

## 1 : 12 Phosphomolybdic Anion Modified Glassy Carbon Electrode

Shaojun Dong\* and Zhe Jin

*Changchun Institute of Applied Chemistry, Academia Sinica, Changchun, Jilin 130 021, People's Republic of China*

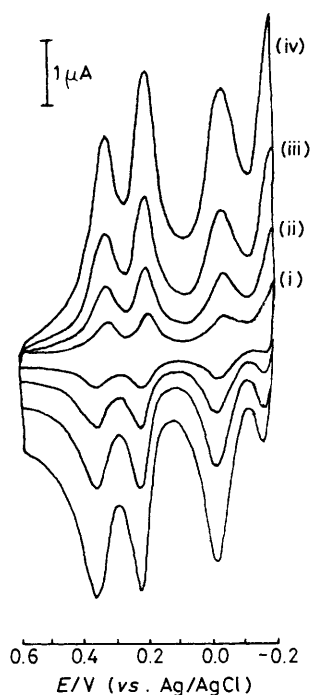
A 1 : 12 phosphomolybdic anion modified glassy carbon electrode has been prepared and its electrochemical behaviour studied.

The modification of electrode surfaces is an active area of research. Clays and zeolites which have special structural features have been used as materials for electrode modification.<sup>1,2</sup> Recently, McEvoy *et al.*<sup>3,4</sup> have described 1:12 silicotungstic acid activated electrodes.

Heteropoly acids (and salts) have attracted considerable attention because of their potential use as homogeneous and

heterogeneous catalysts. Owing to their special structure, they usually undergo a series of one- and two-electron electrode reductions.<sup>5</sup> In this communication, we report the modification of glassy carbon electrodes with a monolayer of the 1 : 12 phosphomolybdic anion ( $\text{PMo}_{12}$ ) and describe their electrochemical behaviour.

A thin film of  $\text{PMo}_{12}$  could be deposited on a glassy carbon



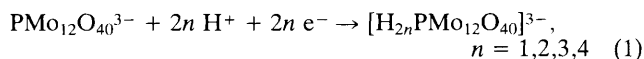
**Figure 1.** C.v. curves of a  $\text{PMo}_{12}$  film modified electrode under different scan rates,  $0.5 \text{ M H}_2\text{SO}_4$ , scan rate: (i) 20, (ii) 50, (iii) 100, (iv) 200  $\text{mV/s}$ .

electrode surface by means of cyclic voltammetry (c.v.) in a solution of  $\text{H}_2\text{SO}_4$  ( $0.5 \text{ M}$ ) containing  $\text{Na}_3\text{PMo}_{12}\text{O}_{40}$  ( $0.01 \text{ M}$ ). Figure 1 shows the c.v. curves of a  $\text{PMo}_{12}$  film modified electrode in  $0.5 \text{ M H}_2\text{SO}_4$  solution under different scan rates. The scan shows three redox couple waves with  $E_m$  [ $E_m = \frac{1}{2}(E_{pa} + E_{pc})$ ] values of 0.35, 0.21, and  $-0.02 \text{ V vs. Ag/AgCl}$  (sat. KCl), respectively. Another, with a clear anodic wave, appears at  $-0.16 \text{ V}$ , but its corresponding cathodic wave is overlapped by the following reduction wave. The peak potential separation of all the redox waves is  $<30 \text{ mV}$  and the

peak potential does not shift with changing scan rate. The peak current ( $i_p$ ) is proportional to the scan rate up to  $5 \text{ V/s}$ . The c.v. curves show the features of an immobilized monolayer.

The stability of the  $\text{PMo}_{12}$  film modified electrode during c.v. scanning depends mainly on the potential range. In a solution of  $0.5 \text{ M H}_2\text{SO}_4$ , it is quite unstable over the potential range of  $0.6$  to  $-0.4 \text{ V}$ , but when the potential range is maintained at  $0.6$  to  $0.2 \text{ V}$ , it is stable over 500 cycles at a rate of  $100 \text{ mV/s}$ .

The acidity of the supporting electrolyte has a marked effect on the electrochemical behaviour of the  $\text{PMo}_{12}$  film modified electrodes. With increasing pH, the c.v. peaks move to more negative potentials, and ultimately the wave shapes become ill-defined. At pH 10, the  $\text{PMo}_{12}$  film on the electrode surface is destroyed and all c.v. curves disappear. The peak potential shifts *ca.*  $60 \text{ mV}$  per unit of pH. Compared with polarographic data,<sup>6</sup> the electrochemical reactions of  $\text{PMo}_{12}$  film modified electrodes can be expressed as in equation (1).



A potentiostatic method has been used to prepare a  $\text{PMo}_{12}$  film modified electrode. At a more negative potential than  $-0.5 \text{ V}$ , the  $\text{PMo}_{12}$  film could not be stabilised on the electrode surface.

Received, 15th July 1987; Com. 1028

## References

- 1 C. G. Murray, R. J. Nowak, and D. R. Rolison, *J. Electroanal. Chem.*, 1984, **164**, 205.
- 2 J. R. White and A. J. Bard, *J. Electroanal. Chem.*, 1986, **197**, 233.
- 3 A. J. McEvoy and M. Gratzel, *J. Electroanal. Chem.*, 1986, **209**, 391.
- 4 B. Keita and L. Nadjo, *J. Electroanal. Chem.*, 1986, **199**, 229.
- 5 M. T. Pope, 'Heteropoly and Isopoly Oxometalates,' Springer, Berlin, Heidelberg, 1983.
- 6 J. M. Furchart and P. C. Souchay, *C.R. Acad. Sci., Ser. C.*, 1968, **266**, 1571.