

Sol-gel-derived graphite organosilicate composite electrodes bulk-modified with Keggin-type α -germanomolybdic acid

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A novel inorganic-organic hybrid material incorporating graphite powder and Keggin-type α -germanomolybdic acid (GeMo_{12}) in methyltrimethoxysilane-based gels has been produced by the sol-gel technique and used to fabricate a chemically bulk-modified electrode. GeMo_{12} acts as a catalyst, graphite powder ensures conductivity by percolation, the silicate provides a rigid porous backbone, and the methyl groups endow hydrophobicity and thus limit the wetting section of the modified electrode. The GeMo_{12} -modified graphite organosilicate composite electrode was characterized by cyclic and square-wave voltammetry. The modified electrode shows a high electrocatalytic activity toward the reduction of bromate, nitrite and hydrogen peroxide in acidic aqueous solution. In addition, the chemically-modified electrode has some distinct advantages over the traditional polyoxometalate-modified electrodes, such as long-term stability and especially repeatability of surface-renewal by simple mechanical polishing.

Introduction

The sol-gel process provides a versatile means for the production of inorganic and inorganic-organic hybrid materials *via* the hydrolysis and condensation of suitable metal alkoxides.¹ The field of silica-modified electrodes started slowly in 1989, but has increased exponentially in the past few years. Recent advances in the various fields and applications of sol-gel electrochemistry were described in several excellent review articles.² Graphite organosilicate composite electrodes (GOSEs) are a new class of carbon electrodes first introduced by Lev's group.³ An important feature of the GOSEs is the ability to produce surface-renewable, bulk-modified electrodes for electroanalytical and electrocatalytic applications. The preparation protocol for GOSEs allows the incorporation of other compounds during the preparation stage itself and hence they can be modified throughout the sample volume. An additional advantage is that the wetting section of the electrode in aqueous solution can be manipulated by the judicious choice of monomer used to prepare the silicate matrix.

Polyoxometalates (POMs) are a large and rapidly growing class of compounds that have attracted much attention in catalysis, medicine, bioanalysis and materials science owing to their chemical, structural and electronic versatility.⁴ One of the most important properties of POMs is their ability to accept various numbers of electrons giving rise to mixed-valency species. Sadakane and Steckhan⁵ have presented detailed accounts of electrochemical properties and electrocatalytic applications of POMs and various procedures for the attachment of POMs onto electrode surfaces. Attachment of these species to electrode surfaces can be achieved by electrodeposition, adsorption, entrapment into polymer matrices, self-assembly, layer-by-layer deposition, and LB methods.⁶ The recent explosive growth of sol-gel science and technology offers several examples of the utilization of POMs as additives in inorganic or inorganic-organic hybrid matrices. Through a sol-gel approach, Judeinstein and Schmidt⁷ trapped POM anions such as $\text{PW}_{12}\text{O}_{40}^{3-}$, $\text{SiW}_{12}\text{O}_{40}^{4-}$ or $\text{W}_{10}\text{O}_{32}^{3-}$ into gel matrices to construct conducting materials with electrochromic

and photochromic properties. Asuka *et al.*⁸ prepared siloxane-POM acid (Keggin-type) composite coatings with antireflective and antistatic properties, and the coatings exhibited good adhesion, transparency, abrasion resistance, hardness and low resistivity. Mayer *et al.*⁹ first synthesized a functionalized POM based on the reaction of trimethoxysilylpropyl methacrylate and the divacant POM, $\gamma\text{-SiW}_{10}\text{O}_{36}^{8-}$. After the reports on the solid-state voltammetric characterization of $\text{PW}_{12}\text{O}_{40}^{3-}$ and $\text{SiW}_{12}\text{O}_{40}^{4-}$ doped in tetraethoxysilane-derived gels,¹⁰ Song *et al.*¹¹ have applied the sol-gel technique to fabricate POM-modified thin film electrodes. Our recent interest has focused on the fabrication of surface-renewable GOSEs bulk-modified with POMs.¹²

GeMo_{12} is a Keggin-type POM with reversible electrochemical behavior;¹³ however, to our knowledge there is no report on the preparation and electrocatalytic study of the GeMo_{12} -modified electrode.⁵ In this paper, we first prepared a new kind of GeMo_{12} /graphite/methylsilicate composite by the sol-gel technique and employed it to fabricate a three-dimensional GeMo_{12} -modified electrode. In the present configuration, the graphite powder contributes to the electrical conductivity by the percolation mechanism,¹⁴ GeMo_{12} is used as a catalyst, the crosslinked silicate backbone provides rigidity in the matrix, and the methyl groups impart hydrophobicity and limit the wetting electroactive section of the modified electrodes when immersed in the electrolyte. The surface-renewable GeMo_{12} -modified GOSE presented a high electrocatalytic activity toward the reduction of bromate, nitrite and hydrogen peroxide.

Experimental

Materials

Methyltrimethoxysilane (MTMOS, >97%) was purchased from ACROS and used without further purification. High purity graphite powder (average particle 0.2–1 μm) was obtained from Shanghai Carbon Plant. $\alpha\text{-H}_4\text{GeMo}_{12}\text{O}_{40}\cdot 14\text{H}_2\text{O}$ (GeMo_{12}) was synthesized according

to the literature method^{13a} and characterized by IR, elemental analysis and TG. The 600 grit emery paper was supplied by Shanghai Sand Wheel Plant. Other chemicals were of analytical grade and used as received.

Ultrapure water obtained from a Millipore Milli-Q water purification system was used throughout the experiments. Solutions with different pH were prepared by mixing the 0.1 M Na₂SO₄ aqueous solution with the 0.1 M Na₂SO₄+0.5 M H₂SO₄ aqueous solution. Solutions were deaerated by argon bubbling prior to the experiments and the electrochemical cell was kept under an argon atmosphere throughout the experiments.

Apparatus

A CHI 660 Electrochemical Workstation connected to a Digital-586 personal computer was used for control of the electrochemical measurements and for data collection. A conventional three-electrode system was used. The working electrode was a glassy carbon electrode, a bare GOSE or a GeMo₁₂-modified GOSE. An Ag/AgCl (saturated KCl) electrode was used as a reference electrode and a Pt gauze as a counter electrode. The glassy carbon electrode was polished with 0.5, 0.3, 0.1 and 0.05 μm $\alpha\text{-Al}_2\text{O}_3$ paste, respectively, washed with distilled water then ultrasonicated in deionized water and acetone successively, and finally dried at room temperature. All potentials were measured and reported *versus* the Ag/AgCl electrode. A Cole-Parmer 3[®] pH meter was used for pH measurements. All the experiments were conducted at $25 \pm 0.5^\circ\text{C}$.

Fabrication of bare GOSEs and GeMo₁₂-modified GOSEs

Bare GOSEs were prepared using the procedure described by Lev and co-workers.^{3,15} The fabrication procedure of GeMo₁₂-modified GOSEs is described as follows. A solution of 0.75 ml methanol containing 7 mg GeMo₁₂, 0.5 ml MTMOS, and 0.03 ml hydrochloric acid (11 M) was ultrasonically mixed for 2 min, then 1.7 g graphite powder was added and shaken on a vortex agitator for an additional 3 min. The mixture was added to glass tubes of 3 mm inner diameter and 8 cm length, and the length of composite material in the tubes was controlled to be about 0.8 cm. In addition, a little extra mixture was retained on the top of the electrodes, and the mixture in the tubes was pressed lightly onto smooth plastic paper with a copper stick through the back. After drying at room temperature for 48 h, the electrodes were polished with 600 grit emery paper to remove extra composite material and wiped gently with weighing paper. Electrical contact was made by silver paint through the back of the electrode.

Results and discussion

Voltammetric behavior of the GeMo₁₂-modified GOSE

As is known, GeMo₁₂ is unstable in neutral and basic aqueous solution and undergoes a series of hydrolysis processes but is fairly stable in acidic aqueous solution;^{13a,16} therefore, electrochemical studies of the GeMo₁₂-modified GOSE were carried out in acidic aqueous solutions.

Fig. 1 shows comparative cyclic voltammograms for a glassy carbon electrode and a bare GOSE in the 1 mM GeMo₁₂+0.1 M Na₂SO₄+0.5 M H₂SO₄ aqueous solution and for a GeMo₁₂-modified GOSE in the 0.1 M Na₂SO₄+0.5 M H₂SO₄ aqueous solution. Redox peaks I–I', II–II' and III–III' correspond to three consecutive two-electron processes.^{13a,b} The redox formal potential of GeMo₁₂ at bare GOSE is more positive than that at a glassy carbon electrode, as is that for the GeMo₁₂-modified GOSE, which may reflect the structural difference between glassy carbon and graphite.¹⁷ In addition, the potential difference value between the

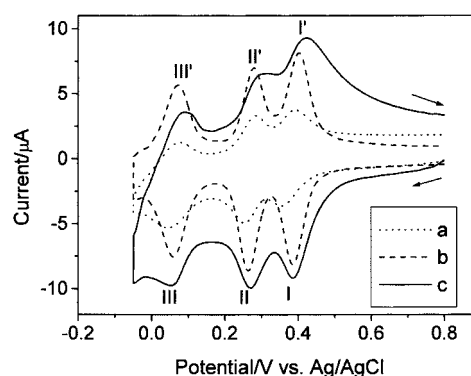


Fig. 1 The comparative cyclic voltammograms of (a) a glassy carbon electrode and (b) a GOSE in the 1 mM GeMo₁₂+0.1 M Na₂SO₄+0.5 M H₂SO₄ solution and (c) the GeMo₁₂-modified GOSE in the 0.1 M Na₂SO₄+0.5 M H₂SO₄ solution. Scan rate: 20 mV s⁻¹.

corresponding anodic and cathodic peaks (ΔE_p) at bare GOSE is obviously less than the theoretical value, 30 mV, for a two-electron reversible redox process,¹⁸ but that at a glassy carbon electrode is about 30 mV, which suggests that GeMo₁₂ is easier to adsorb onto GOSE than glassy carbon. It is not surprising to observe that ΔE_p at bare GOSE is less than that for GeMo₁₂-modified GOSE because the encapsulation of GeMo₁₂ into the TMOS-based gel network may decrease the electron exchange rate between graphite and GeMo₁₂ to some extent.

Fig. 2A presents the cyclic voltammograms of the GeMo₁₂-modified GOSE at different scan rates in the 0.1 M Na₂SO₄+0.5 M H₂SO₄ aqueous solution, and the plots of peak current *versus* scan rate and the square root of scan rate are shown in Fig. 2B. When the scan rate was varied from 20 to

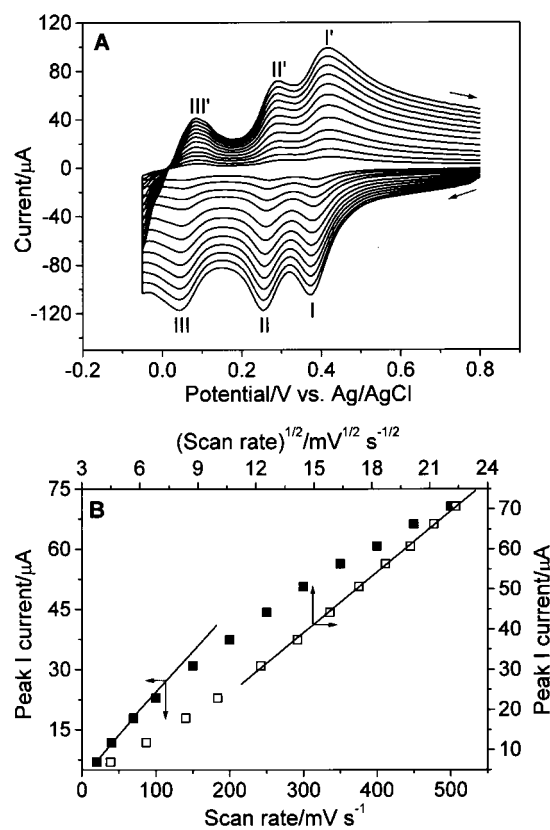


Fig. 2 (A) The cyclic voltammograms of the GeMo₁₂-modified GOSE in the 0.1 M Na₂SO₄+0.5 M H₂SO₄ solution at different scan rates (from inner to outer: 20, 40, 70, 100, 150, 200, 250, 300, 350, 400, 450 and 500 mV s⁻¹). (B) The dependence of anodic peak I currents on scan rates and the square roots of scan rates.

500 mV s^{-1} , the cathodic peak currents were almost the same as the corresponding anodic peak currents and the peak potentials did not change much with increasing scan rate. At scan rates lower than 100 mV s^{-1} , the cathodic I currents were proportional to the scan rate, suggesting that the redox process is surface-confined; however, at scan rates higher than 100 mV s^{-1} , the cathodic I currents were proportional to the square root of the scan rate which indicates that the redox process is diffusion-controlled. The surface concentration of electroactive species, Γ_c , can be approximately calculated by the following equation:¹⁸

$$Q = nFA\Gamma_c \quad (1)$$

where Q is the background corrected charge, A is the electrode geometric surface area, and the other symbols have their usual meanings. The total area under the three reduction peaks at the scan rate of 20 mV s^{-1} corresponds to $ca. 1.5 \times 10^{-9} \text{ mol cm}^{-2}$ of a reactant that undergoes an overall six-electron reduction. It should be pointed out that the calculated surface coverage is an effective attribute of GeMo_{12} molecules per cross section of the electrode and does not reflect the actual number of GeMo_{12} molecules exposed on the electrode top. In addition, if the amount of dopant (GeMo_{12}) is increased, the resulting electrodes present cyclic voltammograms with larger peak currents compared with those of the GeMo_{12} -modified electrode described in this paper.

In the present work, Osteryoung square-wave voltammetry with an excellent sensitivity¹⁷ was adopted to study the pH-dependent electrochemical behavior of the GeMo_{12} -modified GOSE. Fig. 3A shows square-wave voltammograms for the GeMo_{12} -modified GOSE in 0.1 M Na_2SO_4 aqueous solutions with different pH. It can be clearly seen that along with increasing pH, the peak potentials all gradually shift to the more negative potential direction and the peak currents gradually decrease. Reduction of GeMo_{12} immobilized in the

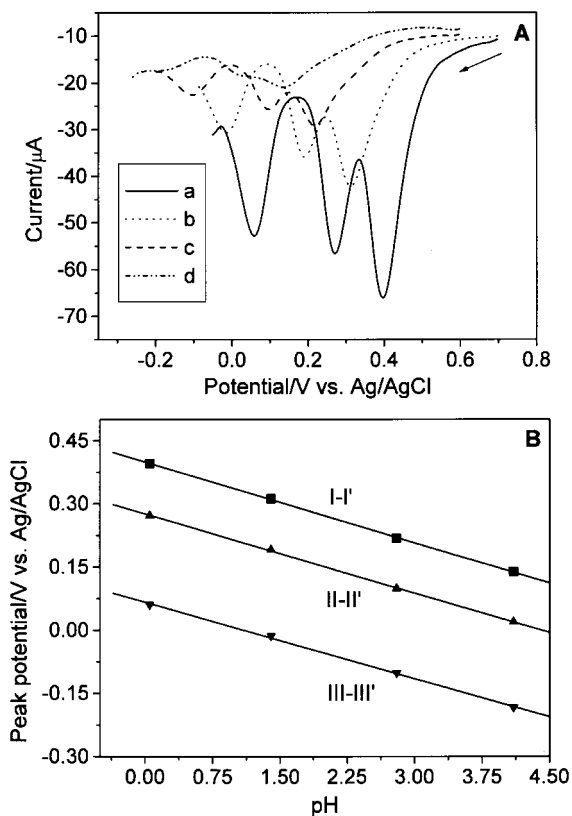
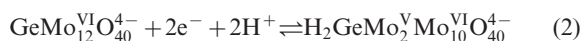


Fig. 3 (A) Osteryoung square-wave voltammograms of the GeMo_{12} -modified GOSE in 0.1 M Na_2SO_4 solutions with different pH: (a) 0.05; (b) 1.40; (c) 2.80; (d) 4.10. Increment: 2 mV; frequency: 25 Hz; scan rate: 50 mV s^{-1} . (B) The relationship between peak potential and pH.

GOSE matrix is accompanied by the evolution of cations from solution to the wetted electroactive section of the electrode to maintain charge neutrality. Along with increasing pH, slower penetration of protons¹⁹ to the wetting section of the GeMo_{12} -modified GOSE should be the reason for the current decrease, and the more negative reduction potentials can be elucidated by the Nernst equation.¹⁸ Plots of peak potentials of the three successive redox waves *versus* pH for the GeMo_{12} -modified GOSE show good linearities in the pH range from 0.05 to 4.10, as shown in Fig. 3B. Slopes in this pH range are -62, -63 and -65 mV per decade for the I-I', II-II' and III-III' couples, respectively, which are close to the theoretical value of -59 mV per decade for the $2e^-/2H^+$ redox process.^{13a,b} The pH-dependent behavior reveals that the charge neutrality is compensated only by protons rather than other cations in the pH range from 0.05 to 4.10. The electrochemical reaction of GeMo_{12} -modified GOSE can be shown as follows:



Electrocatalytic activity of the GeMo_{12} -modified GOSE

Many studies^{5,6} have shown that POMs can be used as reductive electrocatalysts in the following two ways: (i) homogeneously dissolved in the electrolyte solution and (ii) attached to electrode surfaces. For example, Keita *et al.*²⁰ observed that the two-electron-reduced $\alpha\text{-H}_2\text{SiMo}_{12}\text{O}_{40}^{4-}$ can reduce nitrite in acidic solution; Anson's group²¹ and Dong's group²² have applied the iron(III)-substituted Keggin-type POMs [$\alpha\text{-XW}_{11}\text{O}_{39}\text{Fe}^{\text{III}}(\text{H}_2\text{O})^{n-1}$; X = P, As, $n=4$; X = Si, Ge, $n=5$] and the iron(III)-substituted Dawson-type POM [$\text{P}_2\text{W}_{17}\text{O}_{61}\text{Fe}^{\text{III}}(\text{H}_2\text{O})^{8-}$] as catalysts for the reduction of hydrogen peroxide and nitrite; Dong and Jin²³ have prepared the $\alpha\text{-PMo}_{12}\text{O}_{40}^{3-}$ -doped polypyrrole film electrode and observed its electrocatalytic activity towards the reduction of bromate in acidic solution. In our experiments, we found that the GeMo_{12} -modified GOSE also presents good electrocatalytic activity for the reduction of bromate, nitrite and hydrogen peroxide. Fig. 4A presents cyclic voltammograms for the electrocatalytic reduction of bromate at a bare GOSE and bromate at a GeMo_{12} -modified GOSE. No obvious voltammetric response is observed in the potential range from +0.8 to -0.05 V for bromate at a bare GOSE. With the GeMo_{12} -modified GOSE, after the addition of bromate, all three reduction peak currents increase while the corresponding oxidation peak currents decrease, suggesting that bromate is reduced by two-, four- and six-electron-reduced species. It has been noted that the six-electron-reduced species has the largest catalytic activity toward the reduction of bromate. That is to say, the catalytic activity of GeMo_{12} toward bromate increases to the extent that GeMo_{12} is reduced. The catalytic current at peak III is proportional to bromate concentration as shown in Fig. 4B. Electrocatalytic reduction of nitrite and hydrogen peroxide can also be clearly seen from Fig. 5 and Fig. 6. We have noted that two-, four- and six-electron-reduced species of GeMo_{12} all have catalytic activity toward the reduction of bromate and hydrogen peroxide unlike other POM-modified electrodes where only the four- and six-electron-reduced species have electrocatalytic activity.^{5,11b,23}

Repeatability of surface-renewal and stability

Compared with POM-modified film electrodes^{5,6,11,23} fabricated by the conventional methods, the GeMo_{12} -modified GOSEs have certain distinct advantages. One of the main

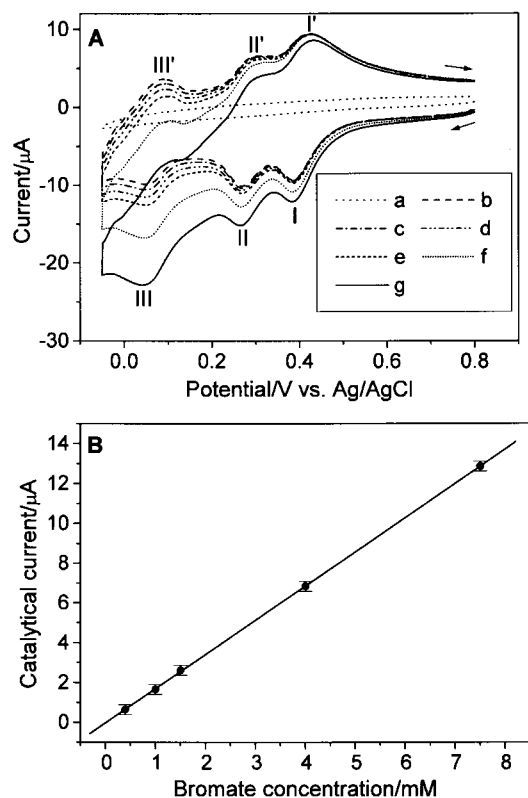


Fig. 4 (A) Cyclic voltammety of (a) a bare GOSE in the 4 mM NaBrO₃+0.1 M Na₂SO₄+0.5 M H₂SO₄ solution and GeMo₁₂-modified GOSE in 0.1 M Na₂SO₄+0.5 M H₂SO₄ solutions containing (b) 0 mM, (c) 0.4 mM, (d) 1.0 mM, (e) 1.5 mM, (f) 4.0 mM and (g) 7.5 mM NaBrO₃. Scan rate: 20 mV s⁻¹. (B) Plot of catalytic current of peak III versus bromate concentration. Error bars show standard deviation for six different electrodes.

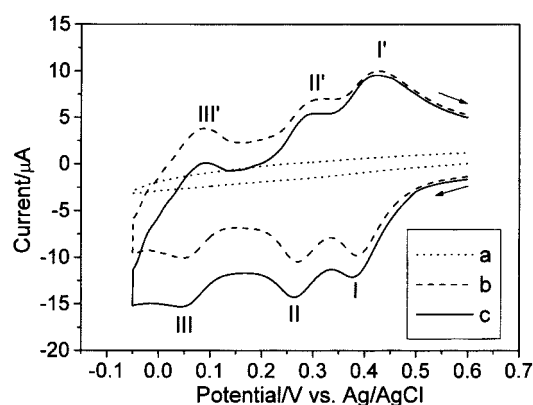


Fig. 5 Cyclic voltammety of (a) a bare GOSE in the 5 mM NaNO₂+0.1 M Na₂SO₄+0.5 M H₂SO₄ solution and GeMo₁₂-modified GOSE in 0.1 M Na₂SO₄+0.5 M H₂SO₄ solutions containing (b) 0 mM and (c) 5 mM NaNO₂. Scan rate: 20 mV s⁻¹.

attractions of the use of GeMo₁₂-modified GOSEs for the electroreduction of bromate, nitrite and hydrogen peroxide is that the surface of the electrodes can be renewed after every use. The hydrophobic methyltrimethoxysilane monomer results in a controlled wetting section of the composite electrode in aqueous solutions.^{2,3,12,15} Hence, a bulk-modified electrode can be polished using emery paper and a fresh surface exposed whenever needed. This is especially useful for the electrocatalytic study since the catalytic activity is known to decrease when the electrode is fouled. Indeed, ten successive polishings resulted in a relative standard deviation (RSD) of 5.8% for a GeMo₁₂-modified GOSE.

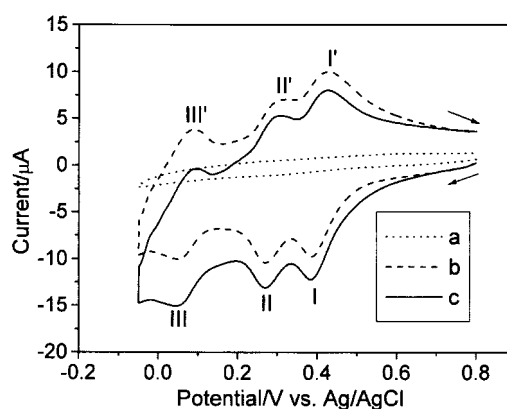


Fig. 6 Cyclic voltammety of (a) a bare GOSE in the 5 mM H₂O₂+0.1 M Na₂SO₄+0.5 M H₂SO₄ solution and GeMo₁₂-modified GOSE in 0.1 M Na₂SO₄+0.5 M H₂SO₄ solutions containing (b) 0 mM and (c) 5 mM H₂O₂. Scan rate: 20 mV s⁻¹.

For small molecules, such as electron-transfer mediators, dyes and complexing agents, simple physical doping in the silicate matrix may result in significant leaching, thus the design and synthesis of the organically-modified silicates have been proposed to construct leak-free chemical sensors.^{4d,f} When the GeMo₁₂-modified GOSE was stored dry at 4 °C, it proved to be very stable. The current response remained almost unchanged for at least 6 months. Only a 3.6% current decrease was found even when the electrode was immersed in a 0.5 M H₂SO₄ aqueous solution for 60 days. We think that the high stability of the GeMo₁₂-modified GOSEs is related to the mechanical and chemical stability and negligible swelling of the silicate matrix,^{1-4,11,12,15} the limited wetting section controlled by methyl groups,^{3,12,15} the strong adsorption of GeMo₁₂ on graphite and the possible host-guest interactions between the doped GeMo₁₂ and silanol groups of the polymer network. In addition, 20 GeMo₁₂-modified GOSEs have almost the same voltammetric behavior in a 0.1 M Na₂SO₄+0.5 M H₂SO₄ solution.

Conclusions

The hydrophobic sol-gel-derived GOSEs modified with POMs, which are exemplified here by the GeMo₁₂-modified GOSEs, promise to compete well with traditional POM-modified film electrodes. The GeMo₁₂-modified GOSEs can catalyze the electroreduction of bromate, nitrite and hydrogen peroxide, and exhibit a distinct advantage of polishing in the event of surface fouling, as well as simple preparation and good chemical and mechanical stability. One of the basic ideas behind the present work was to transfer to CCEs the homogeneous catalytic activities of other unsubstituted, as well as substituted, Keggin-type and Dawson-type POMs. These goals were achieved, and the results will be published in our future papers. In addition, the fundamental research is an important and useful step to demonstrate the viability of this electrocatalytic system in large scale electrolysis.

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