

Fluorination and co-doping of ZIF-8 by ball mill grinding for efficient oxygen reduction electrocatalysis

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The oxygen reduction reaction (ORR) is a common process in a variety of electrochemical devices, like fuel cells and metal air batteries. The sluggish kinetics of the ORR require an electrocatalyst to pass this bottleneck.^[1] Currently, the most used catalytical systems are platinum-based, with several drawbacks, such as the high cost, low availability, and deactivation by CO poisoning.^[2] Efforts are made to develop efficient, durable and low cost catalysts to promote the commercialization of fuel cells.

Non-precious metal catalysts are promising candidates for efficient ORR catalysis. It has been shown that pyrolyzing metal organic frameworks (MOFs) under inert conditions yields carbon-rich materials, with evenly distributed metal sites, which possess promising electrocatalytic activity.^[3] One widely used type of MOF as ORR catalyst precursors is the zeolitic imidazole framework (ZIF) where metal cations are linked through imidazole-based ligands. Their porous nature is partially retained after carbonization, making MOFs very suitable precursor materials.

Herein we report the mechanochemical synthesis and structural analysis of Co-doped ZIF-8 (Zn), as well as two polymorphs (dense and porous) of fluorinated Co-doped CF₃-ZIF-8 (Zn). The samples showed electrochemical performance comparable to platinum after carbonization for 1 h at temperatures ranging between 850 – 1000°C.

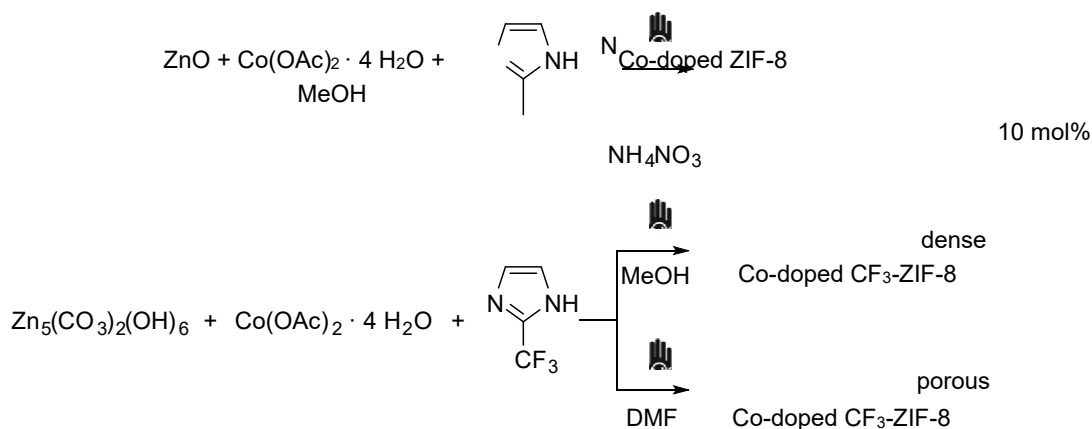


Figure 1: Mechanochemical synthesis of Co-doped ZIF-8 (top) and two polymorphs of Co-doped ZIF-8 (bottom) depending of the grinding liquid.^[4]

1. M. Ghosh, A. K. Basak, S. K. Mazumdar, B. Sheldrick, *Acta Crystallogr.* **1991**, C47, 577.
2. Z. Chen, D. Higgins, A. Yu, L. Zhang, J. Zhang, *Sci* **2011**, 4, 3167.
3. a) A. Morozan, F. Jaouen, *Energy Environ. Sci* **2013**, 6, 1656; b) S. Ma, G. A. Goenaga, A. V. Call, D. J. Liu, *Chemistry—A European Journal* **2011**, 17, 2063-2067; c) X. Wang, J. Zhou, H. Fu, W. Li, X. Fan, G. Xin, J. Zheng, X. Li, *Journal of Materials Chemistry A* **2014**, 2, 14064-14070.
4. M. Rautenberg, M. Gernhard, C. Roth, F. Emmerling (2021) Mechanochemical synthesis and analysis of Co-doped CF₃-ZIF-8 and its application for ORR catalysis. (In preparation)