Cathodic Deposition of Mixed Mo/V Oxyhydroxide Films from V-Substituted Polymolybdophosphate

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Mixed molybdenum and vanadium oxyhydroxide films were prepared on an Au electrode by electroreduction of Keggin-type V-substituted polymolybdophospate. The film-coated electrode exhibited a catalytic activity for the electroreduction of nitrite.

Introduction

Keggin-type heteropolyanions are known to permit multiple electron transfer without the accompanying change in skeleton structure. Although Keggin ions have been the subject of numerous electrochemical studies, there are few reports on their use as a precursor in the electrodeposition of transition metal oxides.[1,2] Our recent work showed that electroreduction of 12-molybdosilicate can produce an electroactive film, and its spectroscopic properties suggested that electron transfer takes place not only on polyatoms but also on the heteroatom of silicon.[3] We present here an electrochemical method for preparing thin films of mixed Mo/V oxyhydroxide from a V-substituted polymolybdophosphate solution. The products were characterized by X-ray photoelectron spectroscopy (XPS) and cyclic voltammetry in Na_2SO_4 solutions with and without nitrite ions.

Experimental

The starting compound, 9-molybdo-3-vanadophosphoric acid ($H_6[PMo_9V_3O_{40}]$, denoted as PMo_9V_3) was synthesized following the procedure described by Tsigdinos et al.[4] Electrodeposition of films was carried out on an Au electrode in an aqueous 0.5 M Na_2SO_4 solution with 0.2 mM PMo_9V_3 by potential cycling between 0 and −0.7 V for 3h at 10 mV s^{-1}. Unsubstituted 12-molybdophosphate ($H_3[PMo_{12}O_{40}]$, PMo_{12}) was also used for comparison purposes. The film-coated electrode was rinsed with water, dried under vacuum, and then subjected to XPS and cyclic voltammetry. Incident X-rays were acquired using an unmonochromatized Al Kα source (1486.6 eV).

Results and Discussion

Wide-range XPS spectra of the films deposited from PMo_9V_3 (a) and PMo_{12} (b) are shown in Fig. 1. Several peaks arising from Mo and O atoms are observed for both samples. In addition, the film prepared with PMo_9V_3 exhibits two peaks assigned to V $2p_{1/2}$ and V $2p_{3/2}$ at 523.5 and 516.2 eV, respectively. This clearly indicates the formation of the film containing V and Mo.

A typical cyclic voltammogram of the Mo/V film-coated electrode in a solution of Na_2SO_4 is depicted in Fig. 2A, in which a redox wave can be seen around −0.5 V. Following the CV scan, XPS measurements were made for the films after being polarized at 0 (a) and −0.7 V (b), and the resulting spectra are shown in Fig. 2B. No significant change induced electrochemically is found in the V 2*p* region, confirming that vanadium ions remain in the film without changing their oxidation state. The Mo 3*d* spectra are composed of four peaks corresponding to two valence states (5+ and 6+) of molybdenum. On the other hand, the O 1*s* signal shows three different peaks assigned to oxide (O^{2-}), hydroxide (OH^-), and adsorbed water, as is expected for a film comprised of oxyhydroxide. As seen from a comparison between the spectra, the contributions of the Mo^{5+} and OH^- peaks are larger for the film obtained at more negative potential. Hence, the voltammetric response observed can be associated with the redox couple of Mo^{5+}/Mo^{6+}, which accompanies the movement of protons for charge compensation. As shown in Fig. 3, addition of $NaNO_2$ to a solution of Na_2SO_4 caused an increase in the cathodic peak current and disappearance of the reoxidation peak. This behavior is consistent with catalytic reduction of NO_2^- by reaction with the reduced form of Mo/V oxyhydroxide.

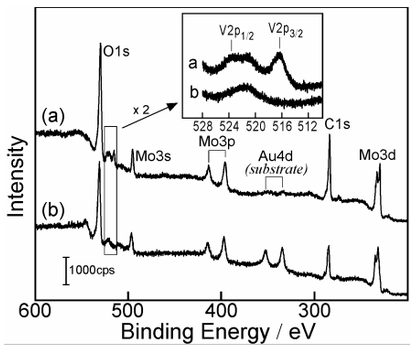

Figure 1 XPS spectra of the electrodeposited films on an Au electrode from 0.5 M Na_2SO_4 solutions containing 0.2 mM PMo_9V_3 (a) and PMo_{12} (b).

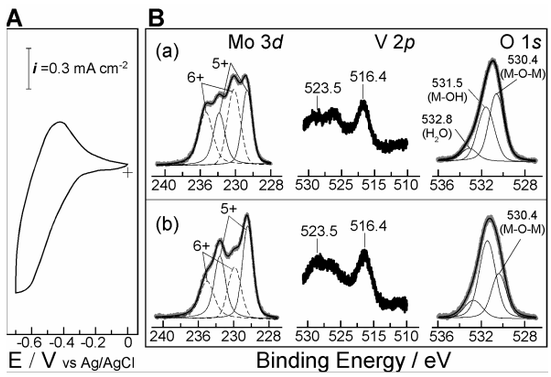

Figure 2 (A) CV of the Mo/V oxyhydroxide film-coated electrode in a 0.5 M Na_2SO_4 solution of pH 3. Scan rate, 20 mV s^{-1}. (B) XPS spectra taken for the films after being polarized at 0 (a) and −0.7 (b) V.

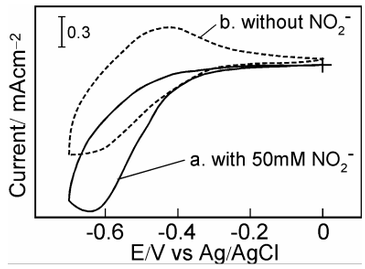

Figure 3 CVs of the Mo/V oxyhydroxide film-coated electrode in 0.5M Na_2SO_4 solutions of pH 3 with (a) and without (b) 50 mM $NaNO_2$. Scan rate, 20 mV s^{-1}.

References

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