

Environmentally Benign Catalysts Based on Heteropolyacids for
Clean Organic Transformations
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Electrochemical/Electrocatalytic Applications of Polyoxometalates

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1. Introduction

Polyoxometalates (POM) are a large family of discrete molecular, self assembled nano-sized anionic metal-oxygen cluster systems composed of edge- and corner-shared MO_6 octahedra where $M = Mo^{VI}, V^V, Nb^V, Ta^V$ and so on [1]. They possess versatile nature in terms of structure, size, high molecular mass, rich redox chemistry, photochemistry, electron and proton transfer/storage abilities, fair thermal stability and lability of the lattice oxygen. These systems have found applications in multidisciplinary areas such as materials [2], nanotechnology [3], medicine [4], surfaces [5], catalysis [6], colloid science [7], electronic materials, [8], sensors [9] and magnetism [10]. These applications are based on the possibility of multiple electron transfer giving rise to lacunary species.

Among the available polyoxometalates, the Keggin-type has received much of the attention. Salts of Keggin-type POM can be classified into two groups: Group A (containing small metal ions like Na^+) and Group B (containing large metal ions like Cs^+). Group A salts show characteristic features such as (i) low surface area, (ii) high solubility in water and (iii) capacity to absorb polar molecules in the bulk. On the other hand, Group B salts have the following characteristics: (i) high surface area, (ii) insolubility in water and (iii) do not absorb molecules.

The Keggin-type POM is an assembly of three kinds of structures, namely, primary, secondary and tertiary structure [11]. In Fig. 1 the schematic representation of the hierarchical structure of the Keggin-type POM is shown.

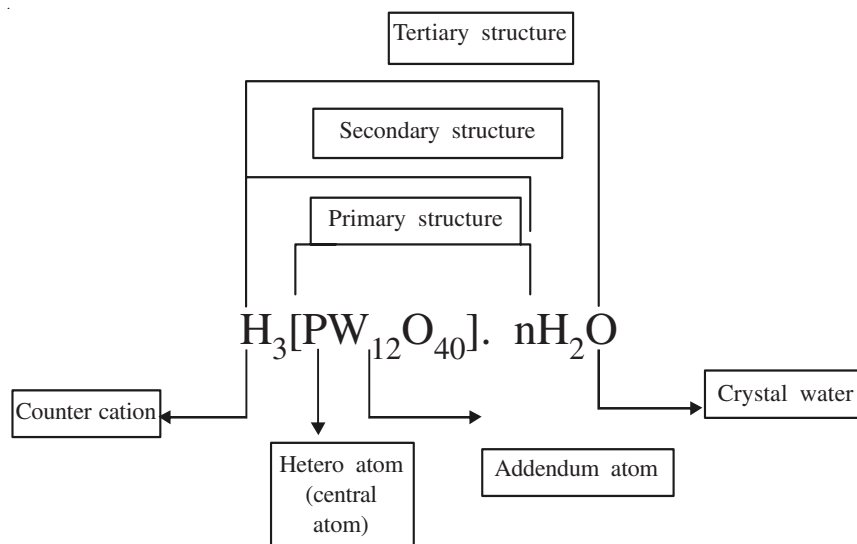


Fig. 1. Primary, Secondary and tertiary structure of Keggin type POM.

The important features such as multi-functionality and structural mobility make POMs unique materials for catalytic applications. The catalytic reactions can be carried out in homogeneous as well as heterogeneous systems. Earlier, POMs were used both in solution and in solid state as acid and oxidation catalysts. In fact, a number of industrial processes [11] have been developed using POMs as catalysts. POMs have been used for a variety of reactions, for example, the formation of carboxylic acids from the corresponding carbonyl compounds, as well as for the dehydrogenation of alcohols, aldehydes and carboxylic acids to form C=C and C=O bonds [12]. A number of vapour-phase oxidation reactions like oxidation of methacrolein and methane have also been developed as industrial processes [13].

Based on POMs' hierarchical structure, it can be demonstrated that there are three completely different modes of catalysis for solid POMs. These are shown pictorially in Fig. 2.

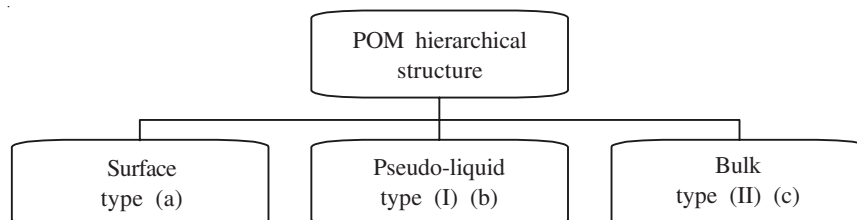


Fig. 2. Three types of catalysis for solid POMs: (a) surface type, (b) pseudo-liquid bulk type (I) and (c) bulk type (II).

POMs are promising solid acids and can replace environmentally harmful liquid acid catalysts such as sulphuric acid [14]. Liquid acids are corrosive and produce a large amount of waste; replacement of the liquid catalysts with 'water tolerant' solid acid catalysts are desirable for developing environmentally benign processes. However, it should be remembered that a high acidity may lead to undesired side reactions and can also lead to quick deactivation due to the formation of heavy by-products. In addition to the various advantages in using solid acids, catalytic reactions can be carried out under milder conditions. In addition the molar catalytic activity of POMs is 10^2 – 10^3 times higher than that of mineral acids.

In principle, mechanisms of homogeneous catalysis by POMs and by ordinary mineral acids are of the same origin. However, since protons are in an encapsulated environment in POMs, the proton transfer reactions are amenable for control.

POMs containing electrochemically inert heteroatoms exhibit redox properties that are attractive for electro-catalysis. The addenda atoms are present in their highest oxidation state in d^0 or d^1 electronic configuration. The electrons are accepted by the addenda ions and if they are identical, the electrons are delocalized on the structural framework by rapid electron hopping or through bridging oxygen ions. The possibility of a given metal ion to accept an electron depends on its nature. There are many examples in the literature of POM clusters with a high number of metallic electrons and are hence even termed as reservoir of electrons [1]. Thus, POMs can undergo electrochemical reduction with retention of the geometry.

Electrochemical investigations of Keggin-type POMs in aqueous or non-aqueous solutions have revealed a sequence of reversible one- or two-electron reduction steps [12]. On reduction, the POMs are converted into heteropoly-blues-mixed valence systems which are intensely blue coloured as a result of intervalence electronic charge transitions. The feature of heteropoly blue formation is a rapid and reversible reduction process. Electronic spectra of reduced POMs show intensified d – d bands in the visible region and intervalence charge transfer (IVCT) bands in the near IR-region.

POMs are many electron oxidants. The limiting number of electrons accepted by a POM molecule without decomposition depends on its composition and reduction conditions and it can reach six or more electrons [15].

The redox processes of POM anions can be studied by several electrochemical methods. By a continuous change of their composition, their redox potentials can be chosen to span a wide range. In solution, the reduction potentials of POMs containing Mo and V are high, as these ions are easily reduced. Oxidative ability decreases generally in the order $V > Mo > W$ -containing POMs. The nature of the heteroatom affects the overall charge of the POM.

2. Electro-catalytic Applications of POMs

The features of POMs such as high stability of most of their redox states, tunable redox potentials without affecting their structure, possibility of multiple electron transfers make POMs attractive as redox catalysts (mediators) for indirect electrochemical processes. In indirect electrochemical reactions a mediator is activated by a heterogeneous redox step at the electrode surface in order to react homogeneously with the substrate in the bulk solution, regenerating the inactivated mediator. Heterogeneous electron transfer between the electrode and the substrate is sometimes slow because of poor interaction. In these cases the electrode reaction occurs only at high over-potentials. Electro-catalysts can minimize the activation energy and hence allow such an electrode reaction to occur at high current density, close to the equilibrium potentials or even considerably below it. Furthermore, suitably designed electro-catalysts can improve not only the reactivity but also the product selectivity. Passivation or film formation on the electrode surface can easily be avoided. Thus, electro-catalytic methods are important for the development of both preparative electrolysis and electrochemical sensors. A large number of organic and inorganic compounds and metal complexes, including biomolecules, have been successfully used as electrocatalysts. However, the number of highly selective and long-time stable redox catalysts is still limited. In this sense, POMs and their transition metal-substituted derivatives have the potential to fill this gap. POMs tend to undergo spontaneous adsorption from aqueous solutions on various electrode substrates like Hg, Au, Ag, glassy carbon and highly oriented pyrolytic graphite (HOPG). Toth and Anson [16] evaluated the electrochemical reduction of nitric oxide and nitrite to ammonia with $(\text{Fe}^{\text{III}}\text{H}_2\text{O})\text{XW}_{11}\text{O}_{39}^{n-}$, where X = Si or Ge ($n = 5$), P, As ($n = 4$), and found the catalysts to have long-term durability. Rong and Pope [17] reported the electro-catalytic oxidation of sulphoxide to sulphone by $\text{Ru}^{\text{V}}(\text{O})\text{PW}_{11}\text{O}_{39}^{4-}$ with greater than 90% current efficiency. Rong and Anson [18] found that benzyl or ethyl alcohol was slowly oxidized to aldehyde by $(\text{CrO})\text{PW}_{11}\text{O}_{39}^{4-}$ generated electrochemically. Steekhan and Kandzia [19] reported the electrochemical cleavage of styrene derivatives to benzaldehydes catalyzed by $\text{RuSiW}_{11}\text{O}_{39}^{5-}$ in a multiphase system.

2.1 Electro-catalytic Reduction: Hydrogen Evolution Reaction

POMs have been used as reductive electro-catalysts for (i) homogeneously dissolved in electrolyte solution and (ii) attached to the electrode surface. Keita and Nadjjo [20] have reported that $\text{SiW}_{12}\text{O}_{40}^{4-}$ can catalyze hydrogen evolution reaction and oxygen reduction in acidic aqueous and organic solutions. The reactive species for the hydrogen evolution reaction are two- or four-electron reduced species, with the four-electron reduced species being more active. For oxygen reduction the first one-electron species is active.

2.2 Amperometric Sensors for Hydrogen Peroxide

POMs have also been used as electro-catalysts for hydrogen peroxide reduction and determination. H_2O_2 sensors are of biological importance. $\text{H}_3\text{PW}_{12}\text{O}_{40}$ is immobilized on the Pt electrode by sol-gel method which is formed using tetraethoxysilane, polyethylene glycol, benzylethyl ether and $\text{H}_3\text{PW}_{12}\text{O}_{40}$. The electrochemical behaviour of the modified electrode is characterized using cyclic voltammetry and found that they show three two-electron redox couples and the electrode is stable for several runs.

2.3 Role of POMs in the Electrochemical Methanol Oxidation

In the last few years, the research on POMs towards electro-catalytic applications has been a topic of widespread technological importance. Ref. [21] has not been cited. Nakajima and Honma [22] employed POM-coordinated Pt catalyst for methanol oxidation. Chojak et al. [23] utilized layer-by-layer method to link Ru-stabilized Pt nanoparticles with POMs to form electro-catalytic network films. It was found to be efficient towards methanol oxidation due to the presence of tungstate units from $\text{H}_3\text{PW}_{12}\text{O}_{40}$ which can provide additional $-\text{OH}$ groups capable of facilitating oxidation of intermediate (CO_{ads}) on Pt. Pan et al. [24] utilized the chemisorptive ability of POMs to modify carbon nanotubes (CNTs) with POMs to form POM-CNT composites. Pt and Pt-Ru nanoparticles were electrochemically deposited on POM-CNT composites and employed as electro-catalysts for methanol oxidation. High specific activity was observed for catalysts containing POMs when compared to POM-free electro-catalysts. Keita et al. [25] utilized $\text{Mo}^{\text{V}}-\text{Mo}^{\text{VI}}$ mixed polyoxometalates for the preparation of POM modified Pt and Pd nanoparticles and shown them as efficient electro-catalysts for methanol and ethanol oxidation. In addition, Pt-POM composites were found to be resistant to poisoning during methanol oxidation. Seo et al. [26] reported 50% higher mass activity and improved stability for POM-modified Pt/CNT catalysts than the POM-free catalysts. Ferrel et al. [27] modified Pt/C with POMs and found a higher performance towards methanol oxidation. This was attributed to the reduced resistance towards charge transfer in Pt/C when modified with highly conducting POM. Due to their electrochemical redox properties and oxidizing abilities, POMs can be potential oxidizing agents. They have proved to be efficient catalysts towards various kinds of oxidation reactions. The data given in Table 1 compares the activity of Pt/C with other electrodes modified by silicotungstic acid (STA) [28].

The points that emerge from data presented in Table 1 are:

- (i) The onset potential for methanol oxidation on Pt/STA is 100 mV less positive than Pt/C electrode and 60 mV less than Pt-Ru/C electrode, showing the better electrocatalytic activity of STA-containing electrodes.

Table 1. Comparison of electro-catalytic activities of various electrodes towards methanol oxidation [28]

Catalyst	EAS (m ² g ⁻¹)	Onset potential (V)	I_f/I_b	Mass activity (mA g ⁻¹ Pt)	Specific activity (mA cm ⁻² Pt)
Pt/C	23.3	0.41	0.80	191	0.81
Pt/STA-C	33.0	0.31	1.11	37	1.12
Pt-Ru/C	17.2	0.30	0.91	204	1.18
Pt-Ru/STA-C	25.6	0.24	1.05	53	1.96
Pt-Ru/C (J.M.)	22.5	0.25	0.95	271	1.20

- (ii) The mass activity follows the order Pt-Ru/STA-C > Pt/STA-C > Pt-Ru/C (J.M.) > Pt-Ru/C > Pt/C.
- (iii) The values of I_f/I_b show that the STA-containing systems show effective removal of the poisoning species on these catalysts.

2.4 Electrochemical Oxygen Reduction Reaction by Pt/STA-C

Kulesza et al. [29] utilized chemisorptive ability of POMs on metal surfaces to form anionic monolayers of POMs on Pt surfaces and immobilized within ultrathin polyaniline film using layer-by-layer method. The formed network films containing POMs were employed as promising electro-catalysts for oxygen reduction reaction. Giordano et al. [30] employed POMs as surface promoters for oxygen reduction. Lu et al. [31] mixed H₃PW₁₂O₄₀ solution with Pt/C and the resulting slurry was coated on glassy carbon electrode and employed as electrode for oxygen reduction reaction in acid solution. The activity was found to be enhanced by about 38% when compared to Pt/C electrode. Karnicka et al. [32] fabricated multilayer network films of conducting polymer, POMs and Pt metal particles on electrodes to combine the attractive physico-chemical properties and reactivity of these materials. Wlodarczyk et al. [33] functionalized Pt nanoparticles coated on glassy carbon with ultrathin films of POM by dip coating method. The resulting electrode was utilized for electro-reduction of dioxygen in acid solution. The activity was found to be enhanced when compared to bare Pt nanoparticles on glassy carbon. The concept of functionalizing Pt nanoparticles with POM was extended to functionalize Nafion-stabilized carbon-supported Pt nanoparticles. The ORR activity of these electrodes was found to be better than conventional electrodes. Kurys et al. [34] have achieved enhanced ORR activity on PAni-H₃PW₁₂O₄₀-V₂O₅ composite electrode. In Fig. 3, the comparison of the activity of Pt/STA-C and Pt/C electrodes under oxygen saturated 0.5 M H₂SO₄ is shown [28]. It is seen that the half-wave potential for oxygen reduction on Pt/STA-C is relatively more positive when compared

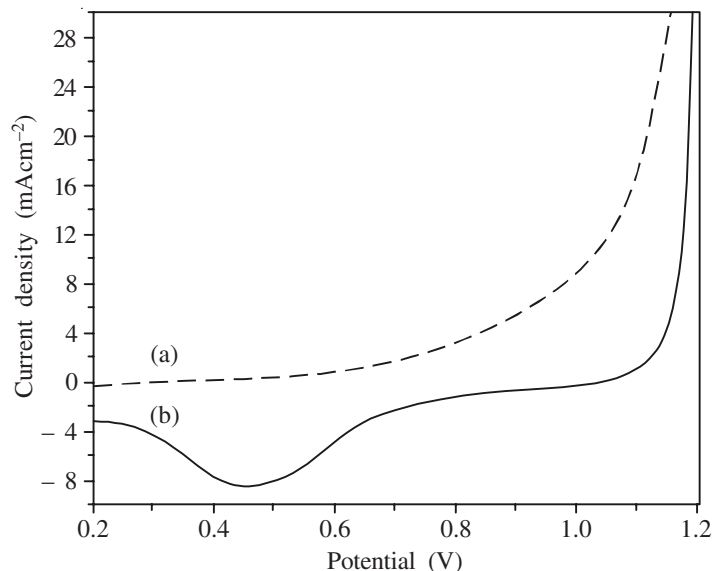


Fig. 3. Overlay of linear sweep voltammograms of (a) Pt/C and (b) Pt/STA-C in O_2 saturated in 0.5 M sulphuric acid at a scan rate of 5 mVs^{-1} [32].

to that in Pt/C. The specific activity on Pt/STA-C (7.6 mA cm^{-2}) is greater than that on Pt-C (4.25 mA cm^{-2}).

2.5 POMs as Electrochemical Super Capacitor Electrodes

The solubility of POMs in typical solvents has caused them to be ignored as active compounds for solid-state applications. Integration of POMs into a conducting polymer matrix to form a hybrid material is an effective way to harness electro-chemical activity. By anchoring them into conducting polymers, the reversible redox chemistry of POM clusters could be combined with that of the conducting polymer. POMs anchored to conducting polymer networks were examined as electrode materials for lithium rechargeable batteries and super capacitors [35]. An inexpensive electrochemical capacitor system with an asymmetric configuration was prepared using POMs and a proton exchange membrane. The prepared electrode showed specific capacitance of 112 F/g [36]. Polypyrrole doped with 10-molydo-2-vanadophosphoric acid, chemically fabricated via vapour transport of monomer showed a specific capacitance of 33.4 F/g [37]. Chemically synthesized polyaniline-doped phosphomolydic acid materials in electrochemical capacitor cells with acidic electrolyte membranes showed remarkable improvement in their cyclability [38]. Keggin-type POMs were effectively doped into poly(3,4-ethylenedioxythiophene) (PEDT) to form organic/inorganic hybrid films by electro-deposition. Other systems generated

by layer-by-layer growth technique of POM on PEDOT and hooked on to carbon or indium–tin oxide conductive glass electrodes also showed capacitance of 0.6 mFcm^{-2} [39]. The hybrid material polyaniline-doped phosphomolybdic acid prepared with the aid of H_2O_2 showed specific capacitance value of 168 Fg^{-1} and PEDOT-doped phosphomolybdic acid prepared by using a similar strategy showed specific capacitance of 130 Fg^{-1} [40]. However, polymers containing POM electrodes are not suitable for long term application, since the polymers undergo degradation. Hence, the idea of anchoring POM on a carbon network would be a desirable strategy to enhance the stability for cycling when used as electrodes for super capacitor applications.

Typical charge discharge behaviour obtained for RuO_2 present in a variety of composites is shown in Fig. 4 in the potential range of 0.0 to 0.7 V in 1.0 M H_2SO_4 at a current density of 3 mAcm^{-2} . The absolute slope value calculated from the discharge curves of the composites decreased with increasing RuO_2 weight percentage in $\text{RuO}_2/\text{STA-C}$. The specific capacitance of each composite was calculated using the expression

$$\text{Specific capacitance } C (\text{Fg}^{-1}) = 'I' (dt/mdV)$$

where I is the current used for charge discharge, dt is the time elapsed for the discharge cycle, m is the mass of the active electrode and dV is the

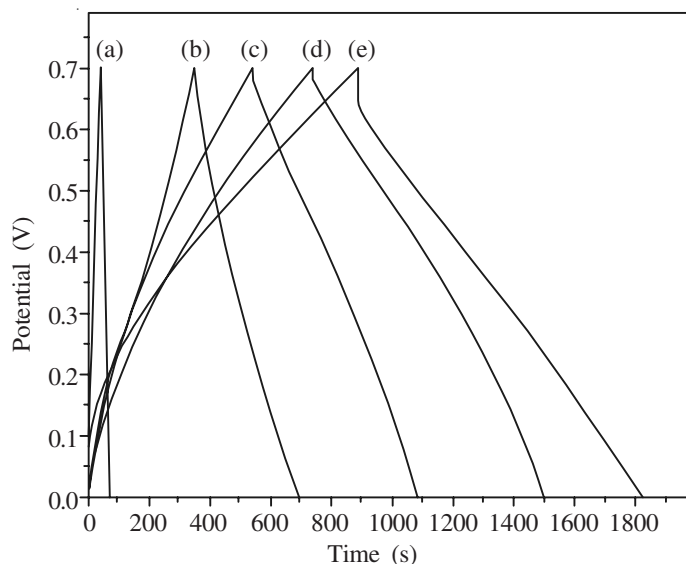


Fig. 4. Galvanostatic charge-discharge studies measured in 1.0 M H_2SO_4 solution between 0.0 V to 0.7 V at 3 mA cm^{-2} for (a) Vulcan XC 72R, (b) 20% RuO_2/C , (c) 10% $\text{RuO}_2/\text{STA-C}$, (d) 20% $\text{RuO}_2/\text{STA-C}$ and (e) 40% $\text{RuO}_2/\text{STA-C}$ [28].

voltage interval of the discharge. The calculated specific capacitance values of various electrodes are given in Table 2.

Table 2. Specific capacitances of various electrodes

Electrode material	Specific capacitance (Fg ⁻¹)
0% RuO ₂ (only Vulcan XC72R)	23
20% RuO ₂ /C	200
10% RuO ₂ /STA-C	325
20% RuO ₂ /STA-C	453
40% RuO ₂ /STA-C	557

The data given in Table 2 show that the POM containing RuO₂ systems are better than simple RuO₂/C systems and these systems showed long-term stability or cycle life.

3. Conclusion

It is known that biological electron transfer processes are facile due to the possibility of modulating and tuning the intermediate environment. This results in appropriate redox potential conditions to effect electron transfer in a facile downhill pathway. Any synthetic system which can mimic biological systems should be capable of being tuned in terms of redox potentials with minimum alteration of the nature and environment of the species. This appears to be possible in POMs.

In Fig. 5 this has been amplified in terms of the redox potential similarities. These excellent possibilities were considered in an earlier publication [41] by us. It appears that the electrochemical applications of POM are at a take-off stage and many exciting applications will be revealed in the near future.

It appears that complex biological electrochemical reactions can be mimicked in the laboratory by heteropoly anions by appropriate modulation of the electron energy levels of the cluster species brought forth by substitution or by alteration of the environment. This may provide a pathway to study a variety of chemical transformations of biological relevance. It is also possible that these systems lead to some devices which can mimic a few of the natural processes. The level of this comparison and the extent to which these systems can run parallel to natural processes are issues that await imagination and execution.

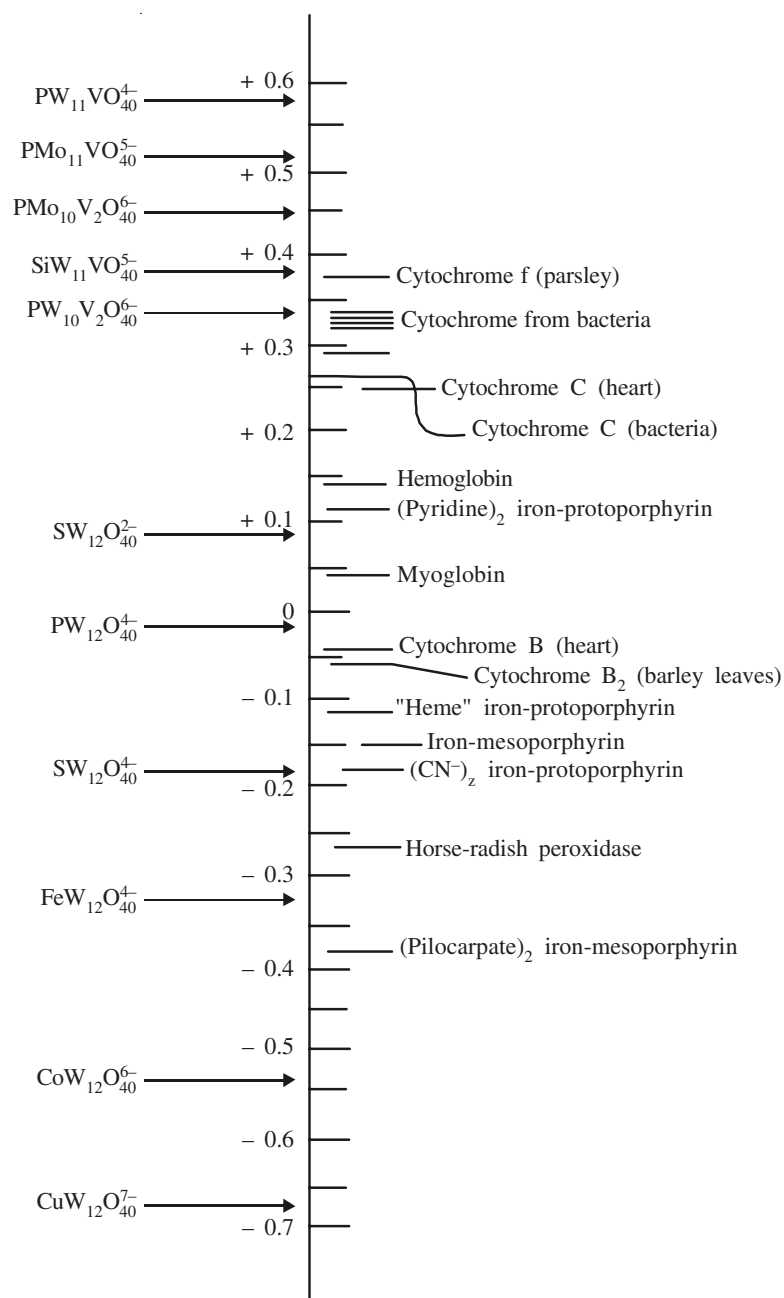


Fig. 5. Redox potentials (in volts) of Fe^{2+}/Fe^{3+} in different biological systems (right side of the scale) and heteropoly anions (left side of the scale) with varying composition [Values were collected from literature] [41].

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