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High-valent metal-oxo intermediates in energy demanding processes: from dioxygen reduction to water splitting

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Four-electron reduction of dioxygen to water and splitting of water to dioxygen are extremely important processes in the context of attaining clean renewable energy sources. High-valent metal-oxo cores are proposed as reactive intermediates in these vital processes, although they have only been isolated in extremely rare cases in the biological systems thereby making the mechanism ambiguous. Recent biomimetic studies have, however, aided in our understanding of the fundamental reactivity of the high-valent metal-oxo species in various reactions relevant to energy conversion. All these studies are summarized in the present review.

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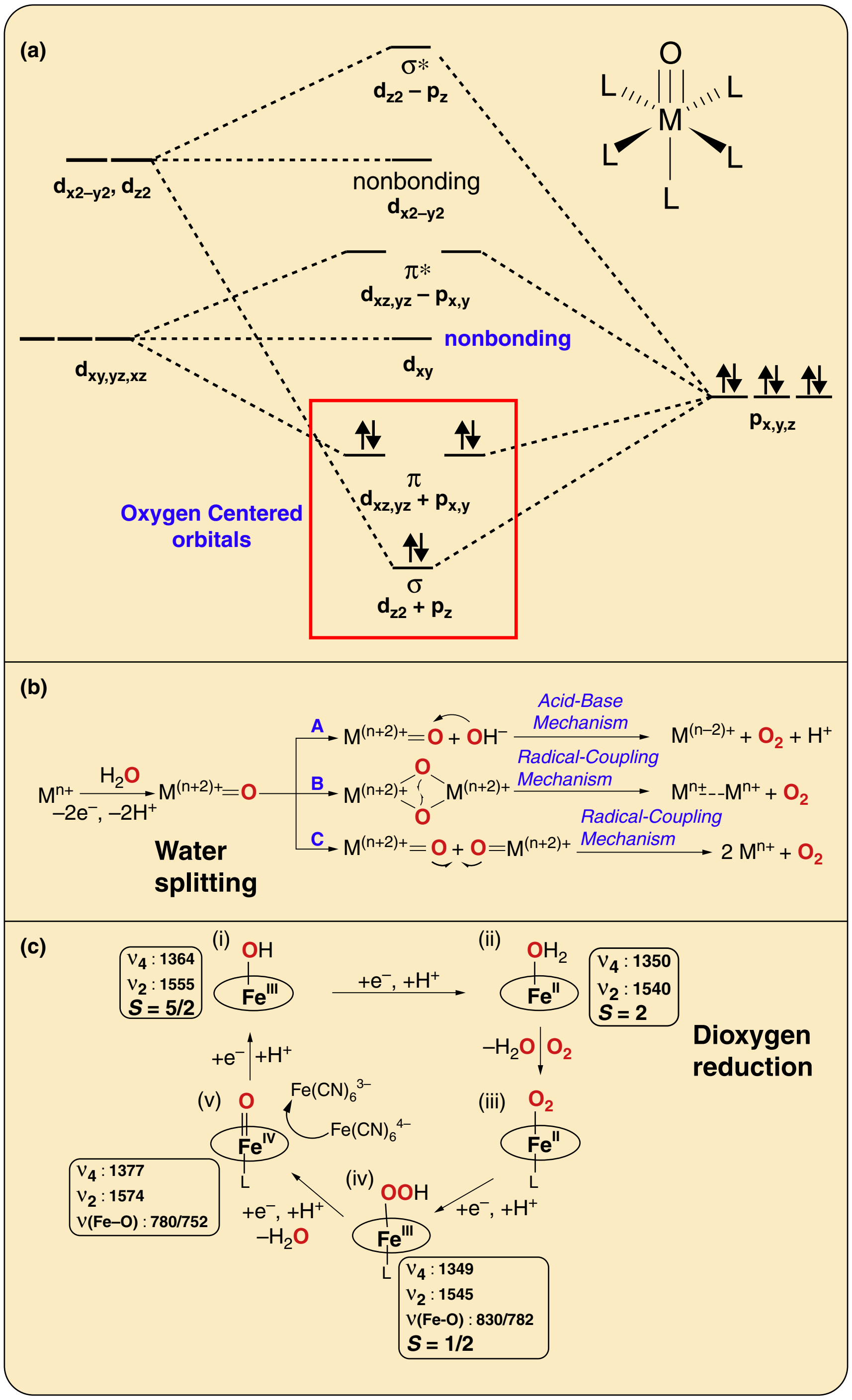
Introduction

The demand for fuel cell technology has increased sharply over the last three decades, as development has been driven by a growing awareness of issues related to anthropogenic climate change and an increase in global energy demand [1]. The most commonly used hydrogen fuel cell involves the oxidation of hydrogen to protons at a platinum anode and the four-electron reduction of O_2 to water at the cathode by Pt impregnated in carbon. The high loadings of this precious metal that are required to achieve appreciable activity have prompted the development of H_2 oxidation [2] and O_2 reduction catalysts [3] based on nonprecious metals. Furthermore, owing to issues of compression and storage, research has been on-going into alternative 'hydrogen-storage' compounds [4], that can guarantee similar performance in a more convenient form. Water is the ultimate candidate as a source for hydrogen underpinning the intense interest in creating artificial systems that use catalysts based on earth abundant elements to achieve the splitting of water into hydrogen and oxygen and their recombination to obtain clean energy in a closed-cycle fuel cell [5–7]. The oxidation of H_2O to O_2 is a four-electron, four-proton process in which O–O bond formation is the key chemical step [8–11]. In photosystem II, these proton-coupled electron transfer (PCET) reactions occur via a tyrosine that is in close proximity to the Mn_4Ca oxygen-evolving complex. Similarly, a range of other metalloenzymes achieve the the challenging tasks of dioxygen reduction [12–16] and hydrogen production [17,18] to fulfill the function of energy supply systems in biology by using cheap and non-toxic metals under ambient conditions of pressure and temperature. However, the large size and relative instability under aerobic conditions of many of these enzymes, and the difficulties associated with their purification process, has led to the search for well-defined molecular complexes for O_2 reduction, water oxidation and hydrogen production.

Advances in our understanding of the mechanism of biological systems may allow vital insights into the prerequisites necessary for the design of efficient catalysts for O_2 reduction and water oxidation by using cheap and readily available first row transition-metals under ambient conditions. High-valent metal-oxo cores have been proposed, and in few cases isolated, as the common reactive intermediates in these biological reactions relevant to renewable energy formation (Figure 1), thereby making them attractive targets for biomimetic synthetic studies. Recent synthetic advances have led to the isolation and characterization of several well-described metal-oxo model complexes, and detailed reactivity studies in conjunction with spectroscopy and theory have helped to understand how the steric and electronic properties of the metal centers modulate their reactivity [19–27]. Although the synthetic metal-oxo complexes have been found to be reactive toward substrates containing weak C–H bonds, in most cases the exhibited reactions are moderate and non-catalytic, with activities falling far short of the activity of the biological catalysts. Moreover, only in extremely rare cases they are found to be efficient in initiating O–O bond formation reactions. Similarly, evidences for the involvement of metal-oxo cores in

Figure 1



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(a) Molecular orbital scheme for a $[M(L)_5O]$ complex in tetragonal symmetry. **(b)** Different possibilities for the metal-oxo mediated O–O bond formation reactions. **(c)** General mechanism for the four-electron reduction of dioxygen to water; the marker bands of the individual intermediate species are given in boxes, with the ν(Fe–O) values ($^{16}O_2/^{18}O_2$) corresponding to those observed for $FeEs_4$ [28••].