

Carbonized ZIF-67 as catalyst for oxygen reduction reaction

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Metal-organic frameworks (MOFs) have garnered considerable scientific attention due to their tuneable characteristics which include surface area, pore structure, and chemical functionalities. Among these, zeolitic imidazolate frameworks (ZIFs) are particularly interesting for their chemical and thermal stability, making them a focal point of extensive research in various fields including catalysis, gas adsorption, electronic devices, and sensors [1]. Within the domain of catalysis, the oxygen reduction reaction (ORR) holds particular significance as a key process [2].

In this study, a novel hydrothermal method employing aqueous solutions at ambient temperature was employed to efficiently synthesize ZIF-67, thereby eliminating the need for harmful organic solvents, and reducing costs. ORR catalysts were fabricated by carbonizing ZIF-67 under an inert atmosphere at different temperatures and ramping times. An essential parameter in the production of ZIF-derived MOFs is the annealing temperature, which appears to govern both the structure of the resultant product and its electrocatalytic performance [3]. It is widely agreed that activity notably decreases at elevated temperatures thus the carbonization was carried out at 800 and 900 °C with different ramp holding time. While cobalt is presumed to act as the catalytic centre, its exact nature remains unclear. Research suggests that combining cobalt with other metals enhances ORR activity compared to using cobalt alone, while others propose that cobalt loading and the atoms surrounding the cobalt ion determine ORR reactivity. In this study, we investigated the influence of carbonization temperature and found that holding the temperature at 800 °C for three hours results in the catalyst with the most positive onset potential for ORR. Additionally, the highest currents were observed in the explored potential range for material treated in this fashion, confirming its excellent properties. The apparent number of exchanged electrons was evaluated using the Koutecky-Levich equation, with the number of exchanged electrons being above three in studied potential range, and close to four at most negative potentials scanned.

Present results suggest that carbonization step can enhance the catalytic behaviour of the material, paving the way for further improvements in energy conversion applications. The fine-tuning of the ZIF-67 temperature transformations addresses challenges associated with increasing energy demands and underscores the potential of ZIF-67-derived materials in electrochemical applications.

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References

1. S. Kouser, A. Hezam, M.J.N. Khadri, S.A. Khanum, *J. Porous Mater.* **29** (2022) 663 <https://doi.org/10.1007/s10934-021-01184-z>
2. J.P. Xuan, N.B. Huang, J.J. Zhang, W.J. Dong, L. Yang, B. Wang, *J. Solid State Chem.* **294** (2021) 121788 <https://doi.org/10.1016/j.jssc.2020.121788>
3. H. Wen, S. Zhang, T. Yu, Z. Yiab, R. Guo, *Nanoscale* **13** (2021) 12058 <https://doi.org/10.1039/D1NR01669E>