

Three-dimensional Carbon-Based Electrocatalysts Templated from FAU and BEA Zeolites.

Leonardo L. dos Santos ^{1*}, Aurélien Habrioux ², Sibele B. C. Pergher ¹, Alexander Sachse ².

¹ Federal University of Rio Grande do Norte, Laboratório de Peneiras Moleculares (LABPEMOL) – IQ 2, st. Senador Salgado Filho 3000, 59078-970 Natal/RN – Brazil.

² Université de Poitiers, Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP) - UMR 7285 CNRS, UFR SFA, Bât. B27, 4 rue Michel Brunet, TSA 51106, 86073 Poitiers Cedex 9 – France.

* leo.leandro25@gmail.com

Abstract

ABSTRACT - Zeolite-templated nanocarbons (ZTNCs) are emerging as advanced materials for energy conversion and storage due to their tunable porosity, high conductivity, and surface functionality. In this study, carbon (C-ZTNC) and nitrogen-doped carbon (CN-ZTNC) materials were synthesized via chemical vapor deposition using ethylene and acetonitrile over FAU and BEA zeolites. CN-ZTNCs exhibited lower density and microporosity, attributed to graphene-like domains formed outside the zeolite template. C-ZTNCs demonstrated enhanced oxygen reduction reaction (ORR) performance, with a half-wave potential of 0.78 V vs. RHE, high selectivity toward OH⁻, and dominant four-electron transfer, making them suitable for application in aqueous rechargeable Zn–air batteries (ZABs). These nanostructured carbons serve as both lightweight gas diffusion electrodes and porous, conductive catalytic supports, offering promising bifunctional activity for ORR/OER processes. This work highlights the structural advantages and catalytic potential of ZTNCs tailored by zeolite type and precursor chemistry.

Keywords: Zeolite-templated nanocarbons, Oxygen reduction reaction, Zinc-air battery, Nitrogen-doped carbon, Electrocatalysis.

Introduction

Rechargeable aqueous zinc-air batteries (ZABs) are promising next-generation energy storage systems due to their high theoretical energy density (~1086 Wh·kg⁻¹), environmental friendliness, low cost, and intrinsic safety. However, their practical application is limited by the sluggish kinetics of the oxygen reduction (ORR) and evolution (OER) reactions, which result in high overpotentials and reduced energy efficiency and cycle stability [1-3].

To overcome ORR/OER limitations in ZABs, developing bifunctional electrocatalysts with high activity, stability, and low cost is essential. Carbon-based materials stand out due to their electrical conductivity, surface tunability, and scalable synthesis [4-5].

Zeolite-templated nanocarbons (ZTNCs) offer additional advantages, including controlled porosity and morphology inherited from the zeolite framework. Nitrogen doping – using precursors like acetonitrile – further improves catalytic performance by enhancing active site density and charge transfer.

This study investigates C-ZTNC and CN-ZTNC cathodes synthesized from FAU (Si/Al = 6.0) and *BEA (Si/Al = 12.5) zeolites, using ethylene and acetonitrile as C and N-C sources, respectively. Comparative analysis revealed how zeolite structure and doping influence electrocatalytic behavior in Zn-air battery systems.

Experimental

a) Synthesis: C-ZTNC and CN-ZTNC were synthesized via chemical vapor deposition (CVD) using ethylene and acetonitrile as precursors, with FAU and *BEA zeolites as templates (2.3 and 2.4 sections of [6]).

b) Electrochemical measurements: ORR activity was assessed in 0.1 M KOH using LSV and RDE in a three-electrode setup, as detailed in [7].

c) Battery testing: ZABs were assembled with NiFeS@ZTNC on Ni foam ($\Delta E = 0.76$ V), Zn anode, 6 M KOH + 0.4 M ZnO electrolyte, and a Sigracet 36 BB GDL. Tests were conducted at 1.353 V.

Results and discussion

Structural and textural characterizations are presented in Figure 1. The XRD confirmed the amorphous carbon nature of the C- and CN-ZTNCs, with no residual crystalline zeolite phases (1.a). The N₂-physisorption data revealed that C-ZTNC materials possess higher microporous volumes and surface areas compared to CN-ZTNCs, reflecting the influence of nitrogen doping on pore development (1.b). SEM and TEM imaging confirmed the formation of nanoscale replicas of the parent zeolites (1.c), while Raman spectroscopy revealed increased structural disorder in CN-ZTNCs (1.d), consistent with the formation of graphene-like domains beyond the template framework.

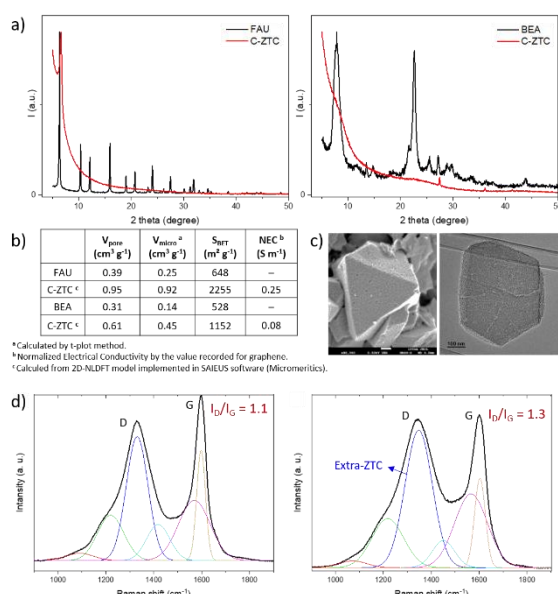


Fig. 1. C- and CN-ZTCN from FAU and *BEA zeolites: (a) XRD, (b) N₂-fis., (c) SEM and MET, (d) Raman.

Figure 2 shows the electrochemical evaluation of oxygen reduction reaction (ORR) activity. The C-ZTCNs displayed higher half-wave potentials and more efficient four-electron transfer mechanisms than CN-ZTCNs at room temperature. Upon thermal activation, the performance of CN-ZTCNs improved significantly, with electron transfer numbers approaching 3.7, indicative of enhanced selectivity toward hydroxyl formation and reduced peroxide generation.

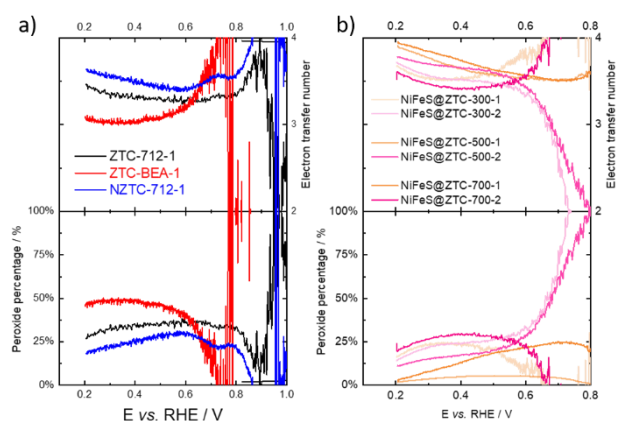


Fig. 2. Polarization curves and number of electrons transferred per oxygen molecule as a function of the applied electrode potential: (a) at room temperature, (b) after thermal activation.

The electrochemical performance of zinc-air batteries (ZABs) employing FAU-derived C-ZTNC as cathode material was evaluated under varying current densities. As shown in Figure 3, the ZAB using NiFe@ZTNC-FAU displayed stable discharge behavior, delivering specific capacities of approximately 280 $\text{mAh} \cdot \text{g}^{-1}$, 360 $\text{mAh} \cdot \text{g}^{-1}$, and

1100 $\text{mAh} \cdot \text{g}^{-1}$ at current densities of 0.5, 1.0, and 5.0 $\text{mA} \cdot \text{cm}^{-2}$, respectively. At 10 $\text{mA} \cdot \text{cm}^{-2}$, the system maintained operational stability, confirming the material's robustness under high current demand. These values are competitive with or superior to those reported for state-of-the-art noble metal-based catalysts. Compared to ZABs assembled with expensive Pt/C-RuO₂ cathodes, the NiFe@ZTNC-FAU system exhibited lower charge overpotentials and greater cycling durability, particularly under limited-capacity regimes [8].

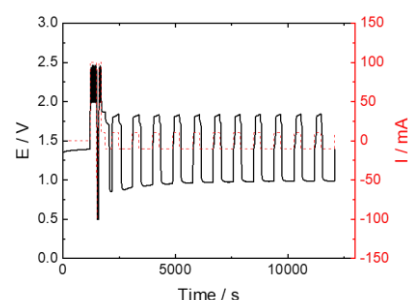


Fig. 3. Electrochemical cycling performance (voltage and capacity variation) of ZAB battery using C-ZTNC from FAU zeolite.

Conclusions

CN-ZTNC derived from FAU zeolite showed high nitrogen content ($\text{C/N} = 12.0$) and a less-condensed aromatic structure than C-ZTNC. Its reduced microporosity, due to graphene-like domains, enhanced electronic conductivity. C-ZTNC exhibited excellent ORR activity ($E_{1/2} = 0.81 \text{ V}$ vs. RHE) and high hydroxide selectivity. CN-ZTNC showed an average electron transfer number of 3.7, favoring the four-electron pathway. Thermal treatment (500–700°C) slightly reduced the half-wave potential (to 0.77–0.78 V), but improved selectivity and efficiency. ZABs using NiFe@ZTNC-FAU cathodes operated stably under high current, showing enhanced electrochemical performance and lower charge overpotentials.

Acknowledgments

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