this assumption (Table 1). The different peaks observed by XRD present patterns that are related to three identified structures, *i.e.* $(\text{Ni}_9\text{Mo})_{0.4}$, $\text{Ni}_{0.16}\text{Mo}_{0.84}$ and MoO_2 (Fig. 1). Table 2 presents the structural parameters of the synthesized NiMo/C materials.

Figure 1: XRD patterns of the NiMo/C electrocatalysts with the peaks for the (α) MoO_2 , (β) $\text{Ni}_{0.16}\text{Mo}_{0.84}$ and (γ) $(\text{Ni}_9\text{Mo})_{0.4}$.

Table 1: Elemental and phases composition determined by X-ray diffraction for the NiMo/C electrocatalysts synthesized in this study. The atomic ratio between brackets is the stoichiometry in the initial metal salt precursor solution.

	Atomic composition	Phase composition / wt. %			
	(determined by) XRD ¹	(Ni ₉ Mo) _{0.4}	Ni _{0.16} Mo _{0.84}	MoO ₂	Ni
Ni	Ni	0 %	0 %	0 %	100 %
NiMo (9:1)/C	Ni _{0.87} Mo _{0.13}	94 %	6 %	0 %	0 %
NiMo (4:1)/C	Ni _{0.78} Mo _{0.15} O _{0.07}	87 %	6 %	7 %	0 %
NiMo (3:1)/C	Ni _{0.85} Mo _{0.15}	91 %	9 %	0 %	0 %
NiMo (2:1)/C	Ni _{0.75} Mo _{0.16} O _{0.09}	85 %	6 %	9 %	0 %
NiMo (1:1)/C	Ni _{0.64} Mo _{0.26} O _{0.10}	65 %	26 %	9 %	0 %

The materials were then characterized in terms of morphology. Figure 2 displays representative TEM images of the synthesized NiMo/C materials. The distribution of the particles on the carbon substrate is homogeneous for Ni/C, NiMo (9:1)/C, NiMo (4:1)/C and NiMo (3:1)/C: only a few agglomerates could be detected (Fig. 2A – D). However, a clear particle distribution break-up is observed for NiMo (2:1)/C and NiMo (1:1)/C, for which two different particle sizes are observed (Fig. 2E – F), as well as the presence of large-sized amorphous MoO₂ structures (Fig. 2E – F). The presence of MoO₂ crystalline residues was also noticed by XRD for NiMo (1:1)/C, NiMo (2:1)/C and NiMo (4:1)/C (Fig. 1 and Table 1).

The local distribution of Ni and Mo in the synthesized electrocatalysts was examined with X-EDS analyses. One must be aware that atomic compositions determined with X-EDS strongly depend on the thickness of the probed area; whatever this bias, Fig. S1 and Table S1 tend to show heterogeneous atomic composition from one particle to the other. On the basis of the

¹ The X-EDS measurements revealed a heterogeneous composition of the catalysts, as described in Fig. S1 and Table S1.

characterizations presented herein, it was considered that the bimetallic catalysts are made of two solid solutions: one being Ni-rich and the other Mo-rich.

Figure 2: Representative TEM pictures and particle size distributions for the NiMo/C electrocatalysts synthesized in this study.

Table 2: Lattice parameter and expansion of the lattice parameter vs. $(\text{Ni}_9\text{Mo})_{0.4}$ and $\text{Ni}_{0.16}\text{Mo}_{0.84}$ for the Ni-rich and Mo-rich phases determined by X-ray diffraction for the Ni-Mo/C electrocatalysts synthesized in this study.

	a (Ni-rich) / nm	Expansion of a vs. $(\text{Ni}_9\text{Mo})_{0.4}$	a (Mo-rich) / nm	Expansion of a vs. $\text{Ni}_{0.16}\text{Mo}_{0.84}$
NiMo (9:1)/C	0.353	0.28 %	0.419	0.48 %
NiMo (4:1)/C	0.353	0.28 %	0.420	0.72 %
NiMo (3:1)/C	0.353	0.28 %	0.421	0.96 %
NiMo (2:1)/C	0.356	1.1 %	0.423	1.44 %
NiMo (1:1)/C	0.356	1.1 %	0.423	1.44 %

According to the XRD analyses, the compositions of these phases are close to (i) the $(\text{Ni}_9\text{Mo})_{0.4}$ solid solution for the Ni-rich and (ii) the $\text{Ni}_{0.16}\text{Mo}_{0.84}$ solid solution for the Mo-rich. A slight expansion of the lattice constant a (see Table 2) was observed compared to $(\text{Ni}_9\text{Mo})_{0.4}$ and $\text{Ni}_{0.16}\text{Mo}_{0.84}$ (*i.e.* for NiMo (1:1) the experimental and theoretical lattice constants for the $(\text{Ni}_9\text{Mo})_{0.4}$ and the $\text{Ni}_{0.16}\text{Mo}_{0.84}$ phases are 0.356 nm vs. 0.352 nm and 0.423 nm vs. 0.417 nm, respectively). This expansion of the lattice constant demonstrates a higher molybdenum content in the Ni-rich and Mo-rich solid solutions than assumed considering the composition of the pure $(\text{Ni}_9\text{Mo})_{0.4}$ and $\text{Ni}_{0.16}\text{Mo}_{0.84}$ solid solutions.

The average crystallite size of the Ni-rich and Mo-rich solid solutions is comparable to the volume-averaged nanoparticle diameter (d_v) determined with TEM, within the standard deviation (Table 3). In general, the Mo-rich phase presents smaller crystallite size (5.5 to 7 nm) whereas the Ni-rich phase has larger crystallite size (8.8 to 13.1 nm), than the volume-averaged nanoparticle diameter. Only the NiMo (1:1)/C electrocatalyst makes exception to this trend: in this case, the size of the Ni-rich and the Mo-rich crystallites are similar (5.9 and 6.0 nm), and close to the volume-averaged diameter of the nanoparticles ($d_v = 6.5 \pm 1.5$ nm).

Table 3: Particle and crystallite size (determined by TEM and XRD, respectively) for the NiMo/C nanoparticles synthesized in this study

	Number-average diameter (d , nm)	Volume-averaged diameter (d_v , nm)	Crystallite domain size / nm		
			Ni-rich	Mo-rich	Ni
Ni	11.1 ± 3.5	16.0 ± 5.0	-	-	13.6
NiMo (9:1)	10.6 ± 3.0	13.2 ± 3.7	10.2	5.5	-
NiMo (4:1)	9.2 ± 3.5	12.9 ± 4.9	10.8	6.4	-
NiMo (3:1)	8.8 ± 2.6	11.2 ± 3.6	13.1	5.7	-
NiMo (2:1)	6.0 ± 2.0	8.2 ± 2.7	8.8	7.0	-
NiMo (1:1)	5.1 ± 1.5	6.5 ± 1.9	5.9	6.0	-

Thus, based on the TEM, XRD and X-EDS results, the morphology of the $\text{Ni}_x\text{Mo}_y/\text{C}$ electrocatalysts is characterized as follows:

- (i) A Ni-rich phase featuring a composition close to the $(\text{Ni}_9\text{Mo})_{0.4}$ solid solution and a diameter comprised between 8.8 and 13.1 nm (Fig. S1-2B);
- (ii) A Mo-rich phase featuring a composition close to the $\text{Ni}_{0.16}\text{Mo}_{0.84}$ solid solution and a diameter comprised between 5.5 and 7 nm (Fig. S1-4B);
- (iii) An amorphous (or crystalline, as observed in XRD for NiMo (1:1)/C, NiMo (2:1)/C and NiMo (4:1)/C) MoO_2 phase, such as observed on Fig S1-3D.

X-ray photoelectron spectroscopy was used to access the composition of the surface and near-surface layers. Figure 3 provides clear experimental evidences of a Ni surface enrichment: the Ni surface content determined by XPS, *i.e.* at 0.3 nm depth, is (i) larger than that estimated from XRD analysis (for example for the NiMo (9:1)/C electrocatalyst the Ni surface content was 92 at. % (Fig. 3) compared to 87 at. % in average (Table 1)) and (ii) decreases while increasing the depth of analysis (Figure 3). The oxygen species detected by XPS (Table S2) were considered as (i) interstitial (*e.g.* in orthogonal sites for NiO) induced by the synthesis passivation step or as (ii) relevant molybdenum oxides – amorphous and crystalline (also showed by XRD, Figure 1 and Table 1). The XPS results of Figure 3 are representative for

inter-particles heterogeneity, supporting the fact that the ‘small’ nanoparticles (5.5 – 7 nm) are Mo-rich, whereas the ‘large’ nanoparticles (9 – 14 nm) are Ni-rich. As such, Ni-rich nanoparticles are probed by XPS at the lowest depths of analysis (Fig. 3) whereas the highest depths of analysis (up to 1.9 nm) include not only the Ni-rich, but also the Mo-rich nanoparticles and the MoO₂ phase.

Figure 3: Nickel atomic content measured at different depths in the NiMo/C electrocatalysts.

The materials were further characterized with regards to their catalytic behaviour towards the electrooxidation reaction of hydrazine.

Figure 4 shows that the mass activity of the Ni/C catalyst synthesized in this study is 14-fold larger than for the Ni/C electrocatalyst ($3.74 \text{ kA g}_{\text{metal}}^{-1}$ vs. $250 \text{ A g}_{\text{metal}}^{-1}$ at $E = 0.2 \text{ V vs. RHE}$) synthesized in Refs ^{24–26}. Obviously, these differences cannot be accounted for by the different hydrazine concentrations employed in these studies (1 M in Sakamoto *et al* works^{25,27} vs. 1.56 M here). Instead, one may assume that a high nickel oxide content inhibited the catalytic activity of the Ni/C catalysts in Refs ^{25,27}. The oxide level is very low in the present study: the oxides observed by XPS (Table S2) are induced by the passivation step and removed during the catalyst electrochemical activation. This demonstrates the clear advantage of the present

wet impregnation synthesis process, which avoids the formation of a thick oxide layer thanks to the use of urea as oxide ‘scavenger’ (Eq. 3).

Figure 4: Positive-going potential scan of hydrazine hydrate oxidation measured on the Ni-Mo/C electrocatalysts. Experimental conditions: 1 M KOH + 5 wt. % Hydrazine hydrate, $T = 333$ K, $\omega = 1600$ rpm, potential scan rate $\nu = 20$ mV s⁻¹.

Table 4: Mass activity of the NiMo/C electrocatalysts for the electrooxidation of hydrazine hydrate. Experimental conditions: 1 M KOH + 5 wt. % Hydrazine hydrate, $T = 333$ K, $\omega = 1600$ rpm, potential scan rate $\nu = 20$ mV s⁻¹.

	Mass activity for hydrazine oxidation / kA g ⁻¹ _{metal}		
	0 V vs. RHE	0.2 V vs. RHE	0.4 V vs. RHE
Ni/C	0.82 ± 0.06	3.47 ± 0.34	6.16 ± 0.75
NiMo (9:1)/C	1.44 ± 0.25	4.55 ± 0.48	7.68 ± 0.96
NiMo (4:1)/C	1.07 ± 0.09	4.37 ± 0.16	7.68 ± 0.36
NiMo (3:1)/C	0.95 ± 0.09	3.89 ± 0.43	6.61 ± 0.85
NiMo (2:1)/C	0.70 ± 0.22	2.94 ± 0.91	5.07 ± 1.69
NiMo (1:1)/C	0.74 ± 0.22	3.53 ± 0.60	6.17 ± 0.95

All the NiMo/C catalysts with a low molybdenum content (*i.e.* < 15 at. %, Table 1) feature higher mass activity than Ni/C, regardless of the potential region considered ($E = 0$ V *vs.* RHE, 0.2 V *vs.* RHE or 0.4 V *vs.* RHE, Table 4). Those activities are also higher than reported in the literature (1.7 kA g_{metal}⁻¹ for Ni_{0.5}Mn_{0.5}/C *vs.* 1.2 kA g_{metal}⁻¹ for Ni_{0.7}Fe_{0.3}/C, 1.4 A g_{metal}⁻¹ for Ni_{0.4}Zn_{0.6}/C and 0.7 kA g_{metal}⁻¹ for Ni_{0.9}La_{0.1}/C at $E = 0.2$ V *vs.* RHE)²⁵⁻²⁷. The activity values presented by Martinez *et al*²⁶ (4 kA g_{metal}⁻¹ for an unsupported Ni_{0.87}Zn_{0.13} catalyst at $E = 0.4$ V *vs.* RHE) are approaching the present ones.

However, a dramatic decrease of the catalysts activity for the electrooxidation of hydrazine is noticed with increasing the Mo content (Table 4). Interestingly, and despite a higher molybdenum content than NiMo (2:1)/C, the NiMo (1:1)/C electrocatalyst features similar performances than the Ni/C catalyst at $E = 0.2$ and 0.4 V *vs.* RHE. Besides, the residual quantity of crystalline molybdenum oxides does not have any significant effect on the mass activity for hydrazine electrooxidation, since no correlation was observed between the current measured at $E = 0$ V *vs.* RHE, $E = 0.2$ V *vs.* RHE and $E = 0.4$ V *vs.* RHE (Table 4) and the oxide content (Table 1).

Therefore, the mass activity enhancement observed for the NiMo/C catalysts with low molybdenum content (*i.e.* < 15 at. %) could be induced by (i) the diminution of the nanoparticles size compared to Ni/C (see. Fig. 2 and Table 3), *i.e.* an increase of the active surface area of the electrocatalyst or/and (ii) a positive effect of the molybdenum as discussed below. It is worth noting that low molybdenum content (< 13 at. %, *e.g.* NiMo (9:1)/C) leads to a diminution of the overpotential for hydrazine hydrate oxidation (see. Fig. 4) compared the overpotential of Ni/C. However, the slightest increase in the molybdenum content (*e.g.* from 13 at. % to 15 at. %) appears to increase the overpotential, suggesting that there is an optimum for the Mo content. This assumption is further supported if one considers the electrocatalysts specific activity (*i.e.* normalized by the specific surface area determined from the TEM micrographs,

Table S4): a dramatic decrease (*i.e.* from $27 \pm 5 \text{ A m}^{-2}_{\text{metal}}$ for NiMo (9:1) to $7 \pm 2 \text{ A m}^{-2}_{\text{metal}}$ for NiMo (1:1) at 0 V vs. RHE) is observed for molybdenum contents $\geq 15 \text{ at. \%}$. It is worth noting, however, that the residual amorphous and crystalline oxide content observed in NiMo (2:1) and NiMo (1:1) (see. Fig. 2) may account for an overestimated specific surface area (Table S4).

In situ FTIR analyses (Fig. 5) were performed to investigate the mechanism of hydrazine electrooxidation. The NiMo (1:1)/C catalyst presents a band ascribed to ammonia deformation at 960 cm^{-1} . Its contribution decreases with an increase in potential, therefore demonstrating lower ammonia production at high potential (Fig. 3B). Despite the fact that ammonia is produced in higher proportions on Ni/C than on NiMo (1:1)/C (see. Table 7), no band was observed at 960 cm^{-1} , suggesting that the adsorption conformation of ammonia differ on the Ni/C electrocatalyst surface. It is worth nothing that the increase in potential results in a faster consumption of the N_2H_4 on the surface and, thus, a diminution of the band intensity observed at 1080 cm^{-1} for Ni/C and NiMo (1:1)/C.

Figure 5: *In situ* FTIR spectra measured during hydrazine hydrate electrooxidation on (A) Ni/C and (B) NiMo (1:1)/C electrocatalysts. All electrode potentials are referred to the RHE scale. Experimental conditions: 1 M KOH + 0.5 wt. % N_2H_4 . Potential sweep rate $\nu = 1 \text{ mV s}^{-1}$

¹. The numbers are relevant for the species described in Table 5. The bands observed at 1450 – 1900 cm⁻¹ wavelength were ascribed to water bending and are presented in Fig. S4.

Table 5: Assignment of IR bands for the spectra displayed in Figure 5.

Number	Wavenumber	Assignment
1	960 cm ⁻¹	NH ₃ deformation
2	1080 cm ⁻¹	-NN stretching ²⁶
3	2340 - 2360 cm ⁻¹	Atmospheric CO ₂

Density functional theory (DFT) calculations with PBE functional were realized to provide further insights into the effect of molybdenum on the hydrazine adsorption conformation and ammonia production. Since (Ni₉Mo)_{0.4} and Ni_{0.16}Mo_{0.84} are presenting known properties close from the Ni-rich and Mo-rich phases, they were discussed in the following part. The adsorption energies of hydrazine on the Ni(111), (Ni₉Mo)_{0.4}(111) and Ni_{0.16}Mo_{0.84}(111) surfaces are given in Table 6 and the corresponding optimized geometries are shown in Figure S5. It is shown that the adsorption energies of hydrazine increase with the surface molybdenum content (Table 6). The adsorption energy of hydrazine is -0.81 eV on the Ni(111) surface, -0.92 eV on the (Ni₉Mo)_{0.4}(111) surface and -1.48 eV on the Ni_{0.16}Mo_{0.84}(111) surface. Thus, hydrazine is for 0.67 eV more stable on the Ni_{0.16}Mo_{0.84}(111) surface than on the Ni(111) surface (Table 6). In addition, hydrazine adsorbs on the Ni_{0.16}Mo_{0.84}(111) surface in a bridge position between two Mo atoms, with N-Mo distances of 2.33 Å and 2.29 Å, while on both the Ni(111) and (Ni₉Mo)_{0.4}(111) surfaces, hydrazine adsorbs in a top position with one nitrogen adsorbed on the surface and the other one oriented towards the solution (Figure S5). Therefore, the DFT calculations suggest that the Mo content in the surface/subsurface layers must significantly impact the catalysts performances, as detailed below.

Table 6: Adsorption energies (ΔE_{ad}) of hydrazine (N_2H_4) and ammonia (NH_3) on the Ni(111), $(\text{Ni}_9\text{Mo})_{0.4}(111)$ and $\text{Ni}_{0.16}\text{Mo}_{0.84}(111)$ surfaces.

System	$\Delta E_{\text{ad}}(\text{N}_2\text{H}_4)/\text{eV}$	$\Delta E_{\text{ad}}(\text{NH}_3)/\text{eV}$
Ni(111)	-0.81	-0.78
$(\text{Ni}_9\text{Mo})_{0.4}(111)$	-0.92	-0.85
$\text{Ni}_{0.16}\text{Mo}_{0.84}(111)$	-1.48	-0.89

The Ni-rich phase is mainly responsible for the enhanced catalytic properties, since an increased nickel Ni-rich content leads to increased catalytic performances (Table 4 and Fig. 4). However, DFT calculations have shown that Mo-containing Ni-rich surfaces and, to a larger extent, Mo-rich surfaces stabilize the N-N bond and avoid ammonia production (*i.e.* fuel losses). However, this stronger N_2H_4 binding and different adsorption position is detrimental to the catalyst activity (Table 4). This may be rationalized by considering the Sabatier principle, which states that the adsorption of the reactive species should be neither too strong nor too weak.

The ammonia generation measurements performed in direct hydrazine fuel cell (see Materials and Methods for the detailed process) support the fact that molybdenum stabilizes the N-N bond (Table 7), since the lowest ammonia production is observed for the catalysts with highest molybdenum content, NiMo (1:1)/C. It can also be emphasized that ammonia production is reduced at high cell voltage, both on Ni/C and NiMo/C, possibly due to a modification of the hydrazine electrooxidation mechanism. Such hypothesis is supported by the change in the NH_3 absorption observed for NiMo (1:1)/C with the potential variation (Fig. 5).

Table 7: Detection of ammonia generation during the hydrazine hydrate oxidation experiments on the NiMo/C electrocatalysts.

	Ammonia Generation at:	
	0.6 V	0.2 V
Ni/C	247 ppm	117 ppm
NiMo (9:1)/C	285 ppm	209 ppm
NiMo (4:1)/C	142 ppm	84 ppm
NiMo (3:1)/C	150 ppm	110 ppm
NiMo (2:1)/C	80 ppm	73 ppm
NiMo (1:1)/C	60 ppm	43 ppm

4. Conclusion

Carbon-supported NiMo catalysts were synthesized using the wet impregnation process, with the adjunction of urea to avoid the formation of MoO₂. The NiMo/C catalysts were composed of 3 distinct phases (i) Ni-rich/C nanoparticles, (ii) Mo-rich/C nanoparticles and, for NiMo (4:1), NiMo (2:1) and NiMo (1:1) (iii) amorphous and/or crystalline MoO₂/C. The NiMo/C catalysts with a low molybdenum content (< 15 at. %) present better catalytic performance for the hydrazine electrooxidation than Ni/C due to a positive effect of the molybdenum. Increasing the molybdenum content led to depreciated catalytic performance, thereby demonstrating the existence of an optimum molybdenum content for hydrazine electrooxidation. *In situ* FTIR measurements and DFT calculations suggest that the presence of molybdenum stabilizes the adsorbed hydrazine, thereby avoiding its decomposition into ammonia. The NiMo (1:1)/C catalyst presents similar mass activity for hydrazine electrooxidation than the Ni/C catalyst at $E = 0.2$ and 0.4 V vs. RHE but its ammonia generation is 4 times lower at a fuel cell voltage of 0.6 V.

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