

Novel template-assisted synthesis of mesoporous nanocarbon catalysts doped with iron and manganese for proton exchange membrane fuel cells

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In the pursuit of widespread proton exchange membrane fuel cell (PEMFC) adoption, operational efficiency challenges persist, particularly related to the cathode and the oxygen reduction reaction (ORR) kinetics in low-pH environments. In these conditions, the sluggish kinetics of the ORR heavily rely on platinum-group metal (PGM) catalysts. Although reducing PGM loading is a potential cost-cutting measure, it often compromises the catalyst's durability, posing a significant challenge in meeting both the durability targets set by the U.S. Department of Energy (DOE) and simultaneously the cost and PGM loading objectives.¹ In the last decades great efforts have been made to develop PGM-free cathodes for low-temperature fuel cells.²

This study addresses and aims to overcome the challenges associated with PEMFCs by exploring alternative PGM-free mesoporous catalysts, with a focus on improving the ORR activity and minimizing undesired Fenton reactions by incorporating iron and manganese as transition metal dopants. The observed enhancements in stability under harsh corrosive conditions showcase the potential of adding manganese to boost the durability of carbon-based PGM-free catalysts. In addition, our investigations underscore the crucial role of hierarchically porous structures in membrane electrode assemblies (MEAs), for enhancing electrocatalytic performance, especially for PGM-free materials where the high loading results in a thick catalyst layer on the electrode.³

The catalysts were prepared through a sustainable synthesis procedure using magnesium acetate as the template precursor and utilizing Honeyol™ (a blend of alkylresorcinols) as the carbon source. Magnesium acetate forms nanoparticles of MgO and MgCN₂ within the carbon matrix during pyrolysis. The nanoparticles are then removed and the final mesoporous material is obtained. The materials prepared with the addition of the template exhibited significantly higher mesoporosity. The performance of the catalysts was similar in RDE testing, displaying a half-wave potential of 0.75 V vs RHE. However, the mesoporous materials achieved much higher peak power density values ($P_{max} = 514 \text{ mW cm}^{-2}$) compared to the less mesoporous material, highlighting the importance of hierarchically porous structures in PGM-free catalysts.

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References

1. R.Y. Wang, D.F. Ruiz Diaz, K.S. Chen, Z. Wang, X.C. Adroher, Mater. Today 32 (2020) 178–203.
2. A. Sarapuu, J. Lilloja, S. Akula, J.H. Zagal, S. Specchia, K. Tammeveski, ChemCatChem 15 (2023) e202300849
3. K. Kisand, A. Sarapuu, J.C. Douglin, A. Kikas, A. Treshchalov, M. Käärik, H.-M. Piirsoo, P. Paiste, J. Aruväli, J. Leis, V. Kisand, A. Tamm, D.R. Dekel, K. Tammeveski, ACS Catal. 12 (2022) 14050–14061.