

Sol-gel-derived carbon ceramic composite electrodes bulk-modified with 1 : 12-silicomolybdic acid

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Received (in Montpellier, France) 10th March 2000, Accepted 4th May 2000

Published on the Web 14th June 2000

1 : 12-Silicomolybdic acid (SiMo_{12}) doped carbon ceramic composite electrodes were fabricated by incorporating SiMo_{12} and graphite powder in a methyltrimethoxysilane-based gel and characterized by cyclic and square-wave voltammetry. It was demonstrated that the chemically modified electrodes were suitable for electrocatalytic reduction of bromate. The electrodes had the remarkable advantage of surface renewal owing to bulk modification, as well as simple preparation, good mechanical and chemical stability and reproducibility.

The high capacity of heteropolyanions (HPAs) to accumulate electrons in their framework and deliver them to an appropriate substrate prompted investigations on their voltammetric and electrocatalytic behavior in the last decades.¹ Many methods have been exploited to attach HPAs onto electrode surfaces, such as electrodeposition, adsorption, encapsulation in organic and inorganic polymeric matrices, layer-by-layer deposition, self-assembly and the LB procedure.^{1–3} A serious drawback in the application of these thin film modified electrodes is their poor long-term stability; moreover, electrode surfaces cannot be renewed in the case of leakage, contamination and passivation.^{1–3} It seems desirable to develop and exploit a new, simple and reliable procedure for preparing HPA-modified electrodes.

Sol-gel-derived hybrid organic-inorganic materials are receiving much attention since they can exhibit the properties associated with both the organic moieties and the inorganic framework.⁴ Since the carbon ceramic composite electrode (CCE) was first prepared by Lev's group,⁵ a great amount of work has been devoted to the fabrication of chemically modified CCEs and to their use as sensors for metal ions, glucose, amino acids and other important chemical and biological substances.⁶ An interesting feature of CCEs is that the active section of the electrodes is not clogged upon repeated polishing, due to the brittleness of the sol-gel silicate backbone, and thus the electrodes can be renewed by a mechanical polish after every use or contamination. The present work reports on the fabrication, voltammetric and electrocatalytic behavior of the first HPA-modified CCE, a 1 : 12-silicomolybdic acid (SiMo_{12}) doped CCE.

Unmodified CCEs were prepared according to the procedure described by Lev and co-workers^{5,6a–e}, which was also used to fabricate SiMo_{12} -doped CCEs with some modifications. Surfaces of unmodified and SiMo_{12} -doped CCEs were both mirror-like and homogeneous. A drop of water deposited on the surfaces did not spread, indicating their apparent hydrophobic nature.

As is known, SiMo_{12} is unstable in neutral and basic aqueous solutions and undergoes a series of hydrolysis processes, but is fairly stable in acidic aqueous solution.¹ So the electrochemical experiments were all performed in acidic aqueous solutions.

Fig. 1 shows the comparative cyclic voltammograms for a glassy carbon electrode, a CCE in 0.5 M H_2SO_4 + 0.1 M Na_2SO_4 + 1 mM SiMo_{12} aqueous solution and a SiMo_{12} -doped CCE in 0.5 M H_2SO_4 + 0.1 M Na_2SO_4 aqueous solution. The pairs of redox peaks I-I', II-II' and III-III' correspond to reduction and oxidation, respectively, each through a two-electron process.^{2f,9} Cyclic voltammetry reveals that the modified CCE is better for SiMo_{12} reduction than the glassy carbon electrode and unmodified CCE as regards the onset potential. The surface coverage was measured by integrating the area under peak I of Fig. 1 (curve c) and was found to be $2.0 \times 10^{-10} \text{ mol cm}^{-2}$.

In order to study the pH-dependent electrochemical behavior of the SiMo_{12} -doped CCE, square-wave voltammetry with an excellent sensitivity was adopted to accurately measure the half-wave potentials ($E_{1/2}$). Fig. 2 shows the Osteryoung square-wave voltammograms for the SiMo_{12} -doped CCE in acidic aqueous solutions with different pH. It can be clearly seen that with increasing pH, the three redox potentials all gradually shift in the more negative potential direction and the peak currents also decrease. Reduction of SiMo_{12} immobilized in the CCE matrix is accompanied by the uptake of protons from the solution to the wetting section of the electrode to maintain charge neutrality. The shift of $E_{1/2}$ and the change of peak current can be explained by the Nernst equation and Fick's first law, respectively. As shown in Fig. 3, plots of $E_{1/2}$ of the three successive redox waves *vs.* pH for the SiMo_{12} -doped CCE present good linearity in the pH range from 0.00 to 3.53. Slopes in this pH range are -59.6 , -66.7 and -64.5 mV pH^{-1} for the I-I', II-II' and III-III' couples, respectively, which are close to the theoretical value of -59 mV pH^{-1} for the $2\text{e}^-/2\text{H}^+$ redox process. As a matter of fact, analogous behavior in SiMo_{12} -modified thin film electrodes

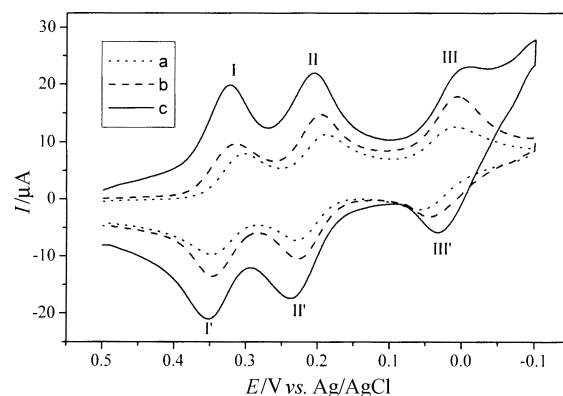


Fig. 1 Comparative cyclic voltammograms of (a) a glassy carbon electrode, (b) a CCE in 0.5 M H_2SO_4 + 0.1 M Na_2SO_4 + 1 mM SiMo_{12} and (c) a SiMo_{12} -doped CCE in 0.5 M H_2SO_4 + 0.1 M Na_2SO_4 aqueous solution. Scan rate is 250 mV s^{-1} .

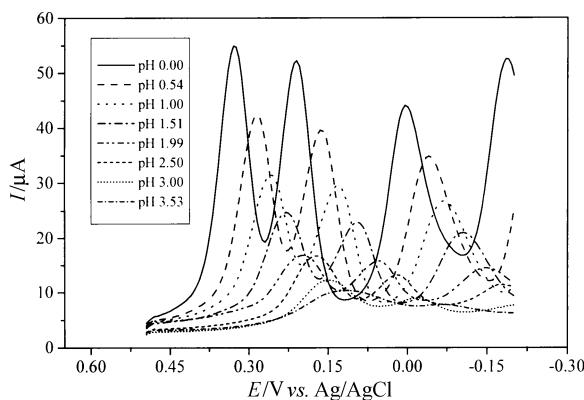


Fig. 2 Osteryoung square-wave voltammograms of a SiMo₁₂-doped CCE in aqueous solutions (H₂SO₄ + 0.1 M Na₂SO₄) with pH of 0.00, 0.54, 1.00, 1.51, 1.99, 2.50, 3.00 and 3.53. Scan rate is 100 mV s⁻¹.

has been described and discussed previously.²⁹ It is evident that the modified CCE can provide a very favorable environment for SiMo₁₂ to perform electron and proton transfers.

The reduction of BrO₃⁻ is totally irreversible at a glassy carbon electrode or an unmodified CCE in acidic aqueous solution. In the present work, we found that the SiMo₁₂-doped CCE showed catalytic activity toward the reduction of BrO₃⁻. The bromate is mainly reduced by the four-electron- (H₄SiMo₈^{VI}Mo₄^{VO}O₄₀) and six-electron-reduced (H₄SiMo₆^{VI}Mo₆^{VO}O₄₀) species in the presence of protons to yield the reduced species containing bromine, and the two-electron-reduced species is regenerated. It can also be seen from Fig. 4 that the six-electron-reduced species has a higher catalytic activity toward bromate than the four-electron-reduced species. So the catalytic activity of SiMo₁₂ toward bromate increases with the extent that SiMo₁₂ is reduced. In addition,

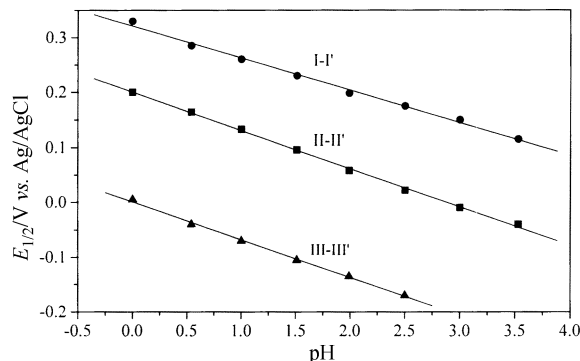


Fig. 3 Plots of $E_{1/2}$ vs. pH for the SiMo₁₂-doped CCE.

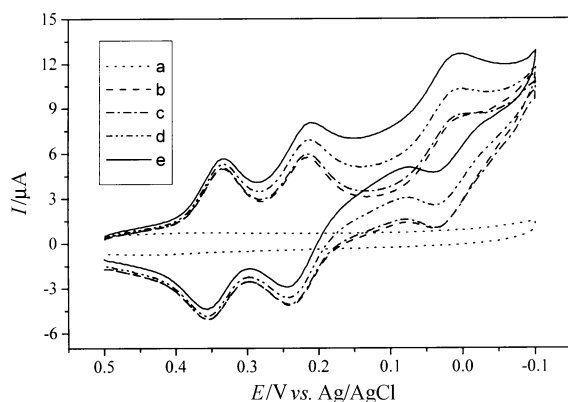


Fig. 4 Cyclic voltammograms of a SiMo₁₂-doped CCE in 0.5 M H₂SO₄ + 0.1 M Na₂SO₄ aqueous solutions containing (b) 0, (c) 0.5, (d) 2, (e) 4 mM NaBrO₃, and (a) an unmodified CCE in the same solution as (e). Scan rate is 40 mV s⁻¹.

the modified electrodes also show good electrocatalytic activity for reduction of iodate, nitrite and nitride oxide.

The hydrophobic methyltrimethoxysilane monomer results in a controlled wetting of the composite electrode in aqueous solutions. Hence, a bulk-modified electrode can be polished using emery paper and a fresh surface exposed whenever needed. This is especially useful for electrocatalytic studies since the catalytic activity is known to decrease when the electrode is fouled. Indeed, ten successive polishings of a SiMo₁₂-doped CCE resulted in a relative standard deviation (RSD) of 3.7% for the peak currents measured by square-wave voltammetry. In addition, little leakage was found when the electrode was immersed in 0.5 M H₂SO₄ aqueous solution for 10 days. We think that the high stability of the SiMo₁₂-doped CCEs is related to the stability of the silicate matrix, the limited wetted section controlled by the methyl group, the strong adsorption of SiMo₁₂ on graphite (due to the large neutral cage (Mo_nO_{3n}),⁷ the aromatic properties of SiMo₁₂ and the conjugated Ti-bonds of graphite), and the possible interactions between the SiMo₁₂ and silanol groups.

In conclusion, we have demonstrated a practical and straightforward method for the construction of HPA bulk-modified electrodes, which are exemplified here by the SiMo₁₂-doped CCEs and which promise to compete well with traditional HPA-modified thin film electrodes. The SiMo₁₂-doped CCEs exhibit reversible voltammetric behavior, high activity for electrochemical reduction, good chemical and mechanical stability, good reproducibility and the distinct advantage of surface renewal by polishing in the event of surface fouling. In addition, the concept described can be extended to fabricate HPA-modified large-scale electrodes for electrolysis and microelectrodes for electroanalysis.

Experimental

Reagents

Methyltrimethoxysilane (MTMOS, 97%) was purchased from ACROS Chemical Company and used without further purification. High purity graphite powder was a product of Shanghai Carbon Plant. Pure SiMo₁₂ was obtained from Beijing Xinhua Chemical Plant, and water content in H₄SiMo₁₂O₄₀·28H₂O was determined by thermogravimetric analysis. Ultrapure water obtained from a Millipore Milli-Q water purification system was used throughout the experiments.

Physical measurements

Electrochemical studies were carried out with a computer-controlled CHI 660 Electrochemical Workstation interfaced to a conventional three-electrode cell. The working electrode was a glassy carbon electrode ($d = 3$ mm), an unmodified CCE, or a modified CCE. An Ag/AgCl (saturated KCl) electrode was used as a reference electrode and a Pt gauze as a counter electrode. Solutions were deaerated by argon bubbling prior to the experiments and the electrochemical cell was kept under argon atmosphere throughout the experiments. A Cole-Parmer 3TM pH meter was used for pH measurements.

Fabrication of SiMo₁₂-doped CCEs

The SiMo₁₂-doped CCEs were fabricated as follows. A solution of 0.75 ml methanol containing 1.88 mg SiMo₁₂, 0.25 ml MTMOS and 0.025 ml hydrochloric acid (11 M) was ultrasonically mixed for 2 min, then 1.875 g graphite powder was added and the mixture shaken on a vortex agitator for an additional 3 min. The mixture was added to glass tubes with 3 mm inner diameter and dried for 24 h at 30 °C. After drying, the electrodes were polished with no. 3 emery paper and the

surface was wiped with weighing paper. Electric contact was made by silver paint through the back of the electrode.

Acknowledgements

The financial support of the Ministry of Science & Technology of China is gratefully acknowledged.

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