PUBLISHED: 28 NOVEMBER 2016 | ARTICLE NUMBER: 16186 | DOI: 10.1038/NENERGY.2016.186

METAL–ORGANIC FRAMEWORKS

Evolved oxygen evolution catalysts

Catalysing the oxygen evolution reaction is central to electrochemical energy conversion technologies such as electrolysis, but the high cost of state-of-the-art precious metal oxide electrocatalysts hinders commercialization. Now, thin sheets of a metal–organic framework are shown to provide a high-performing, cheaper alternative.

Elise M. Miner and Mircea Dincă

As energy generation shifts to a heavier reliance on renewable sources, development of electrocatalytic materials that facilitate electrochemical energy conversion reactions has become a major research focus. One of the most important reactions catalysed by such materials is the oxygen evolution reaction (OER) in which water is oxidized to produce dioxygen. OER is the counterpart of the hydrogen evolution reaction which occurs in electrolysers (Fig. 1), and is central to the charging process in rechargeable metal–air batteries. OER involves removal of four electrons from two water molecules to generate one molecule of dioxygen. This process is kinetically sluggish and typically requires a large overpotential (the additional driving force needed beyond the thermodynamic redox potential to electrocatalyse a reaction) to achieve an appreciable current density or electrochemical reaction rate[1]. State-of-the-art materials for OER are generally based on precious metal oxides such as RuO$_2$, which have limited commercial viability due to their low abundance and high cost. Therefore, the pursuit of electrocatalysts exhibiting high activity for water oxidation as well as durability and low cost has become a focus in the field[2,3]. One class of materials emerging as promising electrocatalysts is metal–organic frameworks (MOFs), which are composed of metal ions or clusters linked by organic ligands to afford crystalline structures. These structures have unprecedented surface areas compared to known materials, and uniform porosity. Now, writing in *Nature Energy*, Shaoqin Liu, Huijun Zhao, Zhiyong Tang, and co-workers report the fabrication of ultrathin Ni–Co MOF sheets featuring coordinatively unsaturated metal sites — open sites for adsorption — that function as robust and highly active OER electrocatalysts[4].

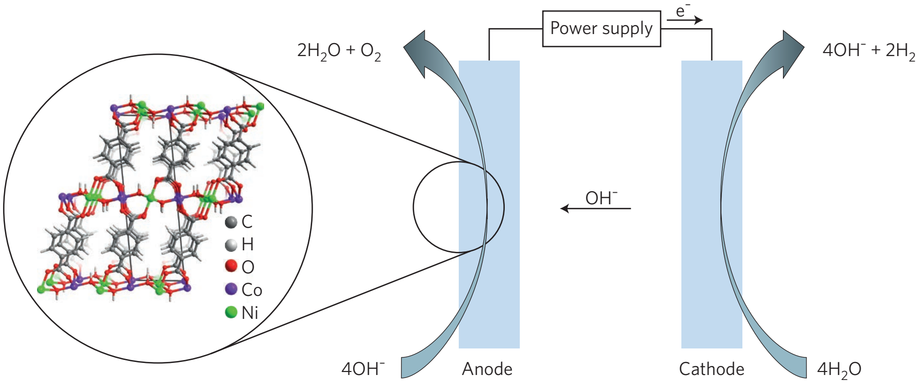

Figure 1 | Thin sheets of Ni–Co metal–organic frameworks (MOFs) as anodic oxygen evolution electrocatalysts in alkaline conditions for electrolyser applications. At the anode, hydroxide ions are oxidized to dioxygen, while at the cathode, water molecules are reduced to dihydrogen. The inset shows the structure of the Ni–Co MOF electrocatalyst.

The ordered structure and tunable ligand fields in MOFs combined with their impressive surface area and metal site isolation marries the well-defined nature of homogeneous molecular catalysts with the active site density and durability of heterogeneous systems. However, the emergence of MOFs as electrocatalysts has only been relatively recent due to their generally electrically insulating nature, caused by redox inactive ligands chelated to hard metal ions which offer a low density of charge carriers and no low-energy charge transport pathway. To overcome this, various solutions have been presented, including controlling the thickness of the MOFs on the electrode to minimize the electron transport distance from the electrode through the poorly conducting active catalysts. Another proposed solution is the development of conductive MOFs that enable electrical conductivity through highly conjugated frameworks[5].

Liu, Zhao, Tang and colleagues prepare ~3 nm thick bimetallic Ni–Co MOF nanosheets by simply combining the benzenedicarboxylic acid ligand with Ni^{2+} and Co^{2+} salts in an organic solvent followed by ultrasonication under ambient conditions. After deposition onto copper foam electrodes, these films exhibit an OER potential of 1.42 V versus the reversible hydrogen electrode to drive the reaction at a current density of 10 mA cm^{-2} in alkaline conditions, which is only 0.19 V over the thermodynamic oxidation potential of water ($E^0 = 1.23$ V). In comparison, to achieve the same current density, RuO$_2$ requires an operating overpotential of 0.28 V under the same conditions. The catalytic performance of the Ni–Co MOF nanosheets on copper foam is characterized by a Tafel slope of 42 mV per decade of current, an indication of fast OER reaction kinetics. Moreover, the current density, catalyst morphology, and crystallinity during potentiostatic measurements at 0.25 V of overpotential remain stable over 200 hours. In addition to impressive OER kinetics and stability, the material affords a 99.3% Faradaic efficiency for the 4 electron oxidation of water, indicating high selectivity for oxygen evolution. The researchers attribute the high activity of the Ni–Co mixed-metal system to enhanced interaction between water and the Ni^{2+} sites due to electron transfer from the Ni^{2+} sites to the Co^{2+} sites; the less filled e_g orbitals of Co^{2+} compared to those of Ni^{2+} (Co^{2+} = d^7 versus Ni^{2+} = d^8) can accept electron density from the Ni^{2+} sites. In turn, the oxidized Ni sites can more readily engage in electron transfer from water, thus offering a lower energy barrier for water oxidation. Indeed, the isostructural monometallic Ni or Co MOFs exhibit diminished OER activity compared to that of the bimetallic system.

Interestingly, the researchers observed that the catalytic activity of the Ni–Co MOF was enhanced when the MOF was deposited on a copper electrode as opposed to a glassy carbon electrode. Further investigation of the nature of the interaction between the MOF and the copper electrode may provide insight into the source of this performance enhancement and how to achieve this performance in the MOF regardless of the substrate. Additional studies on this material could include measuring the electrical conductivity of the MOF to better understand the roles of the MOF thickness and electrical conductivity in allowing electron transport from water to the anode.

Finally, the authors report deposition of the MOF onto the electrode by forming a suspension with a Nafion binder followed by drop-casting the suspension onto the electrode; it could be interesting for future studies to investigate the ability to grow the MOF film directly onto the electrode, instead of using post-synthetic deposition. Growing the MOF onto the electrode could aid in retaining the uniform thickness of the film once on the electrode and maximize the density of coordinatively unsaturated active sites that are available to water as opposed to physically obscured by the Nafion. Growth of MOF films directly onto electrode surfaces for electrocatalytic applications has been explored[6], so this approach may be feasible.

There is still work to be done to fully understand and optimize this system. However, the ultrathin bimetallic MOF sheets introduce several advantages essential to a successful electrocatalyst: rapid mass transport of water to active sites; fast electron transfer from water to the anode on which the ultrathin films are deposited; high density of unsaturated metal sites to maximize activity per geometric surface area; and well-defined, uniform coordination environments around the active sites that enable mechanistic studies and maximize product selectivity. In contrast to many other heterogeneous electrocatalysts, the ability to both introduce different metals into the framework and further functionalize the ligands provides additional opportunities for incrementally tuning the catalyst so that the role of each component of the MOF can be understood in the context of OER. Establishing such structure–function relationships brings about the exciting prospect of further improving the already promising activity and stability of this catalyst. ❒

Elise M. Miner and Mircea Dincă are in the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA.
e-mail: mdinca@mit.edu

References

1. Han, L., Dong, S. & Wang, E. *Adv. Mater.* **28,** 9266–9291 (2016).
2. Kanan, M. K. & Nocera, D. G. *Science* **321,** 1072–1075 (2008).
3. Dincă, M., Surendranath, Y. & Nocera, D. G. *Proc. Natl Acad. Sci. USA* **107,** 10337–10341 (2010).
4. Zhao, S. *et. al. Nat. Energy* **1,** 16184 (2016).
5. Sun, L., Campbell, M. G. & Dincă, M. *Angew. Chem. Int. Ed.* **55,** 3566–3579 (2016).
6. Miner, E. M. *et al. Nat. Commun.* **7,** 10942 (2016).