Exploiting chirality of nickel(II) metal-organic coordination polymers to catalyze Oxygen Evolution Reaction (OER) in Water Electrolysis

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Coordination polymers such as Metal Organic Frameworks (MOFs) and Metal-Hydroxide Organic Frameworks (MHOFs) possess interesting features that make them attractive in the field of catalysis: they are based on cheap and abundant first-row transition metals, have high surface area and porosity, and their properties are tunable by chemical design. In particular, this family of materials proved a viable low cost "green" alternative to state-of-the-art catalysts for the Oxygen Evolution Reaction (OER),[1] now mainly based on rare and expensive metals like Pt and Ir. OER is the bottleneck that limits the energetic efficiency of Electrochemical Water Splitting (EWS), the process allowing to convert electric power to "green H_2". In fact, due to its sluggish kinetics, the OER requires a high overpotential. The latter can be reduced using spin-polarized currents,[2] which can be produced by chiral materials exploiting the Chiral Induced Spin Selectivity (CISS) effect.[3] In particular, a chiral catalyst for OER would promote the formation of ground state O_2 (S = 1) while eliminating by-products with S = 0 (like H_2O_2). However, the exploitation of CISS-active chiral M(H)OFs as enhanced electrocatalysts in EWS is still an unexplored field. In this work we synthesized a family of nanostructured chiral (Ni-C) and achiral (Ni-A) coordination polymers based on Ni^{2+} and dicarboxylic ligands (Fig. 1), with low (1), intermediate (2) or high (3) crystallinity. The catalytic activity and current densities were found systematically higher for the chiral materials than for the achiral analogues (Fig. 1), strongly suggesting that chirality is a viable strategy to design efficient catalysts for EWS and OER. We also performed *in-operando* X-ray absorption spectroscopies, where the Ni catalyst was deposited on the working electrode of an electrochemical cell. The evolution of the XANES and EXAFS spectra as a function of applied potential clearly showed the change of oxidation state and local structure around the metal centers, providing indications about the formation of the elusive and widely debated Ni^{+4} species.

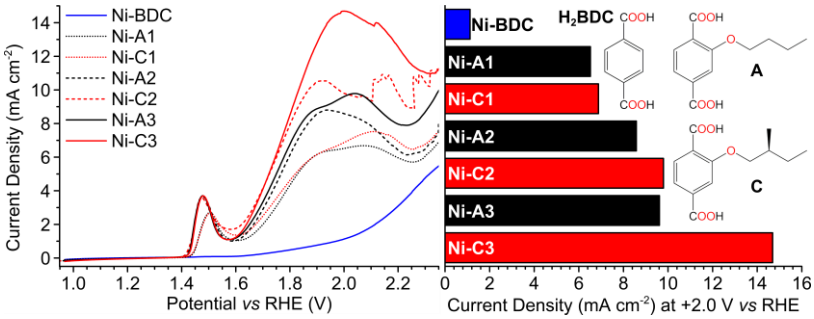

Figure 1. Electrocatalytic activities of the Ni catalysts.

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References:

1. Yuan, S. *et al.*, *Nat. Mater.*, 21 (2022), 673-680.
2. Mtangi, W. *et al.*, *J. Am. Chem. Soc.*, 139 (2017), 2794–2798.
3. Evers., F. *et al.*, *Adv. Mater.*, 34 (2022), 2106629.