

250 years of oxygen chemistry



We look back on the discovery of oxygen in light of its upcoming milestone anniversary and highlight the computational contributions to oxygen reduction and evolution in chemistry.

On 1 August 1774, Joseph Priestley discovered “dephlogisticated air”, later known as oxygen. Now thought of as his [most famous experiment](#), Priestley focused sunlight on a lump of mercuric oxide in an inverted glass container and observed a colorless, odorless, and tasteless gas being released from the lump, which caused a flame. Of this discovery, he wrote¹: “the feeling of [the gas] to my lungs was not sensibly different from that of common air, but I fancied that my breast felt peculiarly light and easy for some time afterwards. Who can tell but that in time, this pure air may become a fashionable article in luxury. Hitherto only two mice and myself have had the privilege of breathing it.” Priestley also observed that this gas kept mice alive about four times as long as similar air quality in closed environments, and that plants released oxygen and “refreshed” the air through the process of photosynthesis.

Now, 250 years later, there have been countless studies on oxygen reactivity, especially on the fundamental electrochemical reactions of oxygen reduction and oxygen evolution. These reactions – the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) – have become especially relevant in recent years, as they are both critical in alternative energy storage systems, such as batteries and fuel cells. In such energy conversion devices, the ORR occurs at the cathode, where oxygen molecules are reduced by electrons. Electrochemically, it is very difficult to break

the O–O double bond in oxygen, meaning that catalysts are often required for bond activation and cleavage. Such slow activity of the ORR on the cathode is one of the main limitations of fuel cell applications. The OER – the reverse reaction of the ORR – releases oxygen and hydrogen from water and is thought of as a promising anodic reaction because it only requires water as a source. However, this process also suffers from slow kinetics and relies on a catalyst to drive the conversion. Although both reactions are essential parts of energy conversion devices, the ideal catalyst in terms of selectivity, activity, and stability, as well as the exact mechanisms of conversion, remains an open question.

Computational chemists have the unique advantage of providing multifaceted insight into chemical reaction mechanisms, particularly at the atom level, which may be difficult (or even impossible) to discern experimentally. In the case of ORR and OER, computational techniques have been applied to a host of tasks, including catalyst design², mechanistic understanding³, and observation rationalization⁴, to name a few, using a range of tools from density functional theory⁵ to machine learning⁶. Together, these efforts have led to an improved understanding of catalyst design and optimization, as well as of the reaction environment – for instance, the role of neighboring ligands and the origin of the overpotential.

Despite the progress made by these approaches, there are still many challenges that the computational chemistry community must address moving forward. For instance, one of the main goals in the field is to develop catalysts that are highly stable and active, but that maintain low overpotentials. De-en Jiang writes in a [Comment](#) that, in order to continue moving towards this target and effectively screen catalyst compositions, computational

scientists need to develop key descriptors for activity, stability, and overpotential, as well as potential machine learning surrogate models for adsorption and elementary-step energetics. Additionally, given that this is a highly collaborative topic, statistical theories still need to be improved to bridge experiments and computation. ORR and OER studies are also subject to the long-standing challenges related to accelerating calculations: while we need ab initio methods that have a strong physical basis to generate training data for machine learning methods, it is well established that those types of density functional theory calculations can become prohibitively expensive and complex.

Looking ahead, there is hope that advanced computing power can help to address the cost and complexity dilemma, and that continued collaboration between computational scientists and experimentalists will result in even more realistic models and greater insights into reactivity. Although challenges remain, it is evident that since the first discovery of oxygen 250 years ago, there has been tremendous progress in understanding the reactivity and importance of oxygen, thanks in part to the numerous computational works on the topic. This progress goes hand-in-hand with the ongoing efforts in renewable energy, and the fields must continue to grow collaboratively. We are holding our breath for continued advances!

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