Iron Redox Chemistry and its Environmental Impacts

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Abstract

This study confirms the growing interest in organic specialized solar cells (OPVs) using polymers as the main active layer. OPVs have gained significant attention due to their high sustainable energy conversion efficiency and the numerous advancements in this field over the past five years. High efficiency and long-term durability may be achieved by mass production of polymeric solar cells, which are very easy to manufacture. This review addresses the most significant issues in this area to enhance OPV devices' solar cells, architecture, performance, stability, and the state of polymer structure development. Thus, research has focused on practical and affordable photovoltaic systems, such as third-generation solar cells, that are easy to produce, have high portable efficiency, and are durable. Many people are interested in studying organic photovoltaics (OPVs) since this study says they have better sustainable energy conversion efficiency than others. The active layer of these cells contains polymers. The processing and mass production of polymeric solar cells allow for great efficiency and actual durability, and they are also easy to work with. This review addresses the most significant issues in this area to enhance OPV devices' solar cells, architecture, performance, stability, and the state of polymer structure development.

Keywords: Iron Redox Chemistry, Environmental Impacts, Organic Photovoltaics (OPVs)

Introduction

Oxidation-reduction reactions, often redox reactions, are chemical processes in which one or more chemical species change their oxidation state. Anschutz et al. (2005) state that the phrase encompasses many processes.

What is iron redox chemistry?
Iron (Fe) is found in greater abundance on Earth than any other redox-active metal. Various host rock lithologies, sediments, and soils include it as nanoparticles, accessory oxide, and ox hydroxide minerals; it may also prevail in the reactive mineral/water interfacial zone.

Iron redox reaction
This process is an example of a redox reaction involving oxidation and reduction. Rhodium ferrocyanide, or iron, is simply Fe. After oxidizing, iron loses some electrons and becomes positively charged, changing its electronic state from neutral elemental (Fe0) to ionic (Fe3+). Little oxygen is now present (Barnes et al., 2009).

Is iron reduced or oxidized
Iron is the reducing agent because its oxidation state changes from {0 3+}. Keep in mind that since oxygen is usually reduced to {2-}, we may infer that the oxidation state of iron in the final product is {3+} (from Fe2O3). Iron (Fe) is abundant on Earth more than any other redox-active metal. It occurs as nanoparticles, accessory oxides, and ox hydroxide minerals in a wide variety of host rock lithologies, sediments, and soils, and it can even dominate in the reactive mineral/water interfacial zone. Environmental cleanup is only one of several emerging uses for Fe oxide nanoparticles to take advantage of the catalytic characteristics of certain mineral surfaces. The interaction between these surfaces and aqueous solutions, organics, pollutants, and other components is greatly affected by their structure, charge, and chemical dynamics. We still don't fully understand how crucial environmental elements like microorganisms, oxygen levels, and natural organic matter impact things. Both living things and inanimate objects can influence important processes occurring at the interface.
Soils, sediments, and marine and lacustrine waters are among the many natural environments where these minerals may be found in their primary and secondary forms. The extremely low solubility of iron(III) (oxyhydr) oxides and the large quantity of iron in the Earth's crust cause this. Other minerals containing iron can also undergo phase transitions and give rise to them. Incorporating, adsorbing, and surface precipitating contaminants into particles—like MN, Ni, Cu, Si, rare earth elements, etc.—is possible throughout the creation process. Soils and groundwater both contain iron. Under some circumstances, it may wreak havoc on groundwater cleanup systems and is quick to participate in redox processes occurring below the earth. The influence of iron chemistry on groundwater is discussed in this column, which aims to provide a larger context.

Background
Iron makes up around 5% of the crustal mass on average. Soil iron concentrations can vary from 0.5 to 5 percent, depending on the soil's origin rocks, the methods of transport, and the soil's general geochemical history. As if its abundance weren't enough, iron is very reactive and clearly shows variations in ambient Eh and pH. Soil and groundwater systems affected by hydrocarbons are especially vulnerable. One form of iron in groundwater systems is reduced soluble ferrous iron (Fe+2), whereas the other is oxidized insoluble trivalent ferric

iron (Fe+3), according to Anderson and Benjamin (1990).

- A significant portion of the iron in shallow subsurface soils is oxidized ferric because of oxygen, which makes about 21% of the atmosphere. Iron hydroxide, also known as Fe (OH) 3, is a result of ferrous iron being oxidized and precipitated. Ferric hydroxide undergoes mineralization as time passes. The most common mineralized ferric iron forms in soils are magnetite (gamma-Fe2O3), lepidocrocite (gamma -FeOOH), hematite (alpha-Fe2O3), and goethite (alpha-FeOOH).

In this table, the iron oxides are presented in the order of increasing crystallinity and decreasing solubility. In neutral pH and oxidizing Eh conditions, the solubility of amorphous hydrous ferric oxide is three orders of magnitude higher at 0.6 μg/L when compared to goethite. Iron is present in high concentrations in several groundwater sources (Barrett & McBride, 2005). Additional processes are at work here.

Iron Complexing

- While ferric iron does not dissolve in water, ferrous iron does. Cathols, organic acids produced by aromatic ring cleavage, are one example of a byproduct of aromatic petroleum hydrocarbon biodegradation that may form soluble complexes with ferric iron and other inorganic and organic ligands. Groundwater in some locations became yellow or orange due to iron oxidation contamination. Many factors affect how long incomplete ferrous iron is to oxidize to a ferric state. Still, the most important ones are temperature, pH, the amount of dissolved oxygen, and the presence of other soluble ions. The time needed to finish the oxidation process increases as the temperature and pH decrease. Oxidation occurs more quickly in solutions with higher dissolved oxygen concentrations (Becker et al., 2001). Take this case in point:
- Ninety percent Fe+2 oxidation at pH 7.0 takes one hour at 21°C and ten hours at 5°C. At 21 degrees Celsius
- According to Z, the oxidation of Fe+2 takes 30 seconds at a pH of 8.0 and 100 hours at a pH of 6.0.

The crucial concentration of dissolved oxygen is two micrograms per liter. Ferrous iron oxidation is a sluggish process below that. Iron fouling of air strippers treating iron-rich groundwater is a common result of the aforementioned processes. Similarly, poorly built recovery wells that pump groundwater can have their screens clogged by these processes. Iron and other transition metals: potential applications and consequences. Pollutants in surface water, groundwater, and soil include organic solvents, hydrocarbons, pesticides, medications, personal care items, heavy metals, and pharmaceuticals. These pollutants are of particular concern because of their widespread usage and their grave dangers to aquatic life, human health, and the environment. Consequently, there has been much study into creating technologies that may remove contaminants from matrices. Thermal, physicochemical, chemical, and biological approaches are the main ways remediation technologies are often classified. The complexity of many polluted systems makes it difficult to design remediation strategies that can remove all toxins. Although older technologies have their uses, they can be time-consuming and expensive. Another problem is removing pollutants to a safe level quickly, efficiently, and at a fair cost (Borch et al., 2010).

Iron and manganese oxides predominate as redox-active components in oxide-rich settings, such as soils and sediments. These metal oxides are available as micro- and nano-sized particles, and their physical and chemical properties can vary greatly. They have an effect on a lot of procedures. Anaerobic decomposition of organic compounds, biogeochemical cycle, trace element availability, organic and inorganic pollutant mobility, redox transformation, and toxicity are all part of this. Soil and water contamination is a common problem, and several solutions have emerged to address this issue by utilizing Fe or MN chemistry. Redox processes mediated by Fe or MN have environmental protection and cleanup engineering applications. Iron remains the most significant reactive substance from an ecological and technological perspective. Various iron compounds have been investigated for their potential usage in environmental remediation technologies and their efficacy against various environmental contaminants. Micro/Nano size zerovalent metal particles, bimetallic reducing compounds, metal oxides/hydroxides, pillared clays, metal-supported silica, and others have been included. Research into the reductive transformation of halogenated chemicals, nitro compounds, and oxyanions using Fe0 or FeII-based materials is one of the most promising areas of study. Catalysts based on iron can be used in engineering to chemically oxidize stubborn contaminants through Fenton reactions. However, there is some evidence that manganese (III/IV) oxides can undergo the oxidative transformation of both naturally occurring organic compounds and xenobiotics. Manganese (III/IV) oxides are a promising class of chemicals with several possible uses in water and soil remediation because of their role in environmental oxidation-reduction processes. Not only that, but further research publications from contributing authors were also presented at the 2011 "Iron and Environmental Chemistry" workshop in Nancy, France (Colón et al., 2008).

Iron species, including their structure, characterization, and surface interactions, were the focus of the workshop's essential and practical aspects. Its secondary objective was to describe the pros and cons of Fe-mediated redox reactions and how they may be used in cleanup efforts.

Included in this special edition are eight papers that were all accepted. Most articles discuss iron's role in remediation procedures, specifically how Fenton oxidation (a modified form of iron) is used.

Microbiology and Iron

Depending on the circumstances, iron may easily be reduced or oxidized. As a result, ferrous and ferric iron redox couples are used in various metabolic activities inside microorganisms. One way to get ferrous iron from organic materials with less solubility is to use ferric iron as the last electron acceptor in biodegradation processes. In addition to anaerobic conditions, an appropriate form of ferric iron must be present. The microbiological availability of ferric iron minerals diminishes with increasing crystallinity. On the flip side, iron-fixing bacteria have a variety of mechanisms at their disposal, such as the ability to oxidize ferrous iron to ferric iron—even in environments with low oxygen levels—and the ability to remove carbon dioxide from ferrous bicarbonate, which leaves insoluble (Cwiertny et al., 2008).

This compound is formed by the precipitation of ferric hydroxide from organic acid complexes that include iron. When iron-rich groundwater is remedied, these reactions usually cause healthy screens, pipe systems, and air strippers to foul with iron (Danielsen & Hayes, 2004).

Effect of Temperature on ORP Sensors

The above Nernst equation states that the ORP is proportional to the sensing system's temperature. In a solution, each redox pair's relative importance determines the magnitude of the temperature impact. Because the presence of electroactive species in a solution is often uncertain, ORP sensors do not often account for temperature. Calibration of ORP sensors must be done at the same temperature as the measurement for them to be used correctly. Because of this, some manufacturers offer tables that show the relative optical potential (ORP) values for the reference electrode and the calibration standard solution at various temperatures (Davis, 1984).

The leap from general chemistry to environmental reduction-oxidation chemistry can be difficult since the field combines biology and geochemistry in novel ways. Microbial respiration is the process that propels reduction-oxidation reactions in the natural world. The connection between cellular metabolism and the environment is established by a network of electron-transfer processes. According to Dimirkou et al. (2002), microbes may release the chemical energy held in reduced carbon compounds by using electron acceptors such as carbon dioxide and molecular oxygen.

Environmental reduction-oxidation chemistry makes use of a variety of electron acceptors that are produced by microbes via the oxidation of biomolecules, organic compounds, and organic waste when oxygen is not present. Therefore, most reduction-oxidation reactions in the environment occur in the zone of biological activity, which is also where organic carbon accumulates.

Biological activity levels govern the creation of zones characterized by the dominance of specific reduction-oxidation processes and the progression of reduction-oxidation reactions in the environment. For molecular oxygen to not be present, conditions must decrease to anoxia, characterized as a very low concentration of O2(aq) in the air. While oxygen (O2) is the final electron acceptor in aerobic respiration, environmental microorganisms begin to employ other electron acceptors in anaerobic respiration as hypoxia progresses (Eary & Rai, 1987).

The electrochemical potential drops due to a chain reaction involving oxidation and reduction that occurs as a consequence of anaerobic respiration, which in turn couples the reduction-oxidation events required for aerobic respiration with changes in microbial communities and respirational mechanisms, allowing for chemical reduction in the environment (Elsner et al., 2004).

Because they influence the bioavailability and mobility of several elements, electron-transfer processes play a crucial role in environmental chemistry. Making the leap from general chemistry to environmental redox chemistry can be difficult since it combines biology and geochemistry in novel ways. The electron transport chain, an essential part of respiration, is the engine that drives environmental redox reactions. According to Environmental et al. (2010), respiration involves a web of electron-transfer processes that releases the chemical energy of reduced carbon molecules by using electron acceptors such as molecular oxygen and carbon dioxide.

Respiration is the original process that gives rise to environmental redox chemistry. During respiration, a number of oxidizing agents take electrons from reduced carbon compounds, such as biomolecules, organic compounds, and organic waste. Organic carbon accumulates in the zone of biological activity, where the majority of environmental redox reactions take place (Gao et al., 2018).

The establishment of zones where particular redox processes dominate, and the advancement of environmental redox reactions are controlled by the degree of biological activity. Conditions with a low concentration of dissolved molecular oxygen, known as anoxia, are required for lowering conditions but are insufficient. Anoxia develops and alters the active microbial population from communities that rely on aerobic respiration to anaerobic respiration, where various chemical substances support respiration instead of molecular oxygen (Ge & Qu, 2003).

Anaerobic respiration reduces the redox potential, which in turn couples the redox reactions required for biological respiration with a multitude of other redox reactions, resulting in a shift in the microbial community and setting the stage for a chemical reduction in the environment (Génin et al., 2001).

There are three main parts to this chapter. To close the knowledge gap between environmental and general chemistry, we will review the fundamentals of redox chemistry. The second one improves the methods used by geochemists to determine and comprehend redox conditions in the natural world. As mentioned earlier, the mechanism that causes soils and groundwater to become acidic is known as anaerobiosis, which is microbial respiration devoid of molecular oxygen. According to Suthersan (2001), anaerobic respiration is structured as an electron transport chain connected to certain ambient electron acceptors, and it produces chemicals that are defined by reducing circumstances. Aerobic settings are indicated by values more than 100 mV, whereas anaerobic situations are indicated by values less than -100 mV. Tables 8.2 and 8.7 show that, at low dye concentrations, the effluents had dissolved oxygen (DO) values between 6.0 and 7.5 mg/L and a redox potential between -32 and -6 mV, respectively. It is possible that the effluent was passively aerated during the sample collection and measurement processes. According to this research, dye degradation may have happened in aerobic and anaerobic environments (Gorski & Scherer, 2009).

Redox reactions are chemical processes in which two molecular species exchange electrons. The two species might be organic or inorganic regardless of the ambient phase (gas, liquid, or solid). A complete redox reaction involves the reduction of one species to its more reduced state followed by its oxidation, or loss of an electron or electrons, by another species. On the flip side, the other species is reduced (takes on one or more electrons) when it enters the reaction in its more oxidized state. Illustrates this procedure in a schematic form. Microbes speed up many redox processes crucial to the environment, but these reactions can only happen when the thermodynamic conditions are right (Gorski & Scherer, 2011).

As mentioned above, tono region mineralogical findings are consistent with redox interpretations grounded in the chemistry of contemporaneous groundwaters. As a qualitative indicator, ferric oxyhydroxides in sedimentary strata at depths less than 30 meters below ground level suggest somewhat oxidizing circumstances. On the other hand, these rocks contain pyrite, which can only be stable in reducing environments at depths over 60 meters. According to Gu et al. (1994), the diagenesis of the Upper and Lower Toki Lignite-bearing Formations led to the precipitation of framboidal pyrite by microbially driven sulfate reduction.

Iron Oxides and in-situ Metal/Organic Adsorption

Amorphous hydrous ferric oxide is an amphoteric ion exchange medium because it can give hydroxyl ions (OH-) for anion exchange or hydrogen ions (H+) for cation exchange. Amorphous ferric oxide may absorb around half a millimole of ionic substance per gram as a general guideline. Complexes of ions include organic compounds that have been ionized, cations of heavy metals, and oxyanions of chromium, arsenic, or selenium. Iron oxides primarily interact with organic compounds soluble in water through their carboxyl and hydroxyl functional groups. For example, consider the organic acids produced during the biodegradation of petroleum hydrocarbons. Morphology and Formation Changing Ferrihydrite into Hematite with Tartaric Acid Encounters several environmental systems use hematite, an iron oxide most stable in soils and sediments and whose common precursor is ferrihydrite. Tartaric acid (L-TA), a prevalent reducing agent in soils, can convert ferrihydrite to hematite by reducing Fe3+ to Fe2+. Here, we looked examined hematite synthesis using L-TA under several conditions, including different starting suspension pH, different aging durations, and different concentrations of L-TA. The objects were analyzed using a combination of X-ray diffraction (XRD), scanning electron microscopy (SEM), and high-resolution transmission electron microscopy (HRTEM). How quickly the hematite solution transformed and what shape the final particles took were both impacted by the initial pHi at which L-TA was injected. The ideal pHi values for a 10-hour aging period at 100 °C with a molar ratio of 1.0% L-TA to Fe(III) were 7 and 11, respectively. After about 20 hours of aging at 100 °C and pHi 7, the transformation was optimized using an L-TA/Fe(III) molar ratio of 1.0%. A dissolution and crystallization process brought about the alteration. The 84 m2/g crystalline corn-like particles were produced using a guided attachment synthesis. Saturating the ferrihydrite surface with L-TA at a molar ratio of 3.0% for Fe(III) hindered the transition. According to Huang et al. (2019), subrounded crystalline particles were produced after aging L-TA/Fe(III) at a concentration of 1.0% for 10 hours at 100 °C.

Mechanisms of Redox that Influence the Iron(II) Flux from Peruvian Shelf Sediments to the Oceanic Mid-Latitude Zone

Distinguishing Biotic and Abiotic Iron Oxidation at Low Temperatures

Due to repeated flooding and drainage, the redox state of paddy soils can change during the rice-growing season. This change may lead to the reductive breakdown of iron oxides and the subsequent formation of iron-containing secondary minerals in rice paddies. The mobility and bioavailability of iron in paddy soils are strongly influenced by the chemical properties of cadmium (Cd) and other metal contaminants. Thus, this work offers a brief synopsis of findings regarding Fe redox changes in paddy and their effects on Cd availability to rice. In this study, we look at some of the latest thinking on iron in paddy soils, the reactions that happen during iron oxidation-reduction, the chemical factors that affect iron redox processes, the amount of Cd that rice can absorb, and how iron transformation affects rice's capacity to translocate Cd. Some directions for future research on iron's effects on the environment (Huang et al., 2019b).

Reducing iron(III) oxide-containing minerals is crucial in the subsurface iron cycle process. To fuel their expansion, certain bacteria, for instance, use a process that combines carbon oxidation and iron reduction. Despite iron oxides' weak electrical conductivity, transferred electrons to an iron oxide material can jump from one iron atom to another using thermal energy. Recent research has used time-resolved X-ray absorption spectroscopy to determine the hopping rates for many phases of iron(III) minerals, confirming a theoretical model of how an electron at one place modifies the locations of neighboring atoms. The processes that change soil mineralogy when decreasing conditions are created by geochemical or biological factors are further explored in this work (Huang Zhang, 2019b).

One of the most common minerals on Earth, iron oxide, and its behavior and impacts on the land and water around it are illuminated by this. This supports the idea that sub-nanoscale chemical reactions in different semiconductors may be studied with time-resolved optical and X-ray methods. Scientists have long known that certain minerals, ions with redox potential, and proteins from living organisms may cause chemical reactions within minerals through the exchange of electrons. But up until now, it was impossible to examine the pace at which electrons hop between atoms inside a nanoparticle to induce change. This research may have provided different results since the same process controls charge collecting in solar energy devices made of metal oxides. Iron's alterations due to electron transfer from other minerals, water, or biological factors are crucial to several important chemical reactions, and iron is everywhere. Elevation of iron(III) oxides causes the substance to gain iron(II) sites. The iron(II) site is not permanent since electrons can go to other places. Soil and surface water mineralogy and chemistry can drastically alter when an electron hops to an iron atom on a mineral's surface, releasing the soluble iron(II) atom into solution (Huang et al., 2018).

The mobility of environmental pollutants is a key reason why iron reduction is crucial. The alteration can also impact the spread of uranium and other pollutants that bind to iron. While larger-particle iron can capture pollutants in filter systems, a soluble form of iron can assist in disseminating the pollution. Understanding the electron hopping rates, which govern iron oxides' reactivity and dissolution rates, will aid in administering some pollutant cleanup operations (Gorski & Scherer, 2009).

"We believe that this work is the starting point for a new area of time-resolved geochemistry," stated Benjamin Gilbert, a scientist at Lawrence Berkeley. "Time-resolved science aims to comprehend the mechanisms of chemical reactions by creating different types of movies" that show the motion of atoms and electrons in real-time during reactions. These concepts and methods have been brought into geochemistry, and we look forward to the future (Gorski & Scherer, 2009).

Recent developments in light source technology have made electron transfer visible by allowing scientists to capture a rapid sequence of images to follow the electron's motion through the iron oxide. The time required for the travel ranges from picoseconds to nanoseconds, influenced by temperature and iron oxide structure. Lead author of the Science article, Jordan Katz, now a scientist at Denison University and formerly of Lawrence Berkeley, said that, like a sports photographer needs a fast shutter speed to capture a moving subject without blurring, observing electron motion required a very brief and intense pulse of X-rays. The X-rays used in this study were produced at Argonne National Laboratory's Advanced Photon Source, as stated by Huang et al. (2019).

The researchers had to come up with a different technique to start the process than adding an electric charge because iron oxide is a semiconductor. They brought a pump-probe method from nano photovoltaics to ultrafast science. First, an electron was injected into the iron using laser light to activate a dye molecule that was surface-sensitive. Researchers from the Center for Nanoscale Materials demonstrated the very rapid light-initiated electron transport using femtosecond optical transient absorption spectroscopy. This speed was faster than their goal, thermally-driven electron hopping. The scientists then used very short bursts of X-rays, similar to the shutter of a camera, to take several pictures of the lightning-fast electron transfer process. Following that, an X-ray spectrum spanning sub-nanosecond time intervals was collected, illuminating the electrons' positions. Exploring the mechanisms of electron transport in both natural and artificial materials, including solar cell efficiency-enhancing nanofilms, might be possible with this technique. Xiaoyi Zhang, a physicist working at the American Physical Society, said, "This opens up studies with many other semiconductor materials." Solar cell research, hydrogen production, catalysis, and electrochemical (battery) energy storage may all benefit from the same approach of initiating reactions using light-induced electrons. The findings might provide light on the inherent energy or electron transport of materials, according to Huang et al. (2019).

The APS is uniquely situated to undertake this type of study.

"We used two different specialties of the APS," stated Karena Chapman, a scientist with the association. The American Physical Society (APS) is a major center for research on nanoparticle dynamics. We can only gain a comprehensive understanding of the increasingly complicated materials we study by integrating our findings from several methods and beamlines (Gorski & Scherer, 2009).

Beamline 11-ID-D provides a detailed look at individual electron hops by letting scientists study activity on many time scales, which reveals all the mechanics underlying energy or electron transfer. The next upgrade to the APS will let scientists see events occurring at a rate greater than 80 picoseconds, or 80 trillionths of a second. Lastly, the scientists will be able to see the process as an electron is injected into the iron or another semiconductor from the photosensitized molecule. Such a process takes a few picoseconds.

Iron-Based Redox Switches in Biology

Due to its exceptional electrochemical characteristics, several biological processes rely on iron as a redox-active cofactor. Iron is used as a cellular redox status sensor in addition to its critical functions in respiration, central metabolism, photosynthesis, nitrogen fixation, and related processes. Iron-based sensors respond to changes in cellular redox status by regulating protein activity through heme, mononuclear iron sites, and Fe-S clusters, which operate as switches. Proteins that serve as iron-based redox sensors in prokaryotes and eukaryotic creatures are reviewed here based on their biochemical descriptions. Redox sensors using Fe-S clusters are the main focus of this work. However, proteins that use heme or novel iron sites are also included (Huang et al., 2019).

Conclusion

Every living thing requires cellular redox status sensors. Due to the high levels of reactive oxygen species (ROS) produced by aerobic respiration, it is essential to keep an eye on oxidative stress and regulate antioxidant systems in these organisms. Obligatory anaerobes must engage stress-response pathways to protect themselves against oxygen and reactive oxygen species (ROS), such as H2O2. Photosynthesis evolved to increase oxygen production to present levels, even though the early Earth was probably anaerobic. One consequence that relies on iron chemistry is the neutralization of H2O2 by mini ferritins, also known as Dps proteins, which Archaea—modern-day "proxies" for ancient anaerobic organisms—developed. Facultative anaerobes adjust their metabolism to accommodate fluctuating oxygen levels by balancing aerobic, microaerobic, and anaerobic processes. The proper functioning of several cellular functions depends on maintaining a specific, limited redox potential window within the cell or its organelle (in eukaryotic creatures).

The coordinated control of antioxidant systems and redox-dependent activities requires a highly sensitive component to changes in the cellular redox environment. Several redox-sensing proteins accomplish this task using thiol residues found in reactive proteins. Chemical modification, selective oxidation, or reduction of these sensor thiols modify protein function and signal transmission in response to redox oscillations. Because of their high sensitivity to both H2O2 and nitric oxide (NO), protein thiols are frequently used as in vivo H2O2 sensors.

However, transition metals whose oxidation states are sensitive to physiologically relevant redox changes can also perform this function. The redox signal might be transformed into a protein frame by altering the coordination number and preferred ligands of specific transition metals through oxidation or reduction. Several applications involving redox processes are associated with iron, in particular. Iron ranks among the Earth's crustal elements in terms of abundance. The fact that iron can change oxidation states and possesses half-filled d orbitals classifies it as a first-row transition element. Several iron enzymes have reaction intermediates that are at higher oxidation levels in their catalytic cycle. On the other hand, ferrous iron ions (II, d6) and ferric iron ions (III, d5) are the two most prevalent oxidation states for iron. Incorporating iron ions into biological activities was easy in the early phases of evolution due to their redox characteristics and availability; these ions are still crucial in modern processes including respiration, photosynthesis, and nitrogen fixation. Iron also reacts with reactive oxygen species (ROS) such as superoxide and hydrogen peroxide. O2 is spin-restricted and unable to absorb pairs of electrons in its lowest energy state, where it is in the triplet spin state. Iron and other transition metals may oxidize oxygen despite the spin constraint because they can give or receive single electrons. The direct conversion of H2O2 to hydroxyl anion and very reactive hydroxyl radical was shown by Fenton over a century ago using ferrous iron. When iron and oxygen metabolites react, hydroxyl radicals are produced, which may damage proteins, lipids, and nucleic acids. The consequences for all forms of life on Earth are dire. Iron, on the other hand, has found new use as a sensor for reactive oxygen species (ROS) and oxygen because of its sensitivity to both chemicals. The reactivity of the metal center may be modulated by carefully attaching iron or an iron cofactor to a polypeptide chain, creating a sensor. A change in protein activity is the biochemical outcome of a regulated iron-mediated redox process, and proteins provide the structural framework necessary to do this.

I will quickly go over the several iron cofactors that are present in protein active sites before I get into the many instances of redox sensors that use iron. A mono-or dinuclear iron core may be generated when an amino acid directly coordinates iron in a polypeptide chain.

Various iron ligands are used in accordance with the iron oxidation state. Certain amino acid side chains, such as His, Cys, and Met, include sulfur and nitrogen ions that are most compatible with ferrous iron (Fe2+), an acid that has a tendency to attach to soft bases. As a powerful Lewis acid, ferric iron (Fe3+) forms strong bonds with the oxygen in the aspartate and glutamate side chains. Cells may produce a variety of cofactors, including the more common iron-only centers and more complex Fe-S clusters arranged in planar [2Fe-2S] or cuboidal [4Fe-4S] patterns. Porphyrin structures, particularly protoporphyrin IX, may also benefit from iron, which can aid in heme synthesis. The following is an expanded description of the mechanisms by which different iron cofactors bind to the active sites of proteins.

Unique properties of Fe-S clusters

Proteins include complex cofactors called Fe-S clusters, composed of iron and inorganic sulfide. Cysteinyl sulfur is one of the most prevalent (but not the only) binding partners for Fe-S clusters in protein active sites, according to Bang et al. (2019). The majority of Fe-S clusters seen in nature are tetranuclear [4Fe-4S] clusters, which have low potentials (about -300 mV) and undergo the [4Fe-4S]2+,+ redox transition. Despite this, several enzymes have [2Fe-2S] clusters and other more complex Fe-S clusters, such as nitrogenase's [8Fe-7S] P cluster (11). In healthy conditions, the predicted redox potential window extends from -600 to +500 mV, and an examination of the proteins comprising Fe-S clusters reveals that most of these proteins span this whole range. Adjusting the redox potentials of Fe-S clusters is necessary for redox-sensor proteins to detect certain oxidants at a medically acceptable concentration threshold. This remarkable property of Fe-S clusters compels us to swiftly survey the myriad of elements that influence the redox potentials of these clusters when bound to proteins.

Ligands have a profound effect on the redox potential of Fe-S clusters. Binuclear [2Fe-2S] Reiske proteins, for instance, have two His residues substituted with imidazolyl groups for two cysteinyl sulfur ligands (Huang et al., 2019). When compared to [2Fe-2S] ferredoxins with complete Cys cluster ligation, the redox potential of Reiske Fe-S proteins is roughly 100 mV higher because of the switch to more neutral cluster ligands. Cluster redox potential is affected by the amount of hydrogen bonding between sulfur ligands in the cluster and the protein backbone or side chains. Hydrogen bonding often raises the reduction potential of a given cluster type, stabilizing its reduced state and decreasing the likelihood of oxidation. As a result of competition between hydrogen bonds and transfer of charges from sulfur to iron, the sulfur ligands' negative charges increase. The correlation between the amount of hydrogen bonds and the absolute change in cluster redox potential is not necessarily linear. But in one instance, the relative reversal of one main-chain NH-S hydrogen bond caused a substantial shift in redox potential between two otherwise similar [2Fe-2S] clusters.

Electrostatic interactions also play a role in regulating redox potential. The result can be greatly affected by the protein's overall shape and, in particular, by the orientation of the amide dipoles concerning the cluster. Nearby charged amino acid side chains will likewise have an electric influence on the cluster. Finally, the quantity of solvent exposure, also known as cluster solvation, is a critical property many proteins use to modify the Fe-S cluster redox potential. The most well-documented example of solvent effects is seen in studies that compare HiPIPs to low-potential bacterial ferredoxins (Fds). While both enzymes use [4Fe-

4S]2+ as their cluster starting point, the reduction potential in HiPIP clusters can be anywhere from +100 to +400 mV. Contrarily, Fd clusters oxidize to the [4Fe-4S]3+ state because their reduction potential is −300 mV or lower. Structural studies show that the HiPiP cluster is located deep inside the protein. While the Fd cluster on the protein's surface is partly accessible, it is largely inaccessible to solvents.

When comparing cluster Fd covalency to HiPIP, a careful examination of the covalency of the Fe-S bonds in all protein types shows a decrease. This effect was recently caused by hydrogen bonding between Fd clusters and water (cluster solvation). Similar findings regarding the HiPIP cluster were documented in the aforementioned study.

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