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Electrochemical Properties of Polyoxometalates as Electrocatalysts

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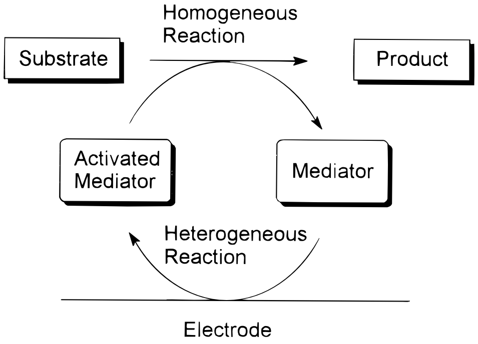
I. General Introduction

The catalytic redox activity of polyoxometalates has attracted much attention in recent years. Heteropolyanions and especially their metal-substituted derivatives have some very useful and interesting properties. Such features include the high stability of most of their redox states, the possibility to tune their redox potentials by changing the heteroions and/or the addenda ions without affecting their structure, the variability of the transition metal cations which can be incorporated into the heteropolymetalate structure, and the possibility of multiple electron transfer. These properties make heteropolyanions attractive as redox catalysts (mediators) for indirect electrochemical processes.

In indirect electrochemical reactions, a mediator (an electrocatalyst) is activated by a heterogeneous redox step at the electrode surface (E process) in order to react homogeneously with the substrate in the bulk solution (C process) regenerating the unactivated mediator. Heterogeneous electron transfer between the electrode and the substrate is sometimes very slow because of poor interaction. In these cases the electrode reaction occurs only at high overpotentials. Electrocatalysts can minimize the activation energy and hence allow such an electrode reaction to occur at high current density close to the equilibrium potential or even considerably below it (electron transfer against the potential gradient).[1] Hence, the redox catalyst (mediator) shuttles the redox equivalents between the substrate and the electrode (Scheme 1).

Scheme 1. Principle of an Indirect Electrochemical Reaction Catalyzed by a Mediator



Furthermore, suitably designed electrocatalysts can improve not only the reactivity but also the product selectivity. Passivation or filming of the electrode surface can also easily be avoided. Thus, electrocatalytic methods are very 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.[1] However, the number of highly selective and long-time stable redox catalysts is still limited. Therefore, heteropolyanions and their transition metal-substituted derivatives have the potential to fill this gap.

There is a vast chemistry of heteropolyanions that involves oxidation/reduction of the heteroatoms and addenda ions. The electrochemical analysis of such species forms the basis not only for the identification of the different species, especially the redox active ones. It is also a means to understand the reactivity and mechanistic behavior of the heteropolyanions as redox reagents and redox catalysts.[2a,3] Recently, attention has been focused on the electrocatalytic behavior of heteropolyanions and some promising results have been reported.[4] Both Keggin- and Dawson-type heteropolyanions have been extensively applied as electrocatalysts.

In this article, we review the present knowledge of the applications of polyoxometalates as electrocatalysts. To provide a sound basis for the understanding of the electrocatalytic processes, in particu-

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lar the heterogeneous E process (see above), section II summarizes the electrochemical behavior of the polyoxometalates. However, as we do not attempt to provide an exhaustive coverage of the electrochemistry of polyoxometalates as such, only the electrochemical properties of polyoxometalates which are investigated as electrocatalysts are summarized. In sections III and IV, the application of polyoxometalates as reductive and oxidative electrocatalysts, is reviewed.

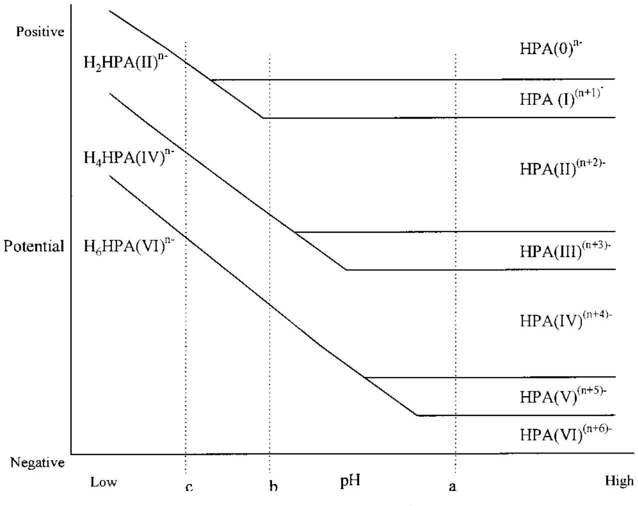
II. Electrochemical Behavior of Heteropolyanions

Although an almost endless number of polyoxometalates has been prepared and characterized, the number of polyoxometalates which have been used as electrocatalysts is limited. Mostly, α-Keggin- and Dawson-type heteropolyanions of phosphotungstate, silicontungstate, phosphomolybdate, and silicomolybdate; mixed-addenda heteropolyanions; and transition metal-substituted heteropolyanions are used as electrocatalysts because of their stability and easy of preparation. In this section, the electrochemical behavior of Keggin- and Dawson-type heteropolyanions, like α-$SiW_{12}O_{40}^{4-}$, α-$SiMo_{12}O_{40}^{4-}$, α-$PW_{12}O_{40}^{3-}$, α-$PMo_{12}O_{40}^{3-}$, α-$(H_2)W_{12}O_{40}^{6-}$, $P_2W_{18}O_{62}^{6-}$, $P_2Mo_{18}O_{62}^{6-}$, their mixed-valence derivatives, and their transition metal-substituted derivatives will be described.

The heteropolyanions undergo several rapid one- and two-electron reversible reductions to produce the so-called "heteropoly blue", and further irreversible multielectron reductions with concomitant decomposition. The electrons are accepted by the addenda ions of the heteropolyanions ($XM_{12}O_{40}^{n-}$ and $X_2M_{18}O_{62}^{n-}$). If the addenda ions are all identical, the electrons are delocalized on the addenda ion oxide framework at room temperature by rapid electron hopping (intramolecular electron transfer).[2a,4b,5] The reduction increases the negative charge density at the heteropolyanions and thus their basicity. As a consequence, the reduction can be accompanied by protonation depending on the pK_a of the produced oxometalates.

Most simply, the relationships between the potentials of the reversible redox pairs of heteropolyanions and the pH can be schematically represented, as shown in Scheme 2. Both Keggin- and Dawson-type heterepolyanions undergo several one-electron reductions in neutral aqueous or organic solution where no protonation can occur (line a in Scheme 2, examples are α-$SiMo_{12}O_{40}^{4-}$, α-$PMo_{12}O_{40}^{3-}$, and $P_2Mo_{18}O_{62}^{6-}$ in neutral organic solvents.). By decreasing the pH, the most negative two one-electron

Scheme 2. Schematic Representation of the Electrochemical Behavior of Heteropolyanions (HPA)[a]



[a] Roman numerals show the number of electrons added to the oxidized anion 0: $(HPA)^{n-}$.

waves convert into one two-electron wave, which is commonly accompanied by the addition of two protons. The odd reduction states I, III, and V disproportionate by protonation (eq 1).

$$2\mathrm{HPA(I)}^{(n+1)-} + 2\mathrm{H}^+ = \mathrm{H_2HPA(II)}^{(n+2)-} + \mathrm{HPA(0)}^{n-} \quad (1)$$

The redox potentials change to positive potential with a slope of ~59 mV/pH with decreasing pH. So at a certain pH two one-electron redox pairs and two two-electron redox pairs (line b, examples are α-$PW_{12}O_{40}^{3-}$ and $P_2W_{18}O_{62}^{6-}$ in 1 M HCl aqueous solution) or three two-electron redox pairs (line c, examples are α-$SiMo_{12}O_{40}^{4-}$, α-$PMo_{12}O_{40}^{3-}$, and $P_2MO_{18}O_{62}^{6-}$ in acidic solution and $P_2W_{18}O_{62}^{6-}$ in 12.4 M HCl aqueous solution) can be observed in a number of electroanalytical studies.

More exactly, the slopes depend on the number of protons and electrons exchanged in the redox process and change when the pH approaches the pK_a values of the oxidized or the reduced form, unless the pK_a values of both forms are similar.

In the case of the Keggin- and Dawson-type heteropolymolybdates, one-electron reduction is found when no protonation takes place or when only one proton is consumed. Two-electron reduction takes place only when two protons are consumed in the cathodic process.

The electrochemical behavior of each of the heteropolyanions exhibits a different feature, because they differ in their redox potentials, their pK_as and their stabilities. They will be described in more detail in the following section.

A. Keggin-Type Heteropolyanions $XM_{12}O_{40}^{n-}$

Keggin-type heteropolyanions can accept a limited number of electrons without decomposition, and in some cases the reduced compounds have been isolated. In general, the reduction potentials of the Keggin-type heteropolytungstates and heteropolymolybdates are controlled by the following factors: (1) The reducibility increases in the sequence α-, β-, and γ-isomers according to the number of rotated M_3O_{13} groups.[2a,3,6] (2) The reduction potential of the one-electron waves decreases linearly with a decrease in the valence of the central metal, i.e., an increase in the negative charge of the heteropolyanions (Figures 1 and 2).[2a,3,4,7-9]

1. Heteropolytungstate (M = W)

Pope and Varga, Jr., studied the reduction of α-$PW_{12}O_{40}^{3-}$, α-$SiW_{12}O_{40}^{4-}$, α-$Fe^{III}W_{12}O_{40}^{5-}$, α-$Co^{II}W_{12}O_{40}^{6-}$, and α-$H_2W_{12}O_{40}^{6-}$ by polarographic and potentiometric methods.[8] In acidic solution (1 M H_2SO_4), electrons can be added without protonation until the charge of the reduced species is −6. Further reduction is always accompanied by protonation, keeping the overall ionic charge at −6. In neutral solutions (pH > 5), reduction proceeds until the charge of the reduced species is −8. In the case of $Fe^{III}W_{12}O_{40}^{5-}$ and $Co^{II}W_{12}O_{40}^{6-}$ the reduction takes place only on the tungsten atoms and no Fe(II) and Co(I) species are observed.

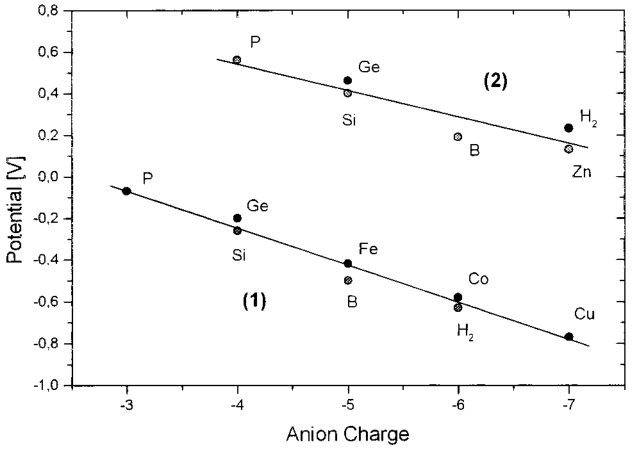


Figure 1. Dependence of the first one-electron reduction potentials on the negative charge: (1) $XW_{12}O_{40}^{n-}$, X = P, Si, Ge, Fe, B, Co, H_2, Cu: and (2) $XW_{11}VO_{40}^{n-}$, X = P, Si, Ge, B, H_2, Zn. The data are taken from ref 7.

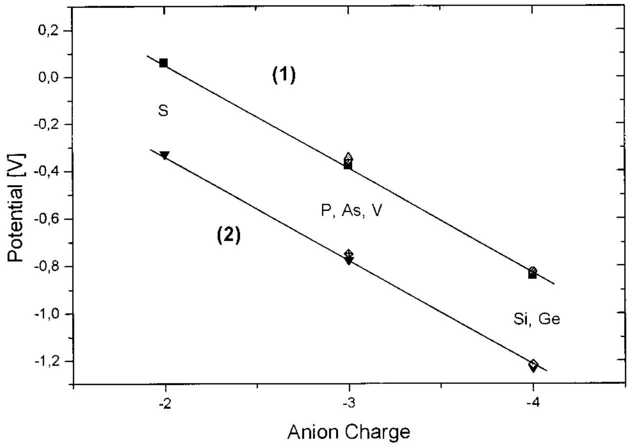


Figure 2. Dependence of the first two one-electron reduction potentials on the negative charge of $XMo_{12}O_{40}^{n-}$: (1) the first one-electron reduction and (2) the second one-electron reduction. The data are taken from ref 9.

In aqueous solution where no protonation accompanies the reduction for α-$XW_{12}O_{40}^{n-}$ (X = P(V), Si(IV), Ge(IV), Fe(III), B(III), Co(II), H_2, Cu(I)) two one-electron reductions are observed. Their potentials are linearly dependent on the ionic charge by −0.18 V per unit charge (Figure 1).[4b,7] A similar trend is also reported in organic solvents.[9]

a. α-Silicon Polyoxotungstate α-$SiW_{12}O_{40}^{3-}$ (X = Si). *i. Aqueous Medium.* Cyclic voltammetry of the α-$SiW_{12}O_{40}^{3-}$ complex in acidic solution shows five reduction waves with the approximate electron ratios 1:1:2:8:12.[10] The first three reductions are reversible and well defined. Reoxidation peaks are observed if the potential scan is stopped before the very beginning of the fourth wave (Figure 3). In 1 M aqueous HCl solution, these reduction waves are located at −0.220, −0.420, and −0.580 V vs SCE, respectively.[11-13] The fourth and fifth reduction are accompanied by chemical reactions of the complex, and the tungsten compounds are adsorbed at the electrode surfaces (see section III.B.3).

The half-wave potentials of the first two polarographic reduction waves, corresponding to two one-

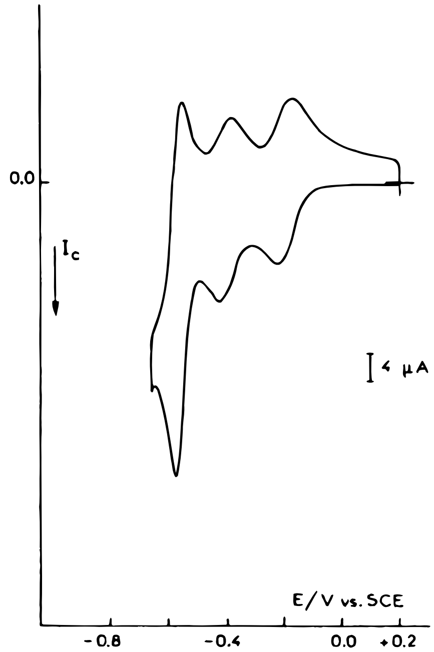


Figure 3. Cyclic voltammogram of $SiW_{12}O_{40}{}^{4-}$ (1 mM) in 1 M $HClO_4$ aqueous solution. Conditions: glassy carbon working electrode, platinum counter electrode, SCE reference electrode, scan rate 100 mV/s. (Reprinted with permission from ref 12. Copyright Elsevier Sequoia S. A., Lausanne.)

electron reductions, were essentially unaltered below pH 5. The third wave, corresponding to a two-electron reduction, moves to more negative potentials by about 59 mV per pH unit.[8,14] Therefore, the waves can be described by the following equations.

$$\alpha\text{-}SiW_{12}O_{40}{}^{4-} + e^- = \alpha\text{-}SiW_{12}O_{40}{}^{5-} \tag{2}$$

$$\alpha\text{-}SiW_{12}O_{40}{}^{5-} + e^- = \alpha\text{-}SiW_{12}O_{40}{}^{6-} \tag{3}$$

$$\alpha\text{-}SiW_{12}O_{40}{}^{6-} + 2e^- + 2H^+ = \alpha\text{-}H_2SiW_{12}O_{40}{}^{6-} \quad 1 < pH < 5 \tag{4}$$

By decreasing the pH of the aqueous solution, the second reduction wave starts to move to more positive potentials and reaches the first wave to produce a two-electron reduction wave (Figure 4).[11−13] In 7 M $HClO_4$ aqueous solution, two successive reversible two-electron reduction waves were observed (Figure 5). Their two-electron reductions are also observed in aqueous HCl solutions at concentrations above 5 M HCl.[15]

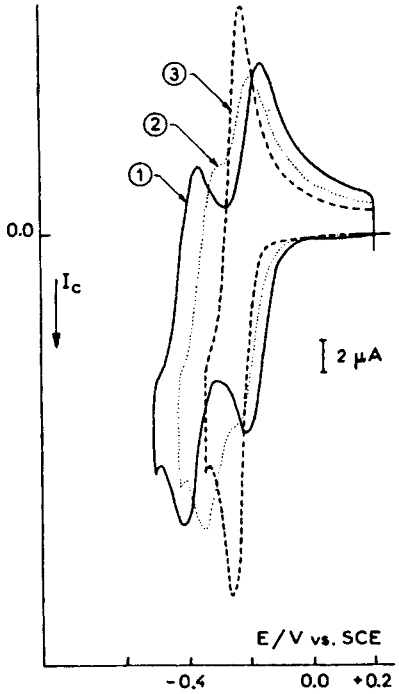


Figure 4. Change of cyclic voltammetric feature of $SiW_{12}O_{40}{}^{4-}$ (1 mM) with perchloric acid concentration in aqueous solution: (1) 1 M $HClO_4$, (2) 4 M $HClO_4$, and (3) 7 M $HClO_4$. Conditions: glassy carbon working electrode, platinum counter electrode, SCE reference electrode, scan rate 100 mV/s. (Reprinted with permission from ref 12. Copyright Elsevier Sequoia S. A., Lausanne.)

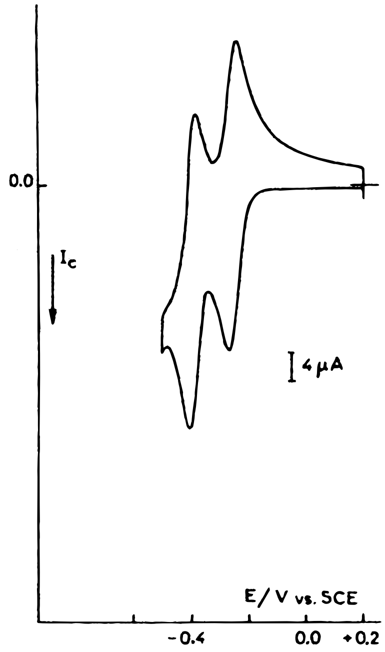


Figure 5. The two two-electron redox waves of $SiW_{12}O_{40}{}^{4-}$ (1 mM) in 7 M $HClO_4$ aqueous solution. Conditions: glassy carbon working electrode, platinum counter electrode, SCE referenece electrode, scan rate 100 mV/s. (Reprinted with permission from ref 12. Copyright Elsevier Sequoia S. A., Lausanne.)

ii. Organic Medium. In DMF (0.1 M $LiClO_4$), cyclic voltammetry of the potassium salt $\alpha\text{-}K_4SiW_{12}O_{40}$ shows five reduction waves.[12,13,16] The reduction peaks of these waves are located at −0.840, −1.060, −1.320, −1.780, and −1.890 V vs SCE. The first two waves are monoelectronic and quasireversible. The third quasireversible wave corresponds to approximately 1.4 electrons per molecule (Figure 6-1). The first redox process is diffusion controlled and chemically reversible. Assuming the one-electron reduced species to be the same as in aqueous 1 M $HClO_4$ solution (eq 2), a very large solvent effect (negative shift in DMF compared with in the aqueous medium) is observed. This effect was also detected in DMSO, *N*-methylformamide, and formamide solutions containing 0.1 M $LiClO_4$. A good correlation of the first one-electron reduction peak potential of $\alpha\text{-}SiW_{12}O_{40}{}^{4-}$ with the acceptor number of the solvent which

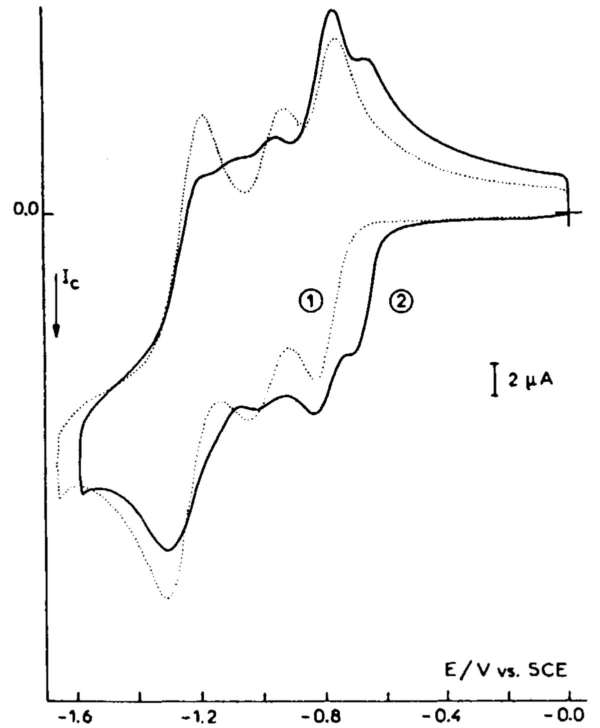


Figure 6. Cyclic voltammogram of α-$K_4SiW_{12}O_{40}$ (1 mM) in DMF + 0.1 M $LiClO_4$ solution: (1) in the absence of acid and (2) in the presence of 2 mM $HClO_4$. Conditions: glassy carbon working electrode, platinum counter electrode, SCE referenece electrode, scan rate 100 mV/s. (Reprinted with permission from ref 13. Copyright Elsevier Sequoia S. A., Lausanne.)

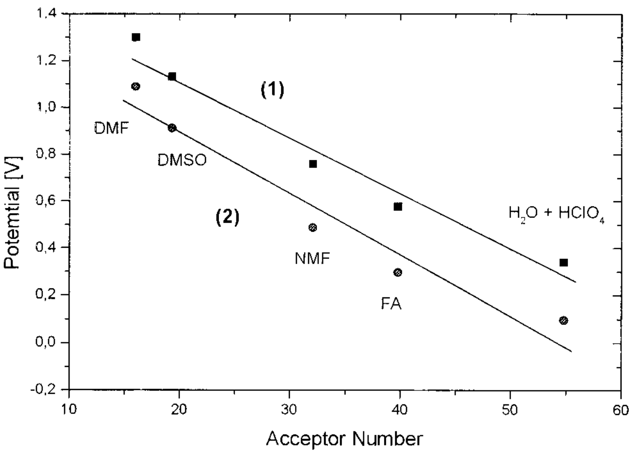


Figure 7. Relationship between the first one-electron reduction peak potential of (1) α-$K_4SiW_{12}O_{40}$ and (2) α-$K_6P_2W_{18}O_{62}$ vs the reduction peak potential of ferrocene and the acceptor number of the solvent. Conditions: glassy carbon working electrode, platinum counter electrode, 0.1 M $LiClO_4$. The data are taken from ref 17.

describes its Lewis acid properties is observed (Figure 7-1).[17] The reduction peak potential shifts linearly to more negative potentials with decreasing solvent acceptor number: H_2O (54.8) > formamide (39.8) > *N*-methylformamide (32.1) > DMSO (19.3) > DMF (16.0).[18] The reduced form (α-$SiW_{12}O_{40}^{5-}$) is better stabilized by solvents that have a higher acceptor number. In a 50% 1,4-dioxane–water mixed-solvent containing 0.5 M H_2SO_4, α-$SiW_{12}O_{40}^{4-}$ undergoes two two-electron reversible reductions. In this solvent system, the one-electron reduced species is destabilized by 1,4-dioxane which has a small acceptor number (10.8).[19]

By addition of acid ($HClO_4$) in DMF, the one-electron waves are converted into two-electron waves in a complex manner, and the shape of the cyclic voltammogram also changes (Figure 6-2).[12] A new reduction peak appears at more positive potential as compared with the original waves, growing until finally the shape of a two-electron reduction is attained. In the cyclic voltammogram of α-$SiW_{12}O_{40}^{4-}$ in DMF + 0.1 M $LiClO_4$ + 0.5 M $HClO_4$ solution, the two two-electron reduction waves and a four-electron reduction wave can be observed. Interestingly, cyclic voltammetry of α-$H_4SiW_{12}O_{40}$ in DMF + 0.1 M $LiClO_4$ shows a different reduction process as compared with those of α-$K_4SiW_{12}O_{40}$ and α-$K_4SiW_{12}O_{40}$ + 4 equiv of $HClO_4$. However, in highly concentrated acidic solution, there is no difference between the cyclic voltammograms of $H_4SiW_{12}O_{40}$ and $K_4SiW_{12}O_{40}$.

b. α-Phospho Polyoxotungstate α-$PW_{12}O_{40}^{3-}$ (X = P). *i. Aqueous Media.* In 1 M $HClO_4$ aqueous solution, five well-defined reduction waves at −0.020, −0.275, −0.590, −0.775, and −0.850 V vs SCE, respectively, are observed. The first, second and third wave correspond to reversible one-, one-, and two-electron reduction processes:[8,13]

$$\alpha\text{-}PW_{12}O_{40}^{3-} + e^- = \alpha\text{-}PW_{12}O_{40}^{4-} \tag{5}$$

$$\alpha\text{-}PW_{12}O_{40}^{4-} + e^- = \alpha\text{-}PW_{12}O_{40}^{5-} \tag{6}$$

$$\alpha\text{-}PW_{12}O_{40}^{5-} + 2\,e^- + H^+ = \alpha\text{-}HPW_{12}O_{40}^{6-} \quad 0 < pH < 3 \tag{7}$$

The last two waves are irreversible and consume more than two electrons. As in the previous case, the reoxidation waves are ill-defined when the potential is scanned up to these last two waves.

The solution of α-$PW_{12}O_{40}^{3-}$ is stable only below pH 1.5, but the reduced species exhibit stability also in solutions of higher pH. The two electron reduction product α-$PW_{12}O_{40}^{5-}$ is inert enough to measure the polarograms also in 1.0 M sodium hydroxide.[20] So the electrochemical investigation in the solution above pH 1.5 is carried out by using the reduced species.

With increasing pH of the solution, the third reversible two-electron wave moves to a more negative potential and splits into two reversible one-electron reduction waves at ca. pH 4[20] (eqs 8 and 9).

$$\alpha\text{-}PW_{12}O_{40}^{5-} + e^- = \alpha\text{-}PW_{12}O_{40}^{6-} \tag{8}$$

$$\alpha\text{-}PW_{12}O_{40}^{6-} + e^- = \alpha\text{-}PW_{12}O_{40}^{7-} \quad pH > 4 \tag{9}$$

When the concentration of hydrochloric acid is increased, the first wave moves toward more negative potential, while the four remaining ones move in the positive direction. However, mergence of the first two one-electron reduction waves into a two-electron reduction wave cannot be observed within the HCl concentration limit, in which $PW_{12}O_{40}^{3-}$ is still soluble.

ii. Organic Media. The cyclic voltammogram of α-$PW_{12}O_{40}^{3-}$ shows four reduction waves in an organic solution. The first one is monoelectronic and the second and third ones are close to each other, their electron numbers being 1 and ~1.17, respectively. The fourth wave is broad and of low intensity, corresponding to ~0.5 electrons per molecule. By adding acid, the peaks shift to more positive potential, but a two-electon reduction is not observed.[13]

c. α-Metatungstate α-$(H_2)W_{12}O_{40}^{6-}$ ($X = H_2$). *i. Aqueous Media.* Polarograms of the α-$(H_2)W_{12}O_{40}^{6-}$ at pH < 3.5 show three reduction waves, indicating two two-electron transfers and one transfer of ~10 electrons.[2a,21] The two-electron waves are reversible and correspond to the formation of α-$H_2(H_2)W_{12}O_{40}^{6-}$ (eq 10) and α-$H_{2+n}(H_2)W_{12}O_{40}^{(8-n)-}$ (eq 11), respectively.

$$\alpha\text{-}(H_2)W_{12}O_{40}{}^{6-} + 2e^- + 2H^+ = \alpha\text{-}H_2(H_2)W_{12}O_{40}{}^{6-} \quad (10)$$

$$\alpha\text{-}H_2(H_2)W_{12}O_{40}{}^{6-} + 2e^- + nH^+ = \alpha\text{-}H_{2+n}(H_2)W_{12}O_{40}{}^{(8-n)-} \quad (11)$$

The half-wave potentials of the two-electron waves move to more negative potential with increasing pH and the waves eventually split into two one-electron waves each, which then remain pH-independent. p*K*s of the α-$H_2(H_2)W_{12}O_{40}^{6-}$ are 4.0 (eq 12) and 6.3 (eq 13) in 1 M NaCl solution.

$$\alpha\text{-}H_2(H_2)W_{12}O_{40}{}^{6-} = \alpha\text{-}H(H_2)W_{12}O_{40}{}^{7-} + H^+ \quad (12)$$

$$\alpha\text{-}H(H_2)W_{12}O_{40}{}^{7-} = \alpha\text{-}(H_2)W_{12}O_{40}{}^{8-} + H^+ \quad (13)$$

The splitting of the first wave occurs at pH 4 (eqs 14 and 15) and the second wave splits when measured in 2.0 M NaOH solution (eqs 16 and 17).

$$\alpha\text{-}(H_2)W_{12}O_{40}{}^{6-} + e^- = \alpha\text{-}(H_2)W_{12}O_{40}{}^{7-} \quad (14)$$

$$\alpha\text{-}(H_2)W_{12}O_{40}{}^{7-} + e^- = \alpha\text{-}(H_2)W_{12}O_{40}{}^{8-} \quad (15)$$

$$\alpha\text{-}(H_2)W_{12}O_{40}{}^{8-} + e^- = \alpha\text{-}(H_2)W_{12}O_{40}{}^{9-} \quad (16)$$

$$\alpha\text{-}(H_2)W_{12}O_{40}{}^{9-} + e^- = \alpha\text{-}(H_2)W_{12}O_{40}{}^{10-} \quad (17)$$

Each of the one- and two-electron reduced complexes can be prepared by controlled potential electrolysis of appropriate solutions.

2. Heteropolyoxomolybdate (M = Mo)

Heteropolyoxomolybdates are reduced more easily than heteropolytungstates.

The first one-electron redox potential of α- and β-$XMo_{12}O_{40}^{n-}$ (X = S, P, As, V, Si, and Ge) depends linearly on the ionic charge of the heteropolymolybdates (Figure 2). The redox potentials of the β-isomers are ~80 mV more positive than those of the α-isomers.[9,22]

a. α-Silicon Polyoxomolybdate α-$SiMo_{12}O_{40}^{4-}$ (X = Si). *i. Aqueous Media.* α-$SiMo_{12}O_{40}^{4-}$ is reduced in aqueous solutions containing acid (HCl, $HClO_4$, H_2SO_4, or HNO_3) in five subsequent steps. Notably, three two-electron reductions, a four-electron reduction, and another two-electron step up to −0.80 V vs SCE [23,24] are observed. Launary et al. reported the pH effect of the first three reversible two-electron reductions (eqs 18−20).[23] The two-electron waves are shifted to more negative potential when the pH is increased, and they are eventually split into one-electron waves. This takes place at pH 2.4 for the first, at pH 9.5 for the second, and in 0.1 M LiOH for the third wave, giving rise to the formation of $SiMo_{12}O_{40}^{5-}$, $SiMo_{12}O_{40}^{6-}$, and $SiMo_{12}O_{40}^{7-}$, respectively.

$$SiMo_{12}O_{40}{}^{4-} + 2e^- + 2H^+ = H_2SiMo_{12}O_{40}{}^{4-} \quad (18)$$

$$H_2SiMo_{12}O_{40}{}^{4-} + 2e^- + 2H^+ = H_4SiMo_{12}O_{40}{}^{4-} \quad (19)$$

$$H_4SiMo_{12}O_{40}{}^{4-} + 2\ e^- + 2\ H^+ = H_6SiMo_{12}O_{40}{}^{4-} \text{ in 0.5 M HCl aqueous solution} \quad (20)$$

ii. Aqueous−Organic Media. The electrochemical behavior of α-$SiMo_{12}O_{40}^{4-}$ has been investigated in aqueous organic mixed-solvent systems containing acid.[15,24−28] In the presence of cyclic ethers such as 1,4-dioxane or THF, $SiMo_{12}O_{40}^{4-}$ undergoes five reversible two-electron cathodic reduction steps, followed by an irreversible two-electron reduction, whereas in the presence of DME, DMF, MeCN, EtOH, or acetone, the cyclic volatmmetry shows four reversible redox couples of two, two, two, and four electrons and an irreversible two-electron reduction wave. This difference is explained by the stabilization of the eight-electron reduced species by the cyclic ethers. $SiMo_{12}O_{40}^{4-}$ is reduced in the presence of the cyclic ethers at more positive potentials than under otherwise identical conditions, however, without organic cosolvents. A negative potential shift, on the contrary, is observed in the presence of DME, DMF, MeCN, and EtOH as cosolvents.[24,28] The positive shift is explained by the interaction between $SiMo_{12}O_{40}^{4-}$ and the cyclic ethers. In contrast to the case of heteropolyoxotungstate (see section II.A.1.a.ii), it is proposed that the cyclic ethers act as Lewis base in the solution.

At low sweep rate (2 mV/s), the fourth cathodic wave becomes ill-defined.[26]

iii. Organic Media. In organic solvents α-$SiMo_{12}O_{40}^{4-}$ undergoes one-electron reduction processes. For example, in MeCN containing 0.05 M nBu_4NClO_4, α-$SiMo_{12}O_{40}^{4-}$ undergoes two reversible one-electron reductions at $E_{1/2} = -0.654$ and −1.059 V vs Ag/Ag$^+$, respectively.[9,22] The one-electron reduction waves are converted into two-electron waves as a function of acid concentration. In MeCN containing 0.05 M nBu_4NClO_4 and 7.2 equiv of CF_3SO_3H, three well-defined reversible two-electron reduction waves can be distinguished in the cyclic voltammogram of α-$SiMo_{12}O_{40}^{4-}$ up to −0.5 V vs Ag/Ag$^+$.

b. α-Phospho Polyoxomolybdate α-$PMo_{12}O_{40}^{3-}$ (X = P). *i. Aqueous−Organic Media.* For phosphopolyoxomolybdate it is difficult to obtain well-defined redox waves in cyclic voltammetry in aqueous electrolytes due to the easy hydrolysis of $PMo_{12}O_{40}^{3-}$. However, it is stabilized by addition of comparatively large amounts of organic solvents. Thus, cyclic voltammetry is usually measured in mixed organic–aqueous solvents containing acid.[15,25,29] Like $SiMo_{12}O_{40}^{4-}$, $PMo_{12}O_{40}^{3-}$ undergoes five two-electron reversible reductions and further irreversible two-electron reductions in the presence of cyclic ethers such as 1,4-dioxane or THF, whereas in the presence of DME, DMF, MeCM, or EtOH four reversible reductions of two, two, two, and four electrons followed by an irreversible two-electron reduction[24] are observed. The reduced α-$PMo_{12}O_{40}$ species are stabilized by the organic cosolvents.[26,29,30] The reduction potentials depend on pH as a results of protonation (eqs 21–23).[5f]

$$PMo_{12}O_{40}^{3-} + 2e^{-} + 2H^{+} = H_2PMo_{12}O_{40}^{3-} \quad (21)$$

$$H_2PMo_{12}O_{40}^{3-} + 2e^{-} + 2H^{+} = H_4PMo_{12}O_{40}^{3-} \quad (22)$$

$$H_4PMo_{12}O_{40}^{4-} + 2e^{-} + 2H^{+} = H_6PMo_{12}O_{40}^{3-} \quad (23)$$

ii. Organic Media. In the cyclic voltammogram of α-$PMo_{12}O_{40}^{3-}$, two or three reversible one-electron reduction waves can be distinguished up to −1.5 V vs Ag/Ag^{+} depending on the solvent.[9,22] In acetone solution containing 0.05 M nBu_4NClO_4, α-$PMo_{12}O_{40}^{3-}$ undergoes two reversible one-electron reductions at $E_{1/2} = -0.661$ and −1.095 V vs Ag/Ag^{+}. On the other hand, cyclic voltammetry of α-$PMo_{12}O_{40}^{3-}$ in MeCN solution containing the same electrolyte leads to three reversible one-electron reduction waves, at $E_{1/2} = -0.170$, −0.585, and −1.313 V vs Ag/Ag^{+}. The reversible one-electron reduction waves convert into reversible two-electron reductions on the addition of acid.

B. Dawson-Type Heteropolyanions $X_2M_{18}O_{62}^{n-}$

Dawson-type heteropolyanions undergo several reversible one-electron reductions in organic and aqueous solvents if no protonation accompanies the reductions. By addition of acid, the one-electron reductions of $P_2Mo_{18}O_{62}^{6-}$ are converted into two-electron waves more easily than in the case of $P_2W_{18}O_{62}^{6-}$ in MeCN. Moreover, one-electron waves of $P_2Mo_{18}O_{62}^{6-}$ in aqueous solutions are not observed even in neutral solutions where the one-electron waves of $P_2W_{18}O_{62}^{6-}$ are observed (see below). This difference between the two isostructural heteropolyanions is rationalized on the basis of size differences of the heteropolyanions and the chiral distortion of $P_2Mo_{18}O_{62}^{6-}$.[2a,31–34]

1. Heteropolyoxotungstate (M = W)

a. Phospho Polyoxotungstate $P_2W_{18}O_{62}^{6-}$ (X = P). *i. Aqueous Media.* In acidic aqueous solution, $P_2W_{18}O_{62}^{6-}$ undergoes four reversible (one, one, two, and two electron) reductions, followed by an irreversible approximately nine-electron reduction[13,20,35] (Figure 8-1). In 1 M HCl aqueous solution, the four reduction peak potentials are located at −0.005, −0.135, −0.610, and −0.805 V vs SCE. Six electrons can be added to $P_2W_{18}O_{62}^{6-}$ without decomposition and the corresponding reoxidation waves are well defined, if the potential is scanned until the beginning of the last irreversible wave. The last irreversible reduction is accompanied by decomposition and the reoxidation waves of the first four reductions become ill-defined if the potential is scanned until the last reduction peak. The four reversible redox waves are summarized as shown in eq 24–27. The two one-electron reductions are indepent of the pH and the third and fourth reversible two-electron reductions are accompanied by protonations (two protons).

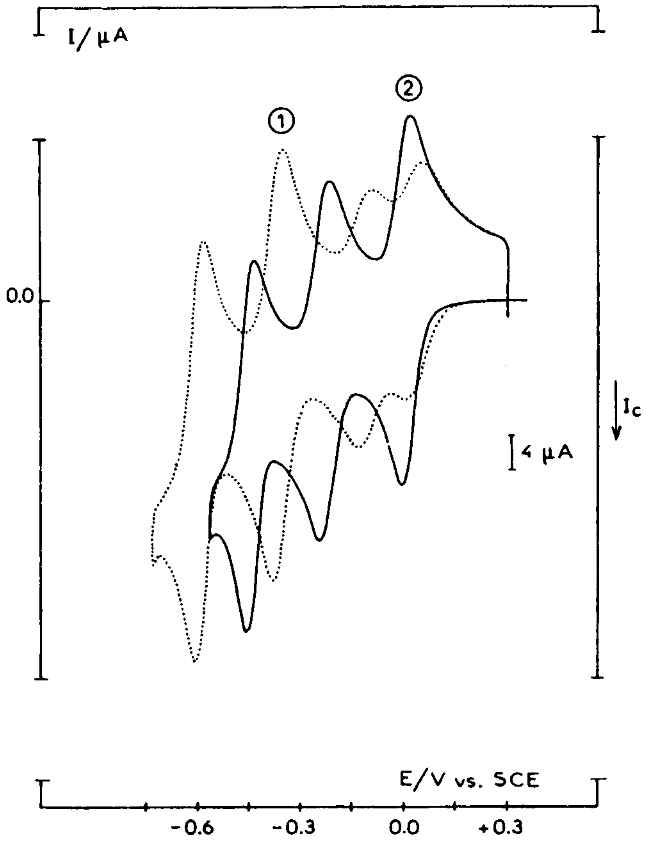


Figure 8. Cyclic voltammogram of α-$K_6P_2W_{18}O_{62}$ (1 mM) in aqueous solution: (1) in 1 M HCl aqueous solution and (2) in 12.4 M HCl aqueous solution. Conditions: glassy carbon working electrode, platinum counter electrode, SCE referenece electrode, scan rate 100 mV/s. (Reprinted with permission from ref 13. Copyright Elsevier Sequoia S. A., Lausanne.)

$$P_2W_{18}O_{62}^{6-} + e^{-} = P_2W_{18}O_{62}^{7-} \quad (24)$$

$$P_2W_{18}O_{62}^{7-} + e^{-} = P_2W_{18}O_{62}^{8-} \quad (25)$$

$$P_2W_{18}O_{62}^{8-} + 2e^{-} + 2H^{+} = H_2P_2W_{18}O_{62}^{8-} \quad (26)$$

$$H_2P_2W_{18}O_{62}^{8-} + 2e^{-} + 2H^{+} = H_2P_2W_{18}O_{62}^{8-} \quad (27)$$
$$0 < pH < 3$$

By increasing the HCl concentration in the solution, the second, third, and fourth reduction waves shift to more positive potentials, whereas the first wave does not move. The second one-electron wave moves closer to the first one-electron wave until they merge into one two-electron wave, resulting in a cyclic voltammogram of three two-electron waves (Figure 8-2).

As the pH of the solution is increased, the third and fourth waves shift to more negative potentials. At pH 6, the third two-electron wave splits into two reversible one-electron waves (eqs 28−29) as does the fourth (eq 30) two-electron wave on reaching pH 8.2 (eqs 31 and 32).

$$P_2W_{18}O_{62}{}^{8-} + e^- = P_2W_{18}O_{62}{}^{9-} \quad (28)$$

$$P_2W_{18}O_{62}{}^{9-} + e^- = P_2W_{18}O_{62}{}^{10-} \quad (29)$$

$$P_2W_{18}O_{62}{}^{10-} + 2e^- + 2H^+ = H_2P_2W_{18}O_{62}{}^{10-} \quad (30)$$
$$6 < pH < 8.2$$

$$P_2W_{18}O_{62}{}^{10-} + e^- = P_2W_{18}O_{62}{}^{11-} \quad (31)$$

$$P_2W_{18}O_{62}{}^{11-} + e^- = P_2W_{18}O_{62}{}^{12-} \quad (32)$$
$$8.2 < pH$$

iii. Organic Media. The electrochemical behavior of $P_2W_{18}O_{62}{}^{6-}$ in DMF solution is similar to that of $SiW_{12}O_{40}{}^{4-}$, as described above.[13] In DMF solution containing 0.1 M $LiClO_4$, the cyclic voltammogram of $P_2W_{18}O_{62}{}^{6-}$ exhibits four redox pairs up to −1.10 V vs SCE. The first wave is monoelectronic and diffusion controlled. On addition of an acid, new waves appear at more positive potential than the first wave and they grow as the acid concentration increases. In DMF solution containing 0.1 M $LiClO_4$ and 0.5 M $HClO_4$, three two-electron pairs are observed up to −1.0 V vs SCE. The first one-electron redox potential of $K_6P_2W_{18}O_{62}$ is reported to show similar solvent effects as that of $K_4SiW_{12}O_{40}$ (Figure 7-2).[17]

2. Heteropolyoxomolybdate (M = Mo)

For the Dawson-type heteropolyoxomolybdate $X_2Mo_{18}O_{62}{}^{n-}$ (X = S, P, As; n = 4, 6), the one-electron reduction proceeds reversibly until the ionic charge of the reduced species reaches −8 in MeCN solution where no protonation accompanies the reduction.[36,37]

a. Phospho Polyoxomolybdate $P_2Mo_{18}O_{62}{}^{6-}$ (X = P). Molybdates are reduced much more readily (∼0.4 V) than the tungstates.[33]

i. Aqueous Media. $P_2Mo_{18}O_{62}{}^{6-}$ undergoes three successive reversible two-electron and a four-electron reduction in acidic solutions.[33,38−40] All reduced species are stable on the cyclic voltammetry time scale. The number of the protons involved in each reducion is the same as the number of transferred electrons.

$$P_2Mo_{18}O_{62}{}^{6-} + 2e^- + 2H^+ = H_2P_2Mo_{18}O_{62}{}^{6-} \quad (33)$$

$$H_2P_2Mo_{18}O_{62}{}^{6-} + 2e^- + 2H^+ = H_4P_2Mo_{18}O_{62}{}^{6-} \quad (34)$$

$$H_4P_2Mo_{18}O_{62}{}^{6-} + 2e^- + 2H^+ = H_6P_2Mo_{18}O_{62}{}^{6-} \quad (35)$$

$$H_6P_2Mo_{18}O_{62}{}^{6-} + 4e^- + 4H^+ = H_{10}P_2Mo_{18}O_{62}{}^{6-} \quad (36)$$
$$pH < 4$$

On increasing the pH of the solution, all three waves shift to more negative potentials. The first and second wave become independent of the pH at pH 4 and ca. pH 8, respectively, without splitting of the two-electron waves into two one-electron waves. The two- and four-electron reduced species are unprotonated under these conditions.

ii. Organic Media. Himeno et al.[37a] as well as Barrows and Pope[37b] reported the electrochemical behavior of $P_2Mo_{18}O_{62}{}^{6-}$ in MeCN. $P_2Mo_{18}O_{62}{}^{6-}$ forms protonated salts such as $(nBu_4N)_{5.5}H_{0.5}P_2Mo_{18}O_{62}$, because of its high negative charge. This acidic proton within the salts affects the voltammetric behavior. If a base like nBu_4NOH is added to neutralize the acidic protons, $P_2Mo_{18}O_{62}{}^{6-}$ undergoes two reversible one-electron reductions in MeCN at −0.60 and −0.73 V vs Ag/Ag^+ (0.01 M in MeCN) containing 0.05 M nBu_4NClO_4. The two one-electron reduction waves are very sensitive to the presence of acid and become ill defined even if there is a trace amount of acid present. The one-electron waves are also sensitive to the presence of water. They are reversible at a water content below 3% (v/v). At a water content of more than 5%, the one-electron waves merge into a two-electron wave.

C. Mixed-Addenda Heteropolyanions

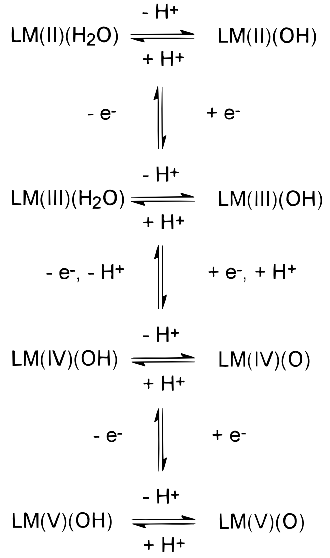
Mixed-addenda heteropolyanions are formed by the substitution of one or more tungsten(VI) or molybdenum(VI) ions in Keggin- and Dawson-type heteropolyanions by another addenda ion like W(VI), Mo(VI), and V(V). By changing the number and the kind of the substituted addenda atoms and the heteroatoms numerous mixed-addenda heteropolyanions can be prepared. Furthermore, X-substituted Keggin-type heteropolyanions, $XM_{12-x}M'_xO_{40}{}^{n-}$ are forming $12!/x!(12 - x)!$ positional isomers.[4a]

By variation of the addenda atoms, the electrochemical character of polyoxometalates can be widely changed. The addenda atoms can be ordered by decreasing oxidizing ability in the following way: V(V) > Mo(VI) > W(VI). In the case of one-electron-reduced mixed-addenda heteropolyanions, the electron is localized on the more reducible atom at room temperature.[4,7,41] For example, in the reduction of $PW^{VI}{}_{11}Mo^{VI}O_{40}{}^{3-}$ and $PW^{VI}{}_{11}V^{V}O_{40}{}^{4-}$, the added electron is accepted by the Mo and V atom, respectively, forming $PW^{VI}{}_{11}Mo^{V}O_{40}{}^{4-}$ and $PW^{VI}{}_{11}V^{IV}O_{40}{}^{5-}$. As for heteroatoms of $XW^{VI}{}_{11}V^{V}O_{40}{}^{n-}$, the reduction potentials decrease linearly with the decrease of their valence or the increase of the negative charge on the heteropolyanions.[7]

D. Transition Metal-Substituted Heteropolyanions

From heteropolyanions (Keggin-type: $XM_{12}O_{40}$ or Dawson-type: $X_2M_{18}O_{62}$), so-called “lacunary heteropolyanions” (Keggin-type $XM_{11}O_{39}$ or Dawson-type $X_2M_{17}O_{61}$) are derived by removing one MO unit. Many transition metals (M′) can fit into this octahedral binding site, giving rise to transition metal

Scheme 3. General Electrochemical Behavior of Transition Metal-Substituted Heteropolyanions



substituted heteropolyanions ($XM_{11}O_{39}M'^{n-}$ and $X_2M_{18}O_{61}M'^{n-}$).

A great number of transition metal-substituted heteropolyanions are reported. However, typically transition metal-substituted heteropolyanions of $SiW_{12}O_{40}$,$^{4-}$ $PW_{12}O_{40}{}^{3-}$, and $P_2W_{18}O_{62}{}^{6-}$ are used as electrocatalysts. In most cases the incorporated metal is the active site for the reactions. Therefore, the electrochemical investigation of the incorporated metals is very important in order to design the electrocatalysts for the desired reaction. The metals incorporated in the heteropolyanions reside in an octahedral environment with one coordination site occupied by a solvent molecule. Because the heteropolyanions are in most cases studied in aqueous solution, the solvent molecule is a labile water molecule. In general, the aquametal(III) is reducible to the aquametal(II) and oxidizable to the corresponding oxometal(IV), hydroxometal(IV), and oxometal(V) derivatives depending on the character of the incorporated metals. In some cases, for example for metals such as Re,[42] the oxometals(V) can be further oxidized to the oxometal(VI) and -(VII) stage (Scheme 3). Especially the hydroxometal and oxometal species are of interest as oxidation catalysts in synthetic application. The formal redox potential depends on several factors. The heteroions and addenda ions of the ligands have the highest influence on the potentials. For example, the redox potential of the incorporated metal increases with increasing formal charge on the heteroion A; for a given oxidation state, the redox potential increases with the size and decreasing electronegativity of X. The redox potential of Mn(III/II) increases with X = B < Zn < Si < Ge < P.[43] Furthermore, the formal redox potential depends on the electrolysis conditions (pH, countercation, additives, and solvents). The redox potential of some transition metals incorporated in heteropolyanions change according to the pH of the solution because of the deprotonation from the aquametal or the hydroxymetal. Incorporation of the transition metal increase the negative charge of the whole heteropolyanions. Such heteropolyanions exist in the electrolyte in an ion-paired formed with countercations. A lot of organic compounds can substitute the water ligand on the transition metal and the redox potential can be controlled by changing the additives. The redox potential can also be changed by using cosolvents.

The heteropolyanion ligands in these complexes undergo two reversible two-electron reductions which are accompanied by the addition of between two and three protons in acidic solutions. Similar to the parent heteropolyanions the two-electron reductions split into two one-electron reductions by increasing the pH of the solutions.[44] The ligand-centered reduction potentials, however, are shifted to more negative values as compared with the parent systems.

The detailed electrochemical behavior of the respective heteropolyanions will be described in the following sections.

III. Electrocatalytic Reduction

Many interesting results have been obtained in the area of electrocatalytic reductions, for example for the hydrogen evolution reaction (h.e.r.) and the oxygen reduction.

A large number of heteropolyanions undergo a series of reversible one- and two-electron reductions, and the reduced heteropolyanions (so-called "heteropolyblue") are the active species.

Heteropolyanions are used as reductive electrocatalysts in the following two ways: (1) homogeneously dissolved in the electrolyte solution and (2) attached to electrode surfaces.

A. Electrocatalysts in Homogeneous Solution

1. Keggin-Type Heteropolyanions

Keita and Nadjo have reported that α-$SiW_{12}O_{40}{}^{4-}$ can catalyze the hydrogen evolution reaction[12,13] and oxygen reduction[45] in acidic aqueous and organic solutions. The reactive species for the hydrogen evolution reaction are two- (eq 3) and four-electron- (eq 4) reduced compounds, the four-electron-reduced species being the more reactive ones. For the oxygen reduction, the first one-electron-reduced species (eq 2) is active.

Dong et al. observed that the first (eq 2) and third (eq 4) reduction waves of α-$SiW_{12}O_{40}{}^{4-}$ exhibit electrocatalytic activities for nitrite reduction in acidic solution at pH < 2 for the former and at a pH of about 4 for the latter.[14] The rate constant governing the nitrite reduction on the first wave of α-$SiW_{12}O_{40}{}^{4-}$ is $3.73 \times 10^3\ M^{-1}\ s^{-1}$.

Unoura et al. reported that α-$SiMo_{12}O_{40}{}^{4-}$ and α-$PMo_{12}O_{40}{}^{3-}$ can be used as electrocatalysts for chlorate ion reduction.[46] The third reduction wave of both the α-$SiMo_{12}O_{40}{}^{4-}$ (eq 20) and the α-$PMo_{12}O_{40}{}^{3-}$ (eq 23) ions corresponding to the reduction process from the four-electron-reduced species to the six-electron-reduced species exhibit catalytic properties in the presence of chlorate ions in 50% (v/v) dioxane–water solution containing 0.5 M H_2SO_4. The chlorate ion is reduced by the six-electron reduced species in the presence of protons to yield chloride and water, and the four-electon reduced species is regenerated. The 12-molybdophosphate is more reactive than the 12-molybdosilicate.

Keita and Nadjo have also reported that two-electron-reduced $\alpha\text{-}H_2SiMo_{12}O_{40}^{4-}$ (eq 18) can reduce nitrite and nitric oxide.[47]

2. Dawson-Type Heteropolyanions

$P_2W_{18}O_{62}^{6-}$ can be used as an electrocatalyst for the nitrite reduction in an aqueous solution.[35] At pH < 3, the reactive species is $P_2W_{18}O_{62}^{7-}$ which is produced by the first reduction (eq 24). By increasing the pH, the $P_2W_{18}O_{62}^{7-}$ loses the reactivity. In solutions above pH 3, the reactive species is $H_2P_2W_{18}O_{62}^{10-}$ which is generated by the fifth reduction wave (eq 30).

3. Transition Metal-Substituted Heteropolyanions

a. Fe-Substituted Heteropolyanions. Attention has not only been paid to iron-substituted heteropolyanions being metaloporphyrine analogues,[48] as oxidation catalysts[4a,49] in combination with stoichiometric oxidants, but also as active electrocatalysts for reductions.

Anson's group[50-52] and Dong's group[53] have investigated the electrochemical behavior of the iron(III)-substituted α-Keggin-type heteropolyanions ($\alpha\text{-}XW_{11}O_{39}Fe^{III}(H_2O)^{n-}$; X = P, As, $n = 4$; X = Si, Ge, $n = 5$) and the iron(III)-substituted Dawson-type heteropolyanion ($P_2W_{17}O_{61}Fe^{III}(H_2O)^{8-}$), respectively, and have applied them as catalysts for the reduction of H_2O_2 and NO_2^-. The iron is the reactive site for both reactions. The catalysts are not deactivated during repetitive cycles between their oxidized and reduced states.

The iron-substituted heteropolyanions have large negative charge densities which would favor ion pairing with countercations or protons. Therefore, the formal potentials of the reversible Fe(III/II) couples and the ligand-centered two two-electron reductions depend on both the pH and the countercation concentration because of competition between protonation and ion pairing.

Nitrite is electrochemically reduced to ammonia with 49% current efficiency in the presence of the iron-substituted heteropolyanions. The catalytic mechanism involves the formation of a nitrosyl complex on Fe(II) as an intermediate (eq 38).

$$2\alpha\text{-}XW_{11}O_{39}Fe^{III}(H_2O)^{n-} + 2e^- = 2\alpha\text{-}XW_{11}O_{39}Fe^{II}(H_2O)^{(n+1)-} \quad (37)$$

$$\begin{aligned}2\alpha\text{-}XW_{11}O_{39}Fe^{II}(H_2O)^{(n+1)-} + NO_2^- + 2\,H^+ = {}& \alpha\text{-}XW_{11}O_{39}Fe^{II}(NO)^{(n+1)-} + \\ & \alpha\text{-}XW_{11}O_{39}Fe^{III}(H_2O)^{n-} + H_2O \quad (38)\end{aligned}$$

$$X = \text{Si, Ge, } n = 5;\ X = \text{P, As, } n = 4$$

The pH dependence of the formation rate of the nitrosyl complex shows that nitrous acid is the reactive intermediate in the reaction when the pH is in the range of 2−8. The iron(II) nitrosyl complex can be further reduced at the reduction potential of the heteropolyanion ligands producing the $Fe^{II}(H_2O)$ complex and ammonia. The NO ligand coordinated to the Fe(II) complex accepts electrons via the heteropolyanion ligand, and not directly from the electrode.

H_2O_2 is also electrochemically reduced in the presence of Fe-substituted heteropolyanions. The cathodic wave corresponding to the reduction of the Fe(III) to the Fe(II) complex exhibits catalytic activity in the presence of H_2O_2 in an aqueous solvent system. The rate constants governing the reaction catalyzed by $\alpha\text{-}SiW_{11}O_{39}Fe^{II}(H_2O)^{6-}$ and $P_2W_{17}O_{61}Fe^{II}(H_2O)^{9-}$ are 9×10^2 and 1.16×10^4 M^{-1} s^{-1}, respectively. Complicated competing reactions including the formation of Fe(II), Fe(III), Fe(IV), and Fe(V) complexes are proposed.[52]

Unfortunately, anodic waves for the formation of higher oxidation states than Fe(III) cannot be obtained for the iron-substituted heteropolyanions in the aqueous buffers. Therefore, their application as electrocatalysts for oxidations is not possible.

b. Ru-Substituted Heteropolyanions. $\alpha\text{-}PW_{11}O_{39}Ru^{III}(H_2O)^{4-}$ can catalyze the hydrogen evolution reaction and the electrochemical reduction of DMSO forming dimethyl sulfide (see also section IV.A).[54] The controlled potential electrolysis of $\alpha\text{-}PW_{11}O_{39}Ru^{III}(H_2O)^{4-}$ in acidic aqueous solution at a potential at which the heteropolyanion ligand is reduced to "heteropolyblue" results in the catalytic hydrogen evolution reaction. The controlled potential electrolysis in sulfate buffer (pH 2) containing DMSO and a catalytic amount of $\alpha\text{-}PW_{11}O_{39}Ru^{III}(H_2O)^{4-}$ at a potential beyond the first heteropolyanion ligand reduction peak produces dimethyl sulfide with a turnover number of 30 in ~50% current efficiency.

c. Lanthanide-Substituted Heteropolyanions. Dong's group has described the electrochemical behavior of heteropolyanion complexes composed of a lanthanide cation and Keggin- or Dawson-type lacunary heteropolyanions in the ratio of 1:2.[2b] The lacunary heteropolyanions ($\alpha\text{-}XM_{11}O_{39}^{n-}$ and $X_2M_{17}O_{61}^{n-}$) act as tetradentate ligands and the lanthanide cations (III) are eight-coordinated by an approximate square antiprism of oxygen atoms.

Bis(Dawson-type arsenotungstate) lanthanides $K_{17}[Ln(As_2W_{17}O_{61})_2]\cdot xH_2O$ (Ln = La, Pr, Sm, Eu, Gd, Dy, Tm, and Yb) undergo three reversible reductions corresponding to two two-electron and one one-electron processes with concomitant protonation. The third reduction waves of all $Ln(As_2W_{17}O_{61})_2^{17-}$ have good electrocatalytic activities for nitrite reduction at pH 5.0.[55]

The electrochemical behavior of bis(Keggin-type mixed-addenda heteropolyanion) lanthanate $Nd(SiMo_7W_4O_{39})_2^{13-}$ was investigated in acidic (pH = 1.0−5.0) aqueous solution where the complex is stable. $Nd(SiMo_7W_4O_{39})_2^{13-}$ undergoes two one- and two two-electron reversible reductions in aqueous solution at pH > 2.5. Except for the first redox couple, all reductions are accompanied by protonation. In a solution below pH 2.5, the first two one-electron waves merge into one two-electron reversible reduction wave. A reduction of bromate to bromide is efficiently catalyzed by the four-electron-reduced

Table 1. Electrocatalytic Reductions by Homogeneously Dissolved Heteropolyanions

catalyst	reduction	condition	ref(s)
$SiW_{12}O_{40}^{4-}$	h.e.r.	acidic solution	12 + 13
	nitrite reduction	buffer	14
	O_2 reduction	triflate buffer (pH 2)	45
$SiMo_{12}O_{40}^{4-}$	chlorate reduction	50% (v/v) dioxane−water (0.5 M H_2SO_4)	46
	nitrite reduction		47
$PMo_{12}O_{40}^{3-}$	chlorate reduction	50% (v/v) dioxane−water (0.5 M H_2SO_4)	46
$P_2W_{18}O_{62}^{6-}$	nitrite reduction	buffer	35
$XW_{11}O_{39}Fe^{III}(H_2O)^{n-}$ (X = P, As, Si, Ge)	nitrite reduction	buffer	51
$SiW_{11}O_{39}Fe^{III}(H_2O)^{5-}$	H_2O_2 reduction	buffer	52
$P_2W_{17}O_{61}Fe^{III}(H_2O)^{8-}$	H_2O_2 reduction	sulfate buffer (pH 3)	53
	nitrite reduction	acetate buffer (pH 5)	53
$PW_{11}O_{39}Ru^{III}(H_2O)^{4-}$	DMSO reduction	sulfate buffer (pH 2)	54
	h.e.r.		
$K_{17}[Ln(AsW_{17}O_{61})_2]$ (Ln = La, Pr, Sm, Eu, Gd, Dy, Tm)	nitrite reduction	acetate buffer (pH 5.5)	55
$Nd(SiMo_7W_4O_{39})_2^{13-}$	bromate reduction	buffer	56

species of $Nd(SiMo_7W_4O_{39})_2^{13-}$ in aqueous solutions regenerating the two-electron-reduced species.[56]

In both cases, the lanthanide metals are not reduced and the coordinated Keggin- and Dawson-type heteropolyanions are the reactive sites.

The results reported in this chapter are summarized in Table 1.

B. Heteropolyanions Attached to Electrode Surfaces

The polyoxometalates are able to be attached onto the electrode by using an interaction between the polyoxometalates and the electrodes. There are three methods commonly used to immobilize polyxometalates onto the electrode surface. The first method is the adsorption of polyoxometalates on the electrode surface by dip coating. The second method is to entrap polyoxometalates into polymers on the electrode surface. The third method is the electrodeposition of polyoxometalates onto the electrode surface within the polyoxometalate solution under constant potential at −1.2 V.

1. Heteropolyanion Adsorbed on Electrode Surfaces

The easiest way to coat electrodes with a heteropolyanion monolayer is by simply soaking the electrode in an acidic aqueous heteropolyanion solution. As reported by Dong et al., this procedure works well for coating both carbon fiber and glassy carbon electrodes with heteropolyanions such as α-$SiMo_{12}O_{40}^{4-}$,[57] α-$PMo_{12}O_{40}^{3-}$,[57–59] $P_2Mo_{18}O_{62}^{6-}$,[40] and $P_2W_{18}O_{62}^{6-}$.[35] If the activity of the monolayer is not sufficient, electrochemical pretreatment of the electrodes provides a convenient alternative: for carbon fiber electrodes, cathodic pretreatment is recommended, whereas for glassy carbon electrodes, anodic pretreatment is the method of choice. Since in all these cases, the heteropolyanions are adsorbed at the electrode surface, the cyclic voltammetric waves show the typical symmetry and linear dependence of the currents on the scan rate that is expected for adsorbed species. Except for this modification, the voltammograms are analogous to those of the dissolved heteropolyanions.

Rong and Anson also reported that $PMo_{12}O_{40}^{3-}$, $P_2Mo_{18}O_{62}^{6-}$, $P_2W_{18}O_{62}^{6-}$, $SiW_{11}O_{39}Fe^{III}(H_2O)^{5-}$, and $PW_{11}O_{39}Fe^{III}(H_2O)^{4-}$ adsorp spontaneously on glassy carbon and edge pyrolytic graphite electrodes.[60a]

The coated electrodes can be rinsed without loss of the heteropolyanion coating, which is actively mediating the reduction of bromate, chromate, H_2O_2, and nitrite just as in the case of the dissolved heteropolyanions.

Heteropolyanions are also able to adsorb on gold[60,61] and mercury electrodes.[60] The adsorbed heteropolyanions increase the negative charge on the surface of the electrode thus influencing the heterogeneous electron-transfer rate between the electrode and the substrate.[60b]

Faulkner's group described that polyoxometalate-based layered composite films on electrodes can be formed due to the fact that heteropolyanions (α-$SiW_{12}O_{40}^{4-}$ and α-$PW_{12}O_{40}^{3-}$) strongly interact with large mono-, multi-, and polyvalent cations.[62a] By immersing the heteropolyanion film into a solution containing these cations, they are coated onto the electrode due to their interaction with heteropolyanions. Subsequently, a second layer of the heteropolyanions can now be coated onto the cation phase. By repeating this procedure, three-dimensional multilayer molecular assemblies can be formed in a controlled way. Robust composite three-dimensional films of α-$SiW_{12}O_{40}^{4-}$ and protonated poly(4-vinylpyridine) were thus formed.

They also performed codeposition of α-$SiW_{12}O_{40}^{4-}$ with $Os(bpy)_3^{2+}$ or $Ru^{III/IV}$-oxo species on the electrode surface and used these modified electrodes for the electrocatalytic oxidation of ascorbic acid and arsenite and the electrocatalytic reduction of nitrite and bromate.[62b]

Shiu and Anson immobilized α-$SiW_{11}O_{39}Fe^{III}(H_2O)^{5-}$ on the electrode-adsorbed tetrapositive tetrakis (4-*N*-methylpyridyl)porphirine and its Co(II) derivative on carbon electrodes by using the dip-coating procedure.[63] These electrodes are electrocatalytically active toward H_2O_2 reduction (section III.A.3.a), but a fast loss of catalytic activity accompanied by the loss of the iron center was observed.

Keita and Nadjo immobilized α-$(H_2)W_{12}O_{40}^{6-}$ onto clay-modified electrode surfaces. Two types of clay films were prepared on glassy carbon electrodes (montmorillonite-modified electrodes[64a] and Zn_2Al-

$(OH)_5X$-modified electrodes (X = Cl^-, NO_3^-, and terphthalic acid)[64b,c]).

In the former case, the sodium cations or acidic protons in montmorillonite are substituted by octadecyltrimethylammonium cations which interact with α-$(H_2)W_{12}O_{40}^{6-}$. Thus prepared montmorillonite-octadecyltrimethyammonium-α-$(H_2)W_{12}O_{40}^{6-}$ electrodes are very stable and can be used for the electrocatalytic reduction of O_2. The two-electron reduced species α-$H_2(H_2)W_{12}O_{40}^{6-}$ (eq 10) can reduce O_2 and α-$(H_2)W_{12}O_{40}^{6-}$ is regenerated.

In the second case, X anions are replaced by α-$(H_2)W_{12}O_{40}^{6-}$ to produce $Zn_2Al(OH)_5(\alpha\text{-}(H_2)W_{12}O_{40}^{6-})$. The choice of pH is very important to optimize the condition for building up this assembly at the electrode surface. The modified electrodes are very stable under various conditions of electrochemical interest. However, application in catalytic processes have not yet been described.

2. Heteropolyanions Entrapped in Polymer Matrixes on Electrode Surfaces

The polyoxometalates can be entrapped into a polymer matrix in a stable way by two methods: First, electrostatic incorporation of the polyoxometalates into a polymer which is already preformed on the electrode surface (two-step method), for example by spin coating or electropolymerization. Then the polymer-coated electrodes are soaked in the solution containing the polyoxometalates. Second, polyoxometalates are immobilized simultaneously with the electropolymerization procedure (one-step method), such that the oxidative polymerization is carried out in the presence of the polyoxometalates.

The polymer matrixes employed are poly(aniline),[47,65,66] poly(pyrrole),[35,63,65,67,74a−c] poly(4-vinylpyridine salt),[19,45,47,68,69] poly(thiophene),[70,71] poly(acetylene),[71,73] poly(1-naphthol),[73] and anionic polymers.[74d]

The interaction between the polymers and the polyoxometalates is stronger than the interaction between the polymers and the small counteranions such as sulfate, chloride, and perchlorate in the electrolyte. Therefore, the polyoxometalates are efficiently immobilized in the polymer matrix and do not exchange with these small anions.

In many cases, the electrochemical behavior of the heteropolyanions incorporated in the polymers is the same as that of the heteropolyanions dissolved in the solutions. In some cases, the polymer environment affects the electrochemical behavior of the immobilized heteropolyanions.

The cyclic voltammogram of $SiW_{12}O_{40}^{4-}$ incorporated in poly(4-vinylpyridine/1,12-dibromododecane) is almost identical with that of the dissolved species in the same electrolyte solution. However, when the acid concentration is increased, the $SiW_{12}O_{40}^{4-}$ incorporated in the polymer undergoes a two-electron reduction at the concentration where the $SiW_{12}O_{40}^{4-}$ dissolved in the same electrolyte solution undergoes yet two one-electron reductions.[69a]

$P_2W_{18}O_{62}^{6-}$ incorporated in poly(4-vinylpyridine/1,12-dibromododecane) undergoes two reversible one-electron reductions followed by two two-electron reductions which is identical with the dissolved species in the electrolyte solution (eqs 24−27).[69a] However, the cyclic voltammogram fo $P_2W_{18}O_{62}^{6-}$ shows three reversible two-electron reduction waves in poly(pyrrole)[35,67f] and poly(1-naphthol).[73a]

The immobilization of $PMo_{12}O_{40}^{3-}$ into poly(4-vinylpyridine) or poly(Ru-vinylbipyridine) results in the merging of the third and fourth reversible two-electron reduction waves into a single four-electron reduction.[19]

The immobilized heteropolyanions can catalyze the reductions summarized in Table 2. In some cases, the heteropolyanion immobilized in a polymer is more efficient than the homogeneously dissolved one. The reactivity of $PMo_{12}O_{40}^{3-}$ toward chlorate reduction is enhanced by immobilizing into the poly(4-vinylpyridine/1,12-dibromododecane) matrix.[45] Many of these systems are especially interesting for sensor application.

Bidan and Farbe developed a valuable nitrogen monooxide and nitrite ion sensor by using electrodes coated by polymer films such as poly(*N*-methylpyrrole), sulfonated polyamide, sulfonated polystyrene, and perfluorinated polysulfonate, which are doped with heteropolyanions $XW_{11}O_{39}M^{III}(H_2O)^{n-}$ (X = Si, Ge, B, P, and As; M = Fe, Rh, Tl, Al, Ga, and In) or $X_2W_{17}O_{62}M^{III}(H_2O)^{7-}$ (X = O and As; M = Fe, Rh, Tl, Al, Ga, and In).[74]

In contrast, the incorporation of α-$SiW_{11}O_{39}Fe^{III}(H_2O)^{5-}$ into polypyrrole or quanternized polyvinylpyridine resulted in a modified electrode which was unstable and/or exhibited only poor electrocatalytic activity. For example, the catalytic anion was lost when the electrode was employed for the catalytic reduction of H_2O_2.[63]

3. Reductive Electrocatalysis by Electrodeposited Polyoxometalates

Since Keita and Nadjo reported the electrodeposition of $SiW_{12}O_{40}^{4-}$ on electrodes in 1985,[75a] a great number of papers have been published in this field. As described in section II.A.1.a.i, the cyclic voltammogram of $SiW_{12}O_{40}^{4-}$ in acidic aqueous solution shows five reduction waves. In aqueous solution containing 0.5 M H_2SO_4 the last two eight- and twelve-electron reduction peaks are located at −0.83 and −0.93 V vs SCE, respectively. These reduction processes are irreversible and accompanied by chemical reactions. Therefore, if the potential is scanned until the potential, at which these reductions occur, the reoxidation peaks of the first three reversible reduction become small and ill defined. Furthermore, if the cycling is continued through the whole reduction range, the hydrogen evolution reaction starts progressively at more and more positive potential until even the first reduction waves of $SiW_{12}O_{40}^{4-}$ can no longer be observed. This electrode modification consists of electrodecomposed $SiW_{12}O_{40}^{4-}$. However, its real structure is not yet totally revealed.[75d,e,76m] But well-ordered two-dimensional arrays have been determined by STM and AFM methods.[75n,p,q] The modification can be carried out on electrode materials such as glassy carbon, gold, mercury, tungsten, and several semiconductors and

Table 2. Electrocatalytic Reductions by Heteropolyanions Entrapped in Polymer Films on Electrode Surfaces

polymer	catalyst	reduction	ref(s)
poly(aniline)	$SiW_{12}O_{40}{}^{4-}$	O_2 reduction	66a
	$PW_{12}O_{40}{}^{3-}$	O_2 reduction	66a
	$SiMo_{12}O_{40}{}^{4-}$	O_2 reduction	66b
		chlorate reduction	66b
		nitrite reduction	47
	$P_2Mo_{12}O_{40}{}^{6-}$	nitrite reduction	47
	$H_2Mo_8O_{26}$	chlorate reduction	66c, d
anionic polymer	$X^1W_{11}O_{39}M^{III}(H_2O)^{n-}$	nitrite/nitrogen monoxide reduction	74c
sulfonated polyamide	$X^2{}_2W_{17}O_{61}M^{III}(H_2O)^{n-}$	nitrite/nitrogen monoxide reduction	74c
sulfonated polystyrene	X^1: Si, Ge, B		
perfluorinated polysulfonate	X^2: P, As		
	M: Fe, Rh, Al, Ga, In, Tl		
poly(3-methylthiophene)	$PW_{12}O_{40}{}^{3-}$	O_2 reduction	70
poly(pyrrole)/poly(*N*-methylpyrrole)	$SiW_{12}O_{40}{}^{4-}$	O_2 reduction	67c
	$PMo_{12}O_{40}{}^{3-}$	O_2 reduction	67i
		chlorate reduction	67i, j
		bromate reduction	67j
	$P_2W_{12}O_{40}{}^{6-}$	O_2 reduction	67f
		nitrite reduction	35
	$Dy(SiMo_{11})_2{}^{13-}$	bromate reduction	67h
	$X^1W_{11}O_{39}M^{III}(H_2O)^{n-}$	nitrite/nitrogen monoxide reduction	74a−c
	$X^2{}_2W_{17}O_{61}M^{III}(H_2O)^{n-}$	nitrite/nitrogen monoxide reduction	74a−c
	X^1: Si, Ge, B		
	X^2: P, As		
	M: Fe, Rh, Al, Ga, In, Tl		
poly(4-vinylpyridine)/1,12-dibromododecane	$SiW_{12}O_{40}{}^{4-}$	O_2 reduction	45
		nitrite reduction	47
	$PMo_{12}O_{40}{}^{3-}$	chlorate reduction	45
		nitrite reduction	47
	$P_2Mo_{12}O_{40}{}^{6-}$	nitrite reduction	47
	α-$P_2W_{11}VO_{40}{}^{6-}$	nitrite reduction	47

Table 3. Exchange Current Densities from Tafel Plots for the Hydrogen Evolution Reaction at Electrodeposited Polyoxometalate Modified Electrode[a]

polyoxometalate	electrode[b]	$-\log(i_o/\mathrm{A\ cm^{-2}})$[c]
α-$H_4SiW_{12}O_{40}$	Pt	2.5−2.8 (3.0−3.3)
	Au	2.5 (5.7)
	W	2.6 (6.8)
	Hg	3.9−4.1 (11.0−12.7)
	GC	2.0−2.3 (7.2−8.5)
α-$H_3PW_{12}O_{40}$	GC	2.3−2.4
+ Fe(III)	GC	2.5
+ Ni(II)	GC	2.6
+ Cu(II)	GC	2.8
α-$H_3PW_{12}O_{40}$	Pt	2.6
+ Fe(III)	Pt	2.7
+ Cu(II)	Pt	3.0
α-$H_4SiMo_{12}O_{40}$	GC	2.0−2.3
α-$H_3PMo_{12}O_{40}$	GC	3.0−3.4
α-$(NH_4)_6H_2W_{12}O_{40}$	GC	2.4−2.6
α1-$K_6P_2W_{17}MoO_{62}$	GC	2.2−2.3
α2-$K_6P_2W_{17}MoO_{62}$	GC	2.2−2.3
α-$K_6P_2W_{18}O_{62}$	GC	2.4−2.5
H_2WO_4 in 12.4 M HCl	GC	2.4−2.5
none	GC	3.97

[a] Deposition conditions: polyoxometalate (1 mM) in 0.5 M H_2SO_4 aqueous solution, Pt (counterelectrode), −1.2 V vs SCE, room temperature. [b] GC: glassy carbon. [c] Negative logarithm of the exchange current density: values in parentheses are those obtained for the unmodified electrodes in 0.5 M H_2SO_4 aqueous solution. All data are taken from refs 75a,g,k.

a large number of iso- and heteropolyanions and tungstate anions are used.[75] The influence on the exchange current densities for the hydrogen evolution reaction is given in Table 3. The modified electrodes are very stable not only in solution at a wide pH range[75l] but also in air. Some electrodes can be kept for several years and still show the same activity toward the hydrogen evolution reaction. In addition, the modified electrodes are electrochemically stable and insensitive to impurities and additives which are usually deleterious to platinum and palladium catalysts.[75k] In addition to the action as catalyst for the hydrogen evolution reaction, the modified glassy carbon electrodes exhibit dramatically enhanced rates for the oxygen reduction ($PW_{12}O_{40}{}^{3-}$ $-\log(i_o/\mathrm{A\ cm^{-2}}) = 5.6$; nonmodified GC $-\log(i_o/\mathrm{A\ cm^{-2}}) = 8.3$) and for the reduction of the hexaamine ruthenium(III) cation.[75c,h] The interpretation of both catalytic processes as being due to the intrinsic catalytic properties of the electrodeposited polyoxometalate has been questioned seriously. There is strong evidence that the catalytic process is due to the deposition of small amounts of platinum at the cathode which stems from anodic corrosion of the platinum anode.[76]

The polyoxometalates immobilized in polymer matrixes can also be reductively modified and then show good activity toward the hydrogen evolution reaction.[19,66a,66b]

The heteropolyanions can be coelectrodeposited together with other metals. Savadogo's group investigated the electrodeposition of nickel or iron electrodes modified by heteropolyanions.[77] With the addition of the heteropolyanions the electrodeposited nickel and iron on electrodes provide better electrocatalytic properties for the hydrogen evolution reaction in acidic and also basic medium. Nickel electrodes codeposited with $SiMo_{12}O_{40}{}^{4-}$ or $PW_{12}O_{40}{}^{3-}$ are better electrocatalyst than platinum for the hydrogen evolution reaction. The heteropolyanion-modified electrodeposited nickel electrodes are less sensitive than platinum to impurity effects for the reaction, while tin and lead impurities in the deposited nickel significantly alter the characteristics of the electrode.

C. Concluding Remarks

In conclusion, some quite interesting properties of polyoxometaletes either in homogeneous solution, deposited on electrodes or incorporated in polymer films at electrodes especially for sensor applications have been developed. In these cases, the best results seem to be obtainable when the polyoxometalate is used for multielectron storage and a transition metal center acts as selective binding site for the substrate (analyte) to be reduced. Further development of this strategy also for synthetic application can be expected. The enhanced hydrogen evolution and the reduction of molecular oxygen at electrodeposited polyoxometalates in many cases seems to involve codepostion of small amounts of platinum. These electrodes are very long-lived and may open up possibilities for organic syntheses such as hydrogenation reaction or the in situ generation of hydrogen peroxide for selective oxidations.

IV. Electrocatalytic Oxidation

A. Transition Metal-Substituted Heteropolyanions

Transition metal-substituted heteropolyanions can be used as oxidative electrocatalysts, as summarized in Table 4. The complexes have been applied as homogeneous oxidation catalyst in both organic and aqueous phase.[2,3] The heteropolyanion ligands are robust under strong oxidative conditions, because they are completely oxidized inorganic compounds, and thus have an important advantage over organometallic complexes such as metalloporphyrin systems, which often decompose under these conditions.

1. Ru-Substituted Heteropolyanions

Oxoruthenium(IV) and oxoruthenium(V) organometallic complexes have attracted considerable interest because of their potential to act as oxygen transfer catalysts.[78] For the same reason, Ru-substituted heteropolyanions were examined with regard to potential application as redox catalysts. Rong and Pope generated $PW_{11}O_{39}Ru^{III}(H_2O)$ (**1**) by reaction of $(Ru(H_2O)_6)^{2+}$ with $PW_{11}O_{39}{}^{7-}$ followed by oxidation with O_2. They investigated the electrochemical properties of Ru in $PW_{11}O_{39}Ru$ in aqueous media and proposed the possibility that this complex might work as an electrochemical oxygen-transfer catalyst.[54]

Cyclic voltammetry of **1** in acidic solution shows three reversible redox couples for the Ru(III/II) (0 to −0.1 V vs SCE at pH 0 to 7), Ru(IV/III) (+0.4 V vs SCE at pH 4, changing with 120 mV per pH unit between pH 0 and pH 4 and with 58 mV per pH unit between pH 5 and pH 7), and Ru(V/IV) (ca. +0.9 V vs SCE at pH 0 to pH 7). These redox couples can be attributed to the aquaruthenium(II), oxoruthenium(IV), and oxoruthenium(V) derivatives according to eqs 40−42 and 44. In acidic solution, at a pH of 0, **1** is oxidized to the oxoruthenium(V) derivative in a single two-electron step according to eq 43.

$$PW_{11}O_{39}Ru^{III}(H_2O)^{4-}\ (\mathbf{1}) = PW_{11}O_{39}Ru^{III}(OH)^{5-} + H^+ \qquad pK_a = 5.1 \quad (39)$$

$$PW_{11}O_{39}Ru^{III}(H_2O)^{4-}\ (\mathbf{1}) + e^- = PW_{11}O_{39}Ru^{II}(H_2O)^{5-} \qquad \text{pH } 0-4 \quad (40)$$

$$PW_{11}O_{39}Ru^{III}(H_2O)^{4-}\ (\mathbf{1}) = PW_{11}O_{39}Ru^{IV}(O)^{5-} + e^- + 2H^+ \qquad \text{pH } 1-4 \quad (41)$$

$$PW_{11}O_{39}Ru^{IV}(O)^{5-} = PW_{11}O_{39}Ru^{V}(O)^{4-} + e^- \qquad \text{pH } 0-7 \quad (42)$$

$$PW_{11}O_{39}Ru^{III}(H_2O)^{4-}\ (\mathbf{1}) = PW_{11}O_{39}Ru^{V}(O)^{4-} + 2\ e^- + 2H^+ \qquad \text{pH } 0 \quad (43)$$

$$PW_{11}O_{39}Ru^{III}(OH)^{5-} = PW_{11}O_{39}Ru^{IV}(O)^{5-} + e^- + H^+ \qquad \text{pH } 5-7 \quad (44)$$

The dielectronic oxidation to generate the oxoruthenium(V) forms the basis of an electrocatalytic oxidation of dimethyl sulfoxide to the sulfone with >90% current efficiency and a moderate total turnover number of 40 for the catalyst (Figure 9).

The application as a reduction catalyst has been reported in section III.A.3.b.

Recently Bart and Anson studied the same system in the presence of π-acid ligands such as pyridine, pyrazine, and their protonated or *N*-methlylated

Table 4. Electrochemical Oxidations Catalyzed by Heteropolyanions

catalyst	substrate	products	conditions	ref(s)
α-$PW_{11}O_{39}Ru(H_2O)^{4-}$	Me_2SO	Me_2SO_2	electrolysis, sulfate buffer (pH 1) 1.1 V vs SCE, divided cell, room temperature	54
	alcohols	carbonyl compounds	acetate buffer (pH 4), room temperature	79
α-$Q_5SiW_{11}O_{39}Ru$[a]	olefins	aldehydes	double-mediator electrolysis CH_2Cl_2-H_2O, $NaIO_3$, undivided cell, 50 °C, PbO_2 anode, Pt cathode	81
α-$PW_{11}O_{39}Cr(H_2O)^{4-}$ $P_2W_{18}O_{61}Cr(H_2O)^{7-}$	alcohols	carbonyl compounds	sulfate buffer (pH 1), room temperature	85
α-$SiW_{11}O_{39}Mn(H_2O)^{6-}$	alcohols	carbonyl compounds	electrolysis, phosphate buffer (pH 6) 1.25 V vs Ag/AgCl, divided cell, room temperature C anode, Pt cathode	87 + 88
α_2-$P_2W_{17}O_{62}{}^{8-}$ α_1-$P_2W_{17}O_{62}{}^{8-}$ α_1-$P_2W_{17}MoO_{62}{}^{8-}$	NADH	NAD^+	phosphate buffer (pH 7), room temperature	89

[a] Q = tetrabutylammoniumion.

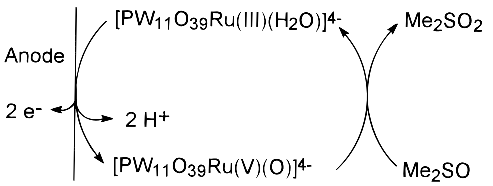


Figure 9. Electrocatalytic oxidation of dimethyl sulfoxide to dimethyl sulfone using $[PW_{11}O_{39}Ru^{III}(H_2O)]^{4-}$ as redox catalyst.

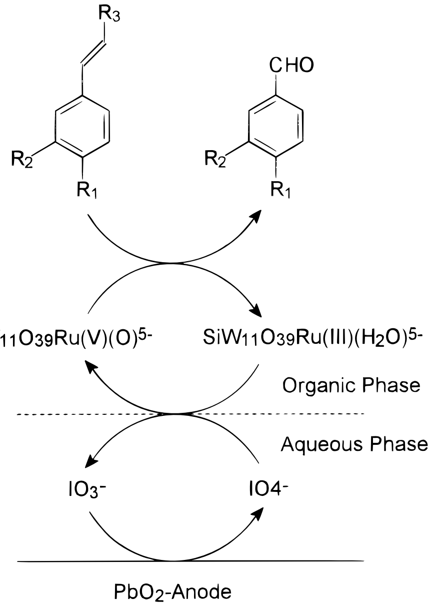


Figure 10. Indirect electrochemical oxidation cleavage of alkenes using a double-mediator system consisting of IO_4^- and ruthenium tungstosilicate.

derivatives. These ligands replace the aqua ligand thus stabilizing the Ru(II) form and shifting the redox potential of the Ru(III/II) couple by 150 mV to more positive values. The Ru(IV/III) and Ru(V/III) couples are no longer present in the cyclic voltammogram because of the absence of an aqua ligand.[79]

It was also shown that the oxoruthenium(V) species formed by electrochemical oxidation of $[PW_{11}O_{39}Ru(H_2O)]^{4-}$ can oxidize alcohols. The catalytic oxidation of benzylic alcohol, 2-propanol, and methanol were investigated by the rotating-disk method. The rate constants obtained for the homogeneous oxidation reaction were about 30 M^{-1} s^{-1} for the benzylic alcohol in acetate buffer at pH 4 and ~9 and 10^{-1} M^{-1} s^{-1}, respectively, for 2-propanol and methanol in the same medium. Compared with other organometallic oxoruthenium(V) complexes such as ruthenium–polypyridine complex the Ru-substituted heteropolyanions are considerable less reactive.[78]

The corresponding tungstosilicate analogue $SiW_{11}O_{39}Ru^{III}(H_2O)$ was first prepared by Neuman and Abu-Gnim. The hydrophobic quaternary ammonium salt of this compound can catalyze the oxidative cleavage of olefins. The selectivity of the oxidation can be controlled by variation of the stoichiometric oxidant.[80] By using $NaIO_4$ as oxidant, olefins can be cleaved to aldehydes in high yields. While the direct electrochemical regeneration of the active oxoruthenium(V) species failed, Steckhan and Kandzia were able to use this complex successfully in a two-phase double-mediator system.[81] The IO_4^- was regenerated at the PbO_2 anode in the aqueous phase and various olefins were converted to the corresponding aldehydes in the organic phase. Up to 200 cycles of the catalyst have be obtained without loss of its activity (Figure 10 and Table 5). As pointed out before, electrochemical investigation and direct electrochemical oxidation of this compound failed yet. X-ray studies showed that the catalyst is a mixture of several isomers.[82]

Table 5. Indirect Electrolytical Cleavage of Aryl-Substituted Olefins[a]

aldehyde	turnover	yield of olefin,[b] (%)	current yield[c] (%)
$R_1, R_2 = CH_2OCH_2$ $R_3 = Me$	206	70	44
$R_1 = OMe, R_2 = H$ $R_3 = Me$	143	59	23
$R_1 = OMe, R_2 = H$ $R_3 = PhOMe-4$	133	78	29
$R_1, R_2 = H, R_3 = Ph$	137	79	57

[a] Conditions: The electrolyses were run galvanostatically with a current density of 8 mA/cm^2 in the presence of the catalyst (~0.5 mol %) on a 2–3 mmol scale. Almost complete conversion is reached within 3.5–5.5 F/mol. [b] Isolated yield. [c] Percentage of theoretical required amount of electroricity. The data are taken from ref 81.

2. Cr-Substituted Heteropolyanions

Oxochromium(V) heteropolyanions have been prepared from the corresponding chromium(III) species using stoichiometric oxidants such as OCl^-, H_2O_2, or iodosylbenzene. Their application as oxygen-transfer reagents has been studied intensively by the groups of Pope[83] and Hill.[84] Catalytic oxidation of alkanes, alkenes, alcohols, and phosphines were thus possible. All results point to a radical-type addition of the oxygen to a double bond.[84] Thus, it was of importance to study the electrochemical behavior of α-$[PW_{11}O_{39}Cr(III)(H_2O)]^{4-}$ and α_2-$[P_2W_{17}O_{61}Cr(III)(H_2O)]^{7-}$ in H_2O in detail to evaluate their potential as electrocatalysts, which was performed by Rong and Anson.[85] While a reduction of chromium(III) to chromium(II) cannot be observed in cyclic voltammograms at pH 1, the electrochemical oxidation at potentials around 1.3 V vs Ag/AgCl directly leads to the oxochromium(V) species in a two-electron quasi-reversible step according to eqs 45 and 46.

$$\alpha\text{-}[PW_{11}O_{39}Cr^{III}(OH_2)]^{4-} = \alpha\text{-}[PW_{11}O_{39}Cr^{III}(O)]^{4-} + 2e^- + 2H^+ \quad (45)$$

$$\alpha_2\text{-}[P_2W_{17}O_{61}Cr^{III}(OH_2)]^{7-} = a_2\text{-}[P_2W_{17}O_{61}Cr^{V}(O)]^{7-} + 2e^- + 2H^+ \quad (46)$$

The electrochemically generated $Cr^V{=}O$ complexes are able to oxidize alcohols to carbonyl compounds (Figure 11). The second-order rate constants for the reactions of both α-$[PW_{11}O_{39}Cr^V{=}O]^{4-}$ and α_2-$[P_2W_{17}O_{61}Cr^V{=}O]^{7-}$ with benzylic alcohol are ~1.5×10^{-3} M^{-1} s^{-1} which is by a factor of 2000 smaller than in the case of the corresponding ruthenium tungstosilicate.

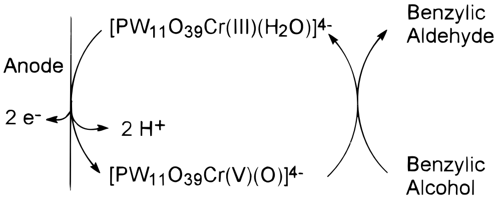


Figure 11. Electrocatalytic oxidation of benzylic alcohol to benzylic aldehyde using $[PW_{11}O_{39}Cr^{III}(H_2O)]^{4-}$ as redox catalyst.

3. Mn-Substituted Heteropolyanions

Manganese-substituted heteropolyanions were first reported in 1970.[43] Pope and co-workers have oxidized some Mn(II)-substituted polyoxotungstenate $XW_{11}O_{39}Mn^{II}(H_2O)$ (X = Si, P, B, and Zn) chemically and electrochemically and characterized the species by spectroscopy.[86] They proposed that the corresponding manganese complex is oxidized to the $Mn^{IV}(OH)$ complex rather than to $Mn^{V}(O)$. The detailed electrochemical behavior of the $SiW_{11}O_{39}Mn$ complex was investigated by Sadakane and Steckhan[87] and the formation of $SiW_{11}O_{39}Mn^{IV}(OH)$ was clearly demonstrated by means of cyclic voltammetry. The cyclic voltammogram of $K_nSiW_{11}O_{39}Mn^{II}(H_2O)^{(6-n)-}$ has no reproducibility and was strongly dependent on the pretreatment of the electrode. Stable cyclic voltammograms of Mn(IV/III) (eq 47) and Mn(III/II) (eq 48) could only be obtained after continuous cycling in cyclic voltammetry (between 1.3 and 0 V vs Ag/AgCl) or by starting the CV from 1.3 V vs Ag/AgCl where the manganese was oxidized to Mn(IV).

$$K_{n-1}SiW_{11}O_{39}Mn^{IV}(OH)^{(6-n)-} + e^- + H^+ = K_{n-1}SiW_{11}O_{39}Mn^{III}(H_2O)^{(6-n)-} \quad (47)$$

$$(E_{1/2} = 0.99 \text{ V vs Ag/AgCl, at pH} = 6.0)$$

$$K_{n-1}SiW_{11}O_{39}Mn^{III}(H_2O)^{(6-n)-} + e^- + K^+ = K_nSiW_{11}O_{39}Mn^{II}(H_2O)^{(6-n)-} \quad (48)$$

$$(E_{1/2} = 0.53 \text{ V vs Ag/AgCl, at pH} = 6.0)$$

This phenomenon was explained as follows: First, the Mn(II) complex exists in two forms; the primarily present labile aquo water ligand can be replaced by the counteranion L ($H_2PO_4^-$ or HPO_4^{2-} in phosphate buffer) (eq 49).

$$K_nSiW_{11}O_{39}Mn^{II}(H_2O)^{(6-n)-} + L = K_nSiW_{11}O_{39}Mn^{II}(L)^{(6-n)-} + H_2O \quad (49)$$

Second, these complexes were oxidized to the Mn (IV) stage (eqs 47, 48, 50, and 51) and the counteranion ligand (L) was replaced by the hydroxy anion (eq 52) to generate $K_{n-1}SiW_{11}O_{39}Mn^{IV}(OH)^{(6-n)-}$.

$$K_nSiW_{11}O_{39}Mn^{II}(L)^{(6-n)-} = K_{n-1}SiW_{11}O_{39}Mn^{III}(L)^{(6-n)-} + e^- + K^+ \quad (50)$$

$$K_{n-1}SiW_{11}O_{39}Mn^{III}(L)^{(6-n)-} = K_{n-1}SiW_{11}O_{39}Mn^{IV}(L)^{(5-n)-} + e^- \quad (51)$$

$$K_{n-1}SiW_{11}O_{39}Mn^{IV}(L)^{(5-n)-} + OH^- = K_{n-1}SiW_{11}O_{39}Mn^{IV}(OH)^{(6-n)-} + L \quad (52)$$

The formation of $K_{n-1}SiW_{11}O_{39}Mn^{IV}(OH)^{(6-n)-}$ was clearly detected by observing the average redox potential by changing the pH and the potassium concentration in the electrolyte.

$$2K_{n-1}SiW_{11}O_{39}Mn^{IV}(OH)^{(6-n)-} + RCH(OH)R' = 2K_{n-1}SiW_{11}O_{39}Mn^{III}(H_2O)^{(6-n)-} + RC(=O)R' \quad (53)$$

The thus-formed complex $K_{n-1}SiW_{11}O_{39}Mn^{IV}(OH)^{(6-n)-}$ could be used for the oxidation of different alcohols via hydride ion transfer (eq 53). It was also demonstrated that this system is effective in the indirect electrochemical oxidation of alcohols (Figure 12, Table 6).[88]

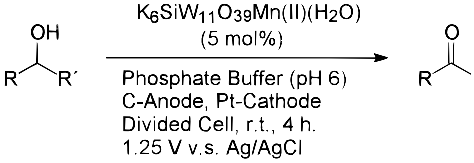


Figure 12. Indirect electrochemical oxidation of alcohols using $K_6SiW_{11}O_{39}Mn^{II}(H_2O)$ as redox catalyst.

Table 6. Indirect Electrochemical Oxidation of Alcohols[a]

alcohols	yields of products (%) ketones	yields of products (%) carboxylic acid	recovery of alcohols (%)	current yields (%)
R = Ph R′ = Me	61		37	48
R = 4-NO₂Ph R′ = H	12	26	34	66
R = 4-ClPh R′ = H	12	24	44	64
R = 4-MeOPh R′ = H	64	16	0	100
R, R′ = −CH=CH(CH₂)₃−	28		69	22

[a] Conditions: $K_6SiW_{11}O_{39}Mn(H_2O)$ (5 mmol %), phosphate buffer (pH = 6), C anode, Pt cathode, constant potential at 1.25 V vs Ag/AgCl, divided cell, room temperature, 4 h.

B. Mixed-Addenda Heteropolyanions

1. V- and Mo-Substituted Heteropolyanions

Recently, Nadjo et al. reported an intensive study of Dawson-type mixed heteropolyanions for the oxidation of NADH.[89] The coenzyme redox couple NADH/NAD$^+$ is one of the most important redox equivalents in biological systems. A great deal of attention has been focused on the regeneration of this coenzyme in its reduced or oxidized form for its application in enzymatic synthesis or in biosensors.[90] Because of its elegance, especially the electrochemical regeneration has attracted much attention.[91] The electrochemical oxidation of NADH directly at the

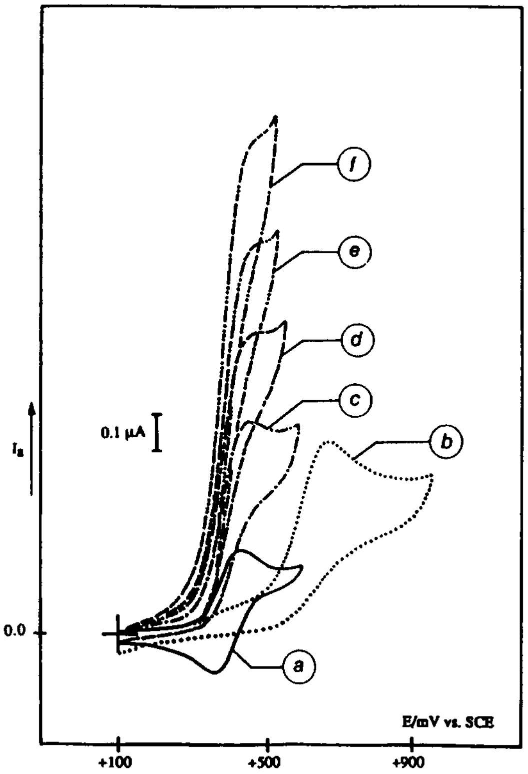


Figure 13. Cyclic voltammogram of $\alpha_2-P_2W_{17}VO_{62}^{8-}$ (1 mM) in phosphate buffer (pH 7): (a) in the absence of NADH, (b) cyclic voltammogram of NADH (1 mM) in phoshate buffer (pH 7), (c–f) in the presence of NADH (c) 0.5 mM, (d) 1.3 mM, (e) 2.1 mM, and (f) 3 mM. Conditions: platinum working electrode, platinum counter electrode, SCE reference electrode, scan rate 100 mV/s. (Reprinted with permission from ref 89a. Copyright Elsevier Sequoia S. A., Lausanne.)

electrode surface is possible if large surface area anodes such as graphite felt are employed.[92] However, high overpotentials are necessary and often fouling of the electrode surface has been observed. Therefore, numerous attempts have been made in order to find suitable redox mediators or electrode modification processes for accelerating the highly irreversible oxidation of NADH. Nadjo et al. found that mixed vanado- and molybdotungstophosphoric systems and their one-electron reduction products are stable in the pH domain of pH 7 and oxidize NADH to NAD^+ efficiently. Figure 13a shows the voltammogram associated with the first redox couple α_2-$P_2W_{17}VO_{62}^{7-}$/α_2-$P_2W_{17}VO_{62}^{8-}$ (eq 54) in pH = 7 phosphate buffer. Figure 13b represents the cyclic voltammogram of the direct oxidation of NADH alone under the same conditions. NADH oxidation catalyzed by α_2-$P_2W_{17}VO_{62}^{7-}$ was clearly observed in cyclic voltammetry (Figure 13c–f). On addition of NADH, the anodic current of the redox pair α_2-$P_2W_{17}VO_{62}^{7-}$/α_2-$P_2W_{17}VO_{62}^{8-}$ increased substantially while the reduction peak current was suppressed. Detailed analytical studies revealed a multistep mechanism involving an initial rate-limiting one-electron transfer. The rate constant of the one-electron NADH oxidation step (eq 55) is ~10^3 M^{-1} s^{-1}, as determined by double potential step chronocoulometry.

$$\alpha_2\text{-}P_2W_{17}VO_{62}^{8-} = \alpha_2\text{-}P_2W_{17}VO_{62}^{7-} + e \quad (54)$$

$$2\alpha_2\text{-}P_2W_{17}VO_{62}^{7-} + NADH = 2\alpha_2\text{-}P_2W_{17}VO_{62}^{8-} + NAD^+ + H^+ \quad (55)$$

α_1-$P_2W_{17}VO_{62}$,$^{8-}$ α_1-$P_2W_{17}MoO_{62}$,$^{7-}$ and $P_2W_{16}V_2O_{62}^{9-}$ can also be used as NADH oxidation electrocatalysts, while the rate for $P_2W_{16}V_2O_{62}^{9-}$ is too small to make it applicable as catalyst.

While large second-order homogeneous rate constants for the reaction between the heteropolyanions and NADH of up to 10^4 M^{-1} s^{-1} could be obtained, neither preparative-scale NAD^+ production nor the more important coupling with a dehydrogenase-catalyzed enzymatic synthesis have yet been performed. For this application, a problem might occur because the optimum pH values are between pH 8 and mostly pH 9 to shift the equilibrium to the oxidized product. Such high pH values are not compatible with heteropolyanions because they start to decompose. Because the heteropolyanions are active as one-electron-transfer agents toward NADH, systems with relatively positive redox potentials have to be applied to obtain high rate constants, for example 480 mV vs SCE for a rate constant of 10^4 M^{-1} s^{-1}. Hydride ion abstracting agent, like quinoide structures, however, can be electrochemically regenerated around 0 V.[93]

C. Concluding Remarks

While transtion metal-substituted and mixed-addenda heteropolyanions are promising candidates for electrocatalytic oxidations, the results observed until now are still quite limited. The rate constants which have been obtained for alcohol oxidations are still too low, especially in the case of aliphatic alcohols. The electrochemical investigations clearly demonstrated that in several cases oxo- or hydroxymetal species, which often are the active species in oxidation reactions, can be electrochemically generated in aqueous media. Further studies are necessary to tune these systems in such a way that their reactivity can be enhanced. Possible starting points are besides the nature of the transiton metal, the selection of addenda ions and the incorporation of ligands, solvents or cosolvents, thus shifting the redox potential in a predictable way.

We believe that transition metal-substituted heteropolyanions because of their unique character, such as tunability of the potentials and variability of the anionic charge without changing the size, in the future will be able to supplement the common anionic electrocatalysts, such as $Fe(CN)_6^{3-}$ or $Mo(CN)_8^{4-}$.

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