

## Electrodeposited Ni-Mo cathodes for hydrogen evolution

Shinsaku Meguro, Teruhito Sasaki, Katsuhiko Asami\*, Takashi Sakaki\*\* and Koji Hashimoto

Tohoku Institute of Technology, Sendai 982-8588 Japan

\* Institute for Materials Research, Tohoku University, Sendai 980-8577 Japan

\*\*Nanyo Research Laboratories, Tosoh Co., Shin-Nanyo, 746-8501 Japan

### Introduction

Enhancement of cathodic activity of nickel for electrolytic hydrogen evolution has been carried out by the formation of nickel alloys such as Ni-S [1], Ni-Mo [1-4] and Ni-Mo-O [5,6]. Recently, the most active Ni-Fe-C electrodes with excellent durability have been prepared by a simple electrodeposition technique [7,8]. For the electrodeposited Ni-Fe-C alloys proton discharge is remarkably accelerated and accordingly the rate determining step for hydrogen evolution is detachment of hydrogen from the cathode surface through combination of two adsorbed hydrogen atoms [8].

Electrodeposition can be applied to the formation of various alloys. Ni-Mo alloys can also be formed by electrodeposition. Although Ni-Mo alloys suffer corrosion under the open circuit condition in hot concentrated alkaline solutions due to the formation of molybdate ion, the cathodic activity of electrodeposited Ni-Mo alloys for hydrogen evolution is expected to be high.

The present work aims to prepare the Ni-Mo alloys with high cathodic activity for hydrogen evolution by electrodeposition and to clarify the effect of the molybdenum addition in enhancing the high activity for hydrogen evolution.

### Experimental Procedures

The basic electrolyte used for electrodeposition at room temperature was an aqueous solution consisting of 60g/l  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ , 7.2g/l  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , 72g/l  $\text{HOOCCH}_2\text{C}(\text{OH})(\text{COOH})\text{CH}_2\text{COOH} \cdot \text{H}_2\text{O}$  (citric acid monohydrate), 6g/l  $\text{H}_3\text{BO}_3$ , 0-5g/l  $\text{Na}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$ . The solution pH was adjusted to 5.0-6.0 by the addition of 4 M NaOH. The electrodeposition was carried out on nickel substrates at a current density of  $6 \times 10^{-3} \text{ Am}^{-2}$  and room temperature under the nitrogen bubbling condition in order to avoid hydrogen coverage of the substrate surface during electrodeposition. The composition of the electrodes thus prepared was analyzed by electron probe microanalysis and the structure of the electrodes was identified by X-ray diffraction using Cu  $K\alpha$  radiation.

The hydrogen evolution activity of the electrodes was examined in 8 M NaOH solution at 90°C. A cell of acrylic resin with the electrodes, platinum counter electrode and an external Hg/HgO/1 M NaOH reference electrode having a reversible potential of 0.950 V for the hydrogen reaction were used. The galvanostatic polarization curves were measured. The ohmic drop was corrected using a current interruption method.

X-ray photoelectron spectroscopy was used for characterization of the surface of the electrodes. A Shimadzu ESCA 850 photoelectron spectrometer was used with Mg  $K\alpha$  excitation for measurements of X-ray photoelectron spectra.

### Results and Discussion

As shown in Table 1, increasing molybdate content of the deposition electrolyte leads to an increase in the molybdenum content of the deposits but to a significant decrease in the deposition efficiency. The molybdenum content of the deposits is also largely affected by solution pH. At pH 5.5 the molybdenum contents of the deposits are particularly high, while at pH 6.0 the molybdenum content reaches the saturation value of about 30 at%.

Table 1 Change in molybdenum content of the deposits with the concentration of  $\text{Na}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$  and pH of the solution for electrodeposition

Concentration of $\text{Na}_2\text{MoO}_4 \cdot \text{H}_2\text{O} / \text{g l}^{-1}$	Molybdenum Content / at%		
	pH 5.0	pH 5.5	pH 6.0
0.5	0.81	1.93	4.81
1.0	15.9	23.2	14.5
1.5	18.6	32.4	29.0
2.0	22.5	35.0	29.5
2.5	32.4	40.7	29.2
3.0	30.0	43.8	31.6

According to X-ray diffraction, low molybdenum alloys were composed of a nanocrystalline fcc phase and increasing molybdenum contents resulted in the formation of amorphous alloy deposits.

When the molybdenum contents of the deposits are insufficient the Tafel slope of hydrogen evolution suggested that the rate determining step was proton discharge. By contrast, the alloys containing about 30 at% molybdenum, which were mostly amorphous, showed the highest activity for hydrogen evolution. For these alloys, because of the fast proton discharge, the rate determining step seems to be desorption of hydrogen from the cathode surface by the combination of two adsorbed hydrogen atoms.

### References

- [1] H. Vanderborre, Ph Vermeiren and R. Leysen, *Electrochim. Acta*, 29 (1984) 297.
- [2] J.-Y. Huot, *J. Electrochem. Soc.* 136 (1989) 1933.
- [3] D. E. Brown, M. N. Mehmood, M. C. M. Man and A. K. Tuner, *Electrochim. Acta* 29 (1984) 1551.
- [4] A. Kawashima, E. Akiyama, H. Habazaki, and K. Hashimoto, *Mater. Sci. Eng.* A226-228 (1998) 905.
- [5] R. Schulz, L. Dignard-Bailey, M. L. Trudeau, J.-Y. Huot and Z. H. Yan, *J. Mater. Res.* 9 (1994) 2998.
- [6] A. Kawashima, T. Sakaki, H. Habazaki and K. Hashimoto, *Mater. Sci. Eng.* A267 (1999) 246.
- [7] K. Suetsugu, T. Sakaki, K. Yoshimitsu, K. Yamaguchi, A. Kawashima and K. Hashimoto, *Chlor Alkali and Chlorate Technology*: R. B. MacMullin Memorial Symposium, H. S. Burney, N. Furuya, F. Hine and K.-I. Ota, Eds. the Electrochemical Society (1999) 169.
- [8] S. Meguro, T. Sasaki, H. Katagiri, H. Habazaki, A. Kawashima, T. Sakaki and K. Hashimoto, *J. Electrochem. Soc.* 147 (2000) 3003.