Electrocatalysis
Electron spin matters

Electrolytic hydrogen production using conventional electrocatalysts suffers from low energy efficiency, due in part to the sluggish nature of the oxygen evolution reaction (OER). Topological chiral semimetals are now explored to facilitate the OER by promoting spin-dependent electron transfer during the reaction.

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Hydrogen is considered a promising renewable energy carrier. It can be produced in water electrolyzers using renewable energy and converted to electricity in fuel cells. Unfortunately, the electrocatalytic reactions behind these devices' energy conversion processes are kinetically sluggish. In particular, oxygen evolution and reduction, which each involve four protons and four electrons, tend to have significant energy penalties associated with them.

The current consensus among electrocatalysis scientists is that the ideal catalyst for these reactions must have an optimal – not too strong but also not too weak – binding energy between the reaction intermediates and active sites on the catalyst surface. Plotting electrocatalytic activity vs. binding energy or another related descriptor allows one to obtain so-called “volcano plots” with an optimal catalyst at the apex, visually representing the well-known Sabatier principle. Since several intermediates are involved in the oxygen reactions, the binding energies of all of them must be optimized. However, linear adsorption-energy scaling relationships between different oxygen-containing intermediates imply this is hardly possible.[1] In other words, surfaces with single active sites will most often have at least one intermediate that is adsorbed either too weakly or too strongly.

This thermodynamic limit results in a minimum overpotential of 0.2-0.4 V. Catalysts with multiple active sites may overcome this limitation, but stabilizing several elements at the surface is challenging. Therefore, concepts that go beyond single activity descriptors and capitalise on unexplored phenomena are required.

Now, writing in Nature Energy,[2] Xia Wang and Claudia Felser at the Max-Planck-Institute for Chemical Physics of Solids and Binghai Yan at the Weizmann Institute of Science and colleagues show that the rate of the OER can be enhanced by using electrocatalysts with intrinsic chiral (Fig. 1a) metallic active sites, which promote in-situ electron spin polarization. The team uses homochiral single crystals of the topological semimetals, RhSi, RhSn, and RhBiS, to showcase the approach, finding a positive correlation between spin-orbit coupling, spin polarization and the OER activity. RhBiS, which has the highest degree of spin-orbit coupling and spin polarization, is more active than RuO_2 – the closest oxide catalyst to the volcano apex that contains only a single metal.

In the most widely accepted OER pathway, the reactant (water or hydroxyl ion in an acidic or alkaline medium, respectively) is converted to the product (molecular oxygen) via four consecutive proton and electron transfer steps in which *HO, *O, and *HOO are the reaction intermediates. Numerous material science solutions, such as alloying, doping, surface modification and defect engineering, have been explored to optimize the binding energies of the intermediates and, hence, the reaction. However, these traditional approaches often overlook magnetic effects on electrocatalytic activities.

Water molecules and hydroxyl ions are singlets (Fig.1b); that is, they have no unpaired electrons, and their total electron spin is zero. On the other hand, molecular oxygen is a triplet – it has two unpaired electrons, and its total electron spin is one. The oxidation of water or hydroxyl ions to oxygen requires a change in the spin state, and extra energy must be supplied for this process. The increased activation barrier (spin barrier) is so significant that chemists call such reactions spin-forbidden reactions. In fact, without spin-orbit coupling, the reaction would not even be possible.[3] Another example of such a reaction is the oxidation of hydrocarbons to H_2O and CO_2 (all singlets) by molecular oxygen (a triplet). Even though these reactions are exothermic, their rate at room temperature is negligibly slow, which, among other things, is crucial to the existence of life on Earth.

The concept of spin selectivity is relatively new in electrocatalysis research. Commonly, the influence of magnetism on electrocatalytic reactions is not considered: the spin orientation of electrons in the catalyst/adsorbate/product is not exploited

(Fig.1c), and the large OER overpotentials are often attributed to scaling relationships between OER intermediates, as discussed above.[1] Alternative – or rather, complementary – theories of oxygen electrocatalysis, including magnetic effects, are rare, and their use is still limited. Such theories postulate that the transition from singlet water to the ground state triplet oxygen takes place through the formation of high energy excited singlet state oxygen. Consequently, higher overpotential is associated with the formation of such intermediates.[4,5] Several approaches have been proposed to overcome this limitation. For example, a constant magnetic field in ferromagnetic electrodes achieves spin polarization and, hence, improves OER kinetics.[6] However, only a few catalytic materials are magnetic.

For nonmagnetic electrodes, coatings by chiral molecules can instead provide spin polarization (Fig.1d).[7] This occurs via the phenomenon known as chirality-induced spin selectivity (CISS), where molecular chirality affects the spin of transported electrons through these molecules (Fig.1a).[8,9] While several successful examples of using this concept have been demonstrated in electrocatalysis, surface modifiers may block metal active sites (if put on the catalyst directly) or introduce additional ohmic barriers (if sandwiched between the catalyst and substrate, as visualized in Fig.1d).

Therefore, a strength of the work from Wang et al. is that the materials they use – RhSi, RhSn, and RhBiS – have intrinsic chirality, meaning that the CISS effect is achieved without surface modifiers (Fig.1e). As a result, the best catalyst, which they find to be RhBiS, has intrinsic activity significantly higher than that of RuO_2 in both alkaline and acidic electrolytes.

The work by Wang and colleagues shows that catalytic activity correlates with the magnitude of spin-orbit coupling, and the researchers introduce this correlation as an activity descriptor for the knowledge-driven design of advanced catalysts for oxygen redox reactions. The direct consequence of this crucial finding is that materials, ideally noble metals-free, with improved spin-orbit coupling and certain degree of spin polarization, should be explored in the future for even higher OER rates. In parallel, more efforts must be put into developing a more robust theory of how CISS affects chemical reactions.[10]

Such fundamental research must also be followed by more practical studies. Thus, the applicability of topological chiral semimetals in real electrolyzers using high surface area nanoparticulate catalysts must be demonstrated. Since spin polarization occurs in the bulk of the catalyst and aligns with the current direction (not surface orientation),[2] such a transition from extended to nanoparticulate surfaces seems feasible. Moreover, the required long-term stability of such multi-component materials in an aggressive reaction environment must be proven.

Nevertheless, while there is still work to be done before conventional catalysts like IrO_2 and Pt are replaced by those engineered with electron spin effects in mind, the work by Wang and colleagues is an important contribution that will necessitate a shift in the conventional electrocatalysis research.

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References:

1 Man, I. *et al.* Universality in oxygen evolution electrocatalysis on oxide surfaces. *ChemCatChem* **3**, 1159-1165, doi:10.1002/cctc.201000397 (2011).

2 Wang, X. *et al.* Topological semimetals with intrinsic chirality as spin-controlling electrocatalysts for the oxygen evolution reaction. *Nature Energy*, doi:10.1038/s41560-024-01674-9 (2024).

3 Chrétien, S. & Metiu, H. O2 evolution on a clean partially reduced rutile TiO2(110) surface and on the same surface precovered with Au1 and Au2: The importance of spin conservation. *The Journal of Chemical Physics* **129**, 074705, doi:10.1063/1.2956506 (2008).

4 Torun, E., Fang, C. M., de Wijs, G. A. & de Groot, R. A. Role of Magnetism in Catalysis: RuO2 (110) Surface. *The Journal of Physical Chemistry C* **117**, 6353-6357, doi:10.1021/jp4020367 (2013).

5 Gracia, J. Spin dependent interactions catalyse the oxygen electrochemistry. *PCCP **19**, 20451,* doi:10.1039/c7cp04289b (2017).

6 Garcés-Pineda, F.A. et al. Direct magnetic enhancement of electrocatalytic water oxidation in alkaline media. *Nature Energy* **4**, 519–525, doi:10.1038/s41560-019-0404-4 (2019).

7 Mtangi, W., Kiran, V., Fontanesi, C. & Naaman, R. Role of the Electron Spin Polarization in Water Splitting. *The Journal of Physical Chemistry Letters* **6**, 4916-4922, doi:10.1021/acs.jpclett.5b02419 (2015).

8 Bloom, B. P., Paltiel, Y., Naaman, R. & Waldeck, D. H. Chiral Induced Spin Selectivity. *Chemical Reviews* **124**, 1950-1991, doi:10.1021/acs.chemrev.3c00661 (2024).

9 Naaman, R., Paltiel, Y. & Waldeck, D. H. Chiral molecules and the electron spin. *Nature Reviews Chemistry* **3**, 250-260, doi:10.1038/s41570-019-0087-1 (2019).

10 Evers, F. *et al.* Theory of Chirality Induced Spin Selectivity: Progress and Challenges. *Advanced Materials* **34**, 2106629, doi: 10.1002/adma.202106629 (2022).

Figure captions:

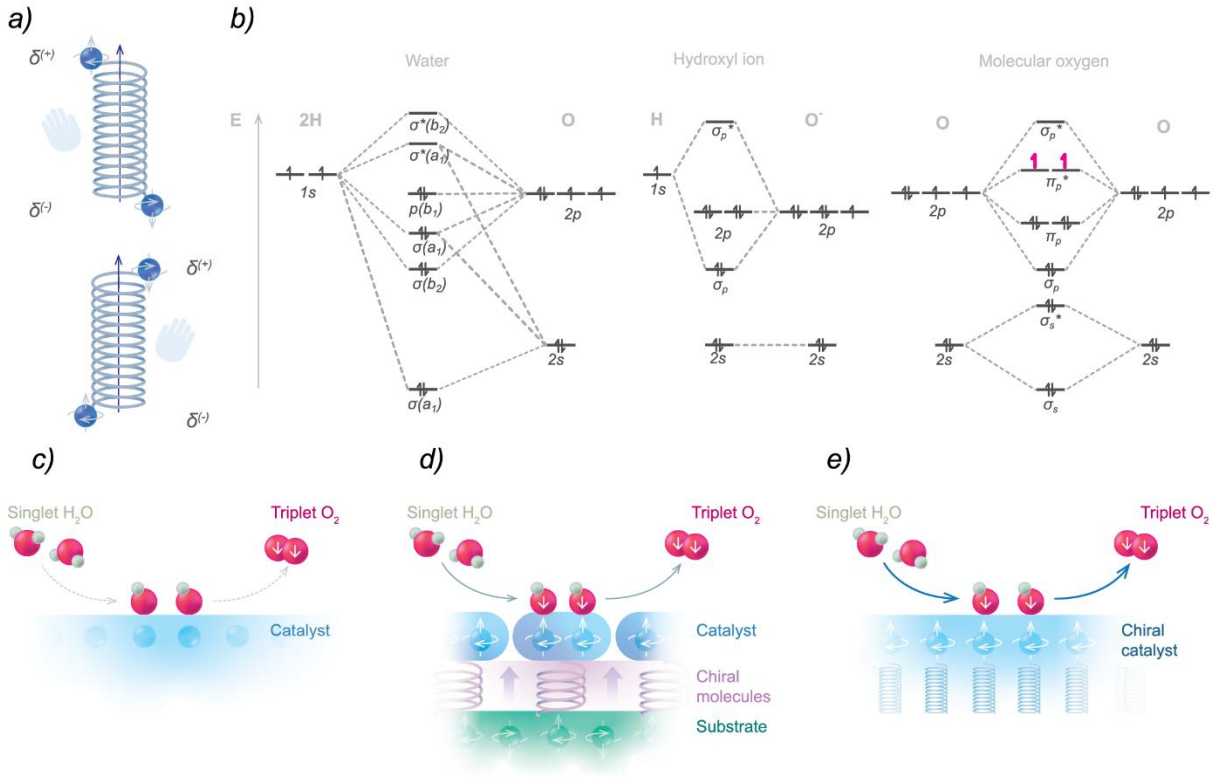

Fig. 1 | Catalysis improvement by chirality-promoted spin-dependent electron transfer. (a) The concept of chirality triggered spin polarization. The electric field (black arrows) induces spin-selective electron displacement to opposite poles of the helices, and their handedness defines the spin orientation. (b) Molecular orbital energy-level diagrams for water and hydroxyl ion - singlets and molecular oxygen - triplet. Oxygen evolution reaction in acid on (c) conventional achiral, (d) chiral molecules modified, and (e) topological chiral electrocatalysts. It is assumed that reacting intermediates in (c) are hydroxyl ions, while those in (d,e) are hydroxyl radicals interacting with spin-polarized electrons in the catalyst. Catalyst active sites, hydrogen, and oxygen atoms are shown in blue, gray, and red, respectively.

Competing interests:

The author declares no competing interests.