Preview

Electrochemical Oxygen Reduction for the Production of Hydrogen Peroxide

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In this issue of *Chem*, Prato and colleagues describe the synthesis of N-doped single-wall carbon nanohorns and their record performance as catalysts for highly selective O_2 reduction to H_2O_2. They outperform metal-based electrocatalysts and set a new benchmark for the sustainable production of H_2O_2 through the oxygen reduction reaction.

The development of economical, stable, and highly active electrocatalysts for the oxygen reduction reaction (ORR) to form water represents a major thrust in the research area of polymer-electrolyte-membrane fuel cells. However, one of the main challenges facing these low-temperature fuel cells is slow ORR kinetics at the cathode, even with the use of Pt-based catalysts.[1] In addition, Pt-based catalysts can suffer from poor catalytic stability and subsequent loss of performance under general operating conditions as a result of their predisposition to dissolution, agglomeration, and sintering.[2,3] In much of the published fuel cell research, the formation of hydrogen peroxide during the ORR is considered undesirable because it lowers efficiency and often affects the stability of the proton-exchange membrane.[4] However, given that hydrogen peroxide is an important industrial chemical with applications in the pulp-and-paper, textile, synthetic-chemical, and waste-water-treatment industries, the ability of a fuel cell to both produce H_2O_2 and generate electricity would be a significant step toward sustainable chemistry and an attractive alternative to the current anthraquinone-based method of H_2O_2 production. This multistep, energy-intensive process requires sequential hydrogenation, oxidation of anthraquinone, and separation of large volumes of solvents, which makes for challenging on-site production.[5] Therefore, the discovery and investigation of stable, earth-abundant ORR catalysts with good selectivity for H_2O_2 are highly valuable.

Several promising studies have focused on selective H_2O_2 production through the ORR by using noble metals and metal alloys, where tuning the relative binding strength of four-electron pathway intermediates and decreasing the propensity to break the O–O bond enables the selectivity to produce H_2O_2 instead of H_2O.[6] Alternatively, carbon materials are particularly attractive because of their global abundance, low cost, high surface area, large pore volume, and good electrical conductivity. Carbon fibers and N-doped porous carbon have previously been found to be active for H_2O_2 production but still have significant room for improvement.[3] The ability to tune the selectivity toward the two-electron or four-electron pathway is one of the main challenges facing these catalysts, because promotion of the ORR often occurs only at high overpotentials, where the production of H_2O is favored.

In this issue of *Chem*, Prato and colleagues have detailed N-doped graphitized carbon nanohorns (CNHs) as active catalysts for the ORR to produce H_2O_2.[7] Research on carbon-supported metal electrocatalysts has yielded materials active for the ORR at industrially relevant electric potentials with moderate faradic efficiency. However, these catalysts are still plagued by challenges of economic scalability and low abundance. By synthesizing a metal-free CNH electrocatalyst, Prato and colleagues have sidestepped common challenges regarding the stability of metal-based materials under harsh ORR conditions. Utilizing thermal annealing of a polydopamine (PDA) polymer, the authors were able to restrict N-doped porous carbon to the nanoscale by coating the CNHs. In a reproducible manner, this approach synthesized a nanocatalyst that has high surface area and long-term stability and is both active and highly selective for the ORR to H_2O_2 at low overpotentials—a vast improvement over previous metal-free carbon electrocatalysts.

CNHs have been widely explored in many applications because of their unique geometry and lack of metal impurities. Given that they can be generated from pure graphite rods, CNHs can be synthesized with high purity and yield. CNHs also offer significant tunability beyond high surface area and large pore volume because heat treatments can add defects to their walls, through which various molecules can be grafted to give excellent properties for numerous applications. Most of the work investigating CNHs has

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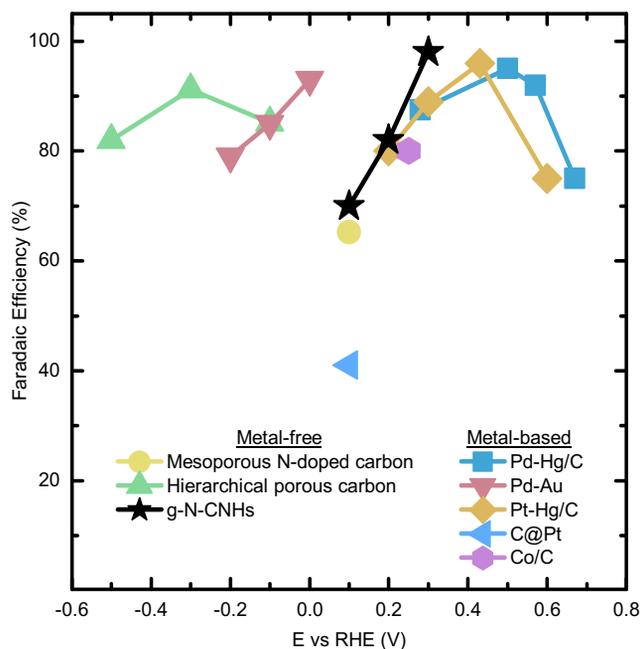
Figure 1. Faradic Efficiency versus Overpotential
Plot of faradic efficiency versus overpotential for state-of-the-art metal-free and metal-based catalysts for H_2O_2 production at acidic pH. Adapted from Prato and colleagues.[7]

centered around their use as catalyst supports for electrocatalysis and drug delivery.[8]

Building upon the versatility of CNHs as supports, Prato and colleagues sought to produce an active metal-free CNH catalyst with a high degree of N-doping through the coating and annealing of polydopamine. The combination of the distinctive properties of the CNH support with a unique method of N-doping allowed the authors to combine several critical features—namely, high surface area and porosity, an optimal distribution of pyridinic and pyrrolic N-atoms, and improved conductivity and facilitation of electron transfer—into a single material. Also, the use of the PDA precursor instead of polypyrrole or polyaniline allowed the incorporation of both a higher $N_{pyridinic}/N_{pyrrolic}$ ratio (1.13 for **g-N-CNHs**, 0.85 for **CNHs@pyrr-700**, and 0.61 for **CNHs@PANI-700**) and a higher overall N atomic percentage (5.56 for **g-N-CNHs**, 6.54 for **CNHs@pyrr-700**, and 6.73 for **CNHs@PANI-700**). As a

result, Prato and colleagues achieved an electrocatalyst that is more selective than current metal-based electrocatalysts[6] (Figure 1) and maintains high selectivity toward H_2O_2 over a wide range of pH values. For instance, they measured faradic efficiencies of 98% in pH 1 and 90% in pH 7.4 with working potentials of 0.3 and 0.65 V versus RHE, respectively. The authors attributed the high selectivity toward H_2O_2 under acidic conditions to the effective protonation of the pyridinic N, which reduces the catalytic center's ability to break the O–O bond. Furthermore, the N-doped CHNs exhibited long-term stability with a constant 33 mmol $g^{-1}h^{-1}cm^{-2}$ H_2O_2 production rate over a period of 24 hr at pH 1.

With a need for the design and development of industrially viable electrocatalysts for the ORR and continued demand for H_2O_2 worldwide, it is vital to explore novel synthetic routes to earth-abundant catalysts.[9] Further exploration of synthetic techniques and the materials they yield

will eventually lead to clean energy and sustainable chemical production. The work by Prato and colleagues is a clear example of how the rational manipulation of materials at the atomic level can lead to new earth-abundant catalysts with superb performance that matches, or even exceeds, that featured by precious-metal-based catalysts.

1. Gasteiger, H.A., Kocha, S.S., Sompalli, B., and Wagner, F.T. (2005). Activity benchmarks and requirements for Pt, Pt-alloy, and non-Pt oxygen reduction catalysts for PEMFCs. Appl. Catal. B *56*, 9–35.

2. Ferreira, P.J., la O', G.J., Shao-Horn, Y., Morgan, D., Makharia, R., Kocha, S., and Gasteiger, H.A. (2005). Instability of Pt/C electrocatalysts in proton exchange membrane fuel cells: a mechanistic investigation. J. Electrochem. Soc. *152*, A2256–A2271.

3. Chen, S., Gasteiger, H.A., Hayakawa, K., Tada, T., and Shao-Horn, Y. (2010). Platinum-alloy cathode catalyst degradation in proton exchange membrane fuel cells: nanometer-scale compositional and morphological changes. J. Electrochem. Soc. *157*, A82–A97.

4. Borup, R., Meyers, J., Pivovar, B., Kim, Y.S., Mukundan, R., Garland, N., Myers, D., Wilson, M., Garzon, F., Wood, D., et al. (2007). Scientific aspects of polymer electrolyte fuel cell durability and degradation. Chem. Rev. *107*, 3904–3951.

5. Liu, Y., Quan, X., Fan, X., Wang, H., and Chen, S. (2015). High-yield electrosynthesis of hydrogen peroxide from oxygen reduction by hierarchically porous carbon. Angew. Chem. Int. Ed. *54*, 6837–6841.

6. Siahrostami, S., Verdaguer-Casadevall, A., Karamad, M., Deiana, D., Malacrida, P., Wickman, B., Escudero-Escribano, M., Paoli, E.A., Frydendal, R., Hansen, T.W., et al. (2013). Enabling direct H_2O_2 production through rational electrocatalyst design. Nat. Mater. *12*, 1137–1143.

7. Iglesias, D., Giuliani, A., Melchionna, M., Marchesan, S., Criado, A., Nasi, L., Bevilacqua, M., Tavagnacco, C., Vizza, F., Prato, M., et al. (2018). N-doped graphitized carbon nanohorns as new forefront electrocatalyst in the highly selective O_2 reduction to H_2O_2. Chem *4*, this issue, 106–123.

8. Li, N., Wang, Z., Zhao, K., Shi, Z., Gu, Z., and Xu, S. (2010). Synthesis of single-wall carbon nanohorns by arc-discharge in air and their formation mechanism. Carbon *48*, 1580–1585.

9. Hunt, S.T., Milina, M., Alba-Rubio, A.C., Hendon, C.H., Dumesic, J.A., and Román-Leshkov, Y. (2016). Self-assembly of noble metal monolayers on transition metal carbide nanoparticle catalysts. Science *352*, 974–978.