

MODIFIED ELECTRODES FOR ELECTROCATALYSIS

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ABSTRACT: Glassy carbon electrode (GCE) surfaces were modified by polymeric ruthenium(II) (vinyl) bipyridine [Poly-Ru (vbpy)₃²⁺] films containing the polyoxometalate ions PMo₁₂O₄₀³⁻ (PMo₁₂), PW₁₂O₄₀³⁻ (PW₁₂), and SiW₁₂O₄₀⁴⁻ (SiW₁₂). The modifications were carried out by reductive electropolymerization of Ru(vbpy)₃²⁺ followed by incorporation of the polyoxometalate anions using an ion exchange method. The modified electrodes were used to catalyze the electroreduction of protons and small oxoanions such as ClO₃⁻, BrO₃⁻, IO₃⁻, and NO₃⁻. Electrodes modified with immobilized PW₁₂ and SiW₁₂ were found to be more effective catalytic reductants than those modified with immobilized PMo₁₂. The catalytic activities of these immobilized polyoxometalates are explained on the basis of their electrochemical behavior in both the free and immobilized states.

KEYWORDS: Electrocatalysis, modified electrodes, oxoanions, and polyoxometalates.

INTRODUCTION

Performing electrochemical reactions at electrode surfaces requires the careful control of the reactivity at the electrode/electrolyte interface. Such control, when it is possible, affects the use of electrochemistry in such areas as analysis, catalysis, and synthesis. By modifying the electrode's surface, a researcher can dictate and control its properties to serve the purpose of a chemical process. In the designed modification process, some of the physicochemical properties of the modifiers are transferred to the electrode's surface, where they enhance such properties as its reactivity, sensitivity, and selectivity.

Because of their chemical stability and their capacity to undergo multi-electron charge transfer reactions, polyoxometalates should be excellent electrocatalysts. A number of reports have discussed the electrocatalytic properties of polyoxometalates and related metal oxide aggregates (Unoura, *et al.*, 1984; Toth, 1990; Toth, *et al.*, 1989; Keita and Nadjo, 1985, 1988a; Kulesza and Faulkner, 1988; Ebersson, 1983; Amadelli, *et al.*, 1990; Navalikhina, *et al.*, 1990). When these electrochemical properties are transferred to a native electrode, its electrochemical properties are enhanced. The transfer is achieved by trapping the polyoxometalate anions in chemically modified layers on the electrode's surface (Murray, 1984). Although widely used in applications based on its electron transfer properties, poly-Ru(vbpy)₃²⁺ (Braddock and Meyer, 1973) is also a potentially useful ion

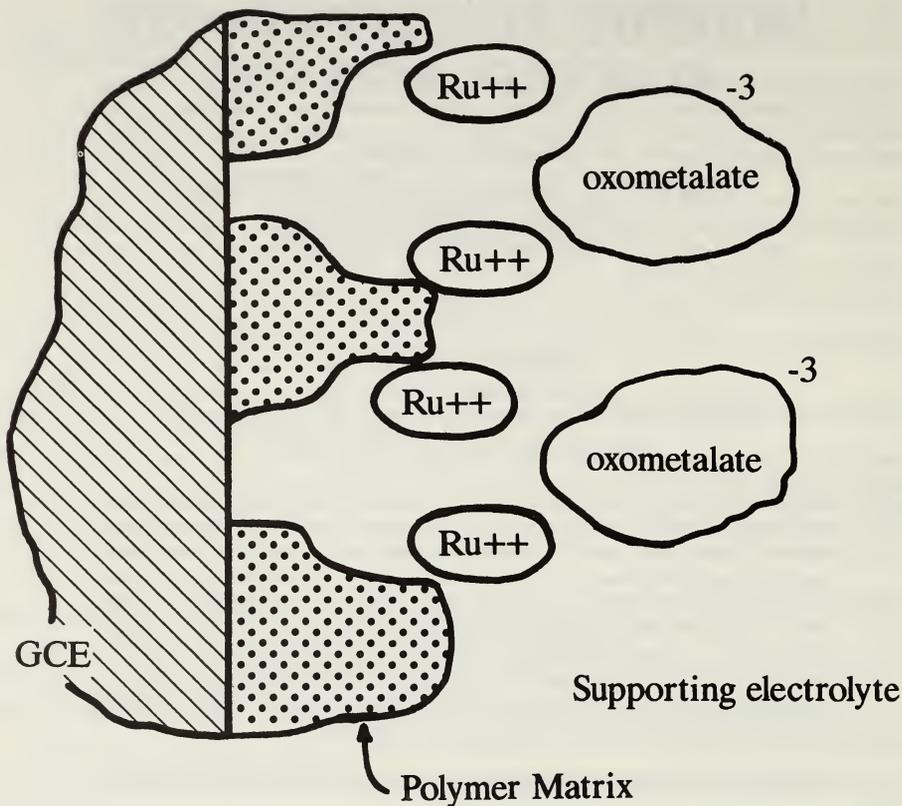


Figure 1. Schematic diagram of a poly-Ru(vbpy)₃²⁺ film containing oxometalate anions on the GCE.

exchange polymer because of its chemical stability, its wide electrochemical window, and its ability to be used in both aqueous and non-aqueous environments.

The electrochemical behavior of immobilized PMo₁₂, PW₁₂, or SiW₁₂ in poly-Ru(vbpy)₃²⁺ has already been studied (Kasem and Schultz, 1995). The present work focuses on the use of electrodes modified with polyoxometalates entrapped in poly-Ru(vbpy)₃²⁺ for the electrocatalytic reduction of H⁺ as well as for the electrochemical reduction of some small oxoanions such as ClO₃⁻, BrO₃⁻, IO₃⁻, and NO₃⁻.

MATERIALS AND METHODS

The PMo₁₂, PW₁₂, and SiW₁₂ heteropolyanions were purchased as phosphomolybdic (Aldrich), phosphotungstic (Fluka), and tungstosilicic (Fluka) acid and used as received. The monomeric reagent, Ru(vbpy)₃²⁺, was prepared from RuCl₃ and 4-vinyl-4'-methyl-2,2'-bipyridine (vbpy) (see Braddock and Meyer, 1973) and isolated as the hexafluorophosphate salt. The vbpy ligand was prepared using the procedure discussed by Abruna, *et al.* (1985) and was characterized by ¹H NMR spectroscopy. Poly(4-vinyl) pyridine (PVP) was purchased from Scientific Polymer Products. Films of poly-Ru(vbpy)₃²⁺ on GCE

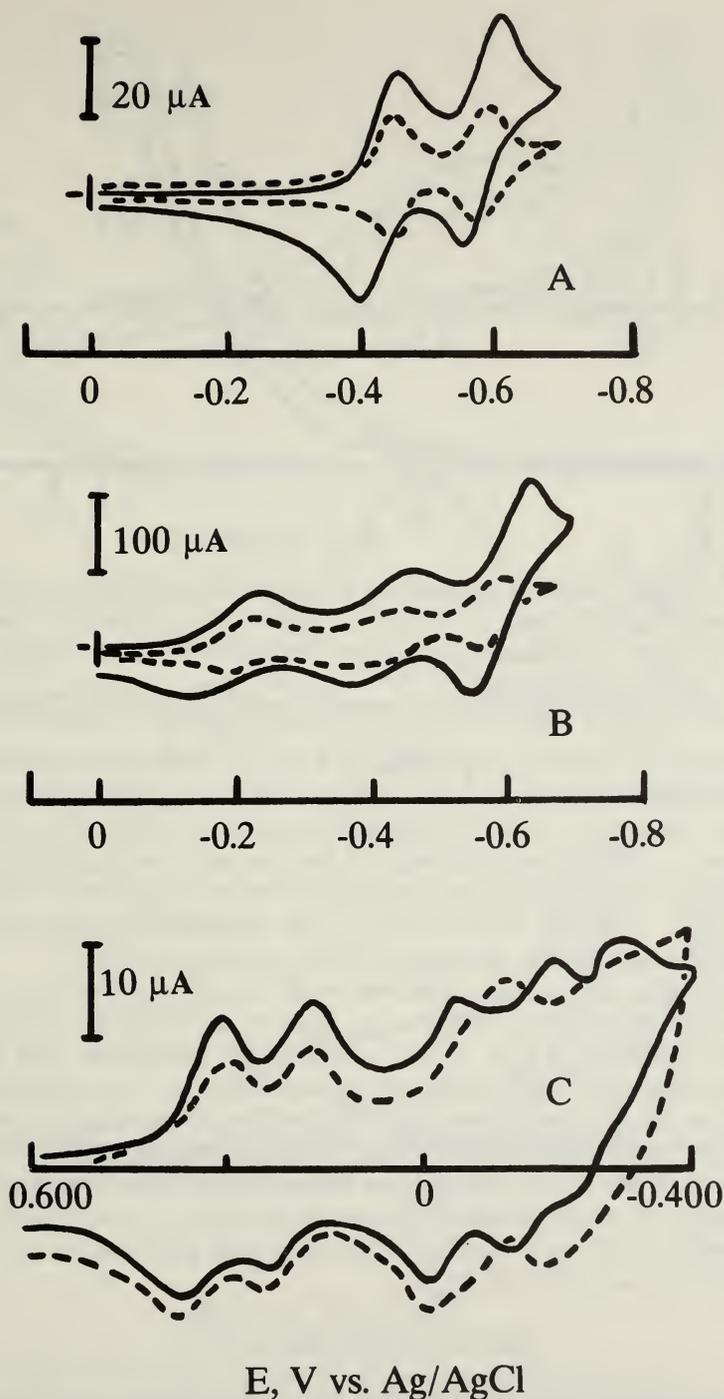


Figure 2. Cyclic voltammograms of 1 mM freely diffusing (—) and immobilized (---) oxometalates in poly-Ru(vbpy)₃²⁺ in 50% dioxane/water containing 0.5 M H₂SO₄: A) SiW₁₂; B) PW₁₂; and C) PMO₁₂. The scan rate was 100 mV/sec.

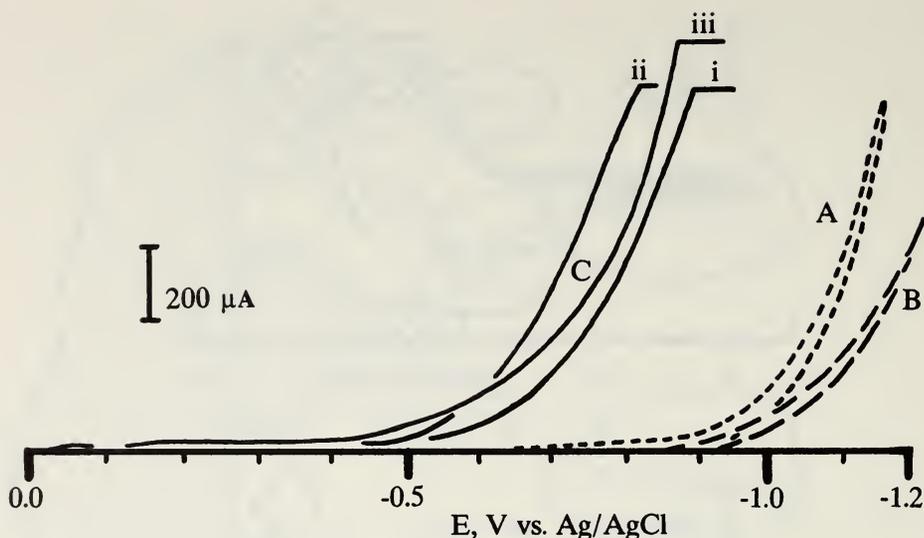


Figure 3. Electrochemical behavior of a bare GCE (A), a GCE modified with multilayers of poly-Ru(vbpy) $_3^{2+}$ films (B), and a GCE modified with multilayers of poly-Ru(vbpy) $_3^{2+}$ films (C) containing PMo $_{12}$ (i), PW $_{12}$ (ii), and SiW $_{12}$ (iii). The scan rate was 100 mV/sec.

were prepared by cycling the potential of a glassy carbon disk electrode (0.071 cm 2 , Bioanalytical Systems) between -0.9 and -1.9 V vs. Ag/AgCl in an acetonitrile solution containing 1-2 mM Ru(vbpy) $_3$ (PF $_6$) $_2$ plus 0.1 M Bu $_4$ NPF $_6$. Scans were carried out at a sweep rate of 200 mV s $^{-1}$ for a period of ca. 8 minutes, resulting in electrodes whose surfaces were covered by between 4×10^{-9} and 9×10^{-9} moles Ru per cm 2 . Films of PVP on GCE were prepared and cross-linked with 1,12-dibromododecane as described by Keita and Nadjo (1988c).

Heteropolyanions were incorporated in the ion polymer films by soaking the modified electrodes for 2-24 hours in aqueous or 50% (v/v) dioxane/water solutions containing 0.5 M H $_2$ SO $_4$ and 0.01 M heteropoly acid (Figure 1 illustrates a modified GCE containing oxometalate ions in a poly-Ru(vbpy) $_3^{2+}$ film). Then, the electrodes were rinsed thoroughly and transferred to reactant-free electrolyte, where their electrochemical response was examined. The surface coverage of anions on the electrode was determined by integrating the area under voltammetric i-E curves (see Braddock and Meyer, 1973). The electrode potentials are reported relative to a Ag/AgCl half-cell whose potential is -45 mV vs. a Saturated Calomel Electrode (SCE)

RESULTS AND DISCUSSION

The electrochemical behaviors of the free and immobilized polyoxometalates under study are recorded in Figure 2. The similarities between the redox behavior of the free and immobilized oxometalates are clearly evident. However, two differences were noted. First, small differences were observed between the behavior of free and immobilized PMo $_{12}$ (Figure 2C), particularly in the third

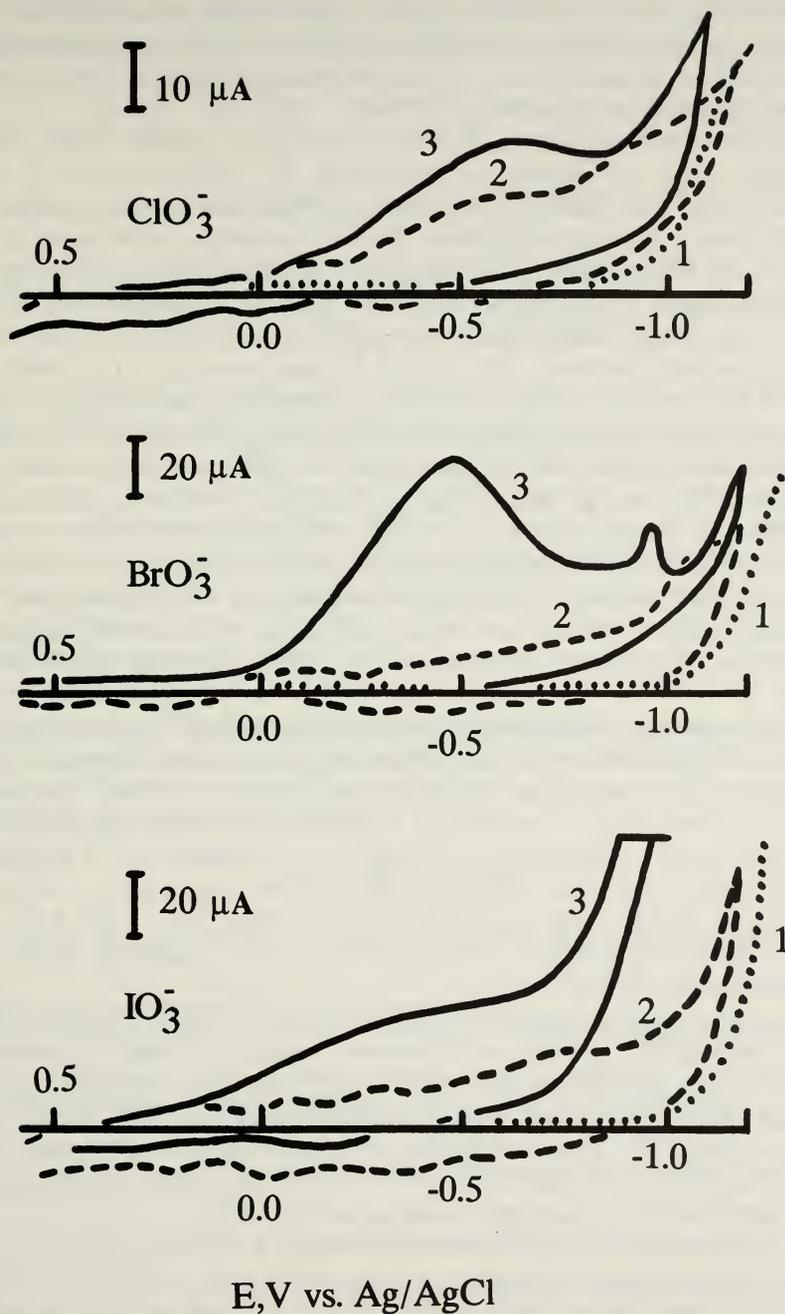


Figure 4. The electrocatalytic reduction of small oxoanions by incorporated PMo_{12} : Trace 1 (···) represents a GCE modified with 6.0×10^{-9} mole/cm² poly-Ru(vbpy)₃²⁺ in 1 M KCl + 0.2 M KClO_3 , KBrO_3 , or KIO_3 ; Trace 2 (- - -) represents a GCE modified with 6.0×10^{-9} mole/cm² poly-Ru(vbpy)₃²⁺ containing 4.4×10^{-10} mole/cm² of PMo_{12} in 1 M KCl; and Trace 3 (—) represents an electrode of trace 2 in 1 M KCl + 0.2 M KClO_3 , KBrO_3 , or KIO_3 . The sweep rate was 20 mV/sec.

and fourth redox waves, which partially overlapped in the immobilized state. The overlapping was attributed to a change in the Lewis acid base characteristics of the host medium (Kasem, 1994). Second, the redox potentials of PMo_{12} are more positive than those of either PW_{12} or SiW_{12} .

Electrocatalytic Reduction. The electrocatalytic activities of the modified electrodes were investigated by comparing the cathodic scan of native, poly-Ru(vbpy) $_3^{2+}$ modified and poly-Ru(vbpy) $_3^{2+}$ /polyoxometalates modified GCE in electrolytes containing the substrate. The electrocatalytic reduction of H^+ in 0.5 M H_2SO_4 by PMo_{12} , SiW_{12} , and PW_{12} ions incorporated in poly-Ru(vbpy) $_3^{2+}$ is illustrated in Figure 3. The overpotential for H^+ reduction is diminished by 0.3-0.5 V relative to its value at bare and poly-Ru(vbpy) $_3^{2+}$ -modified GCE. Noticeable H^+ reduction occurred between -0.5 and -0.7 V, corresponding to the addition of a total of 4 electrons to both PW_{12} and SiW_{12} and 8 electrons to PMo_{12} . Although hydrogen evolution has been detected at the potential of the first SiW_{12} reduction wave (Keita and Nadjo, 1987), apparently several electrons must be added to the polyoxometalate lattices before they can catalyze H^+ reduction efficiently as homogeneous reactants. Keita and Nadjo (1985, 1987, 1988b) have observed efficient H_2 formation under less forcing conditions using surfaces modified by electrodeposited derivatives of polyoxometalates, but the composition of these electrodeposited layers has not been established. The results suggest that W-based polyoxometalates are more effective at H^+ reduction than those based on Mo.

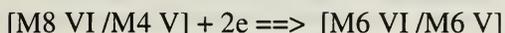
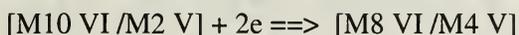
Electrocatalytic reduction of some small oxoanions. The electrochemical reduction of mononuclear oxo complexes of molybdenum and tungsten is known to catalyze the reduction of small inorganic anions (Lahr, *et al.*, 1984). The reactions proceed by inner-sphere mechanisms at labile, water-containing coordination sites on the metal. Similar sites are thought to be available on the periphery of reduced polyoxometalates, and these species have been used to catalyze the reduction of several oxoanions (Unoura, *et al.*, 1984; Toth, 1990; Toth, *et al.*, 1989; Kulesza and Faulkner, 1988; Ebersson, 1983; Amadelli, *et al.*, 1990; Navalikhina, *et al.*, 1990).

The electrocatalytic reductions of ClO_3^- , BrO_3^- , and IO_3^- at poly-Ru(vbpy) $_3^{2+}$ films containing PMo_{12} anions are illustrated in Figure 4. Catalytic current begins to flow at potentials more negative than ca. -0.1 V for ClO_3^- and BrO_3^- and at ca. 0.15 V for IO_3^- . These values coincide with the addition of either six (ClO_3^- and BrO_3^-) or four (IO_3^-) electrons to PMo_{12} . While six electrons are appropriate for the stoichiometric reductions of ClO_3^- to Cl^- and BrO_3^- to Br^- , four electrons are appropriate for the stoichiometric reduction of IO_3^- to IO^- .

A large increase in current occurred around -0.8 V (Figure 3C). The lack of surface analysis makes it difficult to explain this increase in current. Perhaps, as more than 12 electrons were added to the PMo_{12} ion, disproportionation reactions occurred leading to the cathodic deposition of nonstoichiometric aggregates.

The electrocatalytic reductions of ClO_3^- , BrO_3^- , IO_3^- , NO_3^- , and NO_2^- on modified GCE with poly-Ru(vbpy) $_3^{2+}$ films containing PW_{12} and SiW_{12} anions are similar to those shown in Figure 4. A qualitative comparison of the catalytic activities of each modifier towards oxoanion reduction was made based on the normalized charge under each cathodic wave. In general, the modified electrodes with immobilized PW_{12} or SiW_{12} were more efficient in oxoanion reduction than

those modified with immobilized PMo_{12} . The fact that the immobilized polyoxometalate anions become catalytically active after the addition of at least 4 electrons to the metalate network can be understood by considering the following reduction mechanism, which illustrates the electronation reactions (Souhay, *et al.*, 1964):



where M represents either Mo or W (the protonation reactions are not shown).

Reduction from the VI to V oxidation state is accompanied by changes in the M...M distances (Pope, 1983). When the metalate network contains 4 or more M(V), a strain is created within the Keggin structures. Restabilizing these structures under experimental conditions is accomplished by transferring electrons to the substrate and causing the catalytic action. Addition of more electrons to the metalate network increases the M(V) content, which may cause the disproportionation reactions. The existence of multivalent W aggregates in similar compounds, as detected by X-ray photoelectron spectroscopy, is evidence for such disproportionation. Large scale electrolysis and product analysis experiments are needed to determine if each polyoxometalate ion must be charged with a full complement of reducing equivalents before multi-electron catalysis can proceed. Characterization of the mechanisms and products of these reactions will be the subject of future studies.

LITERATURE CITED

- Abruna, H.D., A. Breikss, and D.B. Collum. 1985. Improved synthesis of 4-vinyl-4'-methyl-2,2'-bipyridine. *Inorg. Chem.* 24: 987-988.
- Amadelli, R., G. Varani, A. Maldotti, and V. Carassiti. 1990. Reduction of nitro aromatic compounds by photoreduced heteropolytungstates. *J. Mol. Catal.* 59(3): L9-L14.
- Braddock, J.N. and T.J. Meyer. 1973. Kinetics of the oxidation of $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ by polypyridine complexes of ruthenium(III). *J. Amer. Chem. Soc.* 95: 3158-3162.
- Eberson, L. 1983. Electron-transfer reactions in chemistry. 4. A mechanistic study of the oxidation of p-methoxytoluene by 12-tungstocobalt(III)ate ion. *J. Amer. Chem. Soc.* 105: 3192-3199.
- Kasem, K.K. 1994. Solvent effects on the redox behavior of silicotungstate in mixtures of some oxoanions and their potential analytical applications. *Ann. Chim.* 84: 365-377.
- _____ and F.A. Schultz. in press. Electrochemistry of polyoxometalates immobilized in ion exchange polymer films. *Can. J. Chem.* 73.
- Keita, B. and L. Nadjo. 1985. Activation of electrode surfaces. *J. Electroanal. Chem.* 191: 441-448.
- _____ and _____. 1987. New aspects of the electrochemistry of heteropolyanions. *J. Electroanal. Chem.* 217: 287-304.
- _____ and _____. 1988a. Distribution of oxometalates on polymer-covered electrodes. *J. Electroanal. Chem.* 243: 481-491.
- _____ and _____. 1988b. Surface modification with heteropolyanions. *J. Electroanal. Chem.* 247: 157-164.
- _____ and _____. 1988c. Strategies for entrapping oxometalates in polymeric matrices. *J. Electroanal. Chem.* 255: 303.
- _____, _____, and J.P. Haeussler. 1987. Activation of electrode surfaces; Semiquantitative characterization of electrode surfaces modified with heteropolyanions. *J. Electroanal. Chem.* 230: 85-97.
- Kulesza, P.J. and L.R. Faulkner. 1988. Electrocatalysis at a novel electrode coating of nonstoichiometric tungsten(VI,V) oxide aggregates. *J. Amer. Chem. Soc.* 110: 4905-4913.

- Lahr, S.K, H.O. Finklea, and F.A. Schultz. 1984. Electrocatalytic reduction of oxoanions by aqueous molybdenum-catechol complexes. *J. Electroanal. Chem.* 163: 237-255.
- Murray, R.W. 1984. Electroanalytical chemistry. In: A.J. Bard (Ed.), *Electroanalytical Chemistry, Vol. 13*, pp. 191-368, Marcel Dekker, New York.
- Navalikhina, M.D., I.L. Malkina, and V.I. Garanin. 1990. Hydrogenation of benzene and toluene on nickel catalysts modified with heteropoly tungstates. *Neftekhimiya* 30(1): 26-29.
- Pope, M.T. 1983. *Heteropoly and isopoly oxometalates*. Springer-Verlag, New York, 180 pp.
- Souchay, P., R. Massart, and M. Biquard. 1964. Isomerism and reduction product of the molybdc heteropoly acids. *Proc. Int. Conf. Coordination Chem., Wien*, pp. 394-396.
- Toth, J.E. 1990. Electrocatalytic activities of transition metal substituted heteropolytungstates. Ph.D. Thesis, California Inst. Tech., Pasadena (Diss. Abstr. Int. B, 50(11), 5061; Univ. Microfilms Int., Order No. 9000392).
- _____ and F.C. Anson. 1989. Electrocatalytic reduction of nitrite and nitric oxide to ammonia with iron-substituted polyoxotungstates. *J. Amer. Chem. Soc.* 111: 2444-2451.
- Unoura, K., A. Iwashita, E. Itabashi, and N. Tanaka. 1984. Redox properties of polyoxometalates. *Bull. Chem. Soc. Jap.* 57: 597-605.