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Integration of a non-precious pyrolyzed Cu-doped ZIF as an oxygen depolarized cathode in an advanced chlor-alkali electrolyzer

Tahereh Jangjooye Shaldehi^a, Lele Zhao^b, Teresa Andreu^c, Soosan Rowshanzamir^{a,*}, Ignasi Sirés^{b,*}

^a Hydrogen & Fuel Cell Research Laboratory, School of Chemical, Petroleum and Gas Engineering, Iran University of Science and Technology, Narmak, Tehran 16846-13114, Iran

^b Laboratori d'Electroquímica dels Materials i del Medi Ambient, Departament de Ciència de Materials i Química Física, Secció de Química Física, Facultat de Química, Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain

^c Sustainable Electrochemical Processes, Department of Materials Science and Physical Chemistry & Institute of Nanoscience and Nanotechnology (IN2UB), Facultat de Química, Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain

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ABSTRACT

Oxygen reduction is the critical step in advanced chlor-alkali electrolysis, which has motivated extensive research in catalyst development for improved efficiency and durability. This study investigates the oxygen reduction reaction (ORR) on Cu-based electrocatalysts supported on N-doped carbon (Cu/NC), derived from a Cu-modified zeolitic imidazolate framework (ZIF), and their ultimate performance in a chlor-alkali electrolyzer. Through comprehensive electrochemical characterization in 0.1 M NaOH solution, values of $E_{onset} = 0.87$ V and $E_{1/2} = 0.75$ V (vs. RHE) were obtained, which are competitive with commercial Pt/C despite the superior *j* achieved by the latter in LSV tests. The electron transfer number (*n*) of the optimum Cu/NC was 4, very close to benchmark catalyst Pt/C 20 wt. % (*n* = 3.94). Cu/NC had a low Tafel slope (128 mV dec⁻¹), thus speeding up the ORR on this nanocatalyst. Additionally, chronoamperometry and accelerated durability tests demonstrated the long-term stability of Cu/NC for 10 h. The catalyst was assembled as an oxygen depolarized cathode (ODC) in a purpose-designed advanced chlor-alkali electrolyzer, resulting in a cell voltage of 2.1 V at 1 kA m⁻² and 80 °C, which underscores the potential of Cu-based nanocatalysts to enhance the efficiency and sustainability of chlor-alkali electrolyzer.

1. Introduction

Chlor-alkali electrolysis has been used as a leading industrial process in the United States, Western Europe, and Japan since the 19th century, becoming the primary source of commodity chemicals such as chlorine and sodium/potassium hydroxide throughout the 20th century [1–3]. Membrane-based chlor-alkali technology is one of the most energy-intensive industrial processes. To further reduce energy consumption, oxygen depolarized cathodes (ODCs) have become a suitable alternative to operate the membrane chlor-alkali electrolyzers, since the resulting system configuration allows replacing the conventional hydrogen evolution reaction (HER) [4,5]. The occurrence of reaction (1) and (2) in this type electrolyzers gives rise to the overall reaction (3): $2Cl^{-} \rightarrow Cl_{2(aq)} + 2e^{-} \tag{1}$

$$2H_2O + O_{2(g)} + 4e^- \rightarrow 4OH^-$$
 (2)

$$2H_2O + O_{2(g)} + 4NaCl \rightarrow 2Cl_{2(aq)} + 4NaOH$$
(3)

ODCs are analogous to gas-diffusion electrodes (GDEs), which provide a conductive porous structure for the effective oxygen permeation to eventually carry out the oxygen reduction reaction (ORR) [6,7]. The critical aspect about these electrodes is that the three-phase (*i.e.*, gaseous O_2 /electrolyte/solid electrocatalyst) boundary must be effectively formed [8,9]. The ORR mechanism may involve favorable (4-electron) and unfavorable (2-electron) pathways, which directly affects the stability of the ODCs, since the formation of H_2O_2 via the latter pathway in highly concentrated NaOH electrolyte leads to the precipitation of

* Corresponding authors. E-mail addresses: Rowshanzamir@iust.ac.ir (S. Rowshanzamir), i.sires@ub.edu (I. Sirés).

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 Na_2O_2 [10,11]. Therefore, it is very important to develop highly selective electrocatalysts that prevent the formation of H_2O_2 .

The ORR, a well-known reaction in energy storage and conversion systems such as fuel cells, batteries and electrolyzers, has a sluggish kinetics in both acidic and alkaline media [12]. Researchers have explored numerous materials able to catalyze the ORR at high pH, being platinum the best one [13]. However, this catalyst suffers from dissolution in the concentrated NaOH solution typically employed as the catholyte of a chlor-alkali cell. Silver metal is a good candidate, since it has shown an ORR activity comparable to that of platinum without any traces of dissolution, and it is economically more affordable [14]. Hosseini and Zardari [15] compared the performance of Pt/C-, Ru/C-, and PtRu/C-based ODCs for chlor-alkali electrolysis; in O2-saturated NaOH solution, the bimetallic electrocatalyst showed the highest current density ($j = 2.05 \times 10^{-3}$ A cm⁻²) and the most positive onset potential $(E_{\text{onset}} = 0.75 \text{ V} \text{ vs. Ag}|\text{AgCl})$. To mitigate the excessive cost of RuO₂ and IrO₂, research efforts have been concentrated on the incorporation of different mixed-metal oxides (MMOs) [16,17]. Hosseini et al. [18] investigated the ORR activities of binary and ternary MMO electrodes based on RuO2 nanoparticles supported on Ni mesh for chlor-alkali electrolysis; the voltammetric results in O2-saturated electrolyte revealed a more positive E_{onset} for water reduction using a RuO₂-TiO₂-IrO₂/Ni electrode.

Although the ORR in chlor-alkali electrolysis has been extensively studied using precious metals, from a practical point of view it is mandatory to reduce costs while maintaining a high performance and, consequently, researchers have turned to non-precious metal electrocatalysts in the last decade [19–23]. Specifically, Figueiredo et al. [24] compared the performance of three cathodes (pyrolytic graphite, Cu-free ODC, and 10 % Cu-doped ODC) in chlor-alkali electrolysis at a constant *j* of 2470 A m⁻², at temperatures of 25 and 70 °C; a higher temperature led to a decrease of the overpotential, and the use of Cu-doped ODC was beneficial for reducing the cell voltage. Fujimoto et al. [25] developed electrolytic manganese dioxide (EMD) as the catalyst of ODC for industrial chlor-alkali electrolysis; that catalyst showed an overpotential of ~0.1 V lower than that of Ag catalyst (at *j* of -1.0 A cm⁻²).

Single-atom catalysts (SACs) have become a hot research area in the last decade. These materials are composed of atomically-dispersed metal atoms fixed on a support through strong interactions [26-28]. In order to boost the catalytic performance of SACs, carbon-supported M-N_x moieties can be used (i.e., M-N-C, where M accounts for Fe, Ni, Cu, Co, etc.) [29]. Cui et al. [30] used Cu phthalocyanine as a precursor to synthesize Cu SACs by pyrolysis; they showed that this is a promising non-noble ORR catalyst with a half-wave potential $(E_{1/2})$ of 0.81 V vs. RHE in alkaline medium, being suitable for fuel cell applications. Zeolitic imidazolate frameworks (ZIFs), as one of the well-known metal-organic frameworks, have high chemical and thermal stability [31]. Among ZIFs, ZIF-8 (Zn(MIM)₂, where MIM is 2-methylimidazole) with BET surface areas within a range of 1250–1600 $m^2 \ g^{-1}$ is currently the most widely investigated material for heterogeneous catalysis. ZIF-8 can provide effective anchoring sites for single metal atoms [32,33]. Qu et al. [34] followed a novel strategy to access the large-scale synthesis of Cu SACs, using ZIF-8 via trapping Cu(NH₃)_x species on porous N-carbon under ammonia atmosphere. The catalyst exhibited an Eonset of 0.83 V and 0.99 V vs. RHE for ORR in 0.1 M HClO4 and 0.1 M KOH, respectively. Jin et al. [35] synthesized a similar Cu SAC from ZIF-8 and supported it on carbon fiber paper as the cathode of a Zn-air battery; the catalyst had an E_{onset} and $E_{1/2}$ of 0.93 V and 0.82 V vs. RHE, respectively, and exhibited a 4e⁻ ORR [36]. Lately, some studies have highlighted that bimetallic Cu-based NC catalysts, especially when combined with other metals like Co, enhance the electrocatalytic activity because they benefit from the optimized adsorption and desorption of ORR intermediates upon synergistic interactions between the Cu-Nx sites and additional metal sites, which optimize the adsorption and desorption of ORR intermediates. This synergy can improve the stability and performance in

alkaline conditions [37].

In a recent investigation, we explored the efficacy of non-precious SACs in facilitating the ORR under alkaline conditions using density functional theory (DFT) calculations [38,39]. Our findings revealed that Cu exhibits the highest catalytic activity among different metals atomically dispersed on N-doped carbon support, characterized by a minimal overpotential requirement [38]. Aiming to verify such theoretical study, in the present study, Cu/NC catalysts have been synthesized following a pyrolysis route under N_2 atmosphere. ZIF-8 and cetyl-trimethylammonium bromide (CTAB)-capped Cu-based nanoparticles (NPs) were first synthesized as precursors by solvothermal method. Conventional surface and electrochemical characterization were performed to evaluate the catalytic performance in alkaline medium, whereupon an ODC was built and tested in an advanced chlor-alkali electrolyzer.

2. Experimental

2.1. Chemicals

Zinc nitrate hexahydrate (Zn(NO₃)₂•6H₂O, >99 %), 2-methylimidazole (MIM, 99 %), ethanol and methanol were purchased from Sigma-Aldrich. 2-Propanol dry (max. 0.01 % water, ACS reagent) was acquired from PanReac AppliChem. Copper(II) nitrate trihydrate (Cu (NO₃)₂•3H₂O, pure) and CTAB were provided by Merck. Nafion dispersion (5 wt.%) was purchased from Sigma-Aldrich. Commercial Pt/ C catalyst (20 wt.%) was obtained from Premetek. All aqueous solutions were prepared with high-purity Milli-Q water (Merck Life Science Synergy UV device, resistivity > 18.2 M Ω cm at 25 °C). All reagents were of analytical grade and utilized as received without further purification.

2.2. Synthesis of Cu/ZIF-8 and Cu/NC

In the present study, ZIF-8 was prepared through a simple modification of a published method [40]. As shown in Fig. 1, this so-called step 1 involved the use of two solutions (A and B): Solution A contained 5.4 g of zinc salt dissolved in methanol (300 cm³), and solution B contained 6.6 g MIM dissolved in methanol (300 cm³). Then, the two solutions were mixed by dropwise addition of the latter into the former for 2 h at 400 rpm and room temperature. The precipitate obtained upon centrifugation was washed several times with methanol and then dried overnight at 80 °C in a vacuum oven.

For the synthesis of CTAB-capped Cu-based NPs (step 2 in Fig. 1), first, two solutions named A and B were prepared: Solution A contained 9 g of copper salt dissolved in methanol (150 cm³), and solution B contained 636 mg CTAB dissolved in methanol (150 cm³). Then, a mixture of both solutions was stirred at 75 °C and 400 rpm for 3 h. The NPs, containing Cu in oxidized state, were collected upon centrifugation, washed several times with methanol and then dried for at 80 °C 12 h in a vacuum oven.

As shown in the step 3 of Fig. 1, ZIF-8-encapsulated copper (*i.e.*, Cu/ZIF-8) was obtained through a solvothermal method, and then the Cu/NC catalyst was prepared by pyrolyzing the Cu/ZIF-8 template. Briefly, 1.26 g ZIF-8 was ultrasonically dispersed into 240 ml ethanol for 30 min, and the resulting mixture was stirred at 400 rpm. A solution of 60 cm³ ethanol containing 1.26 g Cu-based NPs was added to the ZIF-8 solution, keeping the mixture in an ultrasonic bath for 30 min. Then, the final mixture was stirred (400 rpm) in a water bath at 80 °C for 1 h to complete the reaction. Finally, the samples were centrifuged, washed three times with ethanol, and dried at 80 °C for 24 h in the vacuum oven. To obtain the Cu/NC catalyst, 1 g of Cu/ZIF-8 was pyrolyzed in a tube furnace under nitrogen atmosphere at 800 °C for 2 h (at 5 °C min⁻¹). Evolving gases like CO served as reducing agents, thus facilitating the conversion of oxidized Cu to Cu(0).

STEP 1



Fig. 1. Synthesis of Cu/NC catalyst in three steps.

2.3. Surface characterization

The synthesized materials were characterized by means of several techniques. For the X-ray diffraction (XRD) analysis, the powders were sandwiched between polyester (Mylar®) films of 3.6 µm thickness. A PANalytical X'Pert PRO "TT2" powder diffractometer of 240 mm of radius was employed, in a configuration of convergent beam with a focalizing mirror and a transmission geometry with flat powder samples sandwiched between low absorption polyester (Mylar®) films of 3.6 µm thickness. The parameters were: Cu K α radiation ($\lambda = 1.5418$ Å), 45 kV and 40 mA, step size of 0.0263° and measuring time of 300 s per step. Fourier transform infrared spectroscopy (FT-IR) analysis was done on a Thermo Scientific Nicolet 6700 device with Smart Orbit Diamond, scanning from 4000 to 500 cm⁻¹ wavenumber and employing OMNIC software. Field-emission scanning electron microscopy (FESEM) was carried out using a JEOL JSM7001F microscope, which operated at 15 kV and was equipped with an Oxford Inca 300 analyzer for energydispersive spectroscopy (EDS). Transmission electron microscopy (TEM) analysis was carried out using a JEOL JEM 2100 microscope at 200 kV. For this analysis, the powders were sonicated in 3 ml of ethanol for 10 min; a drop of suspension was placed onto a holey carbon film supported nickel grid and then, the solvent was evaporated until total drying using a 40 W lamp for 5 min. Thermogravimetric analysis (TGA) was performed on a Mettler-Toledo TGA-851e thermobalance. The powdery samples were placed in alumina crucibles of 70 µL volume. Dry N₂ was supplied at a flow rate of 50 mL min⁻¹, and the samples were heated from 30 to 900 °C, at 10 °C min⁻¹. A blank curve was first obtained for signal correction. X-ray photoelectron spectroscopy (XPS) analysis was carried out in a SPECS system equipped with a highintensity twin anode X-ray source XR50 and using a Phoibos 150 MCD-9 XP detector (2400 V). The analyzer lens had a large area, and the scan mode was Fixed Analyzer Transmission. The excitation energy was 1486.61 eV. The C1s peak with a binding energy of 284.8 eV was used as the internal reference. The spectra were analyzed using Avantage Software.

2.4. Electrochemical characterization

The performance of different materials was investigated using an Autolab PGSTAT 204 potentiostat (Metrohm). A three-electrode cell was equipped with a glassy carbon (GC, diameter of 5.0 mm, Metrohm) tip, inserted into a PTFE casing to serve as a rotating disk electrode (RDE) as the working electrode; a Pt wire and Ag|AgCl (3 M KCl) were employed as the counter and reference electrode, respectively. The GC disk was polished using a PSA-backed white felt cloth from Buehler, containing Micropolish II deagglomerated alumina of 0.3 and 0.05 μ m. The activity of each selected material was investigated by coating the GC surface with a thin layer (loading of 0.2 mg cm⁻²) via drop casting. For this, an ink containing a mixture of 5.0 mg of the catalyst to be tested in 1060 µL of solvent (2-propanol, water, and Nafion dispersion) was prepared. To obtain a good dispersion, the ink was sonicated in an ultrasonic bath for at least 30 min. Before testing, the working electrode was dried in a vacuum oven. All the materials were initially activated in N2-saturated electrolyte, with extensive cyclic voltammetry (CV) cycling recorded at 100 mV s⁻¹ until a stable current was observed. This generally required from 30 to 100 cycles, depending on the material. The CV profiles were recorded in N₂- and O₂-saturated 0.1 M NaOH solutions at room temperature and scan rates of 5–50 mV s⁻¹.

The ORR activity was evaluated in O₂-saturated 0.1 M NaOH solution using linear sweep voltammetry (LSV) at a scan rate of 10 mV s⁻¹. The electron transfer number (*n*) for each material was calculated from the LSV curves through the Koutecky–Levich Eq. (4). In that equation, *j* accounts for the observed current density, whereas *j*_L and *j*_K denote the diffusion-limited and kinetically-limited current density, respectively, with ω representing the RDE rotation rate in rpm; the parameter B is associated with *j*_L and is expressed by the relationship shown in Eq. (5), where *F* corresponds to the Faraday constant (96,485 C mol⁻¹), *C*_{O2} stands for the bulk concentration of O₂ (1.2 × 10⁻⁶ mol cm⁻³), *D*_{O2} represents the diffusion coefficient of O₂ in 0.1 M NaOH solution (1.9 × 10⁻⁵ cm² s⁻¹), and ν denotes the kinematic viscosity of the electrolyte (0.01 cm² s⁻¹) [41].

$$1/j = 1/j_{\rm L} + 1/j_{\rm K} = 1/(B\omega^{1/2}) + 1/j_{\rm K}$$
⁽⁴⁾

$$B = 0.62nFC_0 D_0^{2/3} \nu^{-1/6}$$
(5)

The electrochemically-active surface area (ECSA) of the tested electrocatalysts was assessed by analyzing the non-Faradaic capacitive current linked to the double-layer charging, as observed from the scan rate dependence of the CV curves. For this purpose, a potential range devoid of observable Faradaic reactions was established through stationary CV. This range typically spans *ca.* ± 0.1 V around the opencircuit potential (OCP). Subsequently, the charging current (I_c) was determined from the CVs conducted at various scan rates (ν), and the relationship with the double-layer capacitance (C_{DL}) is as follows:

$$I_{\rm c} = \nu C_{\rm DL} \tag{6}$$

Consequently, plotting I_c against ν results in a linear relationship, with the slope representing the $C_{\rm DL}$ [42,43]. The ECSA of a given catalyst sample is thus calculated according to Eq. (7):

$$ECSA = \frac{C_{\rm DL}}{C_{\rm s}} \tag{7}$$

where C_s is the specific capacitance of the sample, which can be taken as 0.04 mF cm⁻² in 1 M NaOH solution [42,44,45].

Finally, the preliminary stability of the catalysts was evaluated from chronoamperometry tests performed for 10 h in O_2 -saturated 0.1 M NaOH solution. The constant potential was set to 0.4 V vs. RHE, and the working electrode was kept rotating at 1600 rpm during the whole analysis. Please, note that this study was only intended to look for relative stability data (*i.e.*, compared performance of Cu/NC and Pt/C electrocatalysts under strictly analogous conditions), not focusing on

realistic endurance conditions of such materials in the form of practical electrodes. Rather mild conditions were selected because a harsher protocol could be detrimental for the mechanical stability of the ink itself, thus leading to wrong conclusions.

2.5. Fabrication of the oxygen depolarized cathode (ODC) and assembly of the advanced chlor-alkali (ACA) electrolyzer

To evaluate the genuine efficiency of the optimum electrocatalyst within an ACA cell (see Fig. 2), a gas-liquid impermeable ODC was constructed. This ODC comprised three layers: a reaction layer responsible for the catalytic activity, a gas-diffusion layer (GDL) facilitating the gas transport, and a current collector (CC). The GDL utilized was commercial carbon cloth with standard wet proofing to optimize oxygen diffusion while providing a barrier against flooding. A nickel plate was used as CC on the cathode side. The catalyst ink was a mixture that consisted of 33.3 mg catalyst suspended in 10.67 cm³ of solvent (2propanol, Milli-Q water, and Nafion dispersion), and was sonicated for at least half an hour. The ink was divided into 4 equal portions and uniformly applied to one side of four 4 cm \times 4 cm cloth coupons that were previously ultrasonically cleaned with ethanol. After the depletion of the ink, the carbon cloths were completely dried at 80 °C, and then the catalyst-loaded carbon cloths were protected with aluminum foil and kept inside a hot press (6 ton, 210 °C) for 2 h. Natural cooling at room temperature yielded the catalyst-loaded ODC (1 mg cm⁻²). The anode utilized in the ACA electrolyzer setup was a Ti|TiO₂-RuO₂ electrode, whereas a commercial Flemion membrane (pore size < 1 nm, thickness of 200 µm, Asahi Glass, Japan) [46,47] served as the cation exchange membrane within the membrane electrode assembly (MEA), as depicted in Fig. 2. Prior to use, the membrane underwent treatment with an aqueous NaOH solution (30 wt.%) at room temperature for 48 h. In the electrolysis cell, the MEA was formed with the anode and cathode bond to each side. Each electrode and the membrane had an active area of 3 cm \times 3 cm. The analyte consisted of a 300 g m^{-3} NaCl solution and the catholyte comprised humidified oxygen fed behind the ODC. The experiments were conducted at 80 °C, with the current density during brine electrolysis ranging from 1 to 4 kA m⁻². To quantify the amount of NaOH produced, titration was performed using 0.1 M HCl with phenolphthalein solution as the indicator [48]. The caustic current efficiency (CCE) was calculated using the following Eq. (8) [49]:



Fig. 2. Advanced chlor-alkali electrolyzer set-up.

$$CCE = \frac{n_{\text{NaOH}}}{\frac{It}{nF}} \times 100$$
(8)

where n_{NaOH} represents the amount of NaOH generated at the cathode side (mole), while *I* denotes the applied current in the electrolytic cell (A). The variable *t* accounts for the duration of the electrolysis (in seconds), and *n* stands for the number of electrons transferred in the electrolysis.

3. Results and discussion

3.1. Surface characterization

FESEM images were utilized to assess the morphological characteristics of a set of samples that included pre-pyrolysis (i.e., ZIF-8 and Cu/ ZIF-8) and post-pyrolysis (i.e., NC and Cu/NC) specimens (Fig. 3a-d). These images distinctly exhibit clearly defined dodecahedral structures with truncated rhomboids, consistent with the characteristic morphology of parent ZIF-8, as previously documented in the literature. This observation suggests that the surface morphology and overall structure of ZIF-8 remained unchanged upon integration of Cu, aligning perfectly with previous findings [40]. The preservation of the original ZIF-8 morphology despite Cu addition is notable, indicating minimal alteration of the fundamental framework (Fig. 3b vs. Fig. 3a). This aspect becomes significant regarding the maintenance of the integrity and stability of the material, crucial factors determining its performance across diverse applications, including catalysis. In Fig. 3d, some structural damage can be observed, as a result of the phase transformations at high temperature (i.e., pyrolysis of organic framework, reduction of Cu ions to Cu(0)), which are accompanied by uncontrolled gas evolution and thermomechanical stress.

The EDX analysis in Fig. S1 shows the uniform distribution of C, N, O, and Zn within the ZIF-8 sample, demonstrating the well-organized structure of the material. The homogeneous dispersion of Zn

throughout the framework informs about its strong structural stability and effective incorporation of metal nodes. Nitrogen is also uniformly distributed, and serves to introduce N-functionalities that are expected to enhance the properties of the final material, such as catalytic or electrocatalytic activity. The presence of oxygen atoms further contributes to the overall stability of the framework, supporting its potential for future applications. Overall, the uniform distribution of elements highlights the well-defined architecture of the material, which is essential for ensuring high performance under various operation conditions.

Although our synthesis protocol could likely produce copper single atoms [40], TEM image in Fig. 4a illustrates a well-dispersed distribution of metallic copper NPs within the carbon matrix of the Cu/NC sample [50]. Such uniform distribution of the NPs throughout the material confirms the successful Cu incorporation during the synthesis process. Fig. 4b shows the HRTEM analysis, revealing that the copper NPs are embedded within the carbon matrix and protected by a carbon layer (more evident in Fig. S2), in good agreement with the core-shell architecture reported for this type of preparation [51]. This encapsulation prevents the direct exposure of copper to the surrounding environment, improving the stability and durability of the catalyst. Fig. 4c provides a magnified view of the HRTEM image, where the lattice spacing of 0.21 nm corresponding to the (111) crystal plane of Cu(0) can be distinguished. As an excellent electron donor, Cu(0) is expected to enhance the ORR activity by facilitating a more efficient electron transfer.

Other surface and structural results are shown in Fig. 5. To reveal the structural features, Fig. 5a shows the XRD patterns of ZIF-8, Cu-based NPs, Cu/ZIF-8, NC and Cu/NC. The diffractogram of Cu/ZIF-8 aligns closely with that of pristine ZIF-8, corroborating that the crystalline structure of ZIF-8 (body-centered cubic crystal lattice) remained intact upon copper incorporation. This can be explained by the close ionic size similarity between Cu²⁺ (0.71 Å) and Zn²⁺ (0.74 Å) ions. The characteristic peaks of ZIF-8 are thus retained, confirming the stability of the



Fig. 3. FE-SEM images obtained at different magnifications for: (a) ZIF-8, (b) Cu/ZIF-8, (c) N-C, and (d) Cu/NC.



Fig. 4. (a) TEM image of Cu/NC sample. (b) HRTEM image of the same area, and (c) partial enlargement of image b (inset: FFT of Cu/NC nanoparticle).



Fig. 5. (a) XRD analysis of different samples. (b) XPS survey spectrum of Cu/NC. (c) FT-IR analysis of different samples. (d) TGA curves of non-pyrolyzed samples.

framework. On the other hand, the peaks appearing in the XRD pattern of the Cu-based NPs can be attributed to Cu₂(OH)₃(NO₃) (*i.e.*, gerhardtite), a bluish green to emerald green precipitate plausibly formed due to the hydrolysis of copper nitrate during the synthesis. In the inset, the Cu/NC sample shows peaks at 43.4° and 50.4°, corresponding to the (111) and (200) planes of Cu(0), confirming the presence of zero-valent copper in the post-pyrolysis sample, which is consistent with the results obtained in Fig. 4b. Both NC and Cu/NC also show a weak peak around 16° , which may be due to disordered or amorphous carbon. Moreover, the weak and broad peak around 23° in NC is also typically associated with amorphous carbon, arising from the lack of long-range crystalline order. and nitrogen on the Cu/NC catalyst surface, the samples were examined by XPS. The survey spectrum of Fig. 5b evidences the presence of Cu, Zn, C, N and O elements, whereas the finer study of the core levels is presented in Fig. 6.

The high-resolution Cu 2*p* spectrum of the prepared catalyst is shown in Fig. 6a. The peaks at binding energies of 932.6 and 952.6 eV can be attributed to Cu 2*p*_{3/2} and Cu 2*p*_{1/2}, respectively, which can be recognized as Cu(0). The peaks at 934.2 and 955.7 eV are fitted to the same orbitals but assigned to surface Cu(II) species. Since no satellite peaks of Cu(II) were found in the spectrum and considering that it is difficult to distinguish between Cu(0) and Cu(I) simply from the XPS features of Cu 2*p*_{3/2} because of the small difference in their binding energies, Cu LMM analysis was performed to further confirm the presence of Cu(0)

To investigate the surface composition and chemical state of copper



Fig. 6. High-resolution XPS analysis of Cu/NC sample. (a) Cu 2p core-level spectrum. (b) Cu LMM spectrum. (c) N 1s core-level spectrum. (d) Content of different nitrogen types.

chemical state. From the Cu LMM spectrum of Fig. 6b, it was possible to identify a peak at 918.6 eV, which can be attributed to Cu(0) [52]. Therefore, it can be concluded that the surface of the Cu/NC sample is predominantly composed of Cu(0). Fig. 6c shows the core-level spectrum of N 1*s*, whose deconvolution yielded three peaks corresponding to pyridinic, pyrrolic, and graphitic N at 398.4, 400.5, and 403.9 eV, respectively [53]. Accordingly, the content of the three N-functionalities are 59.3 %, 33.7 %, and 7.1 % (Fig. 6d). The C 1*s* spectrum shown in Fig. S3 has been deconvoluted into three distinct peaks, which can be related to graphitic carbon, heteroatom bonding, and plasmonic features, respectively [54]. The high-resolution Zn 2*p* spectrum observed in Fig. S3 exhibits two main peaks at 1021.4 eV (2*p*_{3/2}) and 1044.6 eV (2*p*_{1/2}), attributed to the oxidation state of Zn [55].

The chemical bonds present in the pre- and post-pyrolysis samples was then characterized by FT-IR spectroscopy, as illustrated in Fig. 5c. Comparative analysis revealed a close correspondence between the FT-IR bands of the synthesized ZIF-8 and those reported for that material in previous studies [56,57], thus confirming the successful synthesis of this Cu/NC precursor. Specifically, the entire imidazole ring stretching and bending exhibited a multiple signals ranging from 600 to 1500 cm⁻¹. The C–H vibration was observed within the frequency range of 1100 to 1300 cm⁻¹, whereas the peaks at 1400 and 1450 cm⁻¹ were attributed to the C–N stretching vibration. Furthermore, peaks at 1220 and 1230 cm⁻¹ confirmed the presence of C–N vibration within the imidazole ring. On the other hand, the Cu-N bond vibration in the Cu/ZIF-8 sample was identified within the range of 600–700 cm⁻¹.

Finally, TGA of ZIF-8, Cu NPs, and Cu/ZIF-8 was carried out to

rationally elucidate the events occurring during the preparation of the Cu/NC catalyst via pyrolysis. The TGA curves shown in Fig. 5d reveal minimal weight loss of only 0.7 % between 20 and 200 °C, attributed to the removal of guest molecules (such as methanol or CO₂) from the cavities of all porous samples. Subsequently, the formation of guest-free Cu/Zn(MIM)₂ crystals at 300 °C is indicated by a prolonged plateau, signifying the robust thermal stability of the three-dimensional network, consistent with literature findings [40]. The curves for ZIF-8 and Cu/ZIF-8 exhibit a distinct step attributed to MIM linker decomposition above 300 °C, marking the onset of exothermic decomposition. A gradual weight loss of 23.7 % is observed as the temperature increased from 350 °C to 700 °C, followed by a sharp weight loss of 48.0 % as the temperature escalated from 700 °C to 1000 °C, aligning well with literature reports [40,58]. Notably, the thermal stability of the Cu/ZIF-8 crystal obtained in this study surpasses that of Cu-based MOFs (such as Cu(BDC)) used for catalytic purposes, which undergo decomposition at 200 °C.

3.2. Electrochemical characterization and performance of the chlor-alkali electrolyzer

The cyclic voltammograms depicted in Fig. 7 and S4 illustrate the behavior of Cu/NC and NC samples in 0.1 M NaOH solution under oxygen or nitrogen saturation. In the case of the NC electrocatalyst, the data reveal an indistinguishable electrochemical behavior in both media, suggesting a poor ability for ORR, making it impossible to achieve a clear reduction signal distinct from the high capacitive current of



Fig. 7. Cyclic voltammograms of Cu/NC sample at a scan rate of 10 mV s⁻¹ in N_{2} - and O_2 -saturated 0.1 M NaOH solution.

this carbonaceous sample. In contrast, in the case of the Cu/NC electrocatalyst, a distinct reduction peak starting at around 0.9 V vs. RHE is observed in the O₂-saturated solution (Fig. 7), thus confirming the positive contribution of the Cu species to the catalytic performance (*i.e.*, ORR activity). Furthermore, redox peaks related to the copper species can be identified in both media for this sample [59]. As described in Section 2.4, the average $C_{\rm DL}$ value (= 0.46 mF) can be determined from the plot depicted in Fig. S5, resulting in an ECSA value of 28.7 m² g⁻¹ for the Cu/NC electrocatalyst.

Linear sweep voltammograms were recorded for different samples in O₂-saturated 0.1 M NaOH solution at a scan rate of 10 mV s⁻¹ and a rotation rate of 1600 rpm. As anticipated, the pyrolyzed ZIF-8 (*i.e.*, NC sample) exhibited notably low activity toward the ORR (Fig. 8a). This reaffirms that the impressive activity of the Cu/NC electrocatalyst primarily originates from the positive effect of the core-shell Cu(0) NPs, without discarding the possible contribution of N–coordinated single-atom sites. In Fig. 8a, it is evident that the ORR activity of Cu/NC is comparable to that of commercial Pt/C (20 wt.%), although the latter is still proven superior within almost the whole potential range. This is well exemplified by the characteristic potential values for the ORR: The E_{onset} values of NC, Cu/NC, and Pt/C were determined to be 0.82, 0.87, and 0.94 V, respectively, while the $E_{1/2}$ values were 0.70 V, 0.75 V, and

0.82 V (vs. RHE), respectively. Fig. S6a-c presents the LSV curves of NC, Cu/NC and Pt/C at various rotation rates, which served to calculate the electron transfer number using the Koutecky–Levich relationship (see correlated parameters depicted in Fig. S6d). Fig. 8b illustrates that the *n* value for the ORR using Cu/NC is 4, slightly higher than that found for commercial Pt/C (n = 3.94). Overall, these findings underscore the promising ORR activity of Cu/NC under alkaline conditions.

Although both Pt/C and Cu/NC are equally selective, the observed difference in the limiting current density between them (Fig. 8a) can be attributed to several factors related to the inherent properties and the catalytic environment of each material. Thus, Pt sites are known to provide an efficient binding and desorption of ORR intermediates, which may add to the greater density of total active sites (*i.e.*, higher ECSA due to the enhanced dispersion and smaller size), leading to a higher overall reaction rate.

The excellent activity of Cu/NC was further corroborated by the high kinetic current density and a reduced Tafel slope of 128 mV dec^{-1} , close to that of Pt/C, as depicted in Fig. S7. From the Tafel analysis, it can be concluded that the first electron transfer is the rate-determining step (RDS) of the ORR on the Cu/NC nanocatalyst, confirming our recent computational results [38].

Additionally, the chronoamperometry tests (Fig. 9a) indicated that the stability of the Cu/NC electrocatalyst over a period of 36,000s is comparable to that of the commercial Pt/C. Such good performance is in good agreement with that achieved by Parkash under analogous conditions [40]. Furthermore, accelerated durability testing was conducted to further assess the ORR performance. As illustrated in Fig. 9b, after the 10-h long-term test at constant potential shown in plot (a), the current density of the Cu-based catalyst remained at a value as high as 83.6 %, whereas the current density underwent a lower decrease (*i.e.*, 96.4 % of the initial value) for Pt/C 20 wt.%. Despite the evident superiority of Pt/C, it is worth noting that the Cu/NC behaved quite well considering that an optimization procedure has not been undertaken for long-term performance, unlike the extensive investigation on Pt/C over the years by a large number of researchers.

Following the characterization of the different catalysts through physicochemical and electrochemical analyses, the validation of the Cu/NC electrocatalyst as a suitable material in practice was carried out by preparing an ODC to be tested in the MEA of an ACA electrolyzer. The impact of current density on cell voltage and caustic current efficiency (CCE) was investigated, as depicted in Fig. 10. Our findings reveal a significant correlation between current density and both performance parameters. As the *j* value was increased from 1 to 4 kA m⁻², the cell



Fig. 8. (a) LSV curves obtained in O_2 -saturated 0.1 M NaOH solution at a scan rate of 10 mV s⁻¹ and 1600 rpm for all synthesized materials, compared to commercial Pt/C 20 wt.%. (b) Electron transfer number determined from Koutecky-Levich analysis.



Fig. 9. (a) Chronoamperometry curves obtained for Cu/NC and Pt/C 20 wt.% electrocatalysts in an O₂-saturated 0.1 M NaOH, recorded at E = 0.4 V vs. RHE for 10 h. (b) LSV curves recorded at a scan rate of 10 mV s⁻¹ and 1600 rpm in the same medium for each material, before (continuous lines) and after (dashed lines).



Fig. 10. Caustic current efficiency (CCE) and cell voltage at different current density, using the ACA electrolyzer with a MEA containing an ODC with Cu/NC. Conditions: brine concentration of 300 g m^{-3} and cell temperature of 80 °C.

voltage exhibited an increment from 2.1 to 3 V, respectively. Concurrently, the CCE experienced a decline from 93.8 % to 84.3 % within the same current density range. This decrease is attributed to differences in the kinetics of the desired 4-electron reduction and the undesired partial 2-electron ORR. Increasing the current density leads to a shift of cathode potential towards more negative values, influencing the relative rates of these two reactions. Moreover, higher current densities are expected to be responsible for reducing the CCE due to a plethora of factors such as increased membrane swelling and permeability, enhanced contribution of oxygen evolution, and membrane fouling by chlorine gas at the anode side [60]. For comparison, the commercial Pt/C electrocatalyst was employed in a new ODC, exhibiting a similar trend where an increase in current density from 1 to 4 kA m⁻² resulted in an elevation of cell voltage from 1.9 V to 2.8 V and a decrease in CCE values from 100 % to 89.5 % (Fig. S8). The results achieved with our Cu/NC-based ODC are comparable to those reported by Domga et al. [23]; they used N,P co-doped graphene as electrocatalyst in the ODC of an advanced chlor-alkali electrolyzer, and the CCE experienced a decline from 92.5 % to 87 %within the current density range of 1 to 4 kA m⁻².

4. Conclusions

Improving the ORR performance is pivotal for boosting the efficiency and output of advanced chlor-alkali electrolysis. Inspired by recent computational results that revealed the advantages of Cu-based electrocatalysts for ORR, in this work we have explored the viability of a pyrolyzed Cu-doped ZIF as a potential candidate to replace an expensive precious metal electrocatalyst such as Pt/C. LSV analysis showed that the outstanding activity of the Cu/N-C material in alkaline medium primarily originated from the presence of Cu(0) on the NC framework, without discarding the role of Cu single-atom sites that have been reported to be formed following s similar synthesis procedure. Despite the still higher *j* values and more positive E_{onset} and $E_{1/2}$ values achieved by Pt/C for the ORR, the Cu/NC electrocatalyst was proved to be have quite satisfactorily. Furthermore, the *n*-values of both materials were very similar, and close to 4. Similarly, both catalysts exhibited a similar Tafel slope close to 120 mV dec⁻¹, thus verifying that the first electron transfer is the rate-determining step for the ORR on the Cu-based nanocatalyst. Additionally, the material had a good stability, maintaining the 83.6 % of the reduction *j* after a 10-h durability test. Finally, a designed advanced chlor-alkali electrolyzer cell based on an ODC prepared with the Cu/NC catalyst performed very well, since the output voltage increase and CCE value decrease were analogous to those reported in the literature using modified graphene, and not far from those obtained with Pt/C. Overall, Cu/NC seems a promising material for undertaking further optimization.

CRediT authorship contribution statement

Tahereh Jangjooye Shaldehi: Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. Lele Zhao: Writing – original draft, Methodology, Formal analysis, Data curation. Teresa Andreu: Writing – review & editing, Resources, Methodology. Soosan Rowshanzamir: Supervision, Project administration, Funding acquisition, Conceptualization. Ignasi Sirés: Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Project administration, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.electacta.2025.145929.

Data availability

Data will be made available on request.

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