Electrodeposition of Ni-Mo-P Alloy Coatings

By Y. Zeng, S. Yao and H. Guo

Electrodeposition of Ni-Mo-P alloy coatings from ammoniacal citrate baths was studied, as well as characterization of low overpotential electrocatalysis for hydrogen evolution in alkaline solution. It was observed that the use of cathodes electrodeposited with Ni-Mo-P alloy containing 25 to 29 atomic percent molybdenum, and 0.1 to 0.8 atomic percent phosphorus, relative to Mo for water electrolysis, resulted in decreased overpotential for hydrogen evolution. Some scanning electron microscope (SEM) observations were also made.

Hydrogen has attracted considerable attention as a possible fuel for the future.[1] Although various methods have been proposed for large-scale production of hydrogen fuel from water, water electrolysis remains the simplest method; commercial electrolyzers have been available for many years.[2,3] Most commercial water electrolyzers use nickel electrodes and are operated at 70 to 90 °C in 25 to 35 percent KOH[2,4] to obtain high electrical conductivity, favorable electrode kinetics and minimal corrosion problems. At 80 °C, the specific conductivity of 35 wt percent KOH solutions reaches a maximum value of about 1.5 ohm^{-1} cm^{-1}.[4]

One of the ways of lowering electrical energy consumption in water electrolysis is to reduce the hydrogen evolution overpotential of the electrodes. Deposition of an electrocatalytic coating on the cathode surface has been investigated intensely for many years. Usable results were obtained with the use of steel, nickel or copper cathodes electrolytically covered by an alloy layer. M.H Miles *et al.* have systematically investigated hydrogen evolution of transition metals and their binary alloy electrocatalysis in alkaline[5] and acid[6] solutions. Ni-Zn alloy coatings have been used in water electrolysis processes also.[7]

Our previous experiments have indicated that the amorphous Ni-Mo alloy coatings obtained by electrodeposition have a lower overpotential.[8] Electrodeposition of the ternary Ni-Mo-P alloy coatings and their corrosion behavior were investigated.[9] Electrodeposition of Ni-Mo-P alloy coatings from ammoniacal citrate baths and the characterization of low overpotential electrocatalysis for hydrogen evolution were the primary subjects of this study.

Experimental Procedure

Electrochemical experiments were carried out with H-type glass cells having a single chamber volume of 150 mL. Porous glass was used as a diaphragm. A 30 wt percent KOH solution was used as the electrolyte at 80 ±2 °C. All potentiodynamic and open-circuit decay measurements were carried out on electrodes coated with the Ni-Mo-P alloy electrocatalyst. To minimize problems with oxide films, the test electrodes were first subjected to hydrogen evolution at a constant 500 mA/cm^2 for at least 30 min. The electrode was then transferred to another electrolyzer containing fresh solution. The electrode potential was measured relative to a saturated calomel electrode (SCE). Platinum gauze served as an auxiliary electrode.

The Ni-Mo-P alloy deposits were electrodeposited from ammoniacal citrate solution on copper substrates that were masked on one side. The substrates were degreased in hot alkaline solution at 70 °C and lightly etched with 5 wt percent H_2SO_4 immediately before plating. The composition of the bath is shown in Table 1. Electrodeposition was finished in a 400-mL bath under a cathode moving at 40 times/min. Before electrodeposition, the plating baths not containing NaH_2PO_2 were electrolytically aged (pre-electrolyzed) with a low current density of about 8 mA/cm^2, using titanium grid and platinum gauze as the cathode and anode, respectively. After aging and before plating, NaH_2PO_2 was added. The chemical composition of the alloys was assayed by an energy dispersion spectrometer (EDS). Some scanning electron microscope (SEM) observation was also performed.

Results and Discussion

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If baths were not aged, the appearance of the coatings deteriorated. They peeled or became dark, especially when molybdate concentration was high. Figure 1 shows the effect

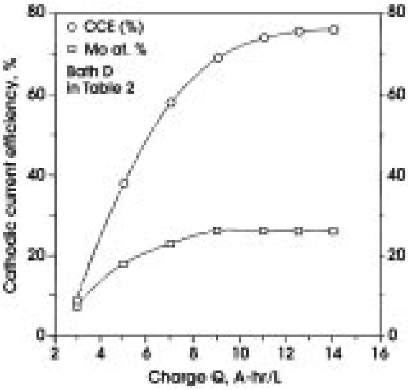


Fig. 1—Effect of current loading for electrolytic aging on Ni-Mo alloy content and current efficiency.

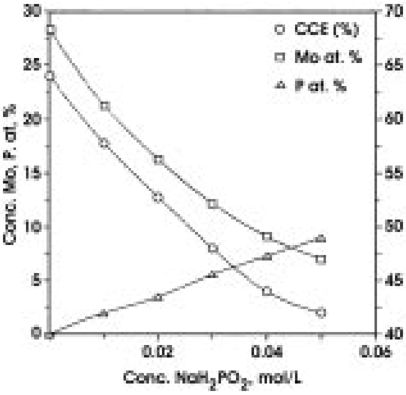


Fig. 2—Effect of NaH_2PO_2 concentration on content of Ni-Mo-P deposits and on current efficiency.

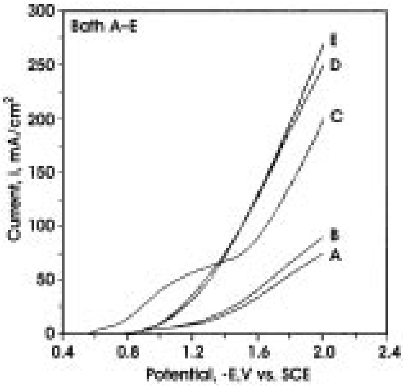


Fig. 3—Potentiodynamic polarization curves for electrolytes with composition as in Table 2. Sweep rate: 2 mV/sec.

of the electric charge loading for electrolytic aging on the content of Mo in electrodeposited Ni-Mo alloy and the cathodic current efficiency (CCE). The cathodic current efficiency and the molybdenum content in the deposit increase as the electric charge loading increases. When the charge loading is greater than 8 A-hr/L, the bath is stable.

Table 1
Composition of Plating Solution

Chemicals	Conc., mol/L
$NiSO_4 \cdot 6H_2O$	0.15
$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	0.1 (Mo)
NaH_2PO_2	0 - 0.05
$Na_3(C_6H_5O_7) \cdot 2H_2O$	0.3
NaCl	0.3
$NH_3 \cdot H_2O$	25 mL/L
Temp.	30 °C
pH	9
Current density	16 A/dm^2

It can be seen in Fig. 2 that the increase of NaH_2PO_2 concentration in the bath has the result of decreasing Mo content and increasing the content of Ni and P in the deposits. Moreover, the cathodic current efficiency (CCE) of deposition decreases as the NaH_2PO_2 concentration is increased.

Steady-state Electrochemical Characteristics

Figure 3 shows the potentiodynamic polarization curves of baths A to E in Table 2. Curves D and E indicate that deposition of the Ni-Mo or Ni-Mo-P alloy occurs at a quite negative potential, whereas nickel deposition from bath C begins at less negative potential by about -0.25 V. Curves D and E for Ni-Mo or Ni-Mo-P alloy deposition are steeper than curve C for nickel. Also, it is shifted toward more negative potential values. Molybdenum and phosphorus belong to the group of elements that cannot be deposited electrolytically and individually from aqueous solution.[10] The polarization curve obtained from Bath B electrolyte without nickel salts resembles the polarization curve obtained from the Bath A electrolyte without metal salts. In these cases, only hydrogen evolution takes place on the cathode. Accordingly, Mo is not deposited individually from the ammonium citrate baths. The possibility of codeposition of these elements with nickel is connected with the occurrence of considerable depolarization accompanying the process of co-discharge of molybdenum complex ions and the formation Ni-Mo-P alloys on the cathode.

The global and partial polarization curves are shown in Fig. 4 for Baths D and E. Figure 4a shows the polarization curves for Bath D without NaH_2PO_2. At the range of low polarization (E > -1.3 V), the current efficiency of the alloy deposition is very low. Hydrogen evolution is observed, as in the case of pure citrate or molybdate-citrate solutions. In the intermediate polarization range between -1.3 and -1.5 V, the hydrogen discharge partial current is nearly potential-independent. The larger the bulk molybdate concentration, the higher this current plateau. For potential between -1.48 and -1.57 V, the partial current for hydrogen evolution rapidly decreases.

Table 2
Electrolyte Composition for Polarization Curves

Chemicals	Baths, mol/L A	B	C	D	E
$NiSO_4 \cdot 6H_2O$	0	0	0.15	0.15	0.15
$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	0	0.1 (Mo)	0	0.1 (Mo)	0.1 (Mo)
NaH_2PO_2	0	0	0	0	0.05
$Na_3(C_6H_5O_7) \cdot 2H_2O$	0.3	0.3	0.3	0.3	0.3
NaCl	0.3	0.3	0.3	0.3	0.3
$NH_3 \cdot H_2O$ (mL/L)	25	25	25	25	25

At more negative potential, the partial current for hydrogen evolution increases more rapidly than nickel and molybdenum discharge, and the current efficiency decreases. In the potential range -1.3 to -2.00 V, the partial currents for nickel and molybdenum increase at the same rate. The alloy composition remains nearly constant at about 28 atomic percent Mo. These results are in agreement with those of E. Chassaing.[11] The global and partial polarization curves are shown in Fig. 4b for Bath E, containing NaH_2PO_2. Comparison of Figs. 4a and 4b reveals that addition of NaH_2PO_2 to the bath greatly decreased the molybdenum partial current and increased the hydrogen evolution partial current, although the effect on the nickel partial current is insignificant. This shows that NaH_2PO_2 hinders the discharge of molybdenum and promotes hydrogen evolution, resulting in decrease of cathodic current efficiency.

The surface morphology of the Ni-Mo-P deposits changes with alloy composition, as shown in Fig. 5. As with electroless Ni-Mo-P alloy,[12] electrodeposited Ni-Mo-P alloy coat-

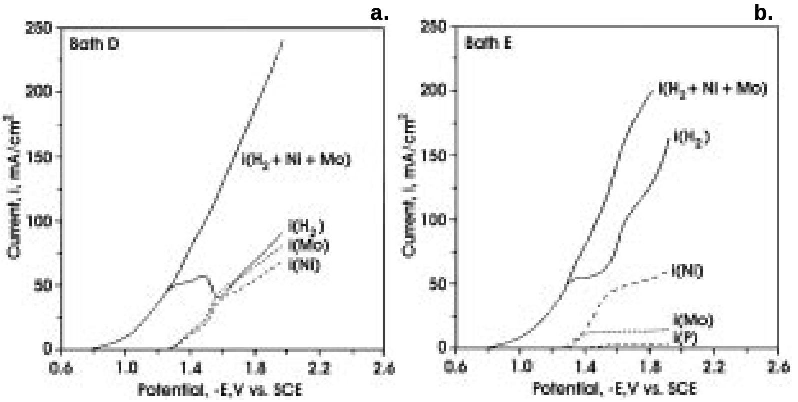


Fig. 4—Global and partial polarization curves for Baths D and E.

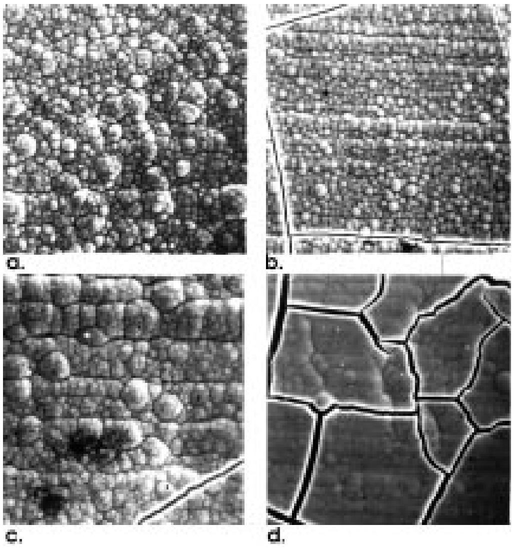


Fig. 5—Surface morphology of Ni-Mo-P coatings by SEM (atomic percent):
(a) Ni73.4Mo26.1P0.5; (b) Ni70.4Mo28.9P0.7;
(c) Ni83.7Mo8.2P8.1; (d) Ni86.6Mo3.3P10.2. 2000X.

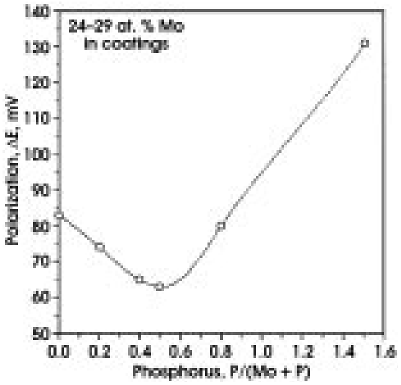


Fig. 6—Dependence of hydrogen evolution polarization, ΔE, on content of P relative to Mo.

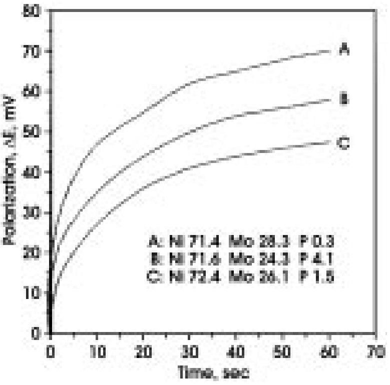


Fig. 7—Open circuit potential decay of electrode coated with Ni-Mo-P alloy.

ings containing a high percentage of Mo and/or P are characterized by internal stresses. Deposits containing more than about 25 atomic percent Mo or 6 atomic percent P have a surface covered with a network of irregular microcracks, and show upheaval of microarea edges. Alloy coatings containing lower content of Mo and P exhibit a uniform surface displaying no cracks.

Ni-Mo-P Coatings as Cathode Material in Hydrogen Evolution

The use of a cathode with Ni-Mo-P coating results in decreased hydrogen overpotential compared with that observed on nickel or nickel-molybdenum cathodes. When the cathodic current density was 200 mA/cm^2, the values measured for the polarization of evolved hydrogen, ΔE, on the cathodes with Ni-Mo-P coatings, ranged from 62 to 131 mV, whereas on the cathodes with Ni and Ni-Mo coatings, the ΔE value is about 300 mV and 83 mV, respectively. The ΔE values depend on the chemical composition of the Ni-Mo-P alloy (Fig. 6). The lowest value, about 62 mV, is found for deposits having a content of P, relative to Mo, of about 0.5 atomic percent.

The structure of the Ni-Mo electrocatalyst was studied extensively by X-ray diffraction.[13] Probably as with the Ni-Mo alloy coatings, the crystal lattices of nickel are changed by co-deposition with Mo and P. This would cause an increase in the number of crystal defects, altering the electronic structure of the metallic matrix, especially the number of electrons in the d-band. Consequently, the Ni-Mo-P alloy would also have a catalytic effect on hydrogen evolution.

Open Circuit Decay Measurements

Figure 7 shows the open circuit potential decay of a typical Ni-Mo-P alloy electrode that was subjected to constant current electrolysis at 500 mA/cm^2 in 30 wt percent KOH. In this case, the potential of the Ni-Mo-P electrocatalyst remained below zero for about one min, indicating the possible absorption of hydrogen into the electrode structure, or existence of hydrogen at a potential more negative than the reversible hydrogen electrode (RHE) potential.[14]

The changes in the electrode potential with time, after open circuit, become flatter and flatter during the first min. This phenomenon may occur when hydrogen desorption from the surface is impeded, constituting evidence for a strong bond between hydrogen atoms and the electrode surface. The content of phosphorus in the Ni-Mo-P alloy coatings is low; however, its presence has a considerable effect on the potential decay.

Conclusions

If the baths were not pre-electrolyzed before deposition, the appearance of the coatings deteriorated—they peeled or became dark, especially when molybdate concentration was high. The concentration of NaH_2PO_2 hinders the discharge of molybdenum and promotes the evolution of hydrogen, resulting in decrease of cathodic current efficiency.

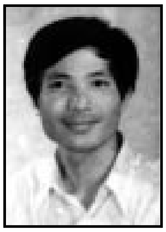
The coatings obtained are compact and adhere well to the copper substrate, with a surface covered with a network of microcracks.

On the cathodes with electrodeposited Ni-Mo-P alloy coatings, hydrogen evolution polarization is low—about 65 mV.

References

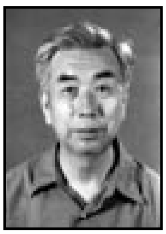
1. W.E. Winsche *et al., Science,* **180**, 1325 (1973).
2. E.A. Chapman, *Chem. Process Eng.,* **46**, 387 (1965).
3. R.L. Costa *et al., Chem. Eng. Progr.,* **63**, 56 (1967).
4. D.H. Smith, *Industrial Electrochemical Processes*, Elsevier Science Publ. Co., New York, NY, 1971; p. 127.
5. M.H. Miles, *J. Electroanalyt. Chem.,* **60**, 89 (1975).
6. M.H. Miles, *J. Electrochem. Soc.,* **123**, 1459 (1976).
7. U.S. patent 4,104,133 (1978).
8. Yue Zeng, Suwei Yao and Hetong Guo, *Plating and Finishing* (Chinese), **16**(3), 9 (1994).
9. Suwei Yao, Yue Zeng *et al., Surf. Technol.* (Japan), **45**(6), 643 (1994).
10. A.T. Wasko, *Elektrochimia molibdena i wolframa' Izd.,* Naukowa Dumka, Kiev, 1977.
11. E. Chassaing *et al., J. Appl. Electrochem.,* **19**, 839 (1989).
12. G.O. Mallory, *Plat. and Surf. Fin.,* **63**, 34 (June 1976).
13. D.E. Brown *et al., Proc. Symp. Electrocatalysis,* **82.2**, 145, Electrochem Soc., New York (1982).
14. B.E. Conway *et al., J. Electrochem. Soc.,* **130**, 1825 (1983).

About the Authors



Yue Zeng is an associate professor in the Department of Chemistry at the Hunan Normal University, Changsha, Hunan 410006, P.R. China. His research includes electroplating, organic electrosynthesis and computer simulation. He has published one book and about 30 papers on electroplating, organic electrosynthesis and computer simulation.

Suwei Yao is an associate professor in the Department of Applied Chemistry at Tianjin University. Her research includes amorphous electroplating and composite plating. She is a member of the Tianjin Electroplating Engineering Society and has published one book and about 60 papers on electroplating and related fields.



Hetong Guo is a professor in the Department of Applied Chemistry at Tianjin University. His research includes electroplating, composite plating and electrolysis. He is chairman of the Tianjin Electroplating Engineering Society, a member of the standing council of the Surface Engineering Association of China and chief of the editorial board of *Plating and Finishing* (Chinese). He has published four books and about 100 papers on electroplating and related subjects.