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Chlorine in NiO promotes electroreduction of CO$_2$ to formate

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ABSTRACT

We report the exceptional finding that NiO, a known electroactive catalyst for the reduction of CO$_2$ to CO, can be tuned to become an active electrocatalyst for CO$_2$ reduction to formate when chlorine is synthetically incorporated into NiO. The CO$_2$ reduction reaction (CO$_2$RR) is carried out on chlorine-containing NiO octahedral particles made by a solid-state synthesis method yielding a Faradaic efficiency (FE) of 70 % for formate production at -0.8 V vs. RHE with a partial current density of 14.7 mA/cm$^2$. XPS confirms the presence of Ni$^{2+}$ and Ni$^{3+}$ species, indicating the existence of uncoordinated Ni. The Ni$^{2+}$/Ni$^{3+}$ ratio increases with the Cl concentrations on NiO. Cl concentrations are also confirmed with STEM-EDX. DFT modeling provides insights into the thermodynamic stability and CO$_2$RR mechanism over the Cl-containing NiO surface. It is suggested that Cl can occupy the defective sites created by oxygen vacancies on the NiO model (O-alpha+Cl). The surface Pourbaix diagrams constructed from DFT indicate the preferred surface terminations favorable at the operating conditions for the CO$_2$RR, which closely agrees with the experimental findings. The O-alpha+Cl has been found to promote CO$_2$RR to formate. Our results create new possibilities in the development of earth-abundant electrocatalysts for selective CO$_2$RR.

1. Introduction

A significant part of the traditional energy value chains uses non-renewable fossil fuels as their primary raw material. These fuels are carbon-based, and their combustion releases carbon as CO$_2$ into the Earth’s atmosphere. The increasing concentration of CO$_2$ in our atmosphere poses a threat to our living environment [1–3]. Capturing CO$_2$ in chemical bonds to make useful compounds is an excellent means of remediation [4]. Thereby, new alternatives for the chemical transformation of CO$_2$ can contribute to a low carbon climate-resilient future.

CO$_2$-recycling, such as the electrochemical conversion of CO$_2$, is an important technology that can effectively produce high-value chemicals using renewable sources. CO$_2$ can be activated at a catalyst surface upon adsorption, which, by subsequent proton and electron transfers, allows chemical transformations of CO$_2$ to carbon compounds, such as C$_1$ (e.g., CO, HCOO$^-$, CH$_4$) and C$_2$ (e.g., C$_2$H$_4$, alcohols) [5,6]. Among the C$_2$ and C$_3$ compounds, formate (HCOO$^-$) is of great interest due to its low toxicity and high H$_2$ carrier capacity (53.4g H$_2$/L) [7]. Metal and metal oxide catalysts (Bi, Cd, Co, Cu, Hg, In, Pd, Pb, Sn, and Zn) exhibit relatively good selectivity for formate at moderate overpotentials (Table S1). To our knowledge, there are no earlier reports on Cl-containing NiO electrocatalysts for electrocatalytic formate production (Tables S1 and S2), demonstrating that the research on NiO electrocatalysts for formate production is still in its infancy. Compared to other approaches that directly use halides (I, Br, or Cl) in the electrolyte to reduce CO$_2$ [8], an ideal catalyst should contain halide species within its structure, as in the case of Cl. The effect of Cl has been showcased by increasing Cu stability during CO$_2$RR [9]. Another advantage is that Cl or other halogens in metals can selectively direct chemical pathways between the competitive processes (i.e., HER and CO$_2$R) [10–14].

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Like Cu, NiO is an abundant earth catalyst for CO$_2$RR. Metallic or oxidized Ni is well-known for selectively producing CO during CO$_2$RR (Table S2) [15,16]. Apart from CO, the electrocatalysis of other chemicals such as formate, using Ni or NiO can extend the functionality of this environmentally friendly catalyst, especially compared to Bi or more expensive metals such as In, Pd, or Sn (Table S1). So far, the highest Faradaic efficiency to formate (FE$_{\text{HCOO}^-}$) reported for the bare Ni electrocatalyst is around 22% at -0.7V vs. RHE, with a partial current density towards formate ($J_{\text{HCOO}^-}$) of 0.24 mA/cm$^2$ [17–19]. More sophisticated systems, such as Ni nanoparticles over MnO$_2$, have achieved FE$_{\text{HCOO}^-}$ = 85% (at -0.85 V vs. RHE) at $J_{\text{HCOO}^-} = 7.2$ mA/cm$^2$ [20]. However, more simple synthetic routes without additional support materials for evaluating the electrocatalytic performance of Ni (or NiO) should be assessed [21].

NiO is an attractive and unexplored option for the design of eco-friendly electrocatalysts (Table S3). A way forward is tuning the active sites on NiO. Although active site tunability is challenging, engineering NiO surface defects can aid in increasing the formate conversion and selectivity. Defect engineering concepts have been applied to NiO for catalytic reactions such as water splitting [22], hydrogen evolution [23], and recently CO$_2$ photoreduction [24]. It has been demonstrated that the electroactivity of NiO can be improved by increasing the number of defects in its structure [25–27]. To reach our aim of engineering defects in NiO, we considered a synthetic route based on electrospinning followed by multiple annealing steps as a potential direction to synthesize Cl-containing NiO. We have found that this approach leads to octahedral NiO crystallites. NiO octahedra have previously been produced using several synthetic routes [28–31]. It has been reported that there exists a relationship between the shape and the addition of halogen or organic ligands to the reaction medium, yielding to (111) faceted NiO [32]. Besides the preferential (111) facets [33–35], doping of NiO with low valence anions has been reported to increase the Ni$^{3+}$/Ni$^{2+}$ ratio leading to the formation of non-stoichiometric nickel oxide. These non-stoichiometric species are uncoordinated species typically induced by defects in the electrocatalyst [5]. From this perspective, incorporating Cl into NiO during the synthesis would be an exciting approach for a high FE$_{\text{HCOO}^-}$ and $J_{\text{HCOO}^-}$ for NiO-based materials.

In this work, NiO is synthesized using a solid-state chemistry approach. As a preparation method, electrospinning of fiber materials is carried out using a NiCl$_2$-PVP precursor solution. The rationale behind the use of electrospinning is that it produces ca. 100 nm-size composite crystals of the desired Cl-containing NiO electrocatalyst after annealing in air. The functionality of Cl-containing NiO is then tested during CO$_2$RR. At 4 h, FE$_{\text{HCOO}^-}$ results in 70%, while for 24 h, the FE$_{\text{HCOO}^-}$ is 63% at -0.8 V vs. RHE with a $J_{\text{HCOO}^-}$ of 13.7 mA/cm$^2$. In both cases, a small amount of CO with Faradaic efficiencies for CO (FE$_{\text{CO}}$) ≤ 3% and Faradaic efficiency for H$_2$ (FE$_{\text{H2}}$) ≤ 15 % have been observed. The density-functional theory (DFT) modeling generates insight into the unexplored reaction mechanism during CO$_2$RR to formate over a Cl-containing NiO surface. The constructed model shows that the filling of oxygen alpha vacancies with Cl play an essential role during CO$_2$RR to formate. The defects can be correlated to non-stoichiometric Ni$^{3+}$ and Ni$^{2+}$ species present in the Cl-containing NiO. XPS analysis demonstrated that the Ni$^{3+}$/Ni$^{2+}$ ratio is proportional to the concentration of Cl. Cl concentrations have also been confirmed with STEM-EDX mapping. For the first time, the results confirm the high electrocatalytic activity of an environmentally friendly NiO electrocatalyst during CO$_2$RR to formate.

2. Methods

2.1. Synthesis of NiO octahedra

NiCl$_2$-PVP (polyvinylpyrrolidone) fibers were used as a precursor for NiO octahedral. The NiCl$_2$-PVP precursor solution was prepared by dissolving NiCl$_2$·6H$_2$O (ACS grade, Sigma Aldrich) in ethanol (ACS grade, Alpha Aesar) until complete dissolution. Then, PVP (MW ~1,300,000 by LS, Sigma Aldrich) and N,N-Dimethylformamide (DMF, anhydrous, Sigma Aldrich) were added to the solutions and stirred magnetically overnight. The final concentrations were 0.22 M (as Ni), 8.09 mM (PVP), and 7.2 M (DMF). The NiCl$_2$-PVP solution was spun using a commercial electrospinning system from IME Technologies (The Netherlands) at 0.5 mL/h. The electrospinning was operated at 18 kV, using a stainless-steel needle of 0.4 mm inner diameter at a separation distance of 12 cm from the needle to the aluminum collector plate. The NiCl$_2$-PVP fibers were collected at 25 °C and relative humidity of 25%. After NiCl$_2$-PVP fiber deposition, the fibers were dried in a furnace at 80°C for 12 h to remove the excess solvent.

The NiCl$_2$-PVP fibers were annealed (Nabertherm LH 15/12) in air, generating NiO octahedra. Two annealing steps were used. First, the fibers were annealed at 350 °C (ramp-up rate 0.5 °C/min) for 1 h to remove the organic components and then annealed at 550 °C (1 °C/min) for 1 h to generate crystalline NiO. The sample was named NiO@Cl-9%. Second, the NiO@Cl-9% sample was annealed at 550 °C (1 °C/min) for 1 h. The sample was then named NiO@Cl-1%. Third, the NiO@Cl-1% was annealed at 550 °C (1 °C/min) for 1 h to evaluate if Cl content varies over the next annealing steps. After annealing the NiO@Cl-1% sample, the Cl concentration remained similar to the untreated NiO@Cl-1%. In all cases, a controlled cooling ramp of 1 °C/min was used in both cases. It should be noted that during NiO@Cl-9% and NiO@Cl-1% preparation, the samples were pressed between two alumina plates (200 g in weight each). The rationale was to generate a compressed NiO fiber film to allow the formation of NiO octahedra.

The NiO drop-casting samples presented in the supporting information were prepared by directly pouring the NiCl$_2$-PVP electrospinning solution into porcelain crucibles and calcined at 550 °C (1 °C/min) for 1 h in air. NiO spin-coating samples from the supporting information were prepared using a Laurell WS-650-23 spin coater. The particles were prepared by pouring 1 mL of the NiCl$_2$-PVP electrospinning solution on top of thermally grown SiO$_2$ on Si wafers and using a spin force of 3000 rpm for 90 s and subsequently at 2300 rpm for 60 s. After spin-coating, the wafers were annealed at 550 °C (1 °C/min) for 1 h in air. Before spin-coating, all SiO$_2$/Si wafers were cleaned with DI water and ethanol. Reduced NiO@Cl-9% (Ni@Red) was used for comparison. Ni@Red was prepared by reducing NiO@Cl-9% in H$_2$ (2% in N$_2$, gas flow: 50 cc/h) at 250 °C (5 °C/min) for 3.5 h.

2.2. Morphological characterization

2.2.1. HR-SEM

High-resolution scanning electron microscopy (HR-SEM) images of samples were taken using a Zeiss MERLIN SEM microscope operated at 2 kV coupled with High-Efficiency Secondary Electron Detector (HE-SE2). Samples NiO@Cl-9% and NiO@Cl-1% were analyzed using a Laurell WS-650-23 spin coater. The particles were prepared by pouring 1 mL of the NiCl$_2$-PVP electrospinning solution on top of thermally grown SiO$_2$ on Si wafers and using a spin force of 3000 rpm for 90 s and subsequently at 2300 rpm for 60 s. After spin-coating, the wafers were annealed at 550 °C (1 °C/min) for 1 h in air. Before spin coating, all SiO$_2$/Si wafers were cleaned with DI water and ethanol. Reduced NiO@Cl-9% (Ni@Red) was used for comparison. Ni@Red was prepared by reducing NiO@Cl-9% in H$_2$ (2% in N$_2$, gas flow: 50 cc/h) at 250 °C (5 °C/min) for 3.5 h.

2.2.2. STEM

Scanning transmission electron microscopy (STEM) was performed in a JEOl ARM 200 CF system operated at 80 kV. The estimated current density during imaging was 14.5 pA while using 68-175 mrad of the annular detector. The estimated current density during imaging was 14.5 pA while using 68-175 mrad of the annular detector
spectrometer. Samples for TEM were prepared by dispersing 5 mg of NiO@Cl-9% and NiO@Cl-1% samples in ethanol and sonicated for 5 min. The suspension was drop cast on Cu grids.

2.2.3. X-ray diffraction

The crystallographic phase of all samples was analyzed by X-ray powder diffraction (D2 PHASER, Bruker) using Cu Kα radiation (λ = 1.5418 Å) operated at 30 V, 10 mA, in a range between 10-85° 2θ, employing a step size of 0.05° and a scan speed of 0.1°/s. Si low background sample holder (Bruker) was used for the powder samples. Commercial NiO (Sigma-Aldrich) is used for comparison.

2.2.4. Chemical surface analysis

X-ray photoelectron spectroscopy (XPS) analysis was performed in a Quantera SXM machine from Physical Electronics using monochromated Al Kα (1486.6 eV). The samples were fixed on double-sided adhesive carbon tape mounted on a stainless-steel holder. Low energy electron flood gun was used to supply the missing photo- and Auger electrons. Low energy argon ions were used to remove the surplus of electrons by the electron flood gun. The electron binding energies were referenced to carbon C 1s at 284.8 eV. The collected core spectra were analyzed using the PHI Multilap V9.9.0.8 software (Physical Electronics, Inc.). High-resolution spectra were fitted using a Lorentzian-Gaussian line fitting and Shirley type to compensate for the background.

2.2.5. Raman measurements

Raman spectroscopy was used to identify the defects present in NiO@Cl-9% and NiO@Cl-1%. An Alpha300 R confocal Raman microscope/spectrometer (WITec, Germany) equipped with an MPlan FL N 100x/0.9 NA air objective (Olympus, Tokyo, Japan) was used. The samples were excited using an excitation laser of 532 nm operated at 5 mW power. The samples were prepared by dispersing 10 mg of a powder sample in one droplet of ethanol and drop-cast on top of glass slides.

2.3. Electrochemical characterization

2.3.1. Electrochemical flow cell

The CO2RR was performed in an in-house designed microfluidic flow cell using a filter-press cell configuration. Working electrodes were prepared by spraying the as-prepared catalyst ink on the carbon gas diffusion layer (Sigracet 25BC) and dried at 80 °C overnight. The ink was prepared using 75% of carbon nanotubes and 25% of binder-catalyst (i.e., binder-NiO@Cl-9%). In this case, the binder composition was PVDF and Nafion 1:1. Then, the binder is mixed 1:1 ratio with the catalyst. The final loading of NiO@Cl-9% was 1.25 mg/cm² (geometrical area 1.8 cm²) in all cases studied. Platinum foil and an Ag/AgCl electrode were used as the counter and reference electrodes.

A previously activated cation exchange membrane (Nafion 115) was used between both compartments, and 0.1M KHCO3 was used as the electrolyte on both sides, recirculated at 15 ml/min. Cyclic voltammetry (-1.1 to 0 V vs. RHE at 10 mV/s) was taken before and after each potentiostat experiment to know the catalyst’s stability. The gas product detection was performed using gas chromatography analysis (490 Micro GC equipment from Agilent technologies) of gas sampled from the headspace during the electrolysis. The system was equipped with two channels - Molsieve 5 A and the PoraPLOT - to analyze the following reaction products: hydrogen (H2) and carbon monoxide (CO), methane (CH4), ethane (C2H6), ethene (C2H4) as well as detection of CO2. NiO-based catalyst produced H2 and CO as main gas products, quantitatively detected in the Molsieve channel with 0.370 min and 1.642 min as retention times. The injector temperature was 110 °C, and the column temperature was set at 80 °C in both channels. The carrier gas was Ar at 200kPa and He at 150 kPa for Molsieve and PoraPLOT channels. Injections were sequentially performed every 5 min, being an injection time 30 ms. The calibration of the equipment for H2 and CO was determined separately by injecting known quantities of pure gas. At the end of the bulk electrolysis, the catholyte was analyzed to quantify the liquid products by HPLC (AMInex column HPX-87X from Bio-Rad). The eluent used was 5 mM of H2SO4 with a 6 mL/min flow rate value at 60 °C. Typically, 10 mL of collected catholyte was mixed with 4M H2SO4 to decrease from pH 6.86 to pH 1–3, corresponding with formic acid formation. It should be noted that all current densities are expressed as cathodic currents. Thus a negative value is used in the manuscript. The Faradaic efficiency for the products was calculated according to the following equation:

\[
FE(\%) = \left( \frac{\text{Nr}}{\text{nF}} \right) \frac{(V)}{Q}
\]

Nr is the number of electrons involved in obtaining the product r (2e− for the formate, CO and H2), n corresponds to the number of r moles generated, F is the Faraday’s constant (96,485 C/mol), and Q is the total charge passed during electrolysis.

2.3.2. Electrochemical surface area

The electrochemical surface area of the NiO@Cl-9% in supporting information was determined by determining the electrochemical double-layer capacitance by CV. The double-layer capacitance measurement can be determined for all catalysts from the slope of the linear relationship between the current density obtained in the non-Faradaic region of the CVs at several scan rates. For that, the catalyst was immersed in 0.1 M KHCO3, continuously purged with N2, and CVs were obtained at scan rates within the range from 5 mV s⁻¹ to 80 mV s⁻¹.

2.4. Mechanistic insights with density-functional theory

2.4.1. First-principles calculations

We have investigated the CO2 reduction with and without Cl atoms using non-collinear spin-polarization first-principles total-energy calculations. Although the NiO nanoparticles show different facets, SEM and TEM images have shown that the most common is the (111) termination. Therefore, we have used the NiO(111) surface to model the CO2 reduction reaction. Total energy calculations were performed in the Vienna Ab initio Simulation Package (VASP) [36-39]. Exchange-correlation energies have been treated according to the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) parameterization [40]. Also, since Ni has d-orbitals with highly correlated electrons, we have included the Hubbard correction (GGA+U) [41]. Previous reports have demonstrated that a value of U = 6.3 and J = 1 eV describes the NiO physical properties very well [42,43]. Therefore, we have used these values in our calculations. The electronic states have been expanded using the projector-augmented wave basis (PAW) [44,45] with an energy cutoff of 425 eV. Van der Waals (vdW) forces have been considered using the Grimme-D3 correction [46,47]. The NiO(111) surface has been simulated employing the supercell method with a 2 × 2 periodicity. Each supercell was formed by a slab and a vacuum space larger than 20 Å to avoid interactions between adjacent slabs; the slab was constructed with 9 atomic layers, where the lower layers were frozen in their ideal positions to simulate the bulk-like environment. In optimizing the geometries, we have required all forces to be less than 0.01 eV/Å and energy differences less than 1 × 10⁻⁴ eV. Integration of electronic states in the Brillouin zone has been performed using a Monkhorst-Pack mesh of 5 × 5 × 1 k-points [48].

2.4.2. Surface formation energy formalism

In order to investigate the stability of different surface terminations with different numbers of atoms and chemical species, we have used the Surface Formation Energy (SFE) formalism adapted to our system, following Refs. [49-53]. In the SFE formalism, we consider thermodynamic equilibrium between the surface and the bulk:
\[ \mu_{\text{Ni}}^{\text{bulk}} + \mu_{O}^{\text{mol}} - \Delta H_f = \mu_{\text{NiO}}^{\text{bulk}} = \mu_{\text{Ni}} + \mu_{O} \]

with

\[ \mu_{\text{Ni}}^{\text{bulk}} \leq \mu_{\text{Ni}} \]

and

\[ \mu_{O}^{\text{mol}} \leq \mu_{O} \]

Where \( \mu \) is the chemical potential of the ith atomic specie, and \( \Delta H_f \) is the enthalpy of formation. Our calculated value of \( \Delta H_f \) is 3.01 eV in good agreement with previous reports [8]. We can write the surface formation energy as follows:

\[ E_s = E_{\text{ads}} - E_{\text{vib}} - \sum n_i \mu_i \]

Where \( E_{\text{ads}} \) is the total electronic energy of the system, and \( n_i \) is the number of atoms of the ith species, \( E_{\text{vib}} \) is the total energy of an arbitrary reference, which in this case is the ideal Ni-terminated surface, and \( \Delta n_i \) is the excess or deficit of atoms of the ith species in comparison with the reference. We plot the SFE as a function of the chemical potential from the reference, which in this case is the ideal Ni-terminated surface, and \( \mu_{\text{NiO}} \) is the most reactive surface as given below:

\[ \frac{1}{2} \Delta H_f = \Delta E_{\text{ads}} \]

Where \( \Delta E_{\text{ads}} \) represents the adsorbent while \( x \) represents the number of hydrogens adsorbed on the NiO(111) model system.

At constant potential and pH, change in free energy of hydrogenation reaction on various absorbate configurations as a function of the number of H atoms adsorbed (n), is given by:

\[ \Delta G = n \mu_{\text{H}_2} + n_k \mu_{PVP} + \Delta G_{\text{ads}} - \Delta G_{\text{vib}} - \Delta G_{\text{H}_2} \]

Where \( \Delta G_{\text{ads}} \) and \( \Delta G_{\text{vib}} \) denote the change in Gibbs free energy upon adsorption of hydrogen on the surface and free energy of the adsorbed state, respectively. \( \Delta G_{\text{ads}} \) can be further written as follows:

\[ \Delta G_{\text{ads}} = \Delta E_{\text{ads}} + \Delta F_{\text{vib}} \]

Here, \( \Delta E_{\text{ads}} \) represents the electronic energy difference while \( F_{\text{vib}} \) is the Helmholtz vibrational energy which can be calculated based on the zero-point vibrational energy contribution \( E_{\text{vib}} = E_{\text{ads}} - E_{\text{vib}} \) and the vibrational entropy \( S_{\text{vib}} \):

\[ F_{\text{vib}} = E_{\text{ads}} - E_{\text{vib}} - T \cdot S_{\text{vib}} = \frac{N_v}{2} \sum \left( \hbar v_i + 2 k_B T \ln \left( 1 - \frac{\hbar v_i}{k_B T} \right) \right) \]

Where \( v_i \) represents the wavenumbers obtained from the vibrational frequencies of hydrogen atom(s) over the surface.

3. Results and discussions

3.1. Preparation, morphology, and composition of electrocatalysts

Electrospinning is extensively used to produce nanofibers of different materials, but in this work, it is employed as a deposition method of NiCl₂-PVP nanofibers (Fig. S1). The NiCl₂-PVP nanofibers are used as precursors for the solid-state synthesis of Cl-containing NiO. The final shape of the NiO depends strongly on the deposition method (Fig. S2). Electrospinning results in the most suitable deposition route for the formation of NiO octahedral crystals (Fig. 1a) when compared with drop casting or spin coating, for which octahedral crystals are not formed (Fig. S2). We propose that the formation of the NiO octahedral Cl-containing NiO@Cl-9% (i.e., NiO with 9%at of Cl) is achieved via the coalescence of NiCl₂-PVP nanofibers (Fig. S1). NiCl₂-PVP nucleates at 550 °C with Cl and PVP acting as ligands, yielding octahedral particles. Under the same conditions, a second thermal treatment is applied to the NiO@Cl-9% leading to the catalyst named NiO@Cl-1% (i.e., NiO with 1at% of Cl) in Fig. 1d. Morphological analysis for NiO@Cl-9% and NiO@Cl-1% can be seen in Fig. 1a and d. The images show the formation of polydisperse NiO octahedra with edge sizes of 1.7 ± 0.6 µm. Morphological variations of NiO@Cl-1% are evidenced in Fig. 1d. Most NiO@Cl-1% octahedral crystals show heavy grooves that originated during the second thermal treatment, most probably due to the removal of Cl. Our hypothesis is compared with other synthetic approaches where the decomposition of the precursors leads to defective NiO crystals [54]. It should be noted that changes in NiO morphology might be expected at higher temperatures than 550 °C [55].

A closer inspection with STEM bright-field (BF) at the surface of the crystallites from NiO@Cl-9% and NiO@Cl-1% is shown in Fig. 1b and e. The relatively low magnification STEM images show a side view of the octahedral crystallites. A significant number of steps and grooves over the NiO@Cl-1% surface (Fig. 1e) caused by the thermal treatment can be seen. Even though it is possible to find smaller crystals with similar features and roughness in NiO@Cl-9% (Fig. 1a), most of the roughness in NiO@Cl-1% is found prominently over average size crystals (Fig. 1d). Similarly, it is possible to find flat facet octahedra in NiO@Cl-1%, although they are very rare and of small dimensions. In Fig. 1e, the high resolution (HR)-STEM annular dark field (ADF) image for NiO@Cl-9% shows part of the edge of the crystal oriented along [101] with lattice planes of spacing 2.3 Å and 2.1 Å that correspond to the (111) and (020) crystallographic planes of the face-centered cubic structure of NiO. [56] This agrees with the crystallographic characteristics of NiO shown in the XRD results displayed in Fig. S3a.

The Cl amount in NiO@Cl-9% and NiO@Cl-1% bulk samples is semi-quantified considering Ni and Cl ratio in SEM-EDX and STEM-EDX. Both methods give similar Cl relative content; therefore, in Table 1, we only display the Cl relative content for NiO@Cl-9% and NiO@Cl-1% as analyzed from STEM-EDX. A 2-fold reduction in Cl atomic concentration is observed for NiO@Cl-1%. The result confirms that part of the Cl is removed during the annealing of the NiO@Cl-9% sample. The Cl distribution over the NiO octahedral can be appreciated in the STEM-EDX mappings of NiO@Cl-9% and NiO@Cl-1%, displayed in Fig. 1f-i and j-m. As can be observed, Cl is distributed mostly over the NiO crystallites, although with a significant reduction in the case of NiO@Cl-1%. A yellow arrow in Fig. 1j highlights the roughness observed in the NiO@Cl-1% surface.

The chemical composition of NiO@Cl-9% and NiO@Cl-1% is investigated with XPS to understand the role of Cl in NiO. High-resolution XPS spectra and the corresponding fitted curves for NiO@Cl-9% (top panel) and NiO@Cl-1% (bottom panel) are presented in the XPS. The XPS spectra correspond to (a) Ni 2p, (b) O 1s, and (c) Cl 2p. In Fig. 2a, the observed binding energies for Ni 2p3/2, 2p1/2 are 854.0 eV and 853.9 eV for NiO@Cl-9% and NiO@Cl-1%, corresponding to lattice NiO in NiO [57, 58]. NiO species are found in NiO@Cl-9% and NiO@Cl-1%, with binding energy at 855.8 and 855.6 eV attributed to uncoordinated Ni, most probably from defective NiO. Similar binding energies for NiO in Ni2O3 or NiOOH could be expected [59-62]. The corresponding Ni 2p3/2 split-orbit peaks appear at 17.5 eV from Ni 2p3/2 signal. The results agree with NiO-based materials using similar precursors (i.e., NiCl2) and other synthetic approaches [63,64]. Raman measurements also confirm NiO and NiO2 species in NiO (Fig. S5).

The fitted peaks for Ni2+ and Ni3+ within the 850-860 eV region for
NiO@Cl-9% and NiO@Cl-1% are integrated for comparison. The ratio between the integrated values is presented in Table 1. It is clear from this table that NiO@Cl-9% has the highest amount of Ni$^{3+}$ species with a Ni$^{3+}$/Ni$^{2+}$ ratio of 4.6. In the case of NiO@Cl-1%, Ni$^{3+}$/Ni$^{2+}$ is close to 1.2, indicating a lower amount of Ni$^{3+}$ species in NiO. A more detailed analysis to explain the relation between Ni$^{3+}$ and Cl is discussed in the DFT section. Fig. 2b shows the XPS spectra and fitted curves for O 1s. The O 1s peaks at binding energies of 529.4 and 529.3 eV for NiO@Cl-9% and NiO@Cl-1% are assigned to oxygen in the NiO lattice [65]. The O 1s peaks at 531 eV label as Ni-O for NiO@Cl-9% and NiO@Cl-1% are associated with Ni-OH, Ni$_2$O$_3$, or non-stoichiometric NiO, probably from oxygen defects [66–69]. The O 1s peak at 532.2 eV for NiO@Cl-1% corresponds to surface OH$^-$ groups, which has been observed before for NiO [59, 66–69]. No nitrogen is detected in all cases, indicating that PVP has been decomposed to oxidized carbon species (Fig. S6) with a total carbon content of 14 at% in NiO@Cl-9% and NiO@Cl-1%. No graphitic carbon has been found, as shown in Figs. S5

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cl content (at%)</th>
<th>XPS Ni$^{3+}$/Ni$^{2+}$ ratio</th>
<th>XPS Ni$^{3+}$/Ni$^{2+}$ ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO@Cl-9%</td>
<td>1.2</td>
<td>9</td>
<td>4.6</td>
</tr>
<tr>
<td>NiO@Cl-1%</td>
<td>0.7</td>
<td>1.5</td>
<td>1.2</td>
</tr>
</tbody>
</table>

NiO@Cl-9% and NiO@Cl-1% are integrated for comparison. The ratio between the integrated values is presented in Table 1. It is clear from this table that NiO@Cl-9% has the highest amount of Ni$^{3+}$ species with a Ni$^{3+}$/Ni$^{2+}$ ratio of 4.6. In the case of NiO@Cl-1%, Ni$^{3+}$/Ni$^{2+}$ is close to 1.2, indicating a lower amount of Ni$^{3+}$ species in NiO. A more detailed analysis to explain the relation between Ni$^{3+}$ and Cl is discussed in the DFT section. Fig. 2b shows the XPS spectra and fitted curves for O 1s. The O 1s peaks at binding energies of 529.4 and 529.3 eV for NiO@Cl-9% and NiO@Cl-1% are assigned to oxygen in the NiO lattice [65]. The O 1s peaks at 531 eV label as Ni-O for NiO@Cl-9% and NiO@Cl-1% are associated with Ni-OH, Ni$_2$O$_3$, or non-stoichiometric NiO, probably from oxygen defects [66–69]. The O 1s peak at 532.2 eV for NiO@Cl-1% corresponds to surface OH$^-$ groups, which has been observed before for NiO [59, 66–69]. The remaining O 1s signal at 532.9 eV for NiO@Cl-9% is assigned to C-O species [59, 70]. No nitrogen is detected in all cases, indicating that PVP has been decomposed to oxidized carbon species (Fig. S6) with a total carbon content of 14 at% in NiO@Cl-9% and NiO@Cl-1%. No graphitic carbon has been found, as shown in Figs. S5.
Fig. 2. XPS spectra for NiO@Cl-9% (top panel), NiO@Cl-1% (bottom panel). XPS spectra recorded for (a) Ni 2p, (b) O 1s, and (c) Cl 2p.

Fig. 3. (a) SEM images of (a1) NiO@Cl-9%, (a2) NiO@Cl-1%, and (a3) Ni@Red. (b) FE and partial current densities after 4 h at -0.8 V for NiO@Cl-9%, NiO@Cl-1%, Ni@Red, and NiO with CNT sprayed over GDE. (c) SEM images of NiO@Cl-9%-CNT electrodes with PVDF: (c1) as prepared, (c2) after 4 h, and (c3) after 24 h of electroreduction. (d) FE and partial current densities of NiO@Cl-9%-CNT-PVDF-GDE for H₂ (4 h), CO (4 h), and HCOO⁻ (4 h) at -0.6, -0.8, and -1.0 V. Note that during CO₂R, the pH of the bulk electrolyte remained at 6.8.
and S6. Additionally, Na (0.6 at%) and Ca (0.5 at%) have been found in this set of samples. The XPS Cl 2p2/3 spectra and fitted peaks are presented in Fig. 2c. The peaks at 199.1 eV (NiO@Cl-9%) and 198.6 eV (NiO@Cl-1%) are typically associated with chloride [67,71]. The low binding energy value for NiO@Cl-1% could indicate an increased electron density due to the Cl loss [67,71,72]. The peak located around 201 eV is likely related to the presence of Cl-organic bonds [73].

3.2. Evaluation of formate production via electrochemical CO₂RR

The functionality of the NiO@Cl-9% is investigated during the CO₂RR to formate. NiO@Cl-1%, reduced Ni (Ni@Red), and commercial NiO (NiO) are used as controls to generate insights into the formate formation mechanisms in NiO@Cl-9%.

Fig. 3a shows a high resolution (HR)-SEM image of the NiO@Cl-9% (Fig. 3a1), NiO@Cl-1% (Fig. 3a2), and Ni@Red (Fig. 3a3). SEM-EDX for NiO is shown in Fig. S7. No Cl is observed for the commercial NiO. The Faradaic Efficiencies (FE) and partial current densities of the different reduction products are presented in Fig. 3b. For these experiments, 1.2 mg/cm² of the NiO@Cl-9%, NiO@Cl-1%, Ni@Red, and NiO catalyst is mixed with carbon nanotubes (CNT) and sprayed over a gas-diffusion electrode (GDE) to overcome CO₂ mass transport issues during CO₂RR. [74] Each prepared GDE is mounted in a continuous flow electrochemical cell in 0.1M HCOO⁻ connected to an online gas chromatograph (GC) to analyze the gas products and ex-situ HPLC to analyze the liquid products.

In Fig. 3b, continuous flow electrochemical measurements under constant voltage have been assessed using various potentials (-0.6, -0.8, and -1.0 V (vs. RHE)). The rationale behind these potentials is that above -0.6 V vs. RHE, hydrogen evolution reaction or CO and -1.0 V (vs. RHE))

The results align with the observations in Fig. 3b and cyclic voltammetry measurements for NiO@Cl-9%-CNT-PVDF in Fig. S8. For CO, the production remains similar between the various applied potentials, such as -0.8V in Fig. 3d. From these results, we can say that the potential window for formate is relatively small compared to Sn (Table S1). However, our results widen the applicability of NiO towards formate, with the advantage of NiO being less costly than Sn and more environmentally friendly than Bi (Tables S1 and S2). To this end, when comparing the total FE (FEΣ) for the various applied potentials, -1.0 V remains the highest with 91.0%. Other FEΣ are 88% (-0.8 V) and 86% (-0.6 V).

Since we aim to demonstrate the functionality of NiO@Cl to produce HCOO⁻, hereafter, the main emphasis is on the synthesized NiO@Cl-9% catalyst, which achieved the highest FEΣCO₃ (ca. 70%) at -0.8 V. Focusing now on the electrochemical results from NiO@Cl-9% in Fig. 3b and d, it is evident that the highest FEΣCO₃ and JCO₃ is found when PVDF is present. The results agree with previous studies, where PVDF acts as a blocking proton agent, which could affect the proton availability and proton transfer rates, stabilizing the CO₂ intermediates [75]. It is important to mention that the presence of PVDF does not change the electrochemical surface area (ECSA) as the NiO@Cl-9%-CNT-PVDF reveals similar ECSA for NiO@Cl-9% and NiO@Cl-9%-CNT-PVDF in Fig. S10 and Table S4.

The long-term stability of NiO@Cl-9%-CNT-PVDF is investigated for 24 h at -0.8 V (Fig. S11). The FEΣ remains close to 90% at a JΣ = 21 mA/cm². FEΣHCOO⁻ reveals an 8% reduction, i.e. FEΣHCOO⁻ = 63% with a JΣHCOO⁻ = 13.3 mA/cm². FEΣHCOO⁻ and FEΣCO₃ reaches 63% with a JΣ = 1.3 mA/cm² after 24 h. Morphological analysis with SEM is carried out to corroborate possible morphological changes in the NiO@Cl-9%-CNT-PVDF GDE after 24 h exposure to electroreduction (Fig. 3c). It is observed that the NiO octahedra are etched. For comparison, SEM of NiO octahedra as-sprayed over the GDE and after 4 h of operation are presented in Fig. 3c1, c2. This observation indicates that variations in morphology can be attributed to the reduction of NiO to Ni and the loss of Cl during CO₂RR [76]. Loss of Cl in Fig. 3c3 could lead to similar structural changes as in NiO@Cl-1% (Fig. 3a2). Loss of Cl might also affect the presence of Ni³⁺, similar to either NiO@Cl-1% (Table 1) or Ni@Red (Fig. S12). It should be noted that Cl losses are complicated to measure in solution at such low catalyst concentrations. However, structural analysis before (Figs. 3 and S13) and after 24 h reaction (Figs. S14-S16) provide insights into morphological changes after CO₂RR. The comparison reveals that NiO morphology is affected when applying a cathodic potential. The Cl concentration in NiO remains close to 0.4 at% after 24 h (Fig. S15). The results evidence a lower Cl concentration, approximately 0.3 at%, than the electrode at 0h (Table 1 and Fig. 3c). XRD analysis does not exhibit structural changes between 0 h and 24 h (Fig. S3).

The reduction of the catalyst is demonstrated with XPS (Fig. S12). Although the Ni@Red (Fig. 3a3) has been exposed to air after its reduction in H₂, it is fair to say that it retains features from reduced Ni. The results indicate that surface species greatly affect the electroreduction of CO₂, Ni³⁺ and reduced Ni species profoundly affect FEΣHCOO⁻ (Fig. 3b). Therefore it is important to understand the type of active site in NiO@Cl-9%. XPS analysis of NiCl₂ and Ni(ClO₂)₂ generates insights on the surface species on NiO@Cl-9% (Fig. S17). NiCl₂ is the main product on the NiO@Cl-9%-CNT-PVDF electrodes. The XPS spectra (Fig. S18) confirm the presence of NiCl₂ and Ni(ClO₂)₂ between NiO or NiOCl species on the NiO catalyst. Fig. S16 suggests that Cl is not coordinated as in Ni(ClO₂)₂, and it has more similarities with NiCl₂. More evidence is provided in Figs. S18 and S19. In Fig. S18, the EELS signal shows the presence of Cl at the surface of the NiO crystallites. In Fig. S19, the Ni L23 edge is used to obtain the L3/L2 ratio and determine the chemical environment of Ni-species in NiCl₂, NiO@Cl-9%, and NiO@Cl-1%. The measurement shows that for NiO@Cl-9%, more points have a lower L3/L2 ratio relative to Ni³⁺.
indicating a higher fraction of Ni$^{2+}$ than NiO@Cl-1%. Note that NiCl$_2$ is used as a reference for the determination of Ni$^{2+}$. Furthermore, electrodes at 0 h and after 24 h of electroreduction from Fig. 3c are analyzed with XPS in Fig. S20. The Ni 3p is used because the Ni 2p overlaps with the F Auger lines of the PVDF. The XPS analysis for Ni 3p confirms the presence of Ni$^{2+}$ and Ni$^{3+}$ species before and after CO$_2$RR (Fig. 3c). A shift to lower binding energy has also been observed in Fig. S20. The shift to lower binding energy might indicate the loss of Cl. Alternatively, the results indicate the reduction of the NiO due to the applied cathodic potential, which can explain the morphological changes in Fig. 3c. We do not discard the possibility that the produced H$_2$ might also reduce NiO to Ni during the application of the cathodic potential [77]. However, considering Faraday law, FE losses due to NiO reduction are estimated to be close to 4% or lower. These losses have not been taken into account in Figs. 3 and S11. Our findings indicate that Cl species can be allocated in defects, such as oxygen vacancies forming three-fold coordination with Ni in the NiO (Fig. 4).

3.3. Modeling of the electrocatalyst surface, thermodynamics, and CO$_2$RR mechanism

To gain mechanistic insights on how Cl-containing NiO surfaces promote CO$_2$ reduction to formate, spin-polarized DFT calculations are carried out. The model accounts for defects present in the NiO (111). The surface formation energy (SFE) for various NiO (111) surfaces is assessed using DFT (Figs. 4 and S21). SFE plots are shown as a function of the chemical potential in a range of chemical potentials varying from -3.0 eV (O-rich conditions) to 0.0 eV (Ni-rich conditions) structures (Fig. 4a). It should be noted that Fig. 4 shows the most stable surface terminations considered. Other NiO surface terminations studied are presented in Fig. S21. From Fig. 4a, b, it can be seen that the only stable structures are the ones with a vacancy (O-alpha model) [78] under oxygen-rich conditions and the octopolar reconstruction (which is formed by a pyramidal-like structure) at intermediated and Ni-rich conditions. [79] Since we are dealing with an environment rich in oxygen, the NiO surfaces are modeled using the O-alpha model. We show the electrostatic potential isosurfaces (EPIs) of the NiO surfaces with and without Cl to demonstrate the reactivity created by Cl substitution of surface hydroxyl groups in Fig. S22. Moreover, the addition of water to the surface should lead to the vacancy configuration for the octopolar reconstruction. Surfaces with vacancies are very reactive, and when Cl interacts with the vacancy is adsorbed on it, forming three-fold coordination with Ni (2 × 2-O alpha + Cl model), which is stable at O-rich and intermediated conditions (gray line) (Fig. 4a and c) over extended pH ranges (Fig. 5). Previous work from Xu et al. has shown that Ni vacancies in a NiO bulk structure result in the presence of Ni$^{3+}$ [59]. We investigated in detail the possible relationship between the presence of Cl and the amount of Ni$^{3+}$ in the structure through the Bader charge analysis [80]. We calculated the Bader charge in pristine NiO bulk as a reference. Our calculations show that the Ni donates 1.28 e to its neighbor O atoms. When a Ni vacancy is present, its neighbor Ni atoms donate 1.37 e to their neighboring O atoms, just as in the case reported in [59]. As previously demonstrated, Cl atoms adsorb on the O vacancy sites. Therefore, when higher Cl content exists on the samples, more NiO-terminating O and OH sites will actually be substituted with Cl. However, increasing the number of O vacancies also requires the presence of Ni vacancies in the octopolar structure. We have calculated the Bader charges of a Cl-covered O-alpha and a Cl-covered O-alpha with a Ni vacancy at different sites. A Ni vacancy is more stable in the third layer than on the surface. The charge donated by the Ni atoms close to Cl and close to the Ni vacancies are 1.25 e and 1.35 e, respectively, showing that Ni vacancies drive Ni$^{3+}$ species. Calculations have also been performed for the octopolar structure, finding similar results: the vacancy becomes more stable at inner layers, and Ni atoms close to it donate more charge (Ni$^{3+}$ is observed around the Ni vacancy). These results explain the increase of the Ni$^{3+}$/Ni$^{2+}$ ratio at the surface structures with higher Cl content.

Surface Pourbaix diagrams shown in Fig. 5 are constructed to assess the thermodynamic stability of favorable surfaces with hydrogen adsorbed as a function of pH and potential [81,82]. In this case, the O-alpha and O-alpha with a chlorine atom on the vacant site (O-alpha+Cl) are chosen because they result in the most stable surface in SFE plot in Fig. 4. The O-alpha without Cl is assessed first. The thermally stable surfaces on the defective O-alpha structure upon adsorption of H atoms at different coverages are shown in Fig. 5 as a function of pH and potential. The H coverage is defined as the number of hydrogen atoms adsorbed per total number of surface oxygen atoms. The Pourbaix diagram shows three terminations to be most favorable in the potential range of -1 to 2.5 V. At potentials over 2.05 V and low pH, the O-alpha surface without the H atoms is found to be stable. The formation of 0.33ML of H atoms is likely from 2.05 to 1.34 V. A large potential range of 0.51 to -1 V favors complete coverage of H atoms over the oxygens in the first layer, as shown in Fig. 5a. On moving to an alkaline medium (pH=14), with a slope of -59 meV per change in pH of 1, these three favourable terminations occur at lower potential ranges. It must be noted that the structure with 1.00 ML of H atoms falls over the potential

![Fig. 4](attachment:image.png) (a) SFE plot vs. the chemical potential for different NiO (111) surface reconstructions. (b) O-alpha model, (c) O-alpha model with a Cl atom filling the vacancy, (d) side view of the model system.
required for oxygen reduction and hydrogen evolution reactions indicated in dashed lines. Furthermore, $\text{H}_2\text{O}$ and NiH$_x$ formation might be possible in the area of the Pourbaix diagram where H$_2$ is produced.

The Pourbaix diagram for the NiO O-alpha vacancy with Cl is presented in Fig. 5b. The vacant site generated by removing oxygen from oxygen terminated nickel oxide (O-alpha) is occupied with a chlorine atom (O-alpha$^+$Cl). The surface is thermally stable surfaces upon H adsorption at varied pH and potential. The non-hydrogenated clean surface is most stable beyond 2.02 V at acidic conditions, while at pH = 14, the range reduces up to 1.19 V. Interestingly, with a decrease in potential, hydrogenation over the clean surface is highly favored, leading to adsorption of 1.00 ML of H atoms in the potential range of 2.02 to -1 V at pH = 0. The observations from Fig. 5a and b clearly indicate the stability of chlorine-containing O-alpha surface compared to the bare O-alpha upon hydrogenation.

An effective catalyst should be highly stable at $U_{\text{SHE}} = 0$. Thus we examined the stability of these hydrogenated surfaces with and without chlorine as a function of pH at $U_{\text{SHE}}$ of 0 [83]. In Fig. S23, the bottom line corresponds to 1.00 ML of H terminated O-alpha+Cl state. The results demonstrate the stability acquired by O-alpha model upon incorporating Cl atoms in its vacant site. The hydrogenated O-alpha and O-alpha+Cl surfaces are favorable at experimental conditions of $U = -0.8$ and pH = 6.8 (highlighted with a black square in Fig. 5). It might be plausible that the local pH at the electrode might further increase during the reaction. O-alpha+Cl surface remains favorable over a wide pH range.
The stability of the O-alpha+Cl is demonstrated in Figs. 4 and 5; further mechanistic insights for CO$_2$RR are generated for O-alpha and O-alpha+Cl in NiO. Since the oxygen atoms of the surface are very reactive and the surface is exposed to hydrogen protons, the oxygen atoms of the substrate are passivated by hydrogen atoms. Therefore, hydrogenated surfaces at the initial step of the reaction are used. The energetics and geometries of some particular states are studied to describe the CO$_2$ reduction reaction in the substrate without Cl (Fig. 6). This includes (i) the initial state in which the molecule and the substrate are not interacting (ZS), (ii) the state in which the CO$_2$ molecule is physisorbed (we call it the intermediate state or IS), (iii) the final state in which the formate is formed after abstracting an H atom, and it is chemisorbed in the oxygen vacancy of the substrate (final state 1 FS1), and the second final state in which the formate and the substrate are not interacting (final state or FS2). The minimum energy path is calculated to consider the kinetics of the reaction. As shown in Fig. 6a, b for NiO, there is an increase in the energy of 0.26 eV, going from ZS to IS. In fact, there is no energy barrier to arrive at this intermediate state. As the reaction evolves, a hydrogen atom from the environment has to bond with the molecule carbon atom, forming an adsorbed formate on the surface (FS1). In this case, there is an energy barrier (call transition state or TS) of 0.19 eV, and the system gains 3.58 eV in energy. However, a large energy barrier of 3.93 eV allows the formate to desorb and reach FS2. Therefore, it prefers to stay on the surface, and our calculations clearly explain why we do not observe formate in our experiments as in the case of NiO@Cl-9%, i.e., the sample with more Cl present (Table 1). This sample also has the highest Ni$^{3+}$/Ni$^{2+}$ suggesting the presence of defects, such as oxygen vacancies (Fig. 4). The energy barrier for the formation of formate without the substrate is 0.31 eV, demonstrating the importance of the Cl-filled vacancies in the NiO surface. In addition to the CO$_2$RR to formate on the chlorinated NiO surfaces, CO formation is considered. CO is obtained through the reaction: CO$_2$ + H$_2$ → CO + H$_2$O. The first reaction step occurs when an H atom of the medium interacts with the O of the CO$_2$ molecule. However, this configuration is less stable (by 0.45 eV). Therefore, since the CO formation is energetically less favorable (Fig. S25), we only focus on the CO$_2$ to formate pathway.

4. Conclusion

Cl containing NiO octahedra are synthesized using a solid-state method. The NiO functionality is demonstrated during CO$_2$RR, yielding to a FE$_{\text{HCOO}^-}$ = 70%, FE$_{\text{H}_2}$ = 15%, and FE$_{\text{CO}}$ = 3%, at -0.8 V vs.
RHE with a total current density of -21 mA/cm² over 4 h operation. Over longer-term operation (i.e., 24 h), the FE to formate lowers to ca. 63%, and the amount of H₂ and CO production remains close to 20 and 6.5% with nearly no changes in the total current density. XPS confirms the presence of Ni²⁺ and Ni³⁺ species in the NiO, and with increasing Cl concentration, the Ni³⁺/Ni²⁺ ratio also increases. It is found that Cl plays a key role in introducing Ni³⁺ presence of Ni. And the amount of H₂ and CO production remains close to 20 and 6.5%.

References


