

Optimizing FeNC materials as electrocatalyst for the CO₂ reduction reaction: Heat treatment temperature, structure and performance correlations

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Abstract

The direct CO_2 electrochemical reduction reaction (CO2RR) into carbon-based chemicals has attracted tremendous attention as a sustainable process for CO_2 utilization. The viability of the process, however, is contingent on finding efficient catalysts based on earth abundant elements. Carbon-based solid catalyst materials doped with nitrogen and transition metals (M-N-C) have emerged as a cost-efficient alternative for the direct electrochemical reduction of CO_2 into CO. These materials contain different N functionalities and MNx moieties which could be involved in the catalytic process. With the aim of gaining insight into the role of these different active sites and how to control their concentration we have prepared 5 polyaniline derived FeNC catalysts by changing the temperature of the heat treatment (750-1050°C). We observed that it is possible to tune the ratio of the different N functionalities by changing the pyrolysis temperature. Furthermore, this had a clear impact on the catalytic performance of this family of FeNC materials. In particular, a higher temperature correlated with a larger FeNx concentration resulting in a high selectivity toward the CO2RR. These results indicate that FeNx moieties play a predominant role in the catalytic process and that the incorporation of such sites to the carbon structure is enhanced by the heat treatment temperature.



The catalytic performance polyaniline derived FeNC catalysts towards the CO_2 reduction reaction can be modified by changing the temperature of the heat treatment during the material synthesis. The catalyst treated at the lowest temperature is the most active one duet to its large electrochemical surface area. The selectivity towards the CO2RR, however, is enhanced with a higher synthesis temperature, which is attribute to large concentration of FeNx, highlighting the importance of such sites on the catalytic performance of MNC materials.

Introduction

The CO₂ electrochemical reduction reaction (CO2RR) is a promising technology for converting waste CO_2 into chemicals as it is a process that can contribute to mitigate climate change on two fronts.¹ On one hand, it is a sustainable option for CO₂ utilization converting it into carbon-based chemicals and fuels. One the other hand, this process could utilize the surplus electricity, produced from intermittent sources such as wind and solar power, avoiding wasting excess of electricity generated during the peaks of production.²

The efficiency of the process relies heavily on the material used as electrocatalyst for the CO2RR. Metallic or partially oxidized copper is usually the catalyst of choice given its unique ability to reduce CO₂ into hydrocarbons.³ This process, however, suffers from poor selectivity since it is accompanied by hydrogen evolution reaction (HER). In addition, CO₂ is reduced to different products mainly CH₄, C₂H₄, CO and formic acid, which hinders the selective formation of one particular product.³⁻⁸ Furthermore, the reaction takes place at high overpotentials which implies important energy loses. Most of these losses can be attributed to the multiple proton/electron transfer steps involved in hydrocarbon production. By contrast, the direct electroreduction of CO₂ into CO is a less hindered process as it involves the transfer of only two electrons and two protons, according to the following reaction:

 $CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$

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The formation of CO is usually accompanied by HER resulting in a mixture of H₂ and CO which in the right proportion, can be used for synthetic fuels production via the catalytic Fischer-Tropsch process.⁹ Pure CO streams, however, are also desired for other processes such as the synthesis phosgene for polyurethane and polycarbonate production.

The first heterogeneous catalysts reported to selectively reduce CO₂ into CO were based on precious metals such as silver and gold on which CO is formed at low overpotentials with high faradaic efficiencies.¹⁰⁻¹² Given their low abundance, these materials are not optimal for developing affordable electrolyzers. Therefore, there is an increasing interest in developing CO2RR catalysts based on earth-abundant elements.

Recently, carbon-based solid catalyst materials doped with nitrogen and nitrogen-coordinated transition metals (M-N-C) have emerged as a selective and cost-efficient alternative to noble metal catalysts for the direct electrochemical reduction of CO₂ to CO.¹³⁻¹⁸ Such materials have been widely studied as an alternative to Pt catalyst for the Oxygen Reduction Reaction (ORR) in cathode's fuel cells.¹⁹⁻²² To explore the possibility of using M-N-C catalyst for the CO2RR Tripkovik et al., performed Density Functional Theory calculations (DFT) on porphyrin-like metal-functionalized graphene structures and found that these materials should in fact be active in the reduction of CO₂.²³ Later, Varela et al. reported that polyaniline (PANI) derived carbon materials exhibit a high selectivity towards CO production with a faradaic selectivity close to 80% at low overpotential (-0.55V vs RHE). Interestingly, they observed high CO selectivity in the presence and absence of a metal center (Fe or Mn).¹³ The activity, however, was dramatically increased by incorporation of a metal to the N-C structure. Indicating that, despite some activity of the N functionalities, the activity of the metal center is dominant. Furthermore, the metal center has been shown to have a crucial role on determining the catalytic performance.^{13,14} In particular, FeNC catalysts present a low onset potential for CO, which has been proposed to be formed via a decoupled proton electron transfer to form (FeNC)- CO_2^- as the key intermediate, followed by an electron transfer to form COOH which then can be reduced to CO and water.²⁴ Combined DFT and experimental studies have found that the high binding energy of the FeNx centers towards CO and CO_2 is responsible for the early CO onset potential on FeNC catalyst.¹⁵ This high binding energy is also responsible for the further reduction of CO to CH₄ which has also been observed as a minor product.

In addition to the nature of the metal center, there are other structural factors that can affect the catalytic activity of MNC materials, such as the coordination environment of the metal center,^{25,26} the presence of different N functionalities and the carbon structure,²⁷⁻²⁹ revealing the complexity of

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these catalysts. Such structural parameters can be affected by the synthesis methods, as it was published in the work by Leonard et al. which showed that the addition of a secondary N precursor affects the ratio of the different N functionalities present in polyaniline based FeNC material.²⁷ For instance, the material prepared with melamine resulted in higher concentration of Fe–N moieties, while the material synthesized using nicarbazin revealed the highest concentration of N-Ox. This difference in composition also resulted in a change in performance toward the CO2RR. Interestingly, when correlating the performance towards the CO2RR with the catalyst composition, it was found that Fe–N moieties are not the only functionalities involved in the catalytic process and that also pyridinic nitrogen is playing a major role on the reduction of CO₂, indicating that there are different possible active sites present in these catalysts.

Herein, we explore the effect of the synthesis heat treatment temperature on the catalysts structure and how it affects its performance towards the CO2RR. In particular, we have prepared 5 polyaniline derived FeNC catalysts changing the temperature of the heat treatment (750-1050°C). The temperature of the heat treatment has been shown to have an effect on performance of MNC catalysts toward the ORR,^{30,31} but its effect towards the CO2RR had not been explore. In this work, we show that the heat treatment temperature affects both the electrochemical surface area and the ratio between the different N functionalities, resulting in a distinct catalytic activity for each of the 5 tested materials. We found that a high micropore area enhances the catalytic activity of this family of materials. The selectivity, however, depends on the nature of the nitrogen incorporated to the material. A larger concentration of FeNx moieties, results in a higher CO2RR selectivity. In particular, we highlight the importance of FeNx moieties which serves as highly selective site for the selectively reducing CO₂. These results contribute to gain a better understanding on the catalytic performance of FeNC catalysts towards the CO2RR.

Results and discussion

A range of FeNC catalysts were synthesized starting from FeCl₃, polyaniline (PANI), Ketjen EC 600JD (AzkoNobel) by varying the synthesis temperature (750, 825, 900, 975 and 1050°C). X-Ray Diffraction (XRD) patterns for the 5 catalysts are shown in Figure S1, showing an amorphous character of the materials. The two broad signals at $2\theta = 24.5^{\circ}$ and $2\theta = 43.5^{\circ}$ can be attributed to the (002) and (100) graphite planes. In addition, residual crystalline inorganic Fe_xS_y species, namely pyrrhotite and pyrite, can be detected on the catalysts prepared at higher temperatures. The presence of such inorganic particles was corroborated by Transmission Electron Microscopy images (Figure S2). Similar to previous works,^{30,32} we observed that on the samples prepare at temperatures $\geq 900^{\circ}$ C

there are nanoparticles embedded in the carbon structure, which makes them difficult to be removed via acid leaching. In addition, the microscopy images in Figure 2 show the amorphous structure of the carbon materials, in which the carbon layers can be distinguish. This, however, is not the case for the FeNC 1050 indicating that the carbon structure is clearly modified when treated at such high temperatures.

The composition of the resulting materials according to elemental analysis and X-ray photoemission spectroscopy (XPS) is given in table 1. Consistent with previous results, the N content diminishes with the heat treatment while the Fe concentration does not show a clear correlation to the heat treatment temperature. The N1s peak revealed the presence of a variety of nitrogen species (Figure 1) including the FeNx confirming that iron has been incorporated to carbon coordinating through nitrogen. Such MNx have been proposed as the predominant active site of MNC catalysts during the CO2RR.^{33,34} The ratio between such N species was found to be dependent on the synthesis temperature, as shown in table 1. As one can expect, a higher temperature results in large graphitization of the MNC materials and thus the ratio of graphitic N increases with temperature, while the concentration of pyridinic N decreases. In addition, the concentration of FeNx increases with the temperature of the heat treatment during the catalysts synthesis indicating that a higher concentration of active sites can be incorporated when treating the materials at elevated temperatures.



Figure 1: High resolution N1s XPS signal of the different Fe-N-C materials showing the contribution

of the different N functionalities a) FeNC 750, b) FeNC 825 c) FeNC 900 d) FeNC 975 and e)FeNC 1050.

Concentration obtained by elemental analysis (%)					
Element	FeNC 750	FeNC 825	FeNC 900	FeNC 975	FeNC 1050
С	66.33	74.41	67.32	78.47	84.88
Ν	11.12	7.19	4.32	3.82	2.75
н	0.57	0.98	0.44	0.44	0.44
S	6.19	1.36	5.50	2.97	2.42
Concentrations obtained by XPS (%) (from figure S3)					
Fe 2P _{3/2}	4.88	5.20	4.40	4.56	4.71
Relative concentration of N functionalities for each catalyst (%) (From figure 1)					
N functionality	FeNC 750	FeNC 825	FeNC 900	FeNC 975	FeNC 1050
Pyridinic	40.76	25.96	24.87	9.92	7.21
Fe-N _x	8.21	13.25	14.04	15.35	15.16
Pyrrolic	37.28	33.45	44.81	43.12	44.97
Graphitic	5.81	13.54	11.51	24.57	25.46
N-O _x	7.95	13.79	4.75	7.00	7.21

Table 1: Elemental composition according to XPS and elemental analysis.

The apparent surface area of the synthesized materials was estimated with BET from the isotherm shown in figure S4. A similar trend to that reported in previous work by Ferrandon et al. ³⁰ and Wu et al³¹ is observed in 2a. The apparent surface area increases with the synthesis temperature

between 750° to 900°C from 536 to 688 m²/g and decreases after 900°C. In our case, however, the FeNC 1050 shows a larger area which could be a result of the change in the carbon structure observed in TEM.

The micropore area, shown in figure 2b, however exhibits a different behavior. As a general trend, higher temperatures during the synthesis resulted in a loss in micropore area being the catalyst treated a 750°C the one with the highest micropore area. For the ORR the micropore area has been shown to be more important than the specific area in determining the activity the MNC catalysts. ^{35,36} In general, large micropore area correlates with a large activity towards the ORR, which can be attributed to higher gas uptake in the microporous structure. If a similar trend is followed during the CO2RR, we would expect a higher activity of the FeNC catalyst.

Finally, we also investigated the relative electrochemical surface area (ECSA) from double layer capacity measurements (Figure 2c and 2d). The larger capacitive current observed on the catalyst prepared at 750°C suggests that this material possess the highest electrocatalytic surface area. Similar to the results from the micropore area there is a decrease in ECSA with increasing the synthesis temperature. Nevertheless, the difference between the catalyst prepare at the 4 higher temperatures is not significant, suggesting that the difference in catalytic performance between these materials can mostly be attributed to differences in the nature of the active sites.



Figure 2: a) Apparent surface area estimated as a function of heat treatment temperature by BET b) Micropore surface area as a function of heat treatment temperature c) Comparison of capacitive current as an estimation of electrochemical surface area of the different catalysts. (CVs recorded at 1 mV/s). d) Double-layer capacitance current on the FeNC catalysts estimate by cyclicvoltammetry as a function of scan rate

Electrocatalytic testing was first carried out by cyclic voltammetry (CV) in presence and absence of CO₂ in a 0.1 M phosphate buffer (Figure 3). The Faradaic currents observed in CO₂-free electrolyte are entirely attributed to the HER, while the Faradaic currents in CO₂-saturated phosphate buffer include the contribution of two processes the HER and the CO2RR. The observed currents on the FeNC catalysts are clearly higher than on the metal free catalyst (Figure S6) confirming the important role that the metal center has on the catalytic process. The incorporation of Fe to the NC material results in a current increase of about 6 times, which indicates that most of the current during the CO2RR can indeed be attributed to the presence of iron. The current from the metal free catalyst, however, is also larger than that of the clean GC plate, showing that despite their lower activity the N functionalities are also involved in the reduction process.

We notice that all 5 catalysts are active towards the competing process as there is a clear reduction current in the absence of CO_2 . However, in all cases there is a larger current when CO_2 is bubbled



through the electrolyte, which indicates that CO_2 is also being reduced when applying negative potentials.

Figure 3: Evaluation of activity for CO2RR vs HER of each FeNC catalyst treated at a) 750, b) 825, c) 900, d) 975 and e) 1050 °C. CVs were acquired at a scan rate of 1 mV/s using a KH_2PO_4/K_2HPO_4 (0.1 *M*) electrolyte with a catalysts loading of 0.75mg/cm²

In figure 3 we observed that the FeNC 750 is the most active catalyst both in the presence and absence of CO₂. This is consistent with the larger electrochemical area indicated by the capacity measurements as well as the larger micropore area. This suggests that higher activity of FeNC 750 can be attributed to a difference in microstructure. The influence of different possible active sites, however, should also be consider, as more nitrogen has been incorporated to the carbon structure of this catalyst. The catalytic activity of the remaining 4 materials is lower than of FeNC 750, however, no significant difference between them is observed, indicating that the activity of these materials indeed correlates with the relative ECSA.

When evaluating CO2RR catalysts, in addition to the activity, a key parameter is the selectivity of the process. A first indication of it is given by the difference in onset potential for the CO2RR and HER. (Figure S7) For our family of catalysts, it seems that this difference is the smallest on FeNC 750 suggesting that despite the high activity this is not a particularly selective catalyst and that most of the current can be attributed to the HER. By contrast, the difference in onset potential for FeNC

1050 is clearly the largest which is an indication that this is the most selective material for the CO2RR.

To corroborate that these materials are in fact reducing CO_2 into carbon-based products, we performed CO_2 electrolysis at a constant potential. The gas phase was analyzed via gas chromatography allowing to quantify the gas products. Consistent with previous studies, CO and H₂ were identified as the major reaction products, together with trace amounts of CH₄.

The obtained faradaic efficiency on the 5 tested materials at -0.95 V vs NHE is shown in figure 4a. Herein, it is clear that the selectivity towards the CO2RR is enhanced by preparing the FeNC catalysts at higher heat treatment temperatures. As suggested by the cyclic voltammetry (Figure 3), FeNC 1050 had the highest faradaic efficiency towards both CO and CH₄ production reaching 62.7% and 2.0% respectively at -0.95V vs NHE. A similar trend is observed in the potential range between - 0.85V and -1.05V vs NHE as shown in figure 4b and 4c confirming that increasing the synthesis temperature of polyaniline derived FeNC catalysts has a beneficial effect on the selectivity towards the CO2RR. Interestingly, the metal free catalyst also exhibited the ability to reduce CO₂ into CO, (Figure S8). The faradaic efficiency, however, was only 13.1% after 15 minutes and 11.6% after 60 minutes of electrolysis and no CH₄ formation was observed. This value is clearly lower compared to the metal containing materials, showing that despite some activity of the N functionalities they are not selective towards the CO2RR.



Figure 4: Selectivity after 15 minutes of CO_2 electrolysis at a constant potential. a) Comparison of product distribution at a constant potential of -0.95V vs NHE b) CO faradaic efficiency as a function of potential and c) CH₄ faradaic efficiency as a function of potential. Electrolyte KH₂PO₄/K₂HPO₄ (0.1 M)

We note that the CO selectivity is lower than that reported on some other FeNC catalysts, which can partially be attributed to a local pH effect. Most of the CO2RR studies are carried out in 0.1M KHCO₃

electrolyte which has a lower buffer capacity resulting in a higher local pH in comparison with KH_2PO_4/K_2HPO_4 buffer. Working in close to neutral pH at the interphase is known to favor the production of CH_4 and H_2 lowering the CO selectivity. ²⁴ Our results, however, are comparable with those obtained in KH_2PO_4/K_2HPO_4 buffer.²⁴ By contrast, the selectivity towards CH_4 is higher than that reported on other MNC catalysts (Table S1). As we discussed previously, the close to neutral local pH favors the production of CH_4 , however, the 2.0% faradaic efficiency is higher than that reported on FeNC in the same electrolyte. This difference with previous results indicates that the material structure is also involved in the observed high CH_4 selectivity.

To understand this difference in electrocatalytic behavior, it is important to look into the catalysts structure. As we have previously discussed, the ECSA has an effect on the catalyst activity. To understand the differences in selectivity, we turn to the different N functionalities. There is a clear difference in the concentration of pyridinic N, which has been proposed as possible active site for CO2RR.^{26,27} In our study however, a lower concentration of pyridinic N correlates with a higher selectivity towards the CO2RR. We note that, different studies on N doped carbon have reported the production of both CO and H₂. Our results show that under the same conditions the metal free NC catalyst yields a high selectivity toward the competing process of the HER. This shows that, despite some activity of the N functionalities towards the CO2RR, they are more active towards HER. The high selectivity of the NC catalyst towards hydrogen production and its low catalytic activity, are strong indicators that the predominant active sites involved are metal sites, most likely iron coordinated to nitrogen to form FeNx.

Table 1 shows that a higher heat treatment temperature also favors the formation of such FeNx sites. MNx functionalities have been proposed as highly selective sites towards the CO2RR. This has been attributed to the nature of the isolated active sites which hinders the HER reaction due to a low binding energy of *H at the on top site. This low binding energy to *H gives an advantage to FeN_x moieties as highly selective sites for the CO2RR³¹ on which the key intermediate (FeNC)-CO₂⁻ is formed without competing with (FeNC)-H formation. Consistently, experimental studies on NiNC catalysts containing exclusively NiN₄ reported faradaic efficiency up to 99% towards CO.³² Therefore, the difference in catalytic activity of our tested materials can be attributed mainly to the concentration of FeNx sites, which are not only the predominant active sites on MNC catalysts, but they are also highly selective in reducing CO₂ to CO. In addition, the higher synthesis temperature increases the graphitization of the FeNC materials which also lowers the concentration of pyridinc

N which, we hypothesizes, are contributing to the competitive process of HER, despite some activity towards the CO2RR.

More interestingly, this study shows that the temperature of the heat treatment has a clear effect on polyaniline derived FeNC materials. In particular, we observed that the concentration of FeN_x functionalities, with respect to other N functionalities, increases with the temperature of the heat treatment during the catalysts synthesis. As a result, the selectivity of the process is clearly enhanced despite some losses in activity which we attribute to a change in microstructure of the carbon support reducing the electrocatalytic surface area.

Finally, we have carried out stability measurements by performing 16 hours electrolysis at a constant potential of -0.95V vs NHE, using three of our catalysts (FeNC 750, FeNC 900 and FeNC 1050). As it can be seen in figure 5a, the three catalysts present a similar behavior, showing a reduction of current density which indicates a loss in activity. Furthermore, figure 5b shows that the CO Faradaic Efficiency also decreases, especially during the first three hours of reaction. We attributed this loss in activity and selectivity to the blocking of the active site by *CO or other reaction intermediates. FeNx functionalities are known to bind strongly to *CO and other intermediates bound through the C atom. By contrast, the also active porphyrinic N should not be blocked and their contribution becomes more important resulting in a higher faradaic efficiency towards H₂. Interestingly, the selectivity towards CH₄ also increased during the first three hours of reaction reaching a constant value of 2.8%, which can mainly by attributed to the lower overall currents. These long electrolysis experiments exhibit another important challenge when it comes to CO2RR catalysts: the stability. In this case the metal center is believed to be key in the observed deactivation. Working with metals that bind weakly to CO should be beneficial for long term electrolysis, despite not producing any products "byond" CO.



Figure 5: Stability test for 16 hours of electrolysis at -0.95 V vs NHE in KH₂PO₄/K₂HPO₄ (0.1 M) for FeNC 750 (black) FeNC 900 (red) and FeNC 1050 (blue) a) Recorded current density b)CO Faradaic efficiency c) CH₄ faradaic efficiency

Conclusions

For this work, we have prepared 5 polyaniline-derived catalysts and shown that by simply changing the synthesis temperature we dramatically affect the catalytic performance of this class of materials. In particular, we observed that the catalyst treated at the lowest temperature (FeNC750) has the largest electrochemical surface area and micropore area, resulting in a higher activity. The selectivity towards the CO2RR, however, is clearly enhanced when the heat treatment temperature is increased. The improvement in the catalytic performance of the FeNC catalyst prepared at higher temperatures is associated with a larger concentration of FeNx which have been proposed to be highly selective sites for the CO2RR. These results highlight the important role played by FeNx sites during the CO₂ electrochemical reduction on MNC catalysts. Furthermore, we show that the concentration of such sites can be tuned by changing the synthesis parameters.

Experimental Section

Material synthesis

For the FeNCs synthesis, we first activated approximately 300 mg of Black Ketjen Carbon EC600 (Akzo Nobel) by heating it under reflux in 35% HNO₃ solution. After 5 hours, the mixture was let to cool down and diluted with \approx 500 mL of water, before filtering. Afterwards the FeNC materials were prepared by dissolving 1 mL of aniline 99.0% in 100 mL of an HCl 0.5 mol/L solution. To this mixture, we added 2.5 g of FeCl₃·6H₂O 99% (our metal source) with constant stirring. Once the solution was homogeneous, we added a (NH₄)₂S₂O₈ solution (2.5 g of (NH₄)₂S₂O₈ in 150 mL HCl 0.5 mol/L) by drop maintaining a 0 °C temperature during the addition to promote a slow aniline polymerization. After 5 h of stirring, 0.2 g of the previously activated Black Ketjen Carbon were added the mixture and left for 48 hours. Then the water was evaporated and the recovered powder was grounded in an agate mortar and heated by 1 h under nitrogen atmosphere at different temperatures for each catalyst (750, 825, 900, 975 and 1050 °C). Subsequently, the solid was dispersed in H₂SO₄ 2 mol/L solution and refluxed for 3 h. The solid was recovered by vacuum filtration, grounded and heated again at the same temperature of the first treatment. We finally gave a second H₂SO₄ reflux and a third heating to each solid. The heat treatments were performed using a MTI oven (model OTF-1200X).

The iron free NC catalyst was prepared following the same procedure without adding $FeCl_3 \cdot 6H_2O$ and with a pyrolysis temperature of 900°C

Material characterization

Powder X-ray diffraction (PXRD) patterns were obtained with Bruker D8 Advance diffractometer equipped with a Cu-K α source (λ =1.54056 Å). TEM images were acquired with a JEOL JEM-2010F microscope applying an accelerating voltage of 200 kV. The textural properties of the samples were obtained by nitrogen physisorption at 77 K using a Micromeritics TriStar surface area and porosity analyzer. Before nitrogen adsorption, the samples were outgassed at 543 K for 12 h. The BET, t-plot and BJH methods were used to calculate specific surface area, pore volume and pore size distributions.

X-ray Photoelectron Spectroscopy measurements were performed using a JEOL JPS-9200, equipped with a dual Mg/Al X-ray source, the Mg source was used with photon energy of 1253.6 eV at 200 W, the analysis area was 3 mm², and all samples were analyzed under high vacuum (1×10^{-8} Torr). Charge correction was made by means of the adventitious carbon (C1s) XPS signal at 284.5 eV. Additionally, elemental analysis were carried out using a Thermo Scientific Flash 2000 elemental analyzer, and a Mettler Toledo XP6 microbalance. Two verification standards were used for the elemental analysis: Methionine (N=9.35 %, C=40.25 %, H=7.43 % and S=21.49 %) and Sulfanilamide (N=16.22 %, C=41.79 %, H=4.66 % and S=18.60 %), both reference material from Thermo Scientific.

Electrochemical measurements

Both capacitive current and activity measurements were controlled by a BioLogic SP-300 potentiostat and were done in a conventional three electrode cell. We used a Ag_(s) |AgCl_(s)|NaCl_(ac)(3 mol/L) electrode (Als Co 012167 RE-1B) as a reference electrode and a platinum mesh as counterelectrode. The working electrode was prepared by depositing different volumes of catalyst suspension on 1 cm² of glassy carbon (25 μ L for activity measurements and 75 μ L for capacitive current experiments). This catalyst suspension was made sonicating a mixture of 15 mg of catalyst with 50 μ L of Nafion 117, 450 μ L of isopropyl alcohol and 500 μ L of ultrapure water by 1 min with a probe sonicator. The electrodes were submerged in a H₂KPO₄/HK₂PO₄ buffer solution (0.1 M, pH=7). Both the capacitive current and the materials activity were measured by cyclic voltammetry. The CVs to evaluate the catalysts' activity were acquired at 1 mV/s at potentials within -0.9 and -0.15 V

vs NHE (under nitrogen atmosphere for HER or with CO_2 bubbling for CO2RR activity). On the other hand, CVs used to measure the capacitive current were done at 1, 3, 5, 7, and 9 mV/s at potentials between -0.53 and -0.15 V vs NHE under nitrogen atmosphere.

Electrolysis experiments

CO₂ electrolysis was carried out in a custom-made two-compartment cell, in which the working electrode was separated from the counter electrode by Nafion membrane. Resistance between reference and working electrode was measured with Potential Electrochemical Impedance Spectroscopy and 50% of it was corrected by the software.

After 15 minutes at constant potential, the gas products were analyzed with a gas chromatograph (Shimadzu GC 2014) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The gaseous compounds H_2 , N_2 , O_2 , CH_4 and CO were separated in a molecular sieve column (Alltech, part no. 57732, 1.65 m × 1/8 in., molecular sieve 13X, 60/80 mesh).

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Keywords

CO₂ electroreduction, electrocatalysis, Polyaniline-derived carbon materials, single-site solid catalysts

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