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Indirect urea electro-oxidation by nickel(III) in alkaline medium: from kinetic and mechanism to reactor modeling

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Abstract

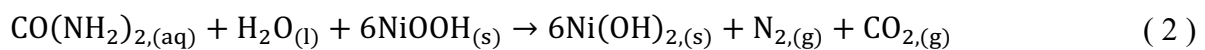
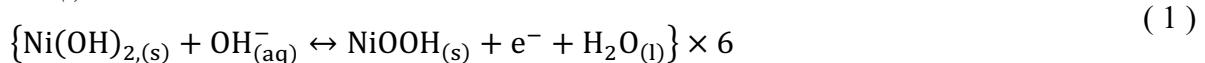
This study consists in the determination of two kinetic laws of urea oxidation (UO) and electro-oxidation (UEO) in alkaline media on nickel(III). Two kinds of active sites were examined, the first one derived from a Ni(OH)₂ powder and the second from a massive nickel electrode. Partial orders of nickel(III) (two for UO and five for UEO) enable concluding about *i*) the urea adsorption on two nickel(III) sites and *ii*) that a multistep oxidation of urea occurs involving five nickel(III) site electro-regenerations. A multi-pathway mechanism is also proposed to explain UEO facilitated by the nickel(III)/nickel(II) mediation system, and to predict the by-products' formation previously identified (NO₂⁻, NH₃, OCN⁻, CO₃²⁻). At last, a model combining the UEO kinetic law previously established, with diffusive and convective transport phenomena was developed. A consistent correlation (maximum deviation of 6%) between laboratory electrolysis results with the model's predictions was obtained under different operating conditions, enabling the validation of this model.

Keywords: Urea electro-oxidation; Ni^(III)/Ni^(II) mediator; Mechanism and kinetics; Heterogeneous coupled reactions; Transport phenomena modeling

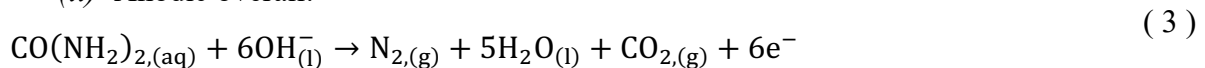
Introduction

Wastewater treatment and energy issues are nowadays major societal problems requiring numerous investments. Previously considered as waste, fresh water that is contaminated by human activity (carbon industry, transportation, etc) and by the primary sector (mining, agriculture) is now recognized as a significant source of pollutants valorization. Interest is enhanced as the waste water production is expected to increase by about 50 % by the year 2050¹. Containing urea (40 %wt.², at around 0.33 mol.L⁻¹), urine constitutes an important source of nitrogen, accounting for nearly 75 % of the nitrogen in watercourses³. Electrochemical oxidation of urea is nowadays studied for meeting various targets, such as electrolyzers⁴⁻⁷ (producing H₂ as an energy carrier), energy production by urea fuel cells⁸⁻¹³, or the development of advanced electrode materials¹⁴⁻¹⁷. Recent investigations^{18,19} have claimed that low-cost electrode materials could be used in alkaline media for efficient urea electro-oxidation (UEO), thus opening promising perspectives for UEO implementation on an industrial scale. In particular, nickel oxides exhibit important catalytic activity regarding urea oxidation in presence of hydroxide ions, which enables a simplified reaction scheme²⁰⁻²² described by the Eqs (1)-(5) to be proposed.

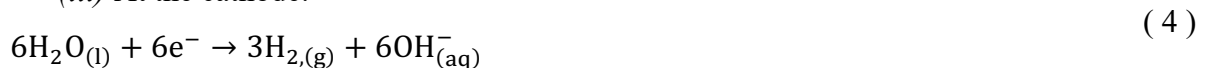
(i) At the anode:



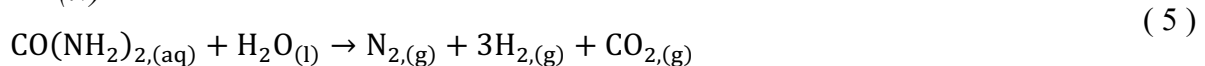
(ii) Anodic overall:



(iii) At the cathode:



(iv) Overall:



The redox system NiOOH/Ni(OH)₂ acts as a redox mediator catalyzing urea mineralization²³.

In such a system, nickel peroxide, NiOOH, is constantly regenerated at the electrode surface by

an electrochemical reaction (ER, Eq. (1)). Six electrons, supplied by 6 NiOOH, are required to achieve a complete mineralization (*i.e.* to be converted into CO₂ and N₂) of one urea molecule according to a heterocatalytic chemical reaction (HCR, Eq. (2)). However, recent works have provided new insights on urea oxidation by demonstrating that, beyond the formation of N₂, various by-products are produced, such as cyanate, nitrite, ammonium and carbonate ions^{24,25}. A deeper knowledge of the reaction scheme coupled to the determination of kinetic laws and the related parameters remain a prerequisite to design and to operate UEO processes on an industrial scale^{26,27}. To the best of our knowledge, only two studies have been devoted to these investigations. By neglecting the catalytic regeneration of the couple NiOOH/Ni(OH)₂ and using Tafel plots, Vedharathinam et al.²⁸ were the first to propose the following simplified kinetic law as in Eq. (6) without determining the kinetic constant k.

$$\text{rate}_{\text{urea}} = k \times [\text{CO}(\text{NH}_2)_2]^{0.3} \times [\text{OH}^-]^2 \quad (6)$$

Later, partial orders of 1.22 and 0.26 for hydroxide ions and urea respectively on a β-NiOOH covered electrode were obtained using cyclic voltammetry and Tafel plots by Singh et al.²⁹. The authors have claimed that: (*i*) the reaction order of urea concentration is independent of the applied potential and (*ii*) increasing the applied potential causes the reaction order of the hydroxide ions to decrease. However, in these studies, experiments were carried out in transient state conditions (*i.e.* high potential scan rate v_{scan}), in which nickel(III) was not constantly regenerated at the electrode surface, as pointed out in our previous study³⁰. As obtained in the mixed ER/HCR regime and at low urea conversion rates, the related values of partial reaction orders allowed neither the understanding of the impact that the secondary reactions (occurring at higher urea conversion rates) may have on the electrochemical system, nor obtaining access to relevant intrinsic kinetic information.

To fill this gap, this paper aims at investigating the kinetics of NiOOH catalytic urea oxidation in an alkaline medium. For this purpose, and since neither explicit rate law nor kinetic models are described in the literature, a novel approach will be suggested, combining studies of the

urea action according to (i) specifically synthesized NiOOH powder and to (ii) electrochemically generated NiOOH sites, carried out under steady state conditions. By implementing catalytic urea oxidation in a suspension of NiOOH solid particles, one can expect to bring new insights on the reaction kinetics by comparing physico-chemical phenomena taking place in the presence of (i) non-regenerated NiOOH sites (adsorption, HCR, desorption) on solid particles or (ii) electrogenerated NiOOH sites (HCR/ER coupling). Results on oxidation kinetics with the synthesized nickel particles will first be studied. The experiments performed in a lab-scale electrolysis cell at low scan rates enabled to determine the key parameters of the kinetic law for the UEO reaction. Furthermore, by combining the newly-established kinetic rate law with the electrolysis results obtained at high urea conversion rates, a detailed mechanism of urea oxidation in alkaline medium on nickel(III) active sites was proposed, allowing the formation of the liquid phase by-products identified by Tatarchuk et al.²⁵ and also in our previous work³⁰. Finally, one can regret a lack of Electrochemical Engineering approach of the UEO processes (cell design, geometry and optimization at pilot and industrial scale)^{31,32} in the state of the art. The present study proposes an original approach enabling the coupled phenomena (electro-oxidation, adsorption, kinetic and mass transport) that occurs during the UEO process to be described. This approach is based on: i) the rigorous determination of the kinetic law; ii) the establishment of the multi-pathway mechanism responsible for the formation of all the liquid phase by-products; and iii) a robust (maximum deviation of 6%) predictive model which, to the knowledge of the authors, has never been applied to UEO. This model will predict the conversion rate of urea during electrolysis at high conversion rates and on a large scale.

Section 2 describe (i) the synthesis pathway of the NiOOH powder and the associated characterization techniques, (ii) the set-up and the analytical technique to monitor the reaction between urea and nickel(III) particles and, (iii) the electrochemical set-up. Section 3 discusses

the kinetic parameters deduced from both chemically and electrochemically synthesized nickel(III) particles, and then elucidates the UEO mechanism. Finally, section 4 is dedicated to the construction of a model that is able to predict the temporal variation of urea conversion during batch electrolysis and its validation by comparison with experimental data.

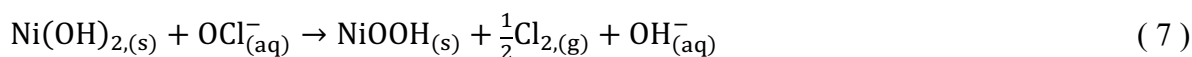
Experimental

Details concerning chemicals (Normapur[®] grade) are reported in §SM. 1 (refer to Table SM1).

NiOOH catalyst powder

Synthesis

The NiOOH powder was synthesized following the protocols developed by Pan et al.³³ and Thimmasandra et al.³⁴. They consisted of oxidizing a Ni(OH)₂ powder at room temperature in the presence of sodium hypochlorite NaOCl and sodium hydroxide NaOH, as Eq. (7) below.



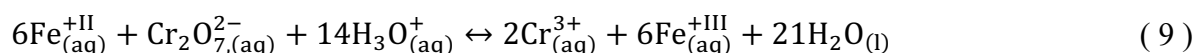
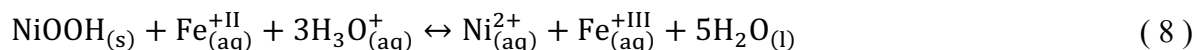
Specifically, NiOOH particles were prepared by mixing 5 g of a commercially available nickel powder (refer to §SM. 1) with a solution containing 400 mL of sodium hypochlorite and 2 g of sodium hydroxide. The reaction was achieved after four hours of magnetic stirring, then the mixture obtained was filtered using a Büchner sintered glass filter; the substance was then washed with 6×60 mL of deionized water. The NiOOH powder was finally dried in an oven at a temperature of 80°C for three days.

Two different concentrations of hypochlorite ($1.76 \times 10^{-1} \text{ mol.L}^{-1}$ and $7.68 \times 10^{-1} \text{ mol.L}^{-1}$) powders, Sample 1 and Sample 2 respectively, were synthesized to vary the nickel(III) purity.

Characterization

Various techniques were used to characterize the initial and the synthesized powders. For sake of clarity, all the results obtained from these methods are reported in §SM. 2.

Firstly, the purity of the nickel(III) particles was quantified by potentiometric back titration using Mohr's salt. An excess of ferrous salt was introduced into a suspension of NiOOH/Ni(OH)₂ particles. After reaction, the excess of ferrous salt was titrated by an acidic solution of potassium dichromate in accordance with Eqs. (8)-(9).



The purity was determined as the ratio of the mass of nickel(III) deduced from the titration to the initial mass of the Ni(OH)₂ powder used in the trial. The set-up related to these experiments is schematically described in Figure SM2.

The crystalline structure of the nickel synthesized powders was studied by XRD analysis using a diffractometer (MiniFlex600 - D/Tex Ultra2, Rigaku[®], Japan) with Cu-K α radiation (40 kV, 15 mA). Data, illustrated in Figure SM4, were collected in the 2 θ range of 5-92 $^\circ$. The step width was 0.02 $^\circ$ with a scan speed of 10 $^\circ$.min⁻¹. From the literature on nickel(III) XRD characterizations³⁴⁻³⁸, the initial powder was well identified as nickel(II) hydroxide β -Ni(OH)₂ with a brucite-type structure. After synthesis, samples 1 and 2 were found to be nickel(III) (in β -NiOOH form), according to diffraction peaks for (001) and (002) crystal faces at 19 and 37 $^\circ$ ³⁹. It is noted that the peaks associated with Ni(OH)₂ disappeared after synthesis. The differences in peak intensities between spectra 2 and 3 could be explained by some differences in crystallinity (a slight amorphous phase could be present in sample 2) which could broaden the diffraction peaks.

Scanning Electron Microscopy (SEM) images were obtained using a microscope (JSM 7100F, JEOL[®], Benelux) operated at 10 kV. As shown in Figure SM5, the morphology of the various particles did not significantly change after the reaction with hypochlorite and the resulting particles could be assumed as spherical in shape with a wide size distribution from 1 to 30 μ m. A laser diffraction particle size analyzer (Mastersizer MS3000, Malvern Instruments[®], United-Kingdom) was used to determine the particle size distributions in terms of number and volume.

The characteristic diameters of the number and volume distributions of the initial and synthesized powders are reported in **Erreur ! Source du renvoi introuvable.**. It should be noted that a slight growth in particle size occurs during synthesis, i.e., the reaction with hypochlorite (mean value – Sample 1: +26% and Sample 2: +10%).

Relative densities of the nickel particles were measured via a helium pycnometer (AccuPyc 1330, Micromeritics[®], United States). They underwent minor modifications both before and after the synthesis (refer to **Erreur ! Source du renvoi introuvable.**).

BET measurements (BELSORP-mini II, BEL[®], Japan) were made to quantify the porosity and specific area of the particles. Since the synthesis reaction of nickel(III) particles consisted in exchanging an electron and a proton, the properties of the particles (porosity, pore diameter, particle size) were slightly modified before and after synthesis. **Erreur ! Source du renvoi introuvable.** summarizes all the physical properties of the initial nickel(II) powder and of the synthesized nickel(III) powders.

These measurements allow us to estimate the number of active sites on the two synthesized powders at 5.2×10^{22} and 1.9×10^{22} atoms per gram of powder, respectively for samples 1 and 2 according to Eq. (10).

$$\frac{\text{sites}_{\text{Ni(III)}}}{m_{\text{cat}}} = \frac{\text{purity} \times \mathcal{N}_A}{M_{\text{NiOOH}}} \quad (10)$$

where m_{cat} is the mass of powders (g), \mathcal{N}_A the Avogadro Number (mol^{-1}) and M_{NiOOH} the molar mass of NiOOH ($\text{g} \cdot \text{mol}^{-1}$).

Kinetics investigations of the reaction between urea and chemically synthesized nickel(III) sites in alkaline medium

Experimental set-up and reaction monitoring

The experimental set-up used to monitor the catalytic oxidation of urea by nickel(III) particles in an alkaline medium, consisted of a closed double-walled thermoregulated reactor operating

in a nitrogen atmosphere (nitrogen was previously humidified to avoid any decrease in the reaction volume) (illustrated §SM. 3, refer to Figure SM6). The reactor initially contained a suspension of 5 g of synthesized powder in 45 mL volume of KOH solution for different concentrations. Ultrapure water 18.2 MΩ.cm was systematically used to prepare suspensions. A strong stirring created by a suitable magnetic bar ($\frac{\phi_{\text{reactor}}}{\phi_{\text{magnetic bar}}} = \frac{6.5}{4.8}$, 800 RPM) ensured that all of the particles were thoroughly suspended. Before introducing urea, the suspension containing the NiOOH/Ni(OH)₂ particles was stirred for 5 min in order to finely disperse the nickel powder into the entire KOH volume. The aqueous deaerated alkaline solution of urea was then injected with a syringe through a septum. Each experiment was performed twice to ensure repeatability. pH was measured to identify the hydroxide ion consumption in order to study the reaction kinetics. To succeed, this method required a precise pH meter (3 digits), calibrated for the appropriate pH range (pH 13-14), and a glass electrode, resistant to the suspension media. To fill these conditions, a Metrohm® Unitrode electrode was used so that the pH could be recorded every 0.5 second with an accuracy of ± 0.001 pH units. Typical examples of the temporal variation of pH recorded in this study are shown in Figure SM7. One could observe that, at the beginning of the recording, a transitional stage occurred corresponding to the time required to reach the perfectly mixed state of the liquid-solid suspension, before injecting the urea alkaline solution (5 mL). The two curves plotted on this figure also highlight the satisfactory repeatability of the experiments when two different solutions of urea in hydroxide solutions were injected in two identical suspensions of nickel(III) particles.

To understand how the reagent concentrations could affect the oxidation kinetic, and subsequently to identify the relevant kinetic parameters, an experimental workplan was established. It allowed varying the hydroxide concentrations from 5×10^{-3} to 5×10^{-2} mol.L⁻¹ and the urea concentrations from 10^{-2} to 3×10^{-1} mol.L⁻¹ (note that the latter value corresponds to the order of magnitude of the urea concentration in human urine). The choice was made to study

synthetic urea solutions with concentrations close to those found in human urine⁴⁰ allowing a rapid preliminary optimization of the system. In addition, the nickel(III) concentration was modified by working with both nickel(III) powders of different purities.

As a preliminary step, it was verified that (i) the chemical reaction that occurred when the alkaline urea solution was put into contact with chemically synthesized nickel(III) particles led to the productions of by-products in the liquid phase identical to those that took place on the bare nickel electrode, and (ii) the total organic carbon (TOC) concentration decreased during the reaction. For this purpose, the analytical procedure established in our previous study³⁰ was used, involving ionic chromatography and non-purgeable organic carbon.

Post-processing of the temporal pH-curves

The instantaneous rate of the reaction described by Eq. (2), expressed in $\text{mol} \cdot (\text{m}^3 \cdot \text{g}_{\text{cat}} \cdot \text{s})^{-1}$ and noted r_{χ} , was defined as the derivative of the extent of reaction, ξ , as a function of time, as shown in Eq. (11).

$$\begin{aligned} r_{\chi} &= -\frac{1}{m_{\text{cat}} \times V} \frac{d\xi}{dt} = -\frac{1}{m_{\text{cat}} \times V} \frac{dn_{\text{CO}(\text{NH}_2)_2}}{dt} = -\frac{1}{m_{\text{cat}} \times V \times v_{\text{Ni}(\text{III})}} \frac{dn_{\text{Ni}(\text{III})}}{dt} \\ &= -\frac{1}{m_{\text{cat}} \times v_{\text{OH}^-}} \frac{d[\text{OH}^-]}{dt} \end{aligned} \quad (11)$$

where m_{cat} is the nickel(III) mass (expressed in grams of catalyst, g_{cat}), v_i the stoichiometric coefficient of the reactant i in Eq. (2), V the reaction mixture volume (assuming the volume constant versus time, m^3) and $n_{\text{Ni}(\text{III})}$ the amount of nickel(III) sites into the solid particles of $\text{NiOOH}/\text{Ni}(\text{OH})_2$ that were accessible to the reagents (urea and OH^-).

The kinetic law of the chemical reaction was assumed to obey Eq. (12).

$$r_{\chi} = k_{\chi} \times [\text{CO}(\text{NH}_2)_2]^{\alpha_{\chi}} \times [\text{OH}^-]^{\beta_{\chi}} \times (\rho_{\text{cat}})^{\gamma_{\chi}} \quad (12)$$

where α_{χ} , β_{χ} , γ_{χ} are the partial orders of the reaction, respectively related to urea, hydroxide, and chemically synthesized nickel(III) sites, k_{χ} the reaction rate constant

$(\text{mol}^{1-(\alpha_\chi+\beta_\chi)} \cdot (\text{m}_{\text{bulk}}^3)^{\alpha_\chi+\beta_\chi+\gamma_\chi-1} \cdot \text{g}_{\text{cat}}^{-(1+\gamma_\chi)} \cdot \text{s}^{-1})$ and ρ_{cat} the mass concentration of nickel(III) per unit of volume ($\text{g}_{\text{cat}} \cdot \text{m}^{-3}$).

Despite the similarity in terms of by-products, the fundamental mechanisms underlying the urea degradation (in particular adsorption/desorption ones) were different, depending on whether the nickel(III) sites used was electrochemically generated or chemically synthesized. For this reason, distinct notations were used for the kinetic law: r_χ for chemically synthesized sites (defined in Eq. (12)) and $r_{\text{E}\chi}$ for electrogenerated sites.

The conversion rate of the HCR reaction, noted X, could be calculated from the pH measurements, according to Eq. (13).

$$X(t) = 1 - \frac{10^{\text{pH}(t)-14}}{10^{\text{pH}_{t=0}-14}} \quad (13)$$

The experimental curves, $\text{pH}(t)$, were systematically smoothed using a polynomial of order 6 as the raw data were slightly noisy, mainly due to disturbances caused by the stirring and specifically by the flow of the solid particles across the pH electrode.

In this work, the initial reaction rates, r_χ^0 , were determined for conversions never exceeding 5 % of the initial hydroxide concentration, and calculated from the slope of the $\text{pH}(t)$ curve measured some seconds after the urea injection. The time period considered to calculate these slopes (typically between 5 s and 50 s) slightly impacted the obtained valued, as shown in Table SM2 (refer to §SM. 4).

Kinetic investigations of the reaction between urea and the electrochemically generated nickel(III) sites in alkaline medium

Experimental set-up

The same set-up as the one developed in our previous study³⁰ was used for determining the partial orders. The three-electrode cell was connected to a potentiostat (PGSTAT 128 N, Metrohm Autolab[®], Switzerland), and consisted of:

- a rotating nickel disk (2 mm diameter) as the working electrode (WE),
- a Hg/HgO as the reference electrode (Origasens, Origalys[®], France),
- a Pt foil (40 mm²) as the counter-electrode (CE).

All trials were repeated three times and the potentials were reported vs. Hg/HgO throughout the article. The temperature of the reaction medium was regulated by flowing a thermostatic solution in the double-jacketed electrochemical cell. Measurements were performed using various concentrations of urea and KOH and four different working electrode surfaces, ranging from 8.7 to 15.4 mm². The latter were elaborated by introducing a thin square shaft into a glass tube filled with alkaline resistant glue and then polished to obtain a smooth rectangular section of bare nickel with surface areas as mentioned above.

Expression of reaction rate

The reaction rate of the HCR on electrogenerated nickel(III) sites, standardized by the electrode surface, is expressed in mol. (m_{elec}² · m_{bulk}³ · s)⁻¹ and defined as the flux density of the superficial chemical reaction by Eq. (14).

$$r_{EX} = k_{EX} \times [\text{CO}(\text{NH}_2)_2]_{(t)}^{\alpha_{EX}} \times [\text{OH}^-]_{(t)}^{\beta_{EX}} \times (S_{elec})^{\gamma_{EX}} \quad (14)$$

where k_{EX} as the reaction rate constant

(mol^{1-($\alpha_{EX}+\beta_{EX}$)} · (m_{elec}²)^{-(1+ γ_{EX})} · (m_{bulk}³) ^{$\alpha_{EX}+\beta_{EX}-1$} · s⁻¹), S_{elec} the surface of the bare nickel

electrode (m_{elec}^2) and $\alpha_{\text{EX}}, \beta_{\text{EX}}, \gamma_{\text{EX}}$ the partial orders of urea, hydroxide, and electrochemically generated nickel(III), respectively.

Results on the kinetic of the catalytic indirect urea oxidation

Case 1: with chemically synthesized nickel(III) sites

Determination of the initial kinetic rate law

The initial rate method is a well-known approach^{41,42}, enabling the partial orders of each reactant to be determined by varying studied reactant concentration while keeping constant the other reactant concentrations and the operating conditions constant (temperature, stirring).

To determine the partial order of urea, noted α_{X} , several temporal pH measurements were performed and the related initial rates, r_{X}^0 , determined. By varying the initial concentration of urea from 0.02 to 0.25 mol.L⁻¹, and by keeping $[\text{OH}^-] = 0.005 \text{ mol.L}^{-1}$ and the nickel particle mass equal to 30 kg_{cat}.m⁻³ (nickel(III) powder - sample 2), the initial kinetic rate law (Eq. (11)) can be written as Eq. (15).

$$r_{\text{X}}^0 = k_{\text{app}} \times [\text{CO}(\text{NH}_2)_2]^{\alpha_{\text{X}}} \quad (15)$$

where k_{app} is the related apparent constant ($\text{mol}^{1-\alpha_{\text{X}}} \cdot (\text{m}_{\text{bulk}}^3)^{\alpha_{\text{X}}-1} \cdot (\text{g}_{\text{cat}} \cdot \text{s})^{-1}$).

The variation of the logarithmic initial reaction rate versus the logarithmic urea concentration, plotted in **Erreur ! Source du renvoi introuvable.-a**, can be assumed linear despite a rather strong dispersion. From the slope of the related straight line, the partial order of urea is found equal to $\alpha_{\text{X}} = 0.2 \pm 0.1$. This low value suggests that the kinetic rate slightly depends on the urea concentration, which can be explained by these assumptions:

- (i) the strong affinity of urea to the nickel peroxide particles. Several works have studied the adsorption of urea molecules on various adsorbents: nickel(II) oxide NiO⁴³, nickel nanoparticles embedded in carbon nanotubes⁴⁴, and nickel(III) sites⁴⁵. Whatever the adsorbent nature, a strong affinity of urea with nickel⁴³ and a low

adsorption energy of urea⁴⁶ have been reported. According to the Langmuir isotherm theory (Eq. (16)), the adsorbate forms a single layer onto an adsorbent surface⁴⁷. The adsorbate (urea) amount can be expressed using the equilibrium constant of the adsorption step, K, and the maximum nickel(III) surface concentration , Γ_{\max} (mol.m⁻²). It is important to keep in mind that a multilayer urea adsorption on the active nickel(III) sites seems hard to envisage due to the steric effects and to the weak affinity of oxygen to nitrogen.

$$\Gamma = \frac{\Gamma_{\max} \times K \times [\text{CO}(\text{NH}_2)_2]}{1 + K \times [\text{CO}(\text{NH}_2)_2]} \quad (16)$$

where Γ the nickel surface concentration (mol.m⁻²).

In this case, the urea superficial concentration on the nickel(III) sites can be simplified ($K \times [\text{CO}(\text{NH}_2)_2] \gg 1$) as Eq. (17).

$$\Gamma = \Gamma_{\max} \quad (17)$$

This means that adsorption is rapid and limited by accessible nickel(III) sites. Once one urea reacts with two nickel(III) sites, the intermediates must desorb and subsequently compete with urea for adsorption on the active sites. The urea concentration remains lower than the amount of nickel(III) sites.

- (ii) the mass transfer limitations of the reagents into the internal nickel oxides layers of core-shell particles⁴⁸.

The same method was implemented for determining the hydroxide partial order, β_x , by varying the related concentration between 0.005 and 0.05 mol.L⁻¹. Here, the simplified initial kinetic rate law can be deduced from Eq. (11) and can be written as Eq (18).

$$r_x^0 = k'_{\text{app}} \times [\text{OH}^-]^{\beta_x} \quad (18)$$

where k'_{app} is the related apparent constant (as $k'_{\text{app}} = k_x \times [\text{CO}(\text{NH}_2)_2]^{0.2} \times (\rho_{\text{cat}})^{\gamma_x}$).

Erreur ! Source du renvoi introuvable.-b presents the variation of the logarithmic initial reaction rate versus the logarithm of the hydroxide concentration, for five different urea

concentrations ranging from 0.01 to 0.3 mol.L⁻¹. These variations are assumed linear and their slopes, determined for various urea concentrations, are reported in **Erreur ! Source du renvoi introuvable.**-c. This leads to $\beta_{\chi} = 0.6 \pm 0.2$. As urea has been found to slightly impact the reaction rate, a small variation of the apparent constants, k'_{app} , as a function of the urea concentration is observed in the inset of **Erreur ! Source du renvoi introuvable.**-d, likely due to some measurement errors. From this, an average value of the apparent constant is found equal to $0.38 \times 10^{-2} \text{ mol}^{0.4} \cdot (\text{m}^3_{\text{bulk}})^{-0.4} \cdot (\text{g}_{\text{cat}} \cdot \text{s})^{-1}$.

By modifying the nickel(III) purity of the synthesized powders (samples 1 and 2, refer to **Erreur ! Source du renvoi introuvable.**) and keeping constant the initial concentrations of urea at 0.3 mol.L⁻¹ and of hydroxide at 0.005 mol.L⁻¹, the partial order of nickel(III), γ_{χ} , can be deduced as Eq. (19).

$$r_{\chi}^0 = k''_{app} \times (\rho_{\text{cat}})^{\gamma_{\chi}} \quad (19)$$

where k''_{app} is the related apparent constant ($\text{mol} \cdot (\text{m}^3_{\text{bulk}})^{\gamma_{\chi}-1} \cdot \text{g}_{\text{cat}}^{-(1+\gamma_{\chi})} \cdot \text{s}^{-1}$).

Considering that the mass concentration of nickel(III), ρ_{cat} , is the product of the mass of powder introduced and the nickel(III) content in the powder, the slope of Eq. (20) allows the reaction order of nickel(III) to be determined.

$$\ln(r_{\chi}^0) = \ln(k''_{app}) + \gamma_{\chi} \times \ln(\text{mass of powder} \times \text{purity}) \quad (20)$$

Finally, γ_{χ} is found almost equal to 1.9 ± 0.2 which can be interpreted as the number of nickel(III) sites (NiOOH in fact) involved in the urea oxidation reaction.

Once the partial orders are determined, the kinetic constant, k_{χ} , is calculated using the values of (i) initial concentrations of the reagents and of (ii) initial rates measured for 35 trials according to Eq. (12). As illustrated in Figure SM8 (refer to §SM. 5), k_{χ} ranges from $k_{\chi, \text{low}} = 0.24 \times 10^{-12}$ to $k_{\chi, \text{high}} = 7.7 \times 10^{-12} \text{ mol}^{0.2} \cdot (\text{m}^3_{\text{bulk}})^{1.7} \cdot \text{g}_{\text{cat}}^{-2.9} \cdot \text{s}^{-1}$, and the average value equal to is $k_{\chi, \text{mean}} = 3.8 \times 10^{-12} \text{ mol}^{0.2} \cdot (\text{m}^3_{\text{bulk}})^{1.7} \cdot \text{g}_{\text{cat}}^{-2.9} \cdot \text{s}^{-1}$.

Therefore, the overall empirical kinetic law of urea oxidation in presence of chemically generated nickel(III) sites can be expressed by Eq. (21).

$$r_x = (3.8 \pm 2.0) \times 10^{-12} \times [\text{CO}(\text{NH}_2)_2]^{0.2} \times [\text{OH}^-]^{0.6} \times \rho_{\text{cat}}^{1.9} \quad (21)$$

It should be kept in mind that (i) as the urea molecules penetrate into the NiOOH/Ni(OH)₂ particles, they are oxidized and the NiOOH is reduced to Ni(OH)₂ and (ii) the urea oxidation products generated then have to diffuse deeper into the particle to encounter another nickel(III) active site and to continue their mineralization. As mentioned above, the occurrence of mass transfer limitations could also contribute to slowing down the reaction rate.

In the case of such synthesized nickel particles, the regeneration of nickel(III) sites cannot occur after being consumed by urea; the UEO by-products must desorb and meet another new nickel(III) site, introducing possible additional mass transport limitation phenomena.

Validation of the initial kinetic rate law by the integral method

In this section, it is assumed that there is no limitation by the mass transport (urea or/and OH⁻), inside or outside of the NiOOH/Ni(OH)₂ particles. Following this assumption, the validity of the kinetic rate law determined previously (Eq. (21)) must be confirmed. To this end, it is necessary to numerically integrate the equation as a function of time and to confront the theoretical temporal evolutions of the reactant concentrations with the experimental data.

Using the integral method for kinetic investigations offers the advantage⁴⁹ to validate the reaction orders and the rate constant value obtained using the initial rate method (*i.e.* at short times and very low OH⁻ conversions below 5 %) for longer periods where high conversions are achieved and where secondary reactions can also occur. The method for doing so entails a comparison between the experimental and predicted temporal variations in OH⁻ concentration in order to validate the law derived from initial kinetics. **Erreur ! Source du renvoi introuvable.** presents the chemical amounts of reactants, initially and at any time, where X represents the hydroxide conversion rate.

Without considering the real accessibility of the nickel(III) sites in the synthesized core-shell particles, the theoretical profiles tend towards the experimental values but significant deviations of magnitude are obtained (deviation > 50 %) and are even greater for the highest reactant concentration (results not shown). In order to describe the physics of the system (*i.e.* spherical layers of NiOOH around a core of Ni(OH)₂), a surface accessibility factor of nickel(III), noted ε , is voluntarily introduced. Such choice is motivated by the fact that (*i*) the spatial distribution of nickel(III) on solid particles is probably not uniform, and (*ii*) the oxidation reaction of urea on nickel particles is a surface reaction, and the by-products and reaction intermediates formed inside the particle consume the OH⁻ ions. This latter consumption, not considered in the kinetic model studied here, will lead to a diffusional limitation of hydroxide ions within the particles. The parameter, ε , offers the advantage to fill this bias. Note that the relating value, not measured, will be the single fitting parameter of the model.

By coupling Eq. (11) expressed as a function of hydroxide ions and Eq. (21), Eq. (22) is obtained.

$$\frac{dX}{dt} = \frac{6m_{\text{cat}}k_{\chi}b^{0.6}}{[\text{OH}^{-}]^0} \times \left(\frac{6a - bX}{6V}\right)^{0.2} \times \left(\frac{(1 - X)}{V}\right)^{0.6} \times \left(\frac{(c' - bX) \times M_{\text{NiOOH}}}{V}\right)^{1.9} \quad (22)$$

The previous equation is numerically solved (using `scipy.integrate.odeint` Python package solving a system of ordinary differential equations), and the theoretical temporal conversion of hydroxide with time is obtained, as reported in **Erreur ! Source du renvoi introuvable.** The surface accessibility factor of nickel(III), ε , used to plot these figures is equal to 2.6 %, suggesting then that a small amount of nickel(III) is available for the chemical reaction. Indeed, after a first cycle of adsorption, the urea molecules having a strong affinity to nickel(III) could induce a “screen effect”, thus reducing the number of nickel(III) sites into the internal layers of the particles. **Erreur ! Source du renvoi introuvable.** also reports a sensitivity study with regard to the chemical kinetic constant, k_{χ} : a maximum deviation of 20 % is observed for the reaction times longer than 600 seconds. The validity of the kinetic rate law is then checked by

considering several initial concentrations of urea and hydroxide ions. Whatever the concentrations, the numerical profiles of the conversion of OH^- do not deviate (maximum deviation of 6 %) from the experimental data for $X < 20\%$ ($\varepsilon = 2.6\%$). As expected, higher conversions are observed when the initial hydroxide ions' concentration is decreased. **Erreur ! Source du renvoi introuvable.** shows that the temporal profiles obtained using the kinetic rate law constant $k_{X,\text{low}}$, $k_{X,\text{mean}}$ or $k_{X,\text{high}}$ determined from the previous section (refer to §SM. 5) correlate very well (maximum deviations of 10 %) with the experimental ones for a period longer than 200 sec. It can be noted that for unfavorable conditions, illustrated in Figure 2-c (*i.e.* the lowest ratio between the initial concentration of hydroxide ions and urea, almost equal to 1.7×10^{-2}), the deviation between the experimental and predictive profiles is higher than 20 % after 600 sec. This slowing down of the urea oxidation could be explained by two assumptions: (*i*) an internal diffusional limitation of the reactants (urea and hydroxide) and by-products in the particles could limit the reaction process after consuming all the nickel(III) active sites on the catalyst surface and (*ii*) a competitive adsorption between the by-products and the reactants could also occur.

Case 2: with the electrochemically synthesized nickel(III) sites on bare nickel electrode

In the present section, the NiOOH sites are electrochemically regenerated on a bare nickel anode and react with urea. As shown in our previous work³⁰, the coupling of the HCR (Urea/NiOOH) with the ER (NiOOH/Ni(OH)₂) allows the continual regeneration of the active nickel(III) sites if the nickel oxide anode is polarized to the appropriated potential. It becomes then possible to study only the HCR and thus to avoid the adsorption/desorption processes as well as the mass transport of urea and oxidation products from one nickel(III) molecule to the other (refer to §3.1.2). For that, the current potential curves have been plotted by applying a potential scan rate lower than $1 \text{ mV}\cdot\text{s}^{-1}$. This technique has been applied here for different

operating parameters, with the aim of establishing the kinetic law of the UEO in presence of electrogenerated NiOOH sites at the anode.

The i-E curves obtained at steady state conditions are showed in **Erreur ! Source du renvoi introuvable.**-a-b-c. From them, the partial orders of urea, hydroxide ions and nickel(III) sites have been determined, as shown in **Erreur ! Source du renvoi introuvable.**-d-e-f respectively.

The potentiostatic polarization of the nickel electrode at the plateau of the i-E curves allows the anode to be covered by Ni(OH)₂ which oxidizes into NiOOH. The urea is oxidized by a chemical reaction with NiOOH which is reduced into Ni(OH)₂, immediately oxidized on the nickel electrode into NiOOH, thus releasing its electron. The newly regenerated NiOOH goes on a new cycle with the urea oxidation intermediate, thus meaning that the urea and its by-products formed could be oxidized by the same nickel system, without any mass transfer limitation. The oxidation process continues until obtaining the final products (N₂, CO₂, etc).

Under steady state conditions, the mass balance on nickel(III) is expressed as Eq. (23).

$$\frac{d\Gamma_{\text{III}}}{dt} = \frac{I_{\text{plateau}}}{n\mathcal{F}S_{\text{electrode}}} - \nu_{\text{NiIII}} \times r_{\text{EX}} \times V \quad (23)$$

where Γ_{III} is the nickel surface concentration (mol.m⁻²), I_{plateau} as the limiting current, observed at the plateau signal (A), n the number of exchanged electron (1, dimensionless), \mathcal{F} the Faraday constant (C.mol⁻¹), ν_{NiIII} the stoichiometric coefficient of nickel(III) and r_{EX} the reaction rate of the HCR on electrogenerated nickel(III) sites (mol. (m_{elec}². m_{bulk}³. s)⁻¹).

It is obvious that after a certain time, the redox system NiOOH/Ni(OH)₂ will reach a steady state until the concentration of urea is sufficient to supply the system. In this case, the accumulation of the nickel(III) at the nickel surface can be assumed equal to zero. The current intensity of the plateau is thus proportional to the reaction rate as Eq. (24).

$$I_{\text{plateau}}^{\infty} = n\mathcal{F} \times V \times \nu_{\text{NiIII}} \times k_{\text{EX}} \times [\text{CO}(\text{NH}_2)_2]^{\alpha_{\text{EX}}} \times [\text{OH}^-]^{\beta_{\text{EX}}} \times (S_{\text{electrode}})^{\gamma_{\text{EX}}+1} \quad (24)$$

where $I_{\text{plateau}}^{\infty}$ is the limiting current in steady state conditions (A).

As for the initial rate method in §3.1.1, by applying the logarithm to Eq. (24) and by varying the molar concentration of one reactant, the partial orders can be deduced, according to Eqs. (25)-

(27).

$$\log(j_{\text{plateau}}^{\infty}) = \log(n\mathcal{F} \times k_{\text{E}\chi} \times [\text{OH}^-]^{\beta_{\text{E}\chi}} \times (S_{\text{electrode}})^{\gamma_{\text{E}\chi}}) + \alpha_{\text{E}\chi} \times \log([\text{CO}(\text{NH}_2)_2]) \quad (25)$$

$$\log(j_{\text{plateau}}^{\infty}) = \log(n\mathcal{F} \times k_{\text{E}\chi} \times [\text{CO}(\text{NH}_2)_2]^{\alpha_{\text{E}\chi}} \times (S_{\text{electrode}})^{\gamma_{\text{E}\chi}}) + \beta_{\text{E}\chi} \times \log([\text{OH}^-]) \quad (26)$$

$$\log(I_{\text{plateau}}^{\infty}) = \log(n\mathcal{F}S_{\text{electrode}} \times k_{\text{E}\chi} \times [\text{CO}(\text{NH}_2)_2]^{\alpha_{\text{E}\chi}} \times [\text{OH}^-]^{\beta_{\text{E}\chi}}) + \gamma_{\text{E}\chi} \times \log(S_{\text{electrode}}) \quad (27)$$

where $j_{\text{plateau}}^{\infty}$ is the limiting current density corresponding to the plateau of the signal in steady state (A.m^{-2}).

The related plots are reported in **Erreur ! Source du renvoi introuvable.**-d-e-f. A value of $\alpha_{\text{E}\chi} = 0.3 \pm 0.1$ is obtained for the partial order of urea, which correlates to the value obtained with chemically synthesized nickel(III) sites (refer to section §3.1.1). The partial order of hydroxide ions is found equal to $\beta_{\text{E}\chi} = 0.9 \pm 0.1$. This value is slightly higher than the previous one ($\beta_{\chi} = 0.6$), which can be attributed to the fact that in addition to urea oxidation, the electrogeneration of nickel(III) requires one hydroxide ion and thus implies a stronger dependence on the chemical rate by hydroxide ions. Lastly, the partial order of nickel(III) is found equal to $\gamma_{\text{E}\chi} = 5.0 \pm 0.5$. This high value would suggest that, during the potentiostatic polarization, a nickel active site is regenerated five times on the electrode surface per adsorbed urea. Since the number of urea adsorption sites onto nickel(III) is continuously electro-regenerated, the adsorbed urea molecule can be completely oxidized without any desorption of intermediates, contrary to the case with chemically synthesized particles, containing sacrificial NiOOH.

Once the partial orders are known, the kinetic constant, noted $k_{\text{E}\chi}$, is deduced using the same method as in section §3.1.1. On the basis of eleven experiments carried out (refer to §SM. 6),

k_{EX} is found to vary in the range from 2.32×10^{24} to 4.24×10^{24} $\text{mol}^{-0.2} \cdot (\text{m}_{\text{elec}}^2)^{-6} \cdot (\text{m}_{\text{bulk}}^3)^{0.2} \cdot \text{s}^{-1}$. The average value is equal to 2.86×10^{24} $\text{mol}^{-0.2} \cdot (\text{m}_{\text{elec}}^2)^{-6} \cdot (\text{m}_{\text{bulk}}^3)^{0.2} \cdot \text{s}^{-1}$ and used for the following calculations. The magnitude of this apparent constant reflects the heterogeneous nature of the HCR reaction. Indeed, the value of the apparent constant is issued from a kinetic law which involves, on the one hand, volume concentrations and, on the other, a superficial concentration (normalized to the catalyst mass for r_{χ}) at a high partial order (2 for r_{χ} and 5 for r_{EX}).

Finally, the proposed kinetic law for the urea oxidation by the electrochemically generated nickel(III) sites can be written as Eq. (28).

$$r_{EX} = (2.86 \pm 1.38) \times 10^{24} \times [\text{CO}(\text{NH}_2)_2]^{0.3} \times [\text{OH}^-]^{0.9} \times (S_{\text{electrode}})^5 \quad (28)$$

Proposed mechanism for the complete urea electro-oxidation

Based on previous work³⁰, **Erreur ! Source du renvoi introuvable.**-a-b propose an overall mechanism for urea degradation involving electrochemically generated nickel(III) sites. The reaction scheme is composed of different pathways leading to the formation of by-products previously identified in the liquid phase.

The urea degradation mechanism from electrogenerated nickel(III) site can be classified into the nucleophilic oxidation reaction class^{50,51} (as for the methanol oxidation on nickel(III)⁵²), involving two pathways successively: (i) electrogenerated $\text{Ni}(\text{OH})_2$ catalyst dehydrogenation reaction followed by (ii) a spontaneous nucleophilic dehydrogenation reaction. Firstly, the urea is adsorbed on a nickel(III) site⁵³, formed by the catalyst dehydrogenation reaction of nickel(II) oxidation. By analogy to the urease action on urea^{54,55}, a second active nickel(III) site is required to pursue oxidation (step 2). Following the first nucleophilic attack on a hydroxide group, two reactional pathways (step 3 and/or step 20) can be considered, favoring the formation of either ammonia (step 5), nitrite (steps 4, 8-19), carbonate ions (steps 4-7), or cyanate ions (steps 20-

22). The formation of ammonia and carbonate ions belongs to the same reactional pathway, thus suggesting an equimolar formation of these by-products over time. The nitrification route on nickel sites shown in **Erreur ! Source du renvoi introuvable.** leads to the formation of nitrite. This route has been already studied by DFT⁵⁶, voltammetry and electrolyzes⁵⁷. This latter route does not rule out the production of nitrogen during oxidation, even if several works^{24,25,30,58} have reported the overoxidation of nitrogen into undesired NO_x compounds at the expense of a nitrogen production. It should be noted that (i) the formation of cyanate (steps 21-22) and nitrite (steps 4, 18, 19) ions occurs in equimolar condition, and (ii) most of the reactions constituting the proposed mechanism require hydroxide ions, and consequently directly decrease the local pH at the electrode surface. The proposed mechanism illustrates a succession of redox reactions between the catalyst (i.e., nickel(III)), both adsorbed urea and oxidation intermediates. The main idea of this mechanism is that nickel(II) is continuously oxidized into nickel(III) at the applied potential, thus providing a continuous source of electrons for UEO. Note that Wang et al³¹ summarized various mechanism found in the bibliography without any quantitative mass balances after electrolyzes. These works consider that the attack of hydroxide ions (strongly alkaline electrolyte) allows deprotonation of adsorbed urea. In the future, one can expect that using *ad hoc* co-catalysts, or even fine controlled potential would make it possible to favor certain mechanistic pathways so as to increase, for example, the yield of nitrogen to the detriment of the nitrite production.^{14,59}

This reaction scheme reflects the complexity of a fully detailed kinetic approach that will require a very large number of experiments so as to be able to determine each elementary kinetic constant (from k_1 to k_{22} , forward and backward).

Global modeling of the urea electro-oxidation

Establishment of the predictive model

Various potentiostatic electrolyses with high conversions of urea have been performed in our previous work³⁰, for which the variations of the concentrations of urea and by-products with electrolysis times have been determined and can be thus used to validate the model. The latter is based on the kinetic data obtained in the previous sections and involves all the physical processes occurring at the anode and in the bulk. Besides, the model is expected to be applicable on a large scale.

A one-dimensional description, as a function of the distance to the electrode, can be considered sufficient (for parallelepipedal electrochemical cells and planar anodes) to solve the mass transport phenomena coupled to the HCR in a porous catalytic layer. A schematic representation of the half-cell is given in **Erreur ! Source du renvoi introuvable.**

The aim here is to model the behavior of the electrochemical system during potentiostatic electrolyses on a massive nickel electrode (supposed in equipotential conditions) of a stirred aqueous solution of urea in an alkaline medium. During the electrode polarization, the following reactions will take place on the nickel compounds; starting with Eq. (29) and followed by Eq (1). At the applied electrolysis potential (*i.e.* the one measured at the diffusion plateau of *i*-E curves, 0.55 V as illustrated in **Erreur ! Source du renvoi introuvable.**), the reaction described in Eq. (29) occurs until the electrode is completely covered by a Ni(OH)₂ layer. Then the catalytic cycle urea/NiOOH/Ni(OH)₂ occurs.



Model assumptions

With the objective of building a robust model, it is necessary to formulate a clear framework and the appropriated assumptions:

(i) Nickel(II) oxidation reaction occurs in a layer of a constant thickness μ which porosity ω , tortuosity τ and surface in contact with the solution remain unchanged throughout the electrolysis. Such assumption is supported by the fact that no significant release of nickel oxides has been measured by inductively coupled plasma (ICP) measurements performed at the end of each electrolysis (detection limit equals 100 ppb). Porosity is evaluated considering that the nickel sites in the reactive layer are disposed as face-centered cubic unit cell with an atomic packing factor estimated at 0.74. Moreover, the tortuosity, τ , is estimated at $\pi/2$ as the ratio between the half-circumference of a sphere ($\pi \times r$) and the diameter of the sphere ($2 \times r$) (corresponding to the shortest path). The diffusion coefficient in the reactive layer ($\delta < z < \delta + \mu$) is then calculated as an effective diffusion coefficient $D_{i,w}^{\text{eff}}$ according to Eq. (30).

$$D_{i,w}^{\text{eff}} = D_{i,w} \times \frac{\omega}{\tau} \quad (30)$$

where $D_{i,w}$ is the diffusion binary coefficient of the specie i in the water ($\text{m}^2 \cdot \text{s}^{-1}$), ω the porosity of the layer of thickness μ (dimensionless) and τ the tortuosity (dimensionless). The values of the urea diffusion coefficient were previously calculated for different KOH concentrations, from the Stokes-Einstein equation³⁰.

(ii) The nickel oxides $\text{Ni}(\text{OH})_2$ and NiOOH are considered here as electronic conductors^{60,61}, making the electronic transfer invariant in the whole μ layer. Most of the electrolyzes are performed under potentiostatic conditions. Since the applied potential is sufficiently anodic to allow (energetically speaking) the immediate conversion of any $\text{Ni}(\text{OH})_2$ released from the HCR to NiOOH , one can assume that after a few minutes' electrolysis, the surface concentrations of $\text{Ni}(\text{OH})_2$ and NiOOH become constant and that the term related to the accumulation of these species is null. It is assumed that all the active sites in the reactive

layer ($\delta < z < \delta + \mu$) are electronic conductors, in contact with the ions in solution. This hypothesis is supported by the following points:

- according to previous work³⁰, one ER/HCR cycle occurs more than 100 times at low scan rates (i.e., $<1 \text{ mV}\cdot\text{s}^{-1}$). The nickel(III) or nickel(II) cannot thus crystallize in an organized lattice, which creates some disorder in this layer²².
- moreover, at the initial time, the massive nickel electrode is only composed of nickel(0). As a result of polarization, the layer thickness grows towards the massive nickel(0) electrode: a previous study using i-E curves highlights that 110 layers of active sites are formed³⁰. For forming a new layer, a hydroxide ion should be present and must diffuse/migrate from the bulk, according to Eq. (1). The water molecules produced should also be removed from the layer by mass transport.

(iii) The geometry of the system is supposed to be independent of the length and width of the reactive layer and the radial diffusion to be negligible. Once formed, NiOOH will react with urea and hydroxide ions according to Eq. (31).

$$r_{\text{Ex}}(\delta \leq z \leq \delta + \mu, t) = k_{\text{Ex}} \times [\text{OH}^-]^{\beta_{\text{Ex}}} \times (S_{\text{elec}})^{\gamma_{\text{Ex}}} \times [\text{CO}(\text{NH}_2)_2]_{(\delta \leq z \leq \delta + \mu, t)}^{\alpha_{\text{Ex}}} \quad (31)$$

$$= k_{\text{app}} \times [\text{CO}(\text{NH}_2)_2]_{(\delta \leq z \leq \delta + \mu, t)}^{\alpha_{\text{Ex}}}$$

where k_{app} is the apparent constant $(\text{mol}^{1-\alpha_{\text{Ex}}}) \cdot (\text{m}_{\text{elec}}^2)^{-1} \cdot (\text{m}_{\text{bulk}}^3)^{\alpha_{\text{Ex}}-1} \cdot \text{s}^{-1}$.

It should be noted that the proposed kinetic equation does not take into account the consumption of nickel peroxide and hydroxide ions during the chemical reactions leading to products and by-products.

(iv) The concentration of urea and hydroxide ions in the layer μ is considered as a spatially continuous function; the nickel particles are assumed to be small enough not to impact the spatial concentration profile.

Governing equations: urea mass balances

From these assumptions, the predictive model gives the urea concentration profile in all areas indicated in **Erreur ! Source du renvoi introuvable.**. Into the bulk, the analyte is assumed to be perfectly stirred, and the urea concentration is therefore considered uniform in the bulk volume, Ω_B . The macroscopic balance of urea can be written as Eq. (32).

$$\begin{aligned}
 & \text{Accumulation flux} + \text{Diffusion flux} + (\text{Feed} + \text{Output})_{\text{flux in continuous reactor}} = 0 \\
 \Omega_B \quad & v^{\text{bulk}} \times \frac{\partial [\text{CO}(\text{NH}_2)_2]_{z \leq 0}}{\partial t} + \left[D_{\text{urea,w}} \times S_{\text{electrode}} \times \frac{\partial [\text{CO}(\text{NH}_2)_2]}{\partial z} \right]_{z=0} \\
 z \leq 0 \quad & + Q \times ([\text{CO}(\text{NH}_2)_2]_{\text{Feed}} - [\text{CO}(\text{NH}_2)_2]_{\text{Output}}) = 0
 \end{aligned} \tag{ 32 }$$

where Q is the volumetric flow rate ($\text{m}^3 \cdot \text{s}^{-1}$).

In the present work, the results are obtained in a batch electrolyzer ($Q = 0$). Unlike in Ω_B , the urea concentration in the diffusion film Ω_F , is subject to spatial variation caused by the urea diffusion phenomenon due to the chemical reaction in Ω_{EC} . The microscopic mass balance can be written as Eq. (33).

$$\begin{aligned}
 & \text{Accumulation flux} + \text{Diffusion flux} = 0 \\
 \Omega_F \quad & (S_{\text{electrode}} \times \delta) \times \left[\frac{\partial [\text{CO}(\text{NH}_2)_2]}{\partial t} - \left[D_{\text{urea,w}} \times \frac{\partial^2 [\text{CO}(\text{NH}_2)_2]}{\partial x^2} \right] \right] = 0 \\
 0 \leq z \leq \delta \quad &
 \end{aligned} \tag{ 33 }$$

In the Ω_{EC} area, the coupling of the HCR to the urea diffusion into the porous solid are the main occurring phenomena. The microscopic mass balance can be written according to Eq. (34).

$$\begin{aligned}
 & \text{Accumulation flux} + \text{Chemical reaction flux} + \text{Diffusion effective flux} = 0 \\
 \Omega_{EC} \quad & (S_{\text{electrode}} \times \mu) \times \left[\frac{\partial [\text{CO}(\text{NH}_2)_2]}{\partial t} + S_{\text{electrode}} \times r_{\text{EX}} \right. \\
 \delta \leq z \leq \delta + \mu \quad & \left. - D_{\text{urea,w}}^{\text{eff}} \times \frac{\partial^2 [\text{CO}(\text{NH}_2)_2]}{\partial x^2} \right] = 0
 \end{aligned} \tag{ 34 }$$

Eq. (34) represents a classical situation of a boundary value problem (shooting method) and its resolution is well documented in other works^{62,63}. The resolution state of the model is a pseudo-steady state where the resolution is established by a succession of steady states, in the mass transport area as well as the electroactive layer, and a transient state in the bulk. The model resolution method is presented in §SM. 7.

Boundary and initial conditions

The following initial and boundary conditions are applied:

- (i) At an initial time, the urea concentration is assumed to be uniform throughout the whole system and equal to the initial concentration in the volume according to Eq. (35).

$$\begin{array}{l} \forall \Omega \\ t = 0 \end{array} \quad C(z, 0) = C_{ini} \quad (35)$$

- (ii) It is considered that the urea does not directly react at the electrode neither with Ni(OH)₂ nor Ni; therefore, the mass flux arriving at the surface of the metal electrode Λ_E and at both frontiers Λ_P of the system, are assumed to zero according to Eq. (36).

$$\begin{array}{l} \forall \Lambda_E, \Lambda_P \\ \forall t \end{array} \quad \left. \frac{\partial [CO(NH_2)_2]}{\partial z} \right|_{z=\Lambda_E, \Lambda_P} = 0 \quad (36)$$

- (iii) The continuity of the concentrations in each Ω domain, especially in the Ω_{EC} area, is ensured by the equality of the concentrations at each Λ boundary of the system following the Eqs. (37)-(38) :

$$\forall t \quad C_{\Omega_B, \Lambda_{BF}}(0, t) = C_{\Omega_F, \Lambda_{BF}}(0, t) \quad (37)$$

$$C_{\Omega_F, \Lambda_{FEC}}(\delta, t) = C_{\Omega_{EC}, \Lambda_{FEC}}(\delta, t) \quad (38)$$

(iv) Since the mass transport properties are significantly different in the domains Ω_F and Ω_{EC} (diffusion constant, thickness, concentration continuity), the equality of urea flux can be described as Eq. (39).

$$\forall t \quad \frac{D_{urea,w}}{\delta} \times \frac{\partial[\text{CO}(\text{NH}_2)_2]}{\partial z} \Big|_{z=\Lambda_{FEC}}^{\Omega_F} = \frac{D_{urea,w}^{eff}}{\mu} \times \frac{\partial[\text{CO}(\text{NH}_2)_2]}{\partial z} \Big|_{z=\Lambda_{FEC}}^{\Omega_{EC}} \quad (39)$$

These changes can be expressed according to a Biot dimensionless number as shown in Eq. (40).

$$Bi = \frac{k_{m,\Omega_F}}{k_{m,\Omega_{EC}}} = \frac{D_{urea,w}}{\delta} \times \frac{\mu}{D_{urea,w}^{eff}} \quad (40)$$

where k_m is the mass transport coefficient (m.s^{-1}).

Comparison between predictions and experimental data

Thicknesses of the diffusion film and the electrocatalytic layer

Two physical dimensions of the system need to be determined prior to the application of the model: the thickness of the diffusion layer, δ , and the thickness of the electrocatalytic layer, μ . Concerning the diffusion layer, the anodic oxidation limit current, observed on the urea diffusion plateau, is proportional to the concentration of the electroactive species. Here, nickel(III) is the electroactive specie, but its concentration will vary proportionally to that of urea according the catalytic cycle already mentioned in the previous section. Then, the following Eq. (41) can be applied.

$$\delta = \frac{n \times \mathcal{F} \times D_{urea,w} \times [\text{CO}(\text{NH}_2)_2]^{bulk}}{j_{plateau}^{\infty}} \quad (41)$$

where $j_{plateau}^{\infty}$ is the limit current density current measured at the diffusion plateau in steady state (A.m^{-2}) at a potential varying from 0.51 to 0.55 V (refer to **Erreur ! Source du renvoi introuvable.**), n the number of exchanged electrons (dimensionless, 1 in case of

nickel(III)/nickel(II)). Considering the values obtained in **Erreur ! Source du renvoi introuvable.**-a for the lowest urea concentration (where the concentration of urea at the electrode is close to 0, the molar flux arriving at the electrode becomes constant), a value of $\delta = (3.4 \pm 0.2) \times 10^{-5}$ m is determined.

The thickness of the electrocatalytic layer has been estimated in our previous study³⁰, by determining the charge transferred during an i-E curve plotted using a massive nickel electrode in a 1 mol.L⁻¹ KOH solution; its value is equal to $\mu = (4.9 \pm 0.4) \times 10^{-8}$ m. This calculation leads to an estimation of 9.74×10^{20} sites.m⁻² of electrode, available at the surface.

Urea electrolysis on nickel electrode: case results and comparison

In order to evaluate the veracity of the model, the experimentally measured urea concentrations in the bulk for various electrolyzes for which high conversions are achieved, will be considered and compared to the ones predicted by the model.

Erreur ! Source du renvoi introuvable. illustrates the spatio-temporal profiles of the urea concentration predicted by the model. The three spatial zones are quite distinct and well represented, allowing a good understanding of the involved processes (Ω_B , Ω_F : transport phenomena / Ω_{EC} : transport phenomena and heterogeneous reaction). A non-linear time scale is represented for better readability of the phenomena occurring.

In the reaction area Ω_{EC} , the flux at the metal electrode (at $z = \delta + \mu$) equals zero. The concentration in this Ω_{EC} zone starts to decrease according to a non-linear profile and tends toward a pseudo-steady state until the chemical regime competes with the diffusion flux from the diffusion film Ω_F . A linear concentration profile in the Ω_F zone is thus obtained.

In the bulk area Ω_B , the assumption of a perfectly stirred batch reactor is equivalent to an identical concentration at all points (at $z < 0$). The breaking slope observed at $z = \delta$ is

representative of the urea fluxes transfer to the electrode. They indicate the discontinuities in the urea fluxes between the two media: liquid Ω_F and the catalytic Ω_{EC} layer of NiOOH/Ni(OH)₂. Both layers exhibit different mass transport properties (diffusion constant, thickness, concentration continuity) according to the Biot number in Eq. (40). In the experimental conditions related to **Erreur ! Source du renvoi introuvable.**, and at a KOH concentration of 5 mol.L⁻¹, this ratio between the mass transfer constants in the diffusion film and in the electrocatalytic layer, respectively, is estimated to be 112, thus reflecting a diffusional limitation in the porous zone compared to the diffusion film.

The inset in **Erreur ! Source du renvoi introuvable.** illustrates the simulated temporal evolution of the urea concentration in the bulk (continuous line), and a good correlation is observed with the experimental points obtained in our previous work³⁰.

Erreur ! Source du renvoi introuvable.-a compares the predicted (continuous line) and experimental (dots) normalized urea concentrations in the bulk, obtained during electrolyzes at different KOH concentrations, using two S/V ratios, where significant conversion rates of urea were reached. Data obtained for a S/V ratio of 8 are extracted from our previous work³⁰. In addition to examining the validity of the model for an enhanced value of S/V ratio, an alkaline electrolysis was carried out using an anode surface of 26 cm² in 130 mL of electrolyte. A good correlation is observed between the experiments and the model since the maximum deviation of urea concentration is observed at 6 %.

An additional validation of the model is performed by comparing the temporal variation of the current predicted by the model according to Eq. (42) with the experimental one.

Electrogenerated Ni^(III) flux = 6 × Urea chemically reacted flux

$$\begin{aligned}
 I &= nFSVv_{\text{Ni(III)}} \int_{z=\delta}^{z=\delta+\mu} r_{\text{E}\chi}(z) \times dz \\
 &= [n\mathcal{F}Vv_{\text{Ni(III)}}k_{\text{E}\chi} \times [\text{OH}^-]^{\beta_{\text{E}\chi}} \times (S_{\text{electrode}})^{\gamma_{\text{E}\chi}+1}] \\
 &\quad \times \int_{z=\delta}^{z=\delta+\mu} [\text{CO}(\text{NH}_2)_2]^{\alpha_{\text{E}\chi}} \times dz
 \end{aligned} \tag{42}$$

As shown in **Erreur ! Source du renvoi introuvable.-b**, the model predicts the current with a maximum deviation of 4 %, thus implying that the main assumption considering a constant temporal superficial concentration of nickel(III) would be verified.

Results of electrolysis indicated in **Erreur ! Source du renvoi introuvable.-c** were obtained using an undivided Metrohm[®] type cell, containing a strongly stirred (1000 RPM) solution. In these conditions, the electrogenerated hydrogen at the cathode (diameter < 1 mm) is dispersed in the bulk, and consequently in the immediate environment of the anode. Strong dispersion of gaseous H₂ increases the gas/liquid interface and facilitates its dissolution (the stationary concentration of hydrogen can achieve its solubility). Under the applied anodic potential (0.55 V), the dissolved hydrogen can be oxidized, and in these conditions the observed current is composed of:

- (i) the urea oxidation current (temporally decreasing);
- (ii) the hydrogen oxidation current^{64–66} induced by the reaction Eq. (43), that first increases until the steady state is reached, *i.e.* a constant gaseous H₂ flux arrived at the anode area.



These facts explain the observed difference of the current between the model and the experimental data, which varies from 1 to 80 %. Note that, this difference will decrease as a

function of time. Indeed, as the urea concentration is depleted, the corresponding fraction of anodic current is decreased, thus implying that the overall current will decrease. In these conditions the hydrogen electrogenerated flux at the cathode decreases.

As the hydrogen is not maintained in the reactor, its contribution to the anode current will also decrease until it is canceled (simultaneously to urea). The difference in current intensity between the theoretical and experimental data corresponds to the 'lost' current, due to the absence of a physical separator.

This undesirable oxidation of hydrogen, which can be considered as a loss of energy efficiency, is a key factor for controlling the thoughtful design of a UEO reactor as already discussed by Hankin et al.⁶⁷.

Conclusions

This work enabled to highlighting and characterizing the kinetics of indirect urea electro-oxidation on active nickel(III) sites in an alkaline medium. NiOOH particles, synthesized from commercial Ni(OH)₂ powder using NaOCl, were characterized by SEM, BET, XRD and particle size analysis. They exhibited spherical shapes and their content in nickel(III) reached 80 %. Compared to Ni(OH)₂ solids, the crystallinity of the synthesized NiOOH particles appears to be much lower than that of the starting powder, reflecting a core-shell geometry. The particles after synthesis, were composed of an amorphous NiOOH shell and a Ni(OH)₂ core.

Firstly, the kinetic study was performed using chemically synthesized nickel(III) particles. By using the method of initial rate of OH⁻ disappearance, the partial reaction order of urea was evaluated at 0.3, highlighting a limitation of the urea adsorption on the active sites of nickel. Subsequently, the partial orders of 0.6 and 1.9, respectively attributed to hydroxide ions and nickel active sites, were determined using the same type of experimental measurements. The dependence of the kinetic rate on hydroxide ions appeared to be low, whereas it was higher for nickel ($\gamma_{\chi} \approx 2$). Although more experiments would be required to precisely identify the

reaction mechanism, an order of 2 against the nickel(III) suggests that urea would bind to two nickel sites either (i) via both amine groups or (ii) via one of the amine groups and the ketone group. Besides, this low dependence of the kinetic rate to dissolved species' concentrations would suggest possible mass transport limitations in the solid spherical particles; indeed, after the consumption of nickel(III), the transformed urea or even the by-products must desorb, and find another nickel(III) available to absorb, to pursue the oxidative process. Moreover, the performed BET analysis showed particles having a low specific surface area ($8.51 \text{ m}^2 \cdot \text{g}^{-1}$), which would tend to incriminate limitation by the mass transport into the particles. This initial kinetic law did not consider the effect of the urea oxidized intermediates on OH^- or nickel(III) consumption, as their initial concentration was close to zero. Since the limitation of the overall process, at least initially, appears to be due to adsorption, these intermediates do not accumulate; they rapidly convert to observed products, and therefore do not affect the kinetic rate. This fact was validated by integration as a function of time, of the initial kinetic law *i.e.* for higher conversion rates. The obtained theoretical variation of the OH^- concentration was successfully compared with the experimental one (maximum deviation of 6 %).

Secondly, the kinetics of indirect electro-oxidation of urea was studied by polarizing a massive nickel electrode which enabled the formation of a catalytic layer $\text{NiOOH}/\text{Ni}(\text{OH})_2$, and thus ensured the urea oxidation thanks to the electrochemical continuous regeneration of the nickel(III) active sites. Under these assumptions, the kinetic rate law showed a partial order of urea close to the previous value (*i.e.* 0.3). However, the order of the nickel surface was found to be high ($\gamma_{\text{EX}} \approx 5$), signifying that the adsorption of urea onto nickel(III) sites was followed by complete oxidation of this urea by five electrochemically generated nickel(III) sites, almost instantaneously due to potentiostatic polarization of the anode at the required potential.

Coupled with the previously performed mass balances, carried out during preparative electrolyses (which demonstrated the presence of various by-products in the liquid phase), the

present kinetic study made it possible to create a relatively complete multi-pathway mechanism (22 sequential steps, four different ways and five urea oxidation products), able to describe the process of indirect electro-oxidation of urea.

Finally, this kinetic study was inserted into a more general predictive model combining (i) mass transport phenomena, in a liquid film and in a solid porous catalytic layer with (ii) indirect electrocatalytic chemical reaction occurring in the previous layer, and finally (iii) assisted by the quasi-instantaneous regeneration of the reaction driving factor *i.e.* the nickel(III) catalytic sites. The resolution of the established model on the basis of the shooting method enabled the prediction of spatio-temporal urea concentration profiles for various operating conditions. These predicted results were compared to the experimental ones for different hydroxide concentrations and S/V ratio. A satisfactory correlation was observed with low (< 5 %) deviations, thus opening interesting perspectives for further larger-scale operations for urea mineralization.

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Notation

Letters

- CE: counter electrode
- E: applied potential (mV vs. Hg/HgO)
- ER: electrogenerated reaction
- \mathcal{F} : Faraday's constant (96 500 C.mol⁻¹)

- I: current (A)
- j: current density ($A.m^{-2}$)
- HCR: heterocatalytic chemical reaction
- n: number of exchanged electron (dimensionless)
- Q: flowrate ($m^3.s^{-1}$)
- t: time (s)
- T: temperature (K)
- UEO : urea electro-oxidation
- V, V_B : suspension volume / electrolyte volume (m^3)
- WE: working electrode
- x: length of the electrode (m)
- X: conversion rate (dimensionless)
- z: distance to the electrode (m)
- δ : diffusion layer thickness (m)
- ϵ : nickel accessibility factor (dimensionless)
- μ : mixed oxides layer length (m)
- τ : tortuosity of the electrocatalytic layer (dimensionless)
- ω : porosity of electrocatalytic layer (dimensionless)
- θ : scattering angle ($^\circ$)
- ξ : extent of reaction (mol)

Subscripts

- d_{10}, d_{50}, d_{90} : percentile value diameters (μm)
- d_{32}, d_{43} : Sauter Mean diameter and De Brouckere Mean diameter (μm)
- $D_{i,w}$: diffusion binary coefficient of the specie i in the water ($m^2.s^{-1}$)
- $D_{i,w}^{eff}$: effective diffusion binary coefficient of the specie i in the water in porous media ($m^2.s^{-1}$)
- $I_{plateau}$: limiting current, observed at the plateau signal (A)
- $I_{plateau}^\infty$: limiting current, observed at the plateau signal in steady state (A)
- $j_{plateau}^\infty$: limiting density current, observed at the plateau signal in steady state ($A.m^{-2}$)
- $k_{app}, k'_{app}, k''_{app}$: apparent constants of $r_\chi(t)$ (variable unit)
- k_m : mass transport coefficient ($m.s^{-1}$)

- k_{χ} : reaction rate constant of r_{χ} ($\text{mol}^{1-\alpha_{\chi}-\beta_{\chi}-\gamma_{\chi}} \cdot \text{m}^{3(\alpha_{\chi}+\beta_{\chi})-3} \cdot (\text{g}_{\text{cat}} \cdot \text{s})^{-1}$)
- $k_{\text{E}\chi}$: reaction rate constant of $r_{\text{E}\chi}$ ($\text{mol}^{1-\alpha_{\text{E}\chi}-\beta_{\text{E}\chi}-\gamma_{\text{E}\chi}} \cdot \text{m}^{3(\alpha_{\text{E}\chi}+\beta_{\text{E}\chi})-2} \cdot \text{s}^{-1}$)
- m_{cat} : mass of powder (g)
- M_{NiIII} : NiOOH molar mass ($\text{g} \cdot \text{mol}^{-1}$)
- n_i : amount of substance i (mol)
- r_{χ} : instantaneous reaction rate for powder nickel(III) study ($\text{mol} \cdot \text{m}^3 \cdot (\text{g}_{\text{cat}} \cdot \text{s})^{-1}$)
- r_{χ}^0 : initial rate of r_{χ} ($\text{mol} \cdot \text{m}^3 \cdot (\text{g}_{\text{cat}} \cdot \text{s})^{-1}$)
- $r_{\text{E}\chi}$: kinetic law obtained on electrogenerated nickel(III) sites ($\text{mol} \cdot \text{m}^2_{\text{electrode}} \cdot \text{s}^{-1}$)
- $S_{\text{electrode}}$: electrode surface (m^2)
- $\alpha_{\chi}, \beta_{\chi}, \gamma_{\chi}$: partial orders of urea, hydroxide, and nickel respectively (dimensionless) determined with nickel-oxides synthesized powders
- $\alpha_{\text{E}\chi}, \beta_{\text{E}\chi}, \gamma_{\text{E}\chi}$: partial orders of urea, hydroxide, and nickel respectively (dimensionless) determined with nickel-oxides electrodes
- Γ_i : superficial concentration of the nickel at the oxidation state i ($\text{mol} \cdot \text{m}^{-2}$)
- Λ_i : model border i
- ρ_{cat} : mass concentration of nickel(III) per unit of volume ($\text{g}_{\text{cat}} \cdot \text{m}^{-3}$)
- $\Omega_{\text{B}}, \Omega_{\text{F}}, \Omega_{\text{EC}}$: model domains respectively, bulk, diffusion film and electrocatalytic layer
- ν_i : stoichiometric number of the reactant i (dimensionless)
- ν_{scan} : potential scan rate ($\text{V} \cdot \text{s}^{-1}$)

Superscripts

- C^{bulk} : bulk urea concentration ($\text{mol} \cdot \text{m}^{-3}$)
- $C^{\text{electrode}}$: electrode urea concentration ($\text{mol} \cdot \text{m}^{-3}$)
- C^{F} : urea concentration at the interface between diffusion film and electrocatalytic layer ($\text{mol} \cdot \text{m}^{-3}$)

Plain Language Summary

The study presents kinetic and mechanistic approaches used as tools for the building of a predictive model enabling the optimization of the urea catalytic oxidation by active nickel sites, simultaneously to the hydrogen cathodic production.

CRedit author statement

G. Hopsort: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing - original draft / **L. Latapie:** Conceptualization, Formal analysis, Investigation, Methodology, Resources / **K. Groenen Serrano:** Conceptualization, Formal analysis, Investigation, Supervision, Validation, Writing - review & editing / **K. Loubière:** Conceptualization, Formal analysis, Investigation, Supervision, Validation, Writing - review & editing / **T. Tzedakis:** Conceptualization, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Supervision, Validation, Writing - review & editing.

Data Availability Statement

All data required to evaluate the conclusions in this paper are present in the paper itself and/or the Supplementary Materials. Additional data that support the findings of this study are available from the corresponding author, upon request. Error bars (where shown) in Figures 1 and 7 show the spread of data observed in duplicate measurements, where independent samples were tested for each measurement. Experimental data shown without error bars are from mean of individual experimental measurements.

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List of Figure Captions:

Figure 1. Kinetic experiments with chemically synthesized nickel(III) sites: measurements of the initial rate versus the concentration of a) urea and b) potassium hydroxide. Graph c) provides the values of β_x as a function of the KOH concentration for different urea concentrations. k'_{app} remains constant whatever the urea concentration, as shown in the graph d). Graph a) was achieved with a 5 mmol.L⁻¹ KOH solution. All these results were obtained with nickel(III) synthesized powder – Sample 2.

Figure 2. Comparison of the experimental temporal evolutions of the hydroxide ion conversion to the ones obtained by numerical solving of the Eq. Erreur ! Source du renvoi introuvable. for different initial concentrations of urea and hydroxide (molar concentration are expressed in mol.L⁻¹). The surface accessibility factor of nickel(III), ϵ , is equal to 2.6 % whatever the graphs.

Figure 3. Kinetic experiments with electrochemically synthesized nickel(III) sites on bare nickel electrode.

Graphs a), b) and c) present j/I -E curves obtained at the steady state ($0.12 \text{ mV}\cdot\text{s}^{-1}$) using a Ni WE immersed in 100 mL of alkaline solutions of urea, thermoregulated at 298 K.

Graph a) effect of urea concentration on the shape of the i -E curves obtained on nickel RDE in alkaline solution of KOH ($1 \text{ mol}\cdot\text{L}^{-1}$) at 1000 RPM with urea concentrations at $0.01 \text{ mol}\cdot\text{L}^{-1}$ (1), $0.05 \text{ mol}\cdot\text{L}^{-1}$ (2), $0.075 \text{ mol}\cdot\text{L}^{-1}$ (3), $0.1 \text{ mol}\cdot\text{L}^{-1}$ (4), $0.2 \text{ mol}\cdot\text{L}^{-1}$ (5) and $0.3 \text{ mol}\cdot\text{L}^{-1}$ (6).

Graph b) effect of KOH concentration on the shape of the i -E curves obtained on nickel RDE in urea solution of $0.3 \text{ mol}\cdot\text{L}^{-1}$ stirred at 1000 RPM with hydroxide concentrations at $0.1 \text{ mol}\cdot\text{L}^{-1}$ (1), $0.25 \text{ mol}\cdot\text{L}^{-1}$ (2), $0.5 \text{ mol}\cdot\text{L}^{-1}$ (3), $1 \text{ mol}\cdot\text{L}^{-1}$ (4) and $1.5 \text{ mol}\cdot\text{L}^{-1}$ (5).

Graph c) effect of the geometric surface area (rectangularly area) of the nickel electrode on the shape of the i -E curves obtained with a urea concentration of $0.3 \text{ mol}\cdot\text{L}^{-1}$ and a KOH concentration of $1 \text{ mol}\cdot\text{L}^{-1}$, using geometrical electrode surfaces equal to 8.7 mm^2 (1), 9.2 mm^2 (2), 10.4 mm^2 (3) and 15.4 mm^2 (4).

The partial orders of urea ($\alpha_{E,\chi}$), hydroxide ions ($\beta_{E,\chi}$) and nickel(III) ($\gamma_{E,\chi}$) were determined from the curves respectively plotted in Figures d), e) and f), deduced from the logarithm plot of the limiting current magnitude (at the diffusion limitation area) as a function of the logarithmic reactant concentration.

Figure 4. Proposed overall mechanism for UEO in alkaline media on a bare nickel anode covered after polarization by the system $\text{NiOOH}/\text{Ni}(\text{OH})_2$. On the left side, a) the mechanism shows the main and side chemical pathways leading to N_2 and CO_2 (under CO_3^{2-} form) as well as the by-products previously identified in the liquid phase³⁰ and b) detailed nitrification route.

Figure 5. a) Schematic representation of the electrochemical half-cell. The large scale includes a perfectly stirred liquid phase and an electroactive layer of nickel oxide mixtures on the metal electrode surface. **b) View of the various sensitive areas including possible limiting physical phenomena.** The enlargement scheme contains three subdomains characterized by the occurrence of different phenomena: (1) a perfectly mixed zone, Ω_B , that is connected to the bulk liquid, (2) a mass transport boundary film Ω_F , and (3) the matrix of the electrocatalytic nickel oxide layer Ω_{EC} at the electrode surface. Each boundary of the system is labeled by Λ . Λ_{BF} represents the boundary between the bulk Ω_B and mass transport boundary film Ω_{EC} areas. Λ_{FEC} represents the boundary between the film Ω_F and electrocatalytic film Ω_{EC} areas. Λ_E and Λ_B represent the massive electrode and wall boundaries of the system, respectively. (illustration adapted from Picioreanu et al.⁶⁸)

Figure 6. Spatio-temporal profiles of the urea concentration during a potentiostatic electrolysis at 0.55 V of a 0.33 mol.L⁻¹ urea solution in alkaline media (5 mol.L⁻¹ KOH), on nickel massive electrode. Inset: dimensionless urea concentrations in the bulk Ω_B measured experimentally (black filled circles) and predicted by the model (red line).

Figure 7. a) Temporal variations of the normalized urea concentration in the bulk during potentiostatic electrolysis on nickel massive electrode in alkaline media. Experimental results are plotted for different KOH concentrations: 1 mol.L⁻¹ (\diamond), 1.5 mol.L⁻¹ (\bullet), 2 mol.L⁻¹ (\blacksquare) and 5 mol.L⁻¹ (\blacktriangle). Filled symbols are obtained with an S/V ratio of 8 m⁻¹. The unfilled symbols are obtained with an S/V ratio equal to 20 m⁻¹. The lines represent the temporal profiles of the urea concentration predicted by the model at each KOH concentration.

(b-c) Experimental and predicted profiles of the current intensity during electrolysis with a distance between electrodes of b) 15 cm using a H-type cell without separator and c) 3 cm

using an undivided Metrohm® type-cell.

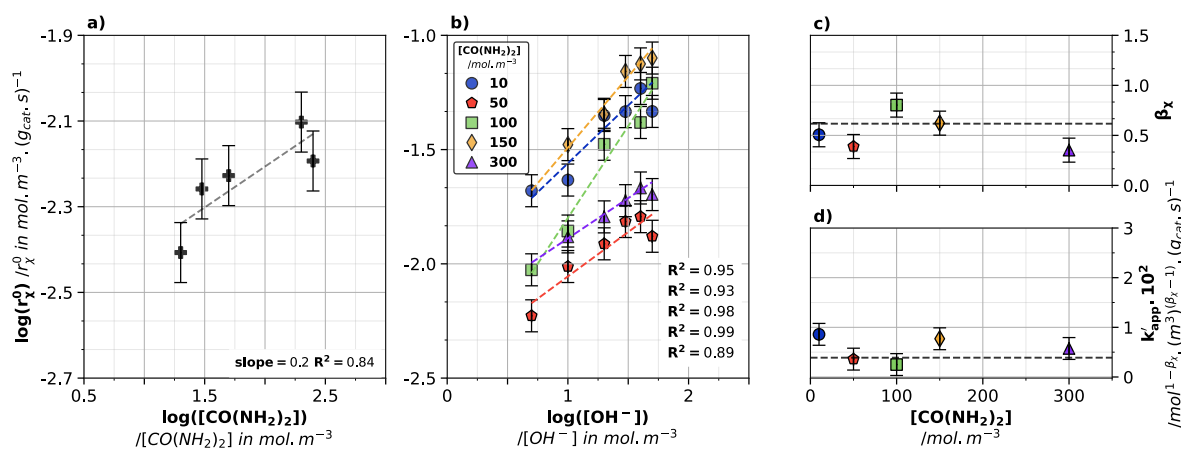


Figure 1

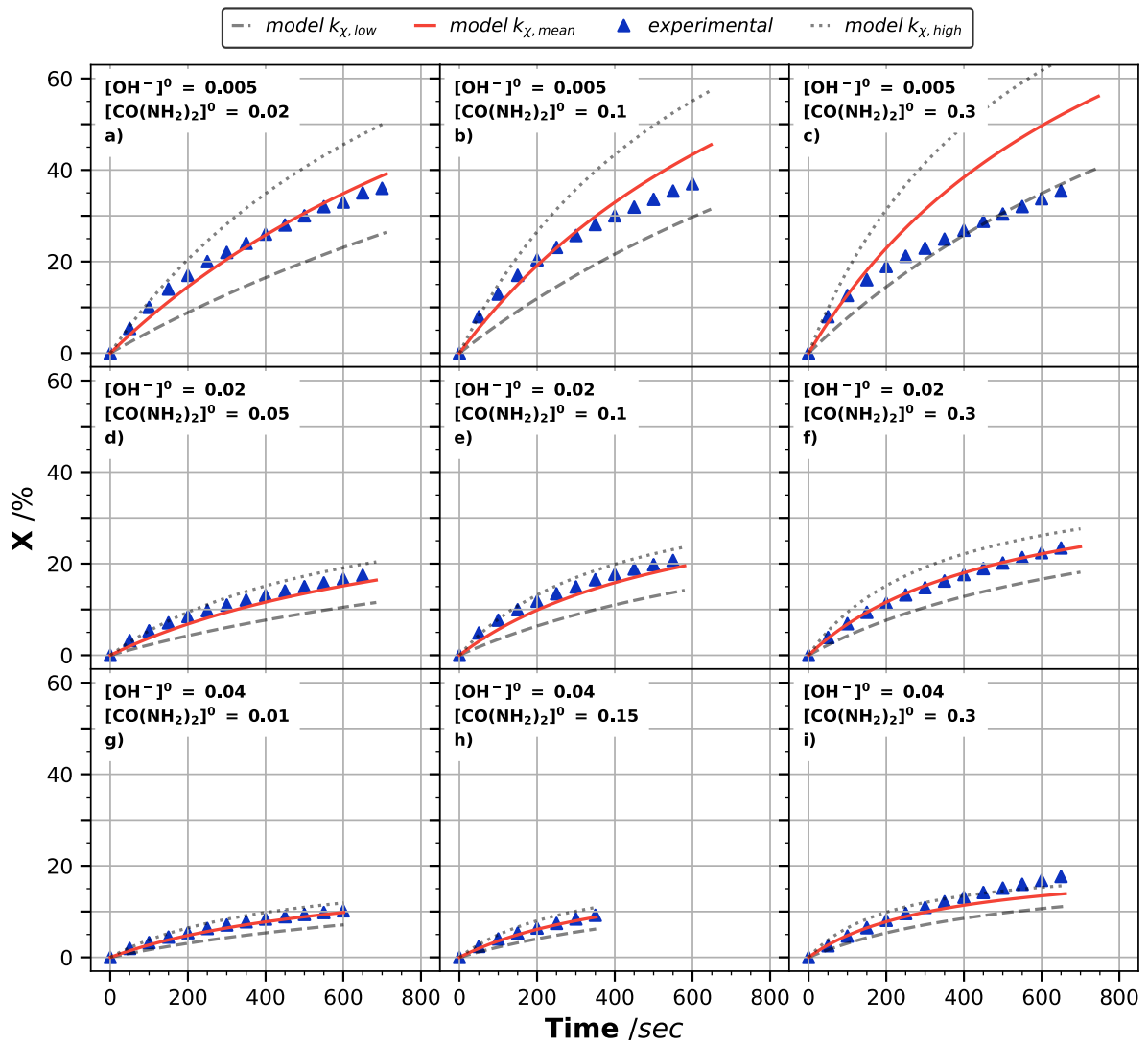


Figure 2

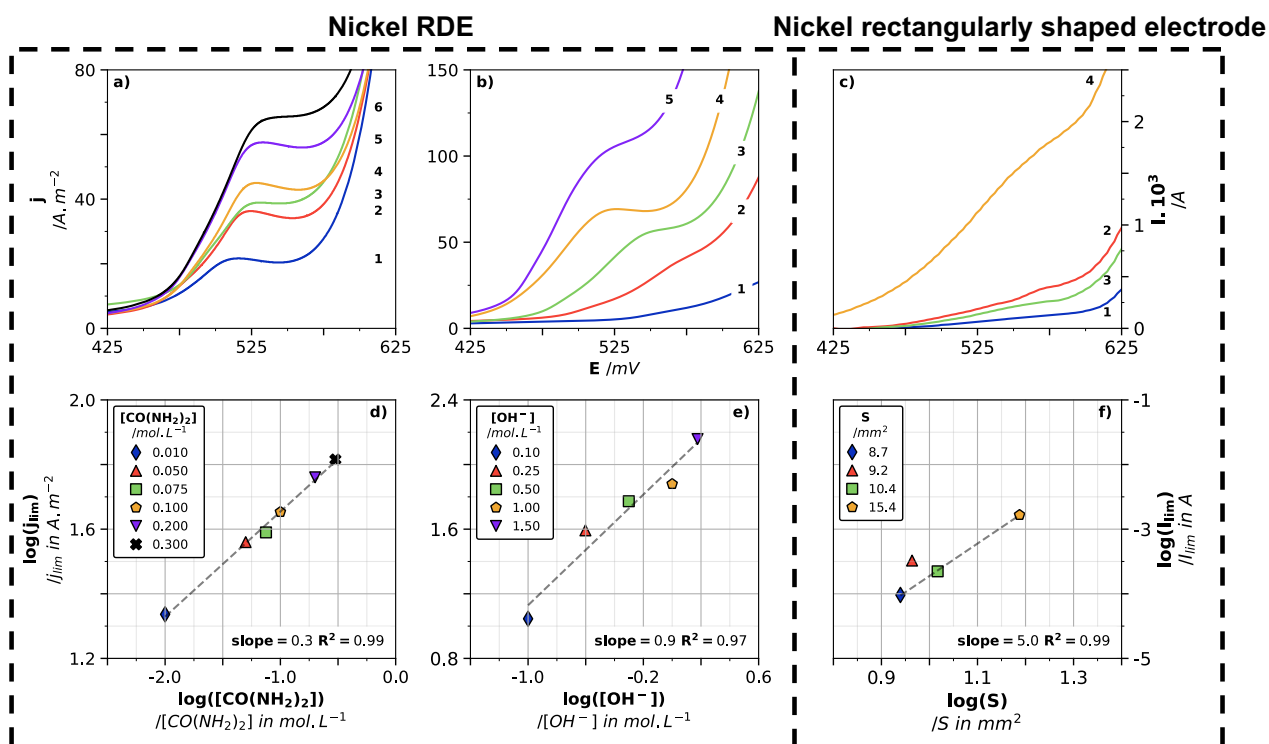


Figure 3

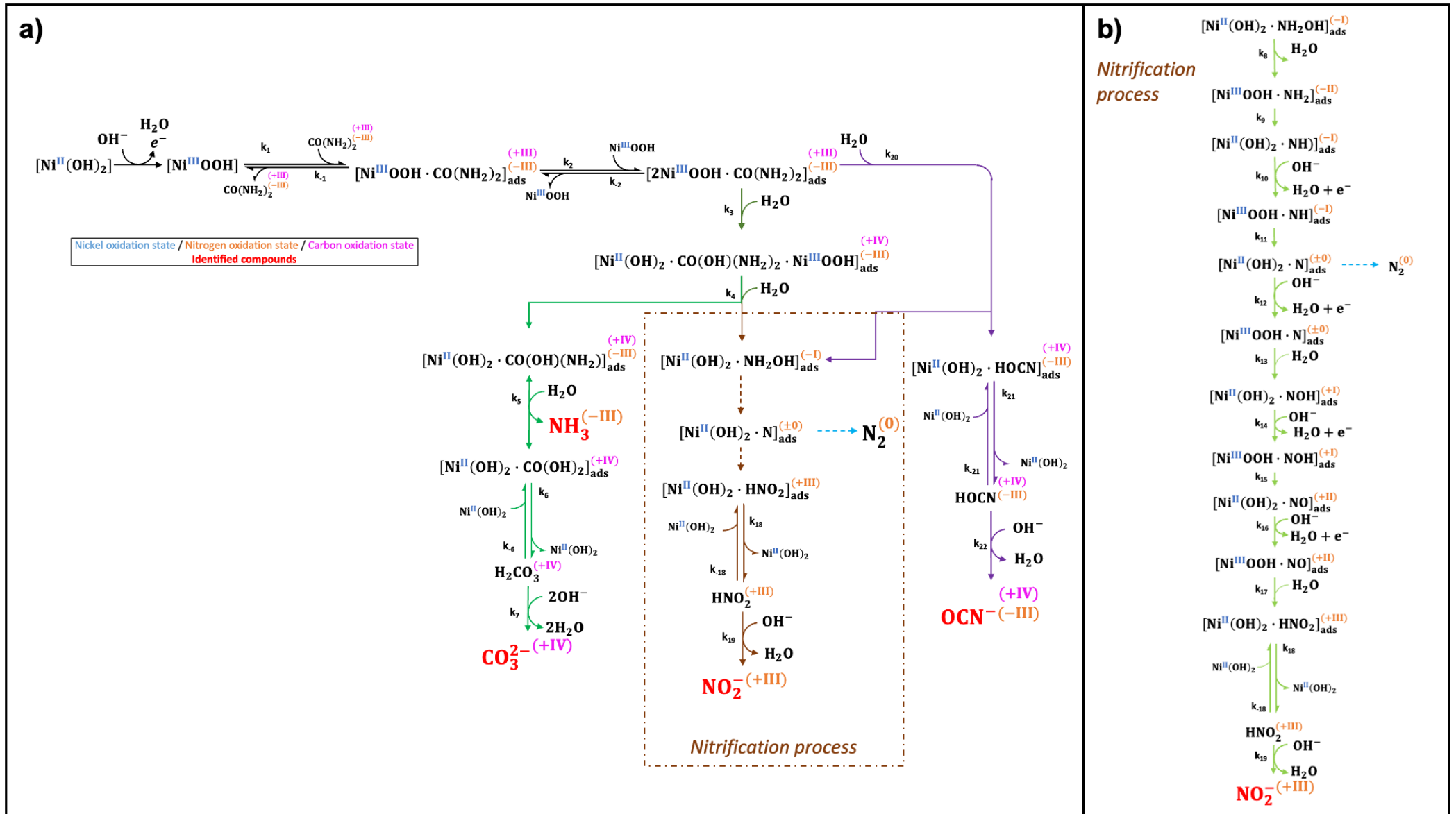
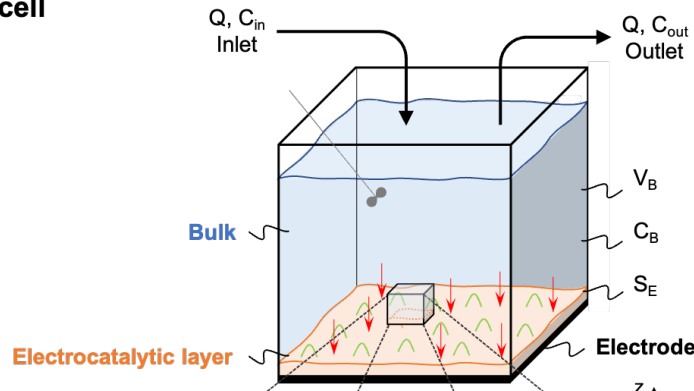


Figure 4

a) Half-cell



b) Anode compartment

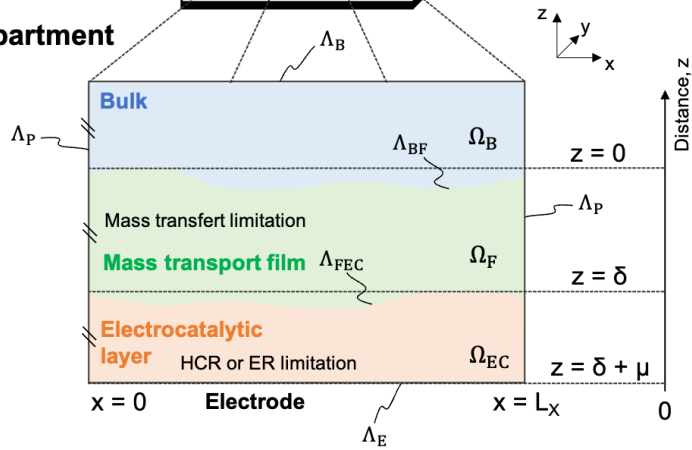


Figure 5

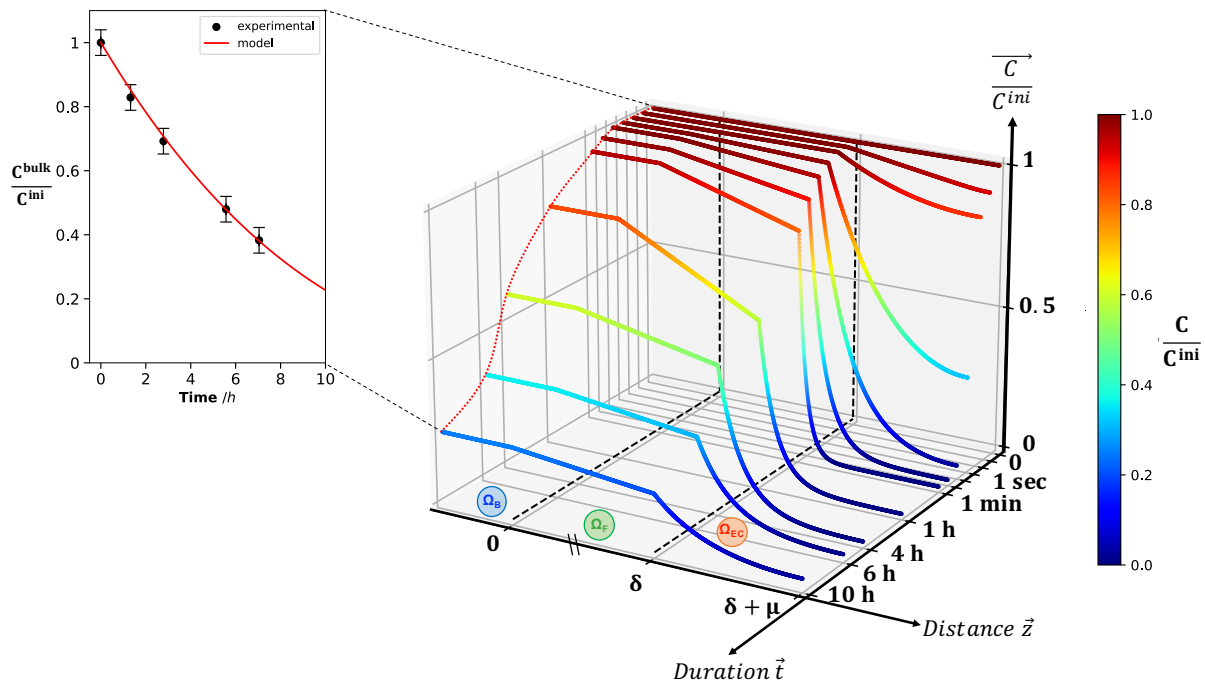


Figure 6

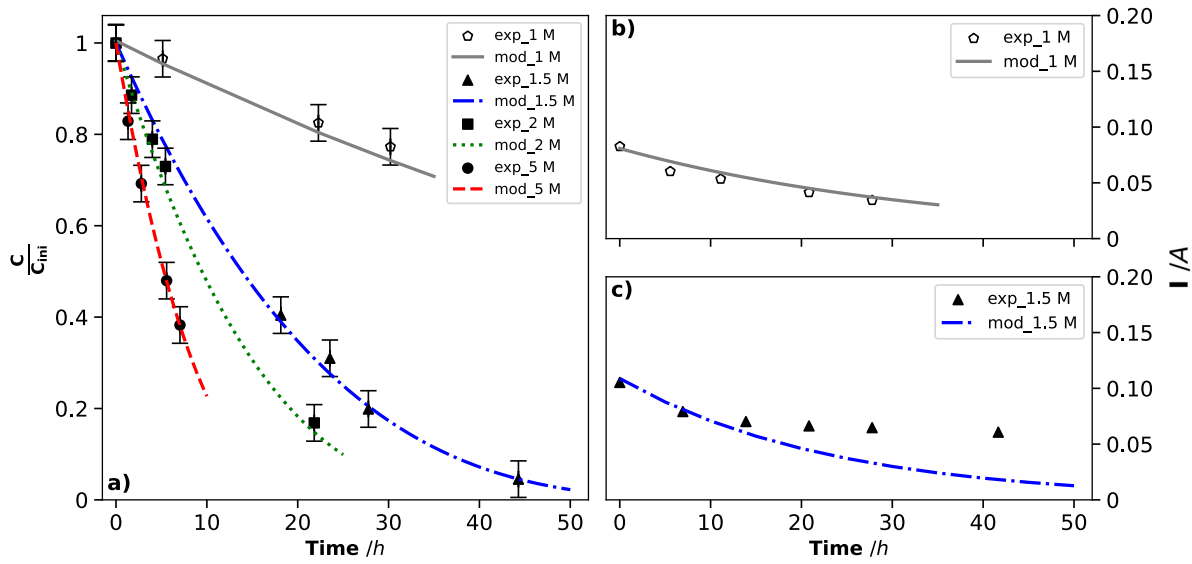


Figure 7

List of Table Captions

Table 1. Physical properties of the initial nickel(II) powder and of the nickel(III) powders.

Table 2. Extent of urea oxidation reaction by chemically synthesized nickel(III) sites where V represents the liquid reaction volume ($4.5 \times 10^{-5} \text{ m}^3$), m_{cat} the mass of powder (5 g), M_{NiOOH} the NiOOH molar mass ($91.7 \text{ g}\cdot\text{mol}^{-1}$) and X the conversion in hydroxide ions.

The corresponding overall reaction is written as $\text{CO}(\text{NH}_2)_2 + 6\text{OH}^- + 6\text{Ni}^{+\text{III}} \rightarrow \text{Products}$.

Table 1

	Purity of nickel(III) content (%)	Density (g.cm ⁻³)	Particle size analysis (μm)										Specific surface area (m ² .g ⁻¹)	Mean pore diameter (nm)
			Volume distribution					Number distribution						
			d ₁₀	d ₅₀	d ₉₀	d ₃₂	d ₄₃	d ₁₀	d ₅₀	d ₉₀	d ₃₂	d ₄₃		
Initial Ni ^(II) powder	0	3.7 ± 0.1	3.9	9.0	16.9	5.4	9.8	0.4	0.5	0.8	5.5	10.0	6.67 ± 0.17	8.2 ± 0.1
Ni ^(III) powder – Sample 1	79 ± 2	3.9 ± 0.1	5.5	12.3	24.0	9.9	13.7	1.3	3.4	8.1	9.9	13.7		
Ni ^(III) powder – Sample 2	29 ± 2	3.8 ± 0.1	4.5	10.0	20.5	7.9	11.4	0.7	1.3	5.3	7.9	11.4	8.51 ± 0.12	7.7 ± 0.1

Table 2

	<i>moles of CO(NH₂)₂</i>	<i>moles of OH⁻</i>	<i>moles of NiOOH</i>	<i>moles of accessible NiOOH</i>
t=0	$a = [\text{CO}(\text{NH}_2)_2]^\circ V$	$b = [\text{OH}^-]^\circ V$	$c = \frac{m_{\text{cat}}}{M_{\text{NiOOH}}} \times \text{purity}$	$c' = c \times \varepsilon$
t	$a - \frac{bX}{6}$	$b(1 - X)$	$c - bX$	$c' - bX$

Supplementary Material

Indirect urea electro-oxidation by nickel(III) in alkaline medium: from kinetic and mechanism to reactor modeling

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Index

SECTION SM. 1: MATERIAL.....	3
SECTION SM.2: PHYSICAL CHARACTERIZATION OF NIOOH.....	4
SECTION SM.3: MONITORING OF THE CATALYTIC OXIDATION BETWEEN UREA AND SYNTHESIZED NICKEL(III) PARTICLE POWDER IN ALKALINE MEDIUM	6
SECTION SM.4: REPEATABILITY OF THE MEASUREMENTS OF THE INITIAL RATE, $r_{\chi 0}$, AS A FUNCTION OF TIME CHOSEN TO CALCULATE THE INITIAL RATE FROM THE CURVE $\text{pH}(t)$	8
SECTION SM.5: VARIATIONS OF THE KINETIC CONSTANT k_{χ} FOR A SAMPLING OF 35 TRIALS	9
SECTION SM.6: VARIATIONS OF THE KINETIC CONSTANT $k_{E\chi}$ FOR A SAMPLING OF 11 TRIALS	9
SECTION SM.7: MODEL RESOLUTION	10
SECTION SM.8: DATA AVAILABILITY	12

Section SM. 1: Material

All the information concerning chemicals and solutions used in this work is summarized in the Table SM1 following:

Table SM1 Indexation of all chemicals and solutions used in this work

CAS n°	Name	Formula	Molecular weight (g.mol ⁻¹)	Purity	Supplier	Batch n°
7681-52-9	Sodium hypochlorite	Na ⁺ OCl ⁻	74.44	14% Cl ₂	VWR Chemicals	21H234009
1310-73-2	Sodium hydroxide	NaOH	40.00	97%	Fisher Scientific	2181225
57-13-6	Urea	CON ₂ H ₄	60.05	>99.5%	Sigma-Aldrich	SLCB9837
1310-58-3	Potassium hydroxide	KOH	56.11	85%	Alfa Aesar	10225535
7789-12-0	Sodium dichromate dihydrate	Na ₂ Cr ₂ O ₇ · 2H ₂ O	298.00	>99%	Aldrich	58692-065
7783-85-9	Ammonium iron(II) sulfate hexahydrate (Mohr's salt)	(NH ₄) ₂ Fe(SO ₄) ₂ · 6H ₂ O	392.14	99%	Sigma-Aldrich	MKBV6451V
7647-01-0	Hydrochloric acid	HCl	36.46	wt.37%	Fisher Scientific	2171489
75-75-2	Methanesulfonic acid	CH ₄ O ₃ S	96.10	99%	Acros Organics	A0419723
<i>Standard for pH</i>						
	Buffer solution pH 7.01				Hanna instruments	3701
	Buffer solution pH 10 (borate)				Fisher Scientific	2187023
	Buffer solution pH 11.00 (boric acid, sodium hydroxide solution/potassium chloride)				Honeywell	L1610
	Buffer solution pH 12.00				Alfa Aesar	R25H066
	Buffer pH 13.00				Reagecon	32520K1
<i>Standard for Ion Chromatography</i>						
7632-00-0	Nitrite in aqueous solution	Na ⁺ NO ₂ ⁻	69.00	996 ± 8 µg.mL ⁻¹	SCP Science	S2009A5024
12125-02-9	Ammonium in aqueous solution	NH ₄ ⁺ Cl ⁻	53.49	1006 ± 7 µg.mL ⁻¹	SCP Science	S200407013
590-28-3	Potassium cyanate	KOCN	81.12	97%	Alfa Aesar	M08F008

At the beginning of the present work, a commercial nickel(III) powder was looked for. A supplier named American Elements provided a green powder with the following designation “99%+ Nickel Oxyhydroxide Nanopowder” (product code : NI-OOH-02-NP / CAS n°55070-72-9). As a reminder, nickel(II) has a light green color. To dispel any doubts about this powder, experiments were carried out by bringing into contact a urea solution with this powder. No chemical reaction could be demonstrated (no decrease of NPOC, no formation of the previously identified by-products), thus suggesting that this powder was made of nickel(II). Several characterization tests were done and confirmed this. Thus, all the results obtained in this article were performed by using this powder. As a precaution, a nickel(II) hydroxide powder from Thermo Scientific (CAS n° 12054-748-7 / Batch n°A0422008 / Molecular weight 92.70 g.mol⁻¹

¹) was purchased. As shown in Figure SM1, where both powders were compared by XDR analysis, they presented the same crystallographic structure.

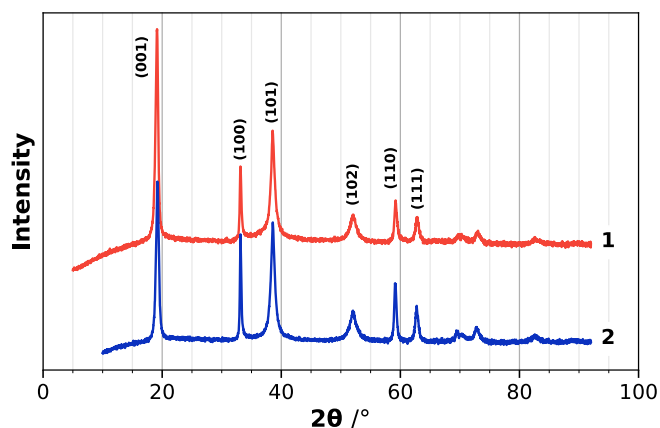


Figure SM1 XRD patterns of the nickel(II) powders purchased from (1) American Elements and (2) Thermo Scientific.

Section SM.2: Physical characterization of NiOOH

- *Set-up used for purity determination of synthesized nickel(III) powder*

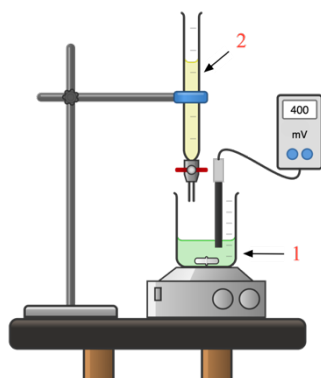


Figure SM2 Schematic representation of the experimental set-up used for determining the purity of the synthesized nickel(III) powder. Label 1 represents the nickel(III) particles dissolved in an acidic oxidized iron(III) solution at $7.20 \times 10^{-2} \text{ mol.L}^{-1}$ and label 2 represents the $\text{K}_2\text{Cr}_2\text{O}_7$ solution at $3.75 \times 10^{-2} \text{ mol.L}^{-1}$.

Figure SM2 describes the experimental set-up used to evaluate the purity of nickel(III) in the synthesized powder. A precise amount of powder (137 mg) was mixed in a beaker filled with a solution composed of 30 mL of deionized water and 2 mL of hydrochloric acid. 882 mg of Mohr's salt was added, corresponding to a large excess of ferrous ions. A stirring period of 5 min was applied to obtain a total oxidation reaction between ferrous ions and nickel(III) particles. The last step consisted in determining the remaining ferrous ions (*i.e.*, the ones that

did not react) by a potentiometric titration with dichromate(VI) potassium. The equivalent volume was deduced from the rise in potential measured by a combined Pt ring electrode Metrohm®. An example of a potential vs. poured volume is shown in Figure SM3:

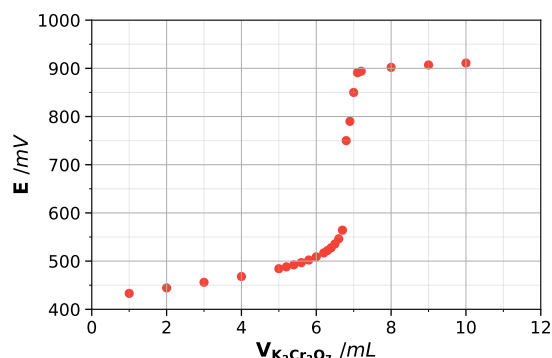


Figure SM3 Potentiometric titration curve involving 32 mL of a solution of nickel(III) particles dissolved in acidic oxidized iron(III) at $7.20 \times 10^{-2} \text{ mol.L}^{-1}$, and a solution $\text{K}_2\text{Cr}_2\text{O}_7$ at $3.75 \times 10^{-2} \text{ mol.L}^{-1}$.

At last, the amount of nickel(III) was equal to the amount of ferrous ions that reacted according to Eq. (SM. 1).

$$n_{\text{Ni(III)}} = n_{\text{Fe(II)}}^{\text{in excess}} - n_{\text{Fe(II)}}^{\text{titration}} \quad (\text{SM. 1})$$

- XRD analysis results

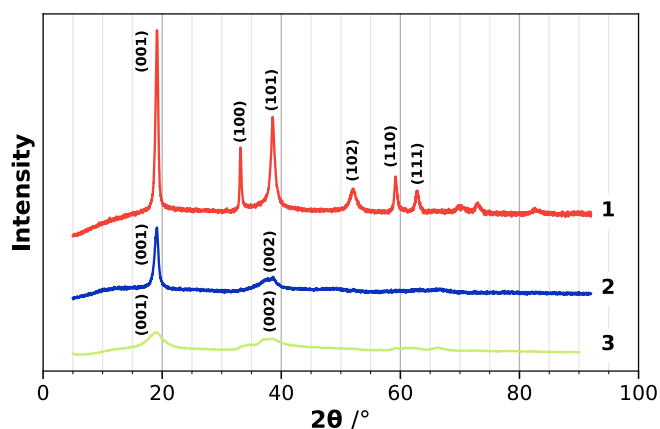


Figure SM4 XRD patterns of (1) commercial Ni(OH)_2 powder, (2) and (3) powders obtained by Ni(OH)_2 oxidation using respectively 0.176 and 0.768 mol.L^{-1} hypochlorite solutions (see §2.1.1).

- SEM analysis results

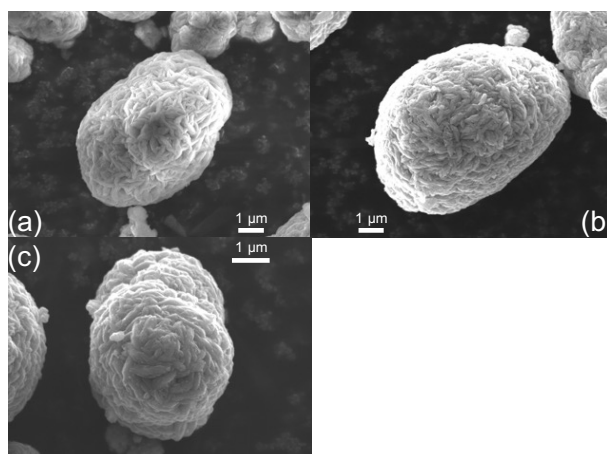


Figure SM5 SEM images of the samples (a) Ni(OH)₂ commercial powder (b) nickel(III) powder – sample 1 (c) nickel(III) powder – sample 2.

Section SM.3: Monitoring of the catalytic oxidation between urea and synthesized nickel(III) particle powder in alkaline medium

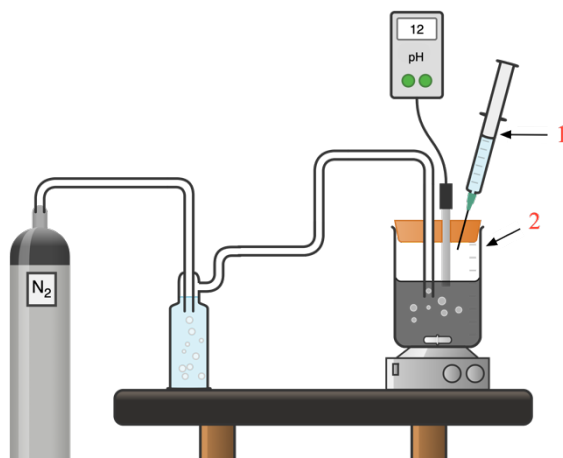


Figure SM6 Schematic representation of the experimental set-up used for studying the kinetics of the catalytic oxidation between urea and nickel(III) particles. Label 1 represents urea in a KOH solution and label 2 represents NiOOH particles in KOH solution in a thermoregulated cell under N₂ atmosphere.

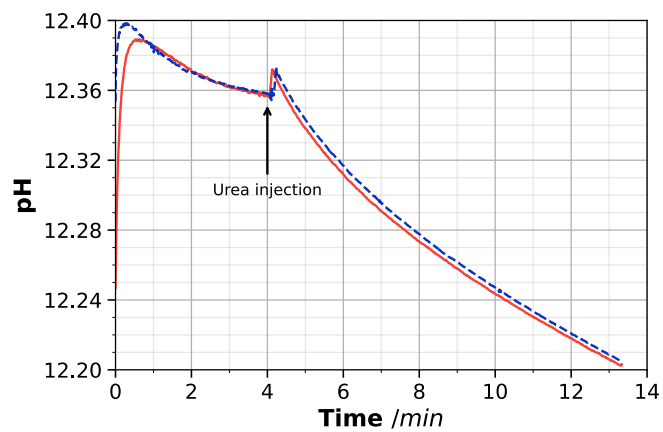


Figure SM7 Typical temporal variations of the pH when an alkaline urea solution was brought into contact with chemically synthesized nickel(III) sites. The repeatability of the results is represented here with two trials (solid and dashed lines).

Section SM.4: Repeatability of the measurements of the initial rate, r_{χ}^0 , as a function of time chosen to calculate the initial rate from the curve $\text{pH}_{(t)}$

To ensure reliable and accurate measurements, the influence of the sampling time on the initial rate was studied. Table SM2 reports the different measures of the initial rate, noted r_{χ}^0 , obtained for five reactant (urea and OH^-) concentrations and sampling times varying from 5 to 50 seconds. The relative standard deviation (RSD) was calculated from each averaged value of r_{χ}^0 . This criterion allows identifying which sampling time was the best choice for determining r_{χ}^0 .

Table SM2 Influence of the sampling on the repeatability of the initial reaction rate r_{χ}^0

Sampling time (s)		Experiment 1		Experiment 2		Experiment 3		Experiment 4		Experiment 5	
		Trial 1	Trial 2	Trial 1	Trial 2	Trial 1	Trial 2	Trial 1	Trial 2	Trial 1	Trial 2
5	r_{χ}^0 (mol.L ⁻¹ .s ⁻¹)	1.23×10 ⁻⁵	1.40×10 ⁻⁵	1.57×10 ⁻⁵	1.64×10 ⁻⁵	2.11×10 ⁻⁵	1.67×10 ⁻⁵	2.32×10 ⁻⁵	1.98×10 ⁻⁵	2.01×10 ⁻⁵	2.01×10 ⁻⁵
	Average	1.31×10 ⁻⁵		1.61×10 ⁻⁵		1.89×10 ⁻⁵		2.15×10 ⁻⁵		2.01×10 ⁻⁵	
	Standard deviation (SD, mol.L ⁻¹ .s ⁻¹)	1.18×10 ⁻⁶		4.97×10 ⁻⁷		3.12×10 ⁻⁶		2.39×10 ⁻⁶		4.11×10 ⁻⁸	
	Relative standard deviation (RSD)	9%		3%		17%		11%		0%	
10	r_{χ}^0 (mol.L ⁻¹ .s ⁻¹)	1.22×10 ⁻⁵	1.38×10 ⁻⁵	1.55×10 ⁻⁵	1.62×10 ⁻⁵	2.08×10 ⁻⁵	1.66×10 ⁻⁵	2.29×10 ⁻⁵	1.96×10 ⁻⁵	2.01×10 ⁻⁵	2.03×10 ⁻⁵
	Average	1.30×10 ⁻⁵		1.59×10 ⁻⁵		1.87×10 ⁻⁵		2.13×10 ⁻⁵		2.02×10 ⁻⁵	
	SD (mol.L ⁻¹ .s ⁻¹)	1.15×10 ⁻⁶		5.02×10 ⁻⁷		3.03×10 ⁻⁶		2.32×10 ⁻⁶		1.84×10 ⁻⁷	
	RSD	9%		3%		16%		11%		1%	
25	r_{χ}^0 (mol.L ⁻¹ .s ⁻¹)	1.18×10 ⁻⁵	1.33×10 ⁻⁵	1.50×10 ⁻⁵	1.57×10 ⁻⁵	2.01×10 ⁻⁵	1.62×10 ⁻⁵	2.22×10 ⁻⁵	1.92×10 ⁻⁵	2.00×10 ⁻⁵	2.11×10 ⁻⁵
	Average	1.25×10 ⁻⁵		1.54×10 ⁻⁵		1.81×10 ⁻⁵		2.07×10 ⁻⁵		2.05×10 ⁻⁵	
	SD (mol.L ⁻¹ .s ⁻¹)	1.08×10 ⁻⁶		4.65×10 ⁻⁷		2.76×10 ⁻⁶		2.11×10 ⁻⁶		8.40×10 ⁻⁷	
	RSD	9%		3%		15%		10%		4%	
50	r_{χ}^0 (mol.L ⁻¹ .s ⁻¹)	1.12×10 ⁻⁵	1.25×10 ⁻⁵	1.43×10 ⁻⁵	1.50×10 ⁻⁵	1.89×10 ⁻⁵	1.56×10 ⁻⁵	2.12×10 ⁻⁵	1.86×10 ⁻⁵	1.97×10 ⁻⁵	2.24×10 ⁻⁵
	Average	1.18×10 ⁻⁵		1.46×10 ⁻⁵		1.73×10 ⁻⁵		1.99×10 ⁻⁵		2.11×10 ⁻⁵	
	SD (mol.L ⁻¹ .s ⁻¹)	9.67×10 ⁻⁷		4.74×10 ⁻⁷		2.35×10 ⁻⁶		1.82×10 ⁻⁶		1.87×10 ⁻⁶	
	RSD	8%		3%		14%		9%		9%	
Average global		1.26×10 ⁻⁵		1.55×10 ⁻⁵		1.83×10 ⁻⁵		2.08×10 ⁻⁵		2.05×10 ⁻⁵	
SD global (mol.L ⁻¹ .s ⁻¹)		5.70×10 ⁻⁷		6.43×10 ⁻⁷		7.39×10 ⁻⁷		7.14×10 ⁻⁷		4.32×10 ⁻⁷	
RSD global		5%		4%		4%		3%		2%	

From these findings, a sampling time of 10 seconds was chosen for calculating all the initial reaction rates.

Section SM.5: Variations of the kinetic constant k_x for a sampling of 35 trials

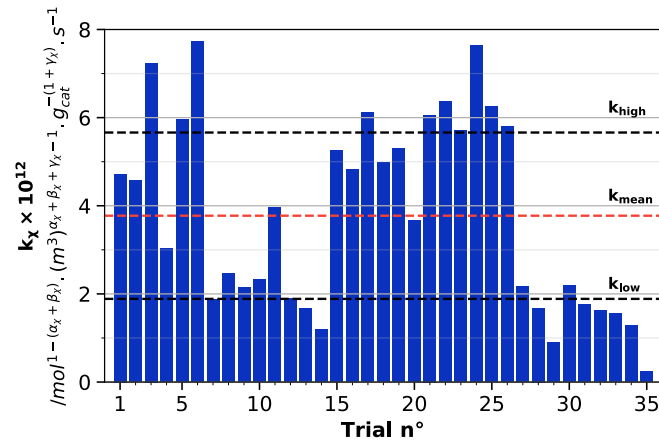


Figure SM8 Distribution histogram of the determined kinetic constant k_x for the 35 experiments carried out. The values were ranged between 2.4×10^{-13} and 7.7×10^{-12} with a mean value at $3.8 \times 10^{-12} \text{ mol}^{0.2} \cdot (\text{m}^3)^{1.7} \cdot \text{g}_{\text{cat}}^{-2.9} \cdot \text{s}^{-1}$.

Section SM.6: Variations of the kinetic constant k_{E_x} for a sampling of 11 trials

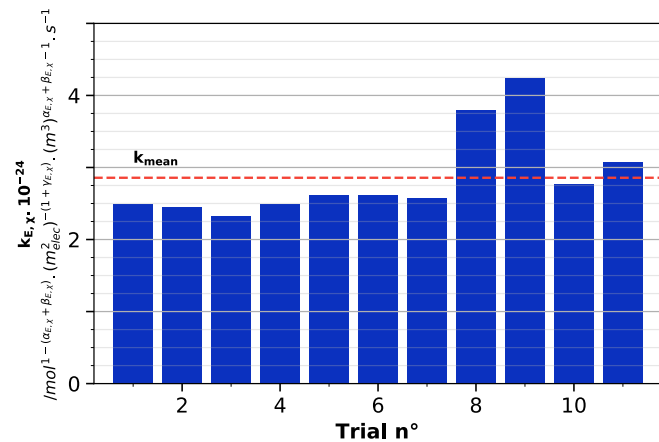


Figure SM9 Distribution histogram of the determined kinetic constant k_{E_x} for the 11 experiments carried out. The values were ranged between 2.32×10^{24} and 4.24×10^{24} with a mean value at $2.86 \times 10^{24} \text{ mol}^{-0.3} \cdot (\text{m}_{\text{elec}}^2)^{-6} \cdot (\text{m}^3)^{0.2} \cdot \text{s}^{-1}$.

Section SM.7: Model resolution¹

I. Initialization

- define all the partial reactional orders, α_{EX} , β_{EX} , γ_{EX} , the kinetic constant, k_{EX} , the tortuosity, τ , and the porosity, ω , of the electrocatalytic layer domain Ω_{EC} , the diffusivity coefficient of urea, $D_{urea,w}$, and the cell volume, V ;
- set the initial concentrations of soluble components in each subdomain: $[\text{OH}^-]_{Vz,t=0}$ and $[\text{CO}(\text{NH}_2)_2]_{Vz,t=0}$;
- set the geometrical surface, $S_{elec}^{geometric}$, and the rugosity of the electrode, Sdr . The Sdr parameter can be considered as the ratio between the area of the ‘real’ developed surface and the area of the ‘projected’ surface. In our case, the Sdr is measured by a 3D optical profiler (S-Neox, Sensofar[®], Spain) and equal to 1.09%.
- calculate the real electrode surface S_{elec} according to Eq. (SM. 2);

$$S_{elec} = S_{elec}^{geometric} \times Sdr \quad (\text{SM. 2})$$

- calculate the kinetic apparent constant, k_{app} ;
- calculate the effective diffusivity coefficient of urea, $D_{urea,w}^{eff}$, into the Ω_{EC} domain;
- set the time $t = 0$ and the time step size $\tau_n = 1$ s;
- set the size and shape of computational sub-domains, Ω_B , Ω_F and Ω_{EC} ;
- initialize all the model fluxes to 0;
- calculate the dimensionless Biot number, Bi defined in Eq. (39).

II. Time stepping (pseudo-steady state)

do

Time step n at time t_n .

A. Dynamics of urea concentration in the electrocatalytic layer Ω_{EC} (steady state)

1. Calculate dimensionless Hatta number

The Hatta number, defined as Eq. (SM. 3), allows to describe the competition, in the Ω_{EC} domain, between the chemical kinetics and the effective diffusion inside the porous solid. Depending on this number, either a chemical or diffusional regime takes place.

$$Ha = \sqrt{\frac{k_{app} \times \mu^2}{D_{urea,w}^{eff} \times [\text{CO}(\text{NH}_2)_2]^{0.7}}} \quad (\text{SM. 3})$$

2. Solve mass balance:

- Solve for urea concentration $[\text{CO}(\text{NH}_2)_2]_{\delta \leq z \leq \delta + \mu}$, $t_n + \tau_n$, the ODE system:

$$\frac{\partial^2 [\text{CO}(\text{NH}_2)_2]}{\partial x^2} - Ha^2 \times [\text{CO}(\text{NH}_2)_2]^{0.3} = 0 \quad (\text{SM. 4})$$

from t_n to $t_n + \tau_n$.

A shooting method for boundary value problems of ODE system was used for stable and accurate integration between t_n and $t_n + \tau_n$. The method consisted in testing

¹ The presentation of the model resolution is inspired from the work of Picioreanu C., Head I.M., Katuri K. P., van Loosdrecht M. K., Scott K., A computational model for biofilm-based microbial fuel cells, *Water Research*. **2007**. doi: 10.1016/j.watres.2007.04.009

different fluxes in $z = \delta$ so as to minimize a target function defined in $z = \delta + \mu$ as a Neumann condition ($\frac{\partial[\text{CO}(\text{NH}_2)_2]}{\partial z}\Big|_{z=\Lambda_E} = 0$).

B. Dynamics of urea concentration in the liquid film layer Ω_F (steady state)

1. Scaling the diffusion flux by the respective mass transport characteristics to the studied area:

$$\text{Biot} \times \frac{\partial[\text{CO}(\text{NH}_2)_2]}{\partial z}\Big|_{z=\Lambda_{\text{FEC}}}^{\Omega_F} = \frac{\partial[\text{CO}(\text{NH}_2)_2]}{\partial z}\Big|_{z=\Lambda_{\text{FEC}}}^{\Omega_{\text{EC}}} \quad (\text{SM. 5})$$

2. Solve mass balance:

- Solve for urea concentration $[\text{CO}(\text{NH}_2)_2]_{0 \leq z \leq \delta}$, $t_n + \tau_n$

$$\frac{\partial^2[\text{CO}(\text{NH}_2)_2]}{\partial x^2} = 0 \quad (\text{SM. 6})$$

C. Dynamics of urea concentration in the bulk Ω_B (transient state)

1. Solve mass balance:

- Solve for urea concentration $[\text{CO}(\text{NH}_2)_2]_{z \leq 0}$, $t_n + \tau_n$

$$V^{\text{bulk}} \times \frac{\partial[\text{CO}(\text{NH}_2)_2]_{z \leq 0}}{\partial t} + D_{\text{urea,w}} \times S_{\text{electrode}} \times \frac{\partial[\text{CO}(\text{NH}_2)_2]}{\partial z}\Big|_{z=\Lambda_{\text{BF}}}^{\Omega_F} = 0 \quad (\text{SM. 7})$$

- Solve for urea concentration $[\text{CO}(\text{NH}_2)_2]_{z=\delta}$, $t_n + \tau_n$

$$[\text{CO}(\text{NH}_2)_2]_{z=\delta} = [\text{CO}(\text{NH}_2)_2]_{z=0} + \delta \times \frac{\partial[\text{CO}(\text{NH}_2)_2]}{\partial z}\Big|_{z=\Lambda_{\text{BF}}}^{\Omega_F} \quad (\text{SM. 8})$$

Section SM.8: Data Availability

Table 1 Data produced by the experiments to obtain Figure 1

Entry	Figure 1-a					
	#1	#2	#3	#4	#5	
$[\text{CO}(\text{NH}_2)_2]$ [mmol. L ⁻¹]	20	30	50	200	250	
$[\text{OH}^-]$ [mmol. L ⁻¹]	5					
Purity of nickel(III) powder	79%					
$r_0^x \times 10^6$ [mol. L ⁻¹ . (g _{cat} . s) ⁻¹]	3.9	5.5	5.9	7.9	6.4	
Entry	Figure 1-b					
	#1	#2	#3	#4	#5	#6
$[\text{CO}(\text{NH}_2)_2]$ [mmol. L ⁻¹]	10					
$[\text{OH}^-]$ [mmol. L ⁻¹]	5	10	20	30	40	50
Purity of nickel(III) powder	79%					
$r_0^x \times 10^6$ [mol. L ⁻¹ . (g _{cat} . s) ⁻¹]	20.8	23.3	44.6	46.3	58.5	46.4
$[\text{CO}(\text{NH}_2)_2]$ [mmol. L ⁻¹]	50					
$[\text{OH}^-]$ [mmol. L ⁻¹]	5	10	20	30	40	50
Purity of nickel(III) powder	79%					
$r_0^x \times 10^6$ [mol. L ⁻¹ . (g _{cat} . s) ⁻¹]	5.9	9.7	12.2	15.3	16.1	13.2
$[\text{CO}(\text{NH}_2)_2]$ [mmol. L ⁻¹]	100					
$[\text{OH}^-]$ [mmol. L ⁻¹]	5	10	20	40	50	
Purity of nickel(III) powder	79%					
r_0^x [mol. L ⁻¹ . (g _{cat} . s) ⁻¹]	9.4	13.9	33.4	41.5	61.7	
$[\text{CO}(\text{NH}_2)_2]$ [mmol. L ⁻¹]	150					
$[\text{OH}^-]$ [mmol. L ⁻¹]	5	10	20	30	40	50
Purity of nickel(III) powder	79%					
r_0^x [mol. L ⁻¹ . (g _{cat} . s) ⁻¹]	20.9	33.2	45.1	69.48	75.0	79.5
$[\text{CO}(\text{NH}_2)_2]$ [mmol. L ⁻¹]	300					
$[\text{OH}^-]$ [mmol. L ⁻¹]	5	10	20	30	40	50
Purity of nickel(III) powder	79%					
r_0^x [mol. L ⁻¹ . (g _{cat} . s) ⁻¹]	2.7	13.1	16.1	18.9	21.5	20.1
Entry	Figure 1-c					
	#1	#2	#3	#4	#5	
β_x [-]	0.5	0.4	0.8	0.6	0.8	
Entry	Figure 1-d					
	#1	#2	#3	#4	#5	
$k'_{\text{app}} \times 10^2$ [mol ^(1-β_x) . (m ³) ^(β_x-1) . (g _{cat} . s) ⁻¹]	0.9	0.4	0.3	0.8	0.6	

Table 2 Data produced by the experiments to obtain Figure 3

Entry	Figure 3-a					
	#1	#2	#3	#4	#5	#6
$[\text{CO}(\text{NH}_2)_2]$ [mmol. L ⁻¹]	10	50	75	100	200	300
$[\text{OH}^-]$ [mol. L ⁻¹]	1					
$S_{\text{electrode}}$ [mm ²]	3.14					
v_{scan} [mV. s ⁻¹]	0.12					
ω_{RDE} [RPM]	1000					
j_{lim} [A. m ⁻²]	21.7	36.3	38.9	45.0	57.6	65.4
Entry	Figure 3-b					
	#1	#2	#3	#4	#5	
$[\text{CO}(\text{NH}_2)_2]$ [mol. L ⁻¹]	0.3					
$[\text{OH}^-]$ [mol. L ⁻¹]	0.1	0.25	0.5	1	1.5	
$S_{\text{electrode}}$ [mm ²]	3.14					
v_{scan} [mV. s ⁻¹]	0.12					
ω_{RDE} [RPM]	1000					
j_{lim} [A. m ⁻²]	11.1	39.1	59.3	75.8	143.8	
Entry	Figure 3-c					
	#1	#2	#3	#4		
$[\text{CO}(\text{NH}_2)_2]$ [mol. L ⁻¹]	0.3					
$[\text{OH}^-]$ [mol. L ⁻¹]	1					
$S_{\text{electrode}}$ [mm ²]	8.7	9.2	10.4	15.4		
v_{scan} [mV. s ⁻¹]	0.12					
$\omega_{\text{magnetic stirrer bar}}$ [RPM]	1000					
j_{lim} [A]	9.9E-5	3.3E-4	2.3E-4	1.7E-3		