

Electrochemical stability of Co–Mo intermetallic compound electrodes for hydrogen oxidation reaction in hot KOH solution

Chang Rae Lee ^{*}, Sung Goon Kang

Surface Engineering Laboratory, Department of Materials Engineering, Hanyang University, 17 Haengdang-dong, Seoungdong-gu, Seoul 133-791, South Korea

Received 23 July 1999; accepted 28 August 1999

Abstract

In order to obtain a hydrogen electrode with high-performance and stability for H₂–O₂ alkaline fuel cells, Brewer-type Co–Mo alloys are manufactured in the 35 to 57 wt.% Mo composition range by an arc-melting method. The electrochemical stability of alloys composed of Co₃Mo and Co₇Mo₆ phases is investigated in hot KOH solution deaerated with N₂ gas by means of electrochemical methods such as cyclic voltammetry, potentiostatic polarization and potentiodynamic polarization. Co–Mo alloy is extensively dissolved because the cobalt in alloy is soluble in hot KOH solution. The dissolution current of the alloys increases with increasing electrolyte temperature, electrolyte concentration and Mo content in the alloy. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Alkaline fuel cell; Co₃Mo; Co₇Mo₆ intermetallic compounds; Hydrogen electrode; Corrosion; Electrochemical stability

1. Introduction

Electrocatalysts with high activity based on the Brewer–Engel theory have been used for hydrogen evolution [1,2] and oxygen evolution [3] in water electrolysis. Since transition metals belong to a wide family of precious metals, they had been researched as replacements for noble metal catalysts. It has been reported [1,4] that when metals such as W, Mo, La, Hf and Zr on the left half side of the transition series in the Periodic Table and with empty or half-filled d-bands are alloyed with metals such as Fe, Co and Ni on the right half of the series and with more filled d-bands, the bond strength and stability of the intermetallic compound phase are maximized and a synergetic effect will occur in the electrocatalyst.

For the hydrogen evolution reaction, the Ni–Mo electrode sintered under H₂ gas exhibits long-time activity with about 70–90 mV in overvoltage at 1000 mA⁻² cm [5]. The electrode prepared by dual combination of molybdenum and cobalt added in situ as anionic of molybdate has been shown to exhibit a remarkable shift in polarization characteristics.

Recently, Fan et al. [6] reported that the catalysts were tested tried as a hydrogen electrode for an alkaline fuel

cell, but there was no reference to the electrochemical stability of the catalyst in hot alkaline solution. The stability of an electrocatalyst depends on the operating conditions, such as overpotential, electrolyte temperature and concentration. Though this type of electrocatalyst has been shown to display long-term activity for the hydrogen evolution reaction in electrolysis, the hydrogen electrode in water electrolysis is polarized respect to the open-circuit potential in a negative direction. In a fuel cell, however the hydrogen electrode is polarized from the equilibrium hydrogen electrode potential in a positive direction. Thus, the hydrogen electrode may be electrochemically unstable in the case of anodic polarization.

In this study, we have investigated the electrochemical stability of Co–Mo (35–57 wt.%) intermetallic compounds in KOH solutions in terms of electrolyte temperature, concentration, and operation potential range.

2. Experimental

2.1. Specimen preparation

For electrochemical corrosion tests, the Co–Mo electrodes were bulk types of specimen with different compositions, as listed in Table 1. The bulk specimen was

^{*} Corresponding author. Fax: +82-2-2296-4560; e-mail: changlee@hymail.hanyang.ac.kr

Table 1
Alloying composition (wt.%) of Co–Mo intermetallic compounds

Alloying element								
Co	100	65	60	55	50	43	0	
Mo	0	35	40	45	50	57	100	

prepared by an arc-melting method with alloying elements (99.9% INCO 255 nickel powder, 99.8% Co powder and 99.9% Mo powder) under an argon atmosphere. Ingots were melted five times and then annealed at 800°C for 6 h under a H₂ gas atmosphere to effect homogenization of the composition. The resulting alloy ingots were cut with a diamond saw, polished mechanically with fine emery papers (2000 grade), and then mounted in plastic holders with epoxy resin.

2.2. Surface analysis

The phase compositions of the alloys were identified by X-ray diffraction (XRD) spectroscopy with Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$). The surface morphology and composition of the electrodes were investigated by scanning electron microscopy (SEM, JEOL JSM-6300) and an EDS analyzer after potentiostatic polarization at -0.75 V (vs. standard hydrogen electrode; SHE) for 1 h.

2.3. Electrochemical polarization

Polarization was carried out in KOH solution which was deaerated with N₂ gas. A computer-controlled potentiostat (EG&G, Model 273) was used to perform the polarization at a scan rate of 1 mV s^{-1} . A Luggin capillary connected to a saturated calomel electrode (SCE) as a reference electrode was placed close to the working electrode, and no correction was made for the internal resistance, iR_{sol} . Platinum net with large surface was used as the auxiliary electrode. Prior to the experiment, the work-

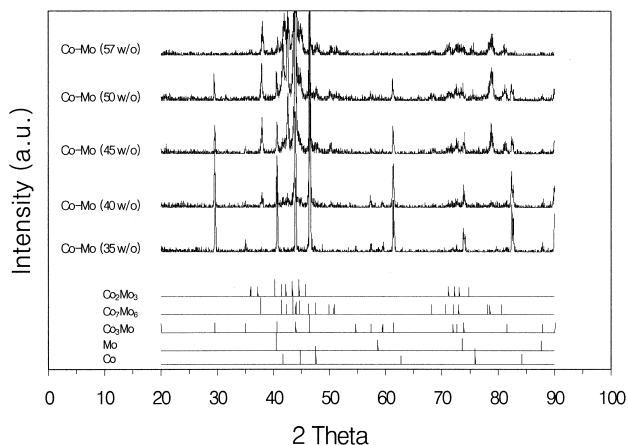


Fig. 1. XRD patterns of Co–Mo intermetallic compounds with a 35 to 57 wt.% Mo composition range.

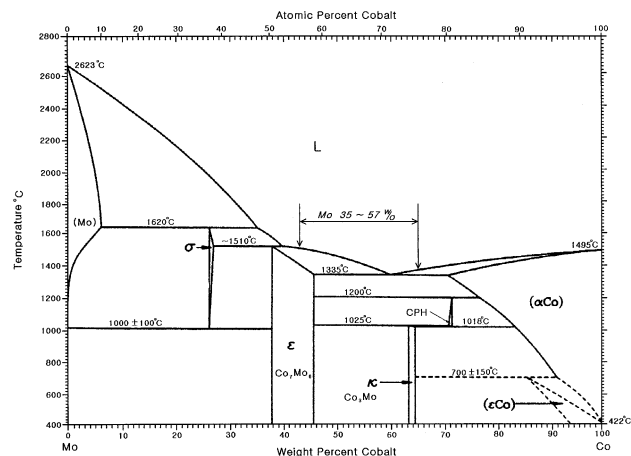


Fig. 2. Equilibrium phase diagram of Co–Mo binary alloy [7].

ing electrode was polished successive with emery paper down to 2000 grade, degreased with alcohol, and rinsed with distilled water. All potentials are reported with respect to the SHE, unless otherwise stated.

3. Results and discussion

3.1. XRD analysis of electrode

The XRD patterns of Co–Mo alloys with various alloying compositions (35 to 57 wt.% Mo) are presented in Fig. 1. The Co–Mo alloys are composed of κ -phase (Co₃Mo) and ϵ -phase (Co₇Mo₆) intermetallic compounds in the chosen composition range. Fan et al. [6] reported that Mo–Co porous electrodes sintered with 9.4 to 70.5 wt.% Mo are composed of Co, Mo, Co₃Mo, Co₇Mo₆ and Co₂Mo₃. In this study, the Co, Mo, and Co₂Mo₃ phases were not observed in electrodes manufactured by means of an arc-melting method. The Co–Mo (35 wt.%) electrode was composed of Co₃Mo phase. On increasing the Mo

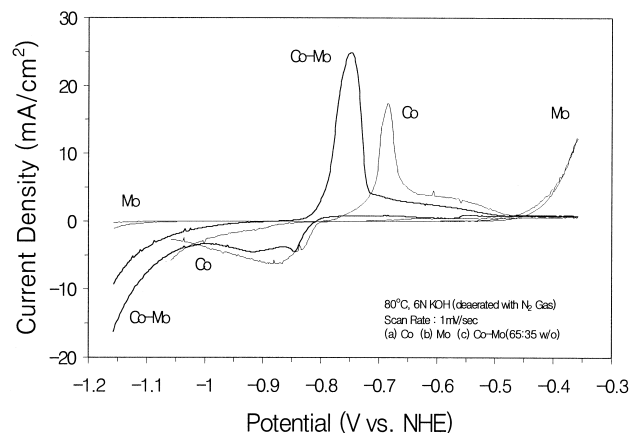


Fig. 3. Cyclic voltammograms for Co–Mo (35 wt.%) intermetallic compound electrode.

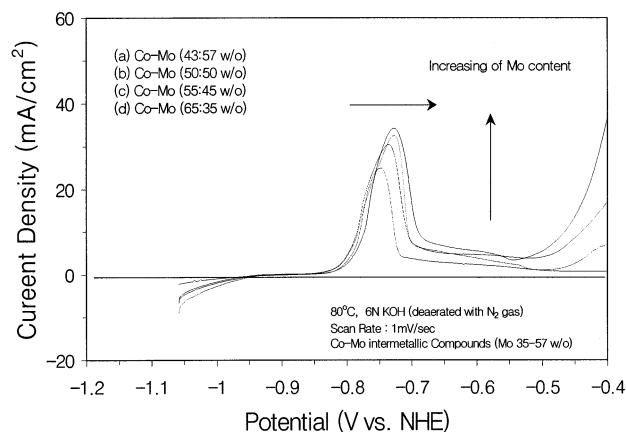


Fig. 4. Effect of molybdenum content on potential and current of first oxidation peak of Co–Mo intermetallic compounds.

content, the Co_7Mo_6 phase appeared such that and Co–Mo (57 wt.%) was composed almost entirely of the Co_7Mo_6 phase, as shown in Fig. 2 [7].

3.2. Cyclic voltammetry

In order to understand the electrochemical behaviour of Co–Mo intermetallic compounds, cyclic voltammetry experiments were carried out by scanning the potential at a rate of 1 mV s^{-1} between -1.3 and -0.3 V (vs. SCE).

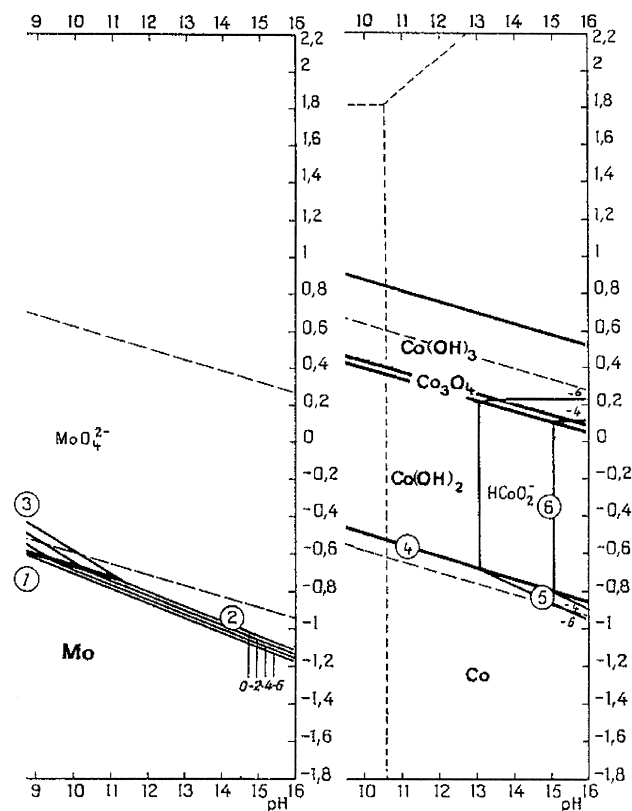


Fig. 5. Potential–pH equilibrium for Co– and Mo–water system at 25°C [8].

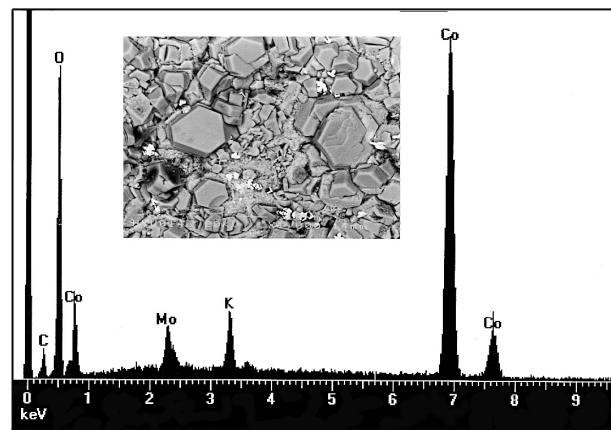


Fig. 6. Backscattered electron micrograph and EDS analysis of Co–Mo (35 wt.%) intermetallic compound (Co_3Mo) after potentiostatic polarization at -0.75 V for 1 h in 6 M KOH solution (deaerated) at 80°C .

The cyclic voltammogram for a Co–Mo (35 wt.%) electrode in 6 M KOH solution deaerated with N_2 gas at 80° is shown in Fig. 3. For the purpose of comparison, the cyclic voltammograms for the alloying elements, i.e., Co and Mo, are also presented. The data show that corrosive dissolution potentials and the first oxidation peak of the Co_3Mo intermetallic compound electrode are shifted to potentials which are more negative than those for the pure alloying elements. Thus, the Co_3Mo phase is unstable compared with the pure alloying elements in hot alkaline solution. It is also found that cobalt is more sensitive to corrosive dissolution than molybdenum in hot KOH solution. The dissolution reaction of cobalt and molybdenum is observed at more positive potentials than -0.8 and -0.75 V , respectively. Also, the maximum dissolution current peak of pure cobalt occurs at a the potential in the region -0.68 to -0.7 V . On the other hand, Co_3Mo intermetallic compound electrode is not dissolved at a potential of -0.87 V and displays a first oxidation peak at -0.77 V .

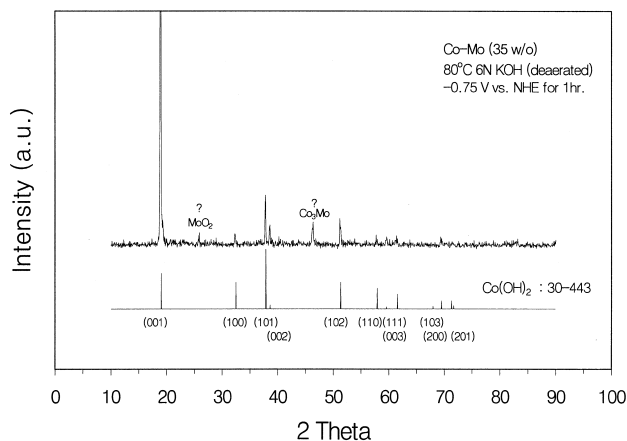
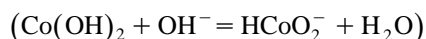
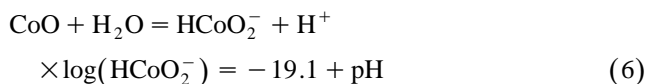
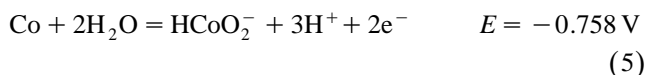
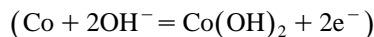
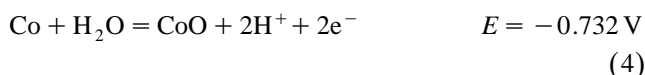
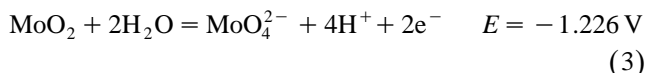
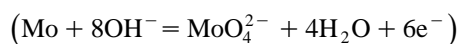
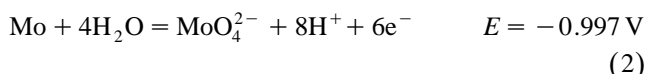
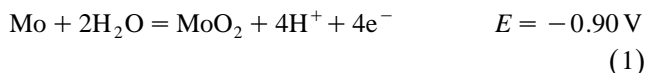


Fig. 7. XRD pattern for Co_3Mo electrode after potentiostatic polarization at -0.75 V for 1 h.

The effect of Mo content on the potential and element of the first oxidation peak of Co–Mo electrodes is shown in Fig. 4. As the Mo content is increased, the first oxidation peak is shifted to more positive potentials. Also, the maximum peak current increases. Thus, it is concluded that the Co_3Mo intermetallic compound is more stable than Co_7Mo_6 phase in hot alkaline solution.

The above results are considered in terms of the E –pH equilibrium diagram at 25°C for alkaline solution, as shown in Fig. 5 [8]. In case of 1 M KOH (pH \approx 14) with a dissolved ion concentration of 10^{-6} mol/l, the following are possible.



$$\times \text{pH} = \log(\text{HCoO}_2^-) + 19.1 = 13.1$$

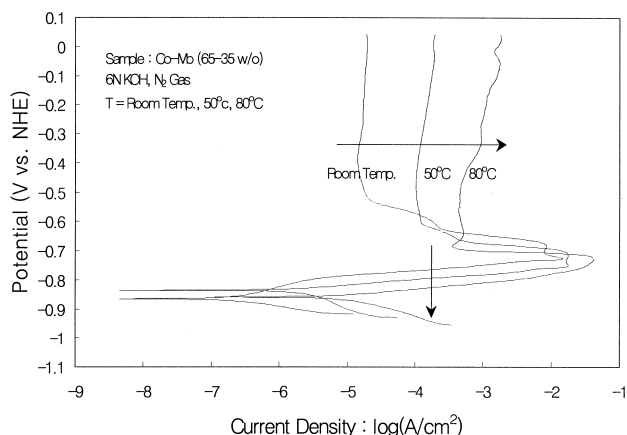


Fig. 8. Effect of electrolyte temperature on anodic polarization curves of Co–Mo (35 wt.%) intermetallic compound.

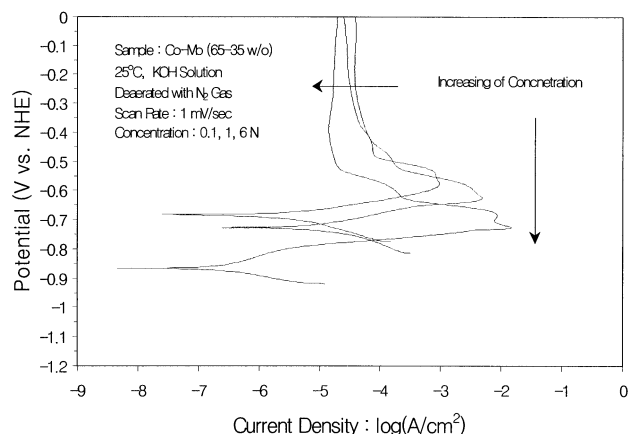


Fig. 9. Effect of electrolyte concentration on anodic polarization curves of Co–Mo (35 wt.%) intermetallic compound.

Molybdenum should dissolve to form MoO_4^{2-} ions in alkaline solution above pH 14. Also, cobalt should dissolve initially to form HCoO_2^- ions rather than a passive film of $\text{Co}(\text{OH})_2$ in solution above pH 13.1. As the potential is increased, the $\text{Co}(\text{OH})_2$ passive film develops on the electrode surface. By contrast, the molybdenum can dissolve at more negative potentials than the dissolution potential of cobalt. Thus, it is concluded that the Mo in the Co_3Mo intermetallic compound is first dissolved to give MoO_4^{2-} ions and then the compound, which has a DO_{19} type superlattice structure [9] becomes unstable. Thus, Co in the Co_3Mo intermetallic compound must dissolve at a more negative potential than pure cobalt in order to form stable structure. On increasing the molybdenum content in the Co–Mo intermetallic compound, dissolution of Co may be enhanced. Clearly, it is necessary to examine in detail the initial dissolution behaviour in order to define the corrosion mechanism of Co–Mo intermetallic compounds.

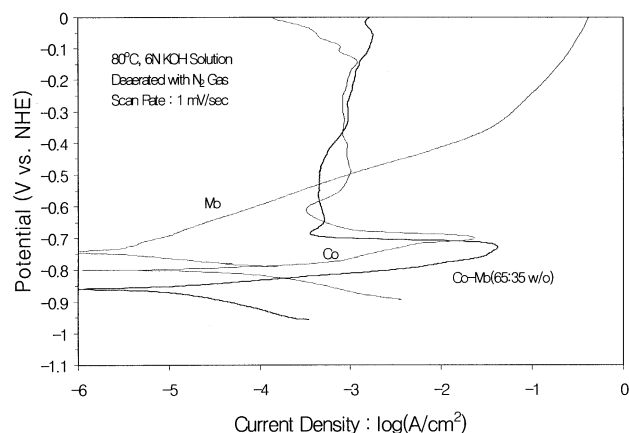


Fig. 10. Anodic polarization curves for pure Co, Mo and Co–Mo intermetallic compound.

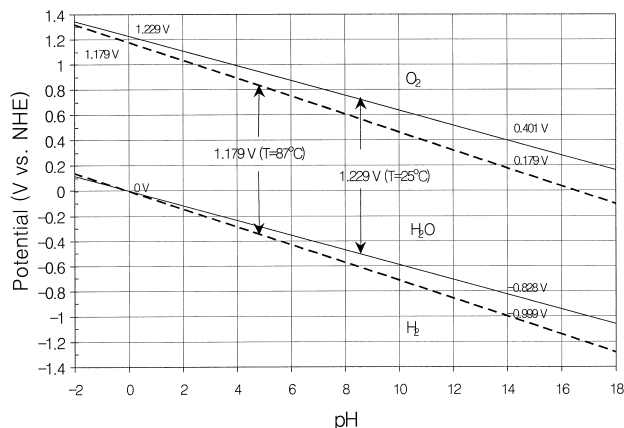


Fig. 11. Equilibrium potential–pH diagram for operation conditions of alkaline fuel cell.

3.3. Formation of hydroxide film on electrode

In order to investigate the hydroxide film formed on the electrode surface at the first oxidation peak potential, the Co_3Mo intermetallic compound electrode was polarized potentiostatically at -0.75 V for 1 h. After potentiostatic polarization, EDS analysis of the Co_3Mo electrode indicated that the surface composition was almost cobalt and oxygen, as shown in Fig. 6. Small amounts of molybdenum and potassium were also detected. XRD analysis indicated that a passive film of $\beta\text{-Co}(\text{OH})_2$ was formed on the electrode surface, as shown in Fig. 7. This suggests that the cobalt component in Co–Mo intermetallic compounds is less stable than pure cobalt in alkaline solution. The Co–Mo alloy was severely dissolved at potentials more positive than -0.87 V in hot KOH solution. Therefore, cobalt dissolved from a Co–Mo electrode is deposited as cobalt hydroxide on the surface of the electrode.

3.4. Effect of temperature and concentration

The effect of electrolyte temperature on the electrochemical characteristics of a Co–Mo (35 wt.%) alloy is shown in Fig. 8. The dissolution current in the active potential region increases with increasing electrolyte temperature. The primary passive potential (E_{pp}) is shifted to an active potential region and the limiting current at E_{pp} is increased. The potential of the Co–Mo (35 wt.%) electrode occurs at -0.85 to -0.87 V in 6 M KOH deaerated solution. Thus, the Co_3Mo intermetallic compound can be used for an AFC hydrogen electrode at potentials negative than -0.87 V. The effect of electrolyte concentration on the electrochemical behaviours of the Co–Mo (35 wt.%) electrode is given in Fig. 9. The open-circuit potential (E_{oc}) and the passive potential (E_{pp}) are shifted to more negative potentials with increasing concentration. The dissolution current of the electrode results from dissolution of

cobalt in activated potential region. The electrochemical parameters are dependent on concentration rather than on temperature. The anodic polarization curves for pure Co, Mo and Co–Mo intermetallic compound are shown in Fig. 10. The dissolution current of the electrode results from dissolution of cobalt in activated potential region.

In summary, since the hydrogen electrode in an alkaline fuel cell is operated at an overpotential of 0.1 V (i.e., from -1.0 to -0.9 V) in 80°C , 6 M KOH, as shown in Fig. 11, Co–Mo intermetallic compound electrodes without corrosion problems, such electrodes cannot, however, be employed at an overpotential of 0.1 to 0.2 V because of serious dissolution.

4. Conclusion

Brewer type Co–Mo (35 to 57 wt.%) alloys which are composed of Co_3Mo and Co_7Mo_6 intermetallic compounds are unstable in hot KOH deaerated solution. In the active potential region, these electrodes are seriously attacked due to the dissolution of the cobalt element. In particular, the Co–Mo intermetallic compound becomes unstable with increasing Mo content. This means that the Co_3Mo phase is more stable than the Co_7Mo_6 phase in hot alkaline solution. Also, the dissolution current of the alloys increases with increasing temperature and concentration of the electrolyte. In the active potential region, the electrode potential is shifted in the negative-potential direction with increasing electrolyte concentration. Thus, it is concluded that the Brewer type Co–Mo electrodes can be used as hydrogen electrodes without corrosion problems. In an alkaline fuel cell, the hydrogen electrode can be operated in the potential region from -1.0 to -0.9 V, which is located below the corrosion potential. If the hydrogen electrode is used at an overpotential above 0.1 V, however, the Co–Mo intermetallic compound electrode will suffer extensive dissolution in hot alkaline solution.

References

- [1] M.M. Jaksic, *Electrochim. Acta* 29 (1984) 1359.
- [2] H. Wendt, *Electrochemical Hydrogen Technology*, Elsevier, New York, 1990, p. 35.
- [3] L. Vracar, B.E. Conway, *Electrochim. Acta* 35 (1990) 1919.
- [4] M.M. Kasic, *Int. J. Hydrogen Energy* 12 (1987) 727.
- [5] D.E. Brown, M.N. Mahmood, A.K. Turner, S.M. Hall, P.O. Fogarty, *Int. J. Hydrogen Energy* 7 (1982) 405.
- [6] C. Fan, D.L. Piron, M. Rojas, *J. Hydrogen Energy* 19 (1994) 29.
- [7] T.B. Massalski, *Binary Alloy Phase Diagrams*, Vol. 2, 2nd edn., ASM International, USA, 1990.
- [8] M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, Pergamon, Oxford, 1966.
- [9] M. Hansen, *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958, p. 482.