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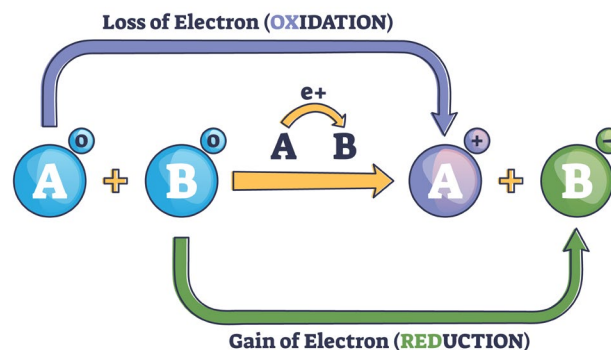
Professor Craig L. Hill

Redox Buffers: Self-Regulating Catalysts for Chemical Oxidation

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REDOX REACTION



Balancing Electrochemical Potential in Reactions

Many people are familiar with the concept of pH buffering. When acids or bases are added to a buffered solution, the buffer minimises fluctuations in acidity, keeping conditions stable. A comparable principle applies to electrochemical potential in chemical reactions. The free energy difference describes a solution's ability to gain or lose electrons, and it governs how easily oxidation–reduction (redox) processes can occur. In practical terms, electrochemical potential is a measure of the driving force that pushes electrons from one molecule to another. If the potential swings too high or too low during a reaction, electron transfers may slow down, stop altogether, or produce unwanted side products. Controlling this 'voltage' is therefore as important as controlling acidity with pH buffers.

Stable electrochemical potential is essential. Without it, redox reactions may become erratic, wasting energy and reducing yields. For decades, biologists have recognised that nature maintains redox balance through buffering systems, such as the glutathione system in living cells. This system helps protect against oxidative stress by keeping electron transfer reactions within safe operating ranges. Yet, despite such biological precedents, chemists had not succeeded in creating artificial catalysts with a built-in redox buffering capacity—until now.

Polyoxometalates and the Quest for Self-Regulation

Addressing this challenge, the team focused on the properties of polyoxometalates (POMs). These are large, cage-like molecular clusters composed of transition metals such as molybdenum, tungsten, or vanadium, connected by oxygen atoms. Their size and architecture give them remarkable stability, but their most significant property is redox flexibility, since POMs can store and release multiple electrons without breaking apart. This means they can act as rechargeable electron reservoirs, smoothing out fluctuations in a chemical reaction.

The researchers developed a system based on a specific POM known as hexavanadopolymolybdate (PV_6Mo_6). When dissolved in acetonitrile and paired with copper ions, this molecule formed a two-component catalyst with remarkable properties. Unlike traditional catalysts, which require careful external control, this hybrid system could regulate its own redox state automatically. In effect, it functioned like a chemical thermostat, keeping the electron transfer conditions within an optimal window while still accelerating the target reaction.

Converting Smelly Thiols into Odourless Compounds

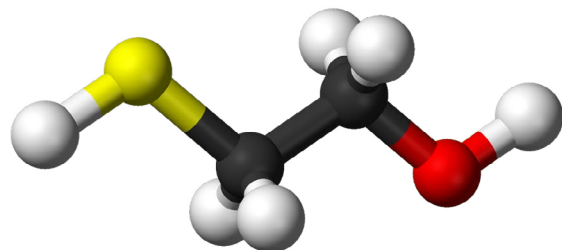
To demonstrate the power of their system, the researchers selected a class of compounds notorious for their unpleasant odour: thiols. These sulphur-containing molecules occur in petroleum products and waste streams. They are detectable at extraordinarily low concentrations, which is why they are deliberately added to domestic gas supplies as a safety warning. But thiols also pose a significant challenge for industries seeking to minimise pollution and improve working environments.

When thiols are oxidised to disulfides, their volatility and odour are dramatically reduced. Traditional oxidation catalysts can perform this transformation, but often require harsh conditions involving high temperatures, corrosive oxidants, or significant energy input. The system devised by Dr Geletii and Prof Hill was able to achieve the same conversion under ambient conditions, using only oxygen from the air as the oxidising agent. In chemistry, the efficiency of this process is measured by the conversion rate – the percentage of starting material transformed into the desired product within a given timeframe.

Chemical reactions often demand precise control over their operating conditions to proceed efficiently. While chemists routinely use pH buffers to stabilise acidity levels, far less attention has been directed towards stabilising the electrochemical potential of solutions during oxidation–reduction reactions.

At Emory University, Dr Xinlin Lu, Dr Yuri Geletii, and Prof Craig Hill have pioneered a catalytic system that not only drives chemical reactions, but also acts as its own redox buffer. By automatically maintaining conditions optimal for electron transfers while converting malodorous thiols into odourless compounds, this innovation points to a new generation of catalysts that adjust themselves, delivering both efficiency and environmental benefits.

High conversion rates are essential in industry because they indicate not only that a catalyst is active but also that it uses resources effectively, with minimal waste. In tests with 2-mercaptoethanol as a representative substrate, the new catalyst system achieved rapid and near-complete conversion in under an hour, far outperforming either component alone.



Synergy Between Polyoxometalates and Copper

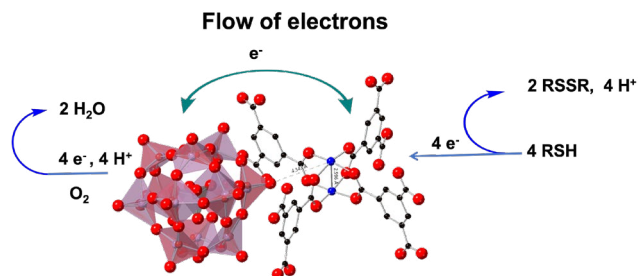
A crucial discovery was that neither component of the system—POM or copper—was sufficient on its own. Only in combination did they deliver such striking results. The mechanism underlying this synergy is both elegant and efficient:

1. The polyoxometalate acts as a multistep redox buffer. It can accept as many as six electrons without destabilising, maintaining the solution's electrochemical potential within a narrow range.
2. The copper ions, cycling between copper(II) and copper(I), serve as intermediaries. They accept electrons from the thiol substrates and transfer them to the polyoxometalate.
3. Finally, oxygen from the atmosphere re-oxidises the reduced POM, regenerating the active form of the catalyst.

This three-way interplay creates a self-sustaining catalytic cycle. The result is consistent, high-yield oxidation of thiols, carried out under mild conditions, without the instability that typically plagues redox processes.

To probe how the catalyst operated, the researchers employed spectroscopy. This analytical technique shines ultraviolet and visible light through a sample and records how much is absorbed. Molecules absorb different wavelengths depending on the arrangement of their electrons, so shifts in absorption reveal when electrons are gained or lost. Because oxidation and reduction change electron states, this is a powerful way to track redox processes in real time. By applying the method during catalysis, the team observed that

the POM maintained steady reduction states throughout most of the reaction. Only once the thiol substrate was nearly depleted did the system shift to different electron levels. This provided clear, direct evidence that the POM was functioning as a redox buffer, stabilising the electrochemical potential during the reaction.



$$E = E_o + 0.059 \cdot \text{Log}(\{POM_{ox}\}/\{POM_{red}\}) + 0.059 \cdot \text{Log}(\{Cu2\}/\{Cu1\}) + 0.0295 \cdot \text{Log}(\{RSSR\})$$

From Solution to Solid-State Catalysts

For real-world applications, liquid-phase catalysts are often impractical. Industrial processes favour solid catalysts, which can be easily recovered, recycled, and integrated into continuous systems. To meet this requirement, the team embedded their POMs within metal-organic frameworks (MOFs), porous crystalline structures with well-defined channels. In particular, they used the copper-based framework HKUST-1 to produce composite materials denoted POM@HKUST. Within this hybrid, the POMs occupy the internal pores while copper ions form part of the framework structure. This close spatial arrangement allowed electron transfer between the POM and copper to proceed efficiently.

The results were highly encouraging. The solid catalysts retained the same synergistic activity as the liquid-phase system and displayed excellent stability. However, the molybdenum-based composites could be reused repeatedly without degradation, while tungsten analogues broke down after limited use. So, not all POMs performed equally well. This was surprising because the two sets of compounds had very similar electrochemical potentials when in isolation.

The explanation lay in the mechanism of electron transfer. Molybdenum-based POMs facilitate inner-sphere electron transfer, where the donor and acceptor molecules briefly form a chemical bond through which the electron moves. This bond stabilises the

exchange, making the transfer efficient and reliable. In contrast, tungsten-based POMs rely on outer-sphere electron transfer, where electrons move without bond formation, and is less efficient for sustaining complex catalytic cycles.

Towards Industrial and Biological Applications

The significance of this work extends beyond thiol deodorisation. Oxidation reactions underpin vast sectors of the chemical industry, including fuel processing, polymer synthesis, and pharmaceutical manufacturing. A catalyst that is both efficient and self-regulating offers considerable economic and environmental advantages. By eliminating the need for harsh oxidants or elevated temperatures, the system devised by Dr Geletii and Prof Hill reduces waste, energy consumption, and costs.

Equally important is the conceptual advance. Incorporating redox buffering directly into catalytic systems could transform the way chemists approach reaction design. Instead of relying on external controls to maintain optimal conditions, future catalysts may be designed to regulate themselves dynamically, just as biological enzymes often do.

The biological parallels are striking. Cells rely on redox buffering to maintain homeostasis, ensuring that critical metabolic pathways function despite constant environmental fluctuations. By mimicking these strategies, synthetic catalysts not only achieve technical improvements but also provide deeper insight into how life itself manages chemical reactivity.

The development of self-regulating catalysts represents a culmination of decades of work exploring electron transfer in POMs. The team's findings illustrate how a detailed understanding of fundamental chemistry can lead directly to innovations with wide-ranging industrial relevance. This research demonstrates that catalysts can be more than passive accelerators of reactions: they can be active managers of their own operating environment, sustaining efficiency and stability in ways that echo the sophistication of biological systems.



Article written by Neelam Parihar.

MEET THE RESEARCHERS



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Dr Yurii V. Geletii received his MS in Chemistry with Honors in 1976 and his PhD in the Chemistry of Fast Processes in 1979, under the supervision of Prof A. E. Shilov, both from the Moscow Institute of Physics and Technology, Russia. He began his scientific career at the Institute of Problems of Chemical Physics (IPCP) of the Russian Academy of Sciences, where he worked as a Junior and Senior Researcher from 1979 to 1992 and again from 1996 to 1999. He held a position of a Principal Investigator in the Laboratory of Coordination Chemistry CNRS (Toulouse, France) from 1992 to 1996.

He joined Emory University's Department of Chemistry as a Senior Researcher in 1999, where he contributed to cutting-edge research in catalysis and artificial photosynthesis until his retirement in 2023. Dr Geletii's research focuses on the kinetics of chemical reactions, homogeneous catalysis, and the chemistry of transition metal complexes and polyoxometalates. He has authored over 170 scientific publications, holds 3 patents, and has been cited more than 9,000 times, reflecting his significant impact in the field of inorganic and catalytic chemistry.

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Dr Craig L. Hill is the Goodrich C. White Professor of Chemistry at Emory University, a position he has held since 1996. He retired from full-time academic service in October 2025, concluding a distinguished career that has profoundly influenced the fields of catalysis, inorganic chemistry, and green energy research.

Prof Hill earned his BA with High Honors from the University of California, San Diego in 1971, and his PhD in Chemistry in 1975 from the Massachusetts Institute of Technology, under the supervision of Prof G. M. Whitesides. He completed an NSF Postdoctoral Fellowship at Stanford University with Prof R. H. Holm in 1977. His pioneering research has focused on catalysis, multifunctional nanomaterials, artificial photosynthesis, and the chemistry of inorganic clusters and polyoxometalates. A highly cited scientist with an h-index of 102, Prof Hill has authored approximately 700 publications, 31 patents, and delivered over 500 invited and plenary lectures worldwide. He has trained more than 150 graduate students and postdoctoral fellows, shaping future leaders in chemistry.

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FURTHER READING

X Lu, T Cheng, Y V Geletii, J Bacsá, CL Hill, Reactivity and stability synergism directed by the electron transfer between polyoxometalates and metal-organic frameworks, *Catalysis Science & Technology*, 2023, 13, 5094–5103. DOI: <https://doi.org/10.1039/D3CY00569K>

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