Corrosion properties of Ni-Nb & Ni-Nb-M (M = Zr, Mo, Ta & Pd) metallic glasses in simulated PEMFC conditions

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Abstract. The corrosion behaviour of (Ni₆₀Nb₄₀) and Ni-Nb-M (M = Zr, Mo, Ta & Pd) melt-spun ribbons was studied by electrochemical and chemical methods at PEMFC environments. The doping of Mo, Pd and Ta decreased the corrosion and passivation current densities, whereas the addition of Zr induced the opposite effect. To understand the change of corrosion behaviour induced by these additional elements, the surface composition and surface oxide layer thickness were analyzed by XPS method.

1. Introduction
Proton exchange membrane (PEM) fuel cells are the most promising candidates for stationary and portable applications because of their high efficiency, high energy density, low operating temperature, low noise, rapid recharging and no emission of polluting materials using hydrogen [1]. By substituting metallic glass, for the present separator material (i.e., graphite), the performance of the fuel cell could be improved [2]. Metallic glass possesses excellent corrosion resistance due to the absence of crystalline defects such as grain boundaries, segregations and dislocations. Particularly, Ni-based compositions are quite resistant to general and localized corrosion in alkali and most acids and have high mechanical strength [3, 4].

It has been reported that the Ni₆₀Nb₄₀ alloy is very close to the eutectic composition in the Ni-Nb phase diagram [5] and that the glassy alloy of this composition exhibits high corrosion resistance. Although the Ni₆₀Nb₄₀ alloy is well known for the formation of the amorphous structure under high cooling rates, its corrosion property has not been investigated thoroughly. In this paper, the corrosion behaviours of binary Ni₆₀Nb₄₀ alloy and its ternary alloys formed by the alloying of passivating elements such as Pd, Zr, Mo and Ta were studied in the PEMFC conditions.

2. Experimental
Potentiodynamic and potentiostatic polarization experiments were carried out using autolab equipment with PGSTAT10. All amorphous ribbons prepared by melt spinning technique were polished with 2400 grit SiC paper, ultrasonically cleaned in acetone for 5 minutes, followed by rinsing with deionised water and finally used as working electrode. Ag/AgCl and platinum foil were used as reference and counter electrodes, respectively, in 1M H₂SO₄ + 2ppm F⁻ at 80°C with either hydrogen or pressurized air bubbling conditions. The immersion tests were carried out by refluxing the ribbons in a round bottom flask fitted with a condenser for 168 hours under the above experimental conditions.

[1] V. S. Vasantha, H.-S. Chin, and E. Fleury, “Corrosion properties of Ni-Nb & Ni-Nb-M (M = Zr, Mo, Ta & Pd) metallic glasses in simulated PEMFC conditions,” in *The 13th International Conference on Rapidly Quenched and Metastable Materials*, IOP Publishing, 2009, pp. 1–2.

[2] V. S. Vasantha, H.-S. Chin, and E. Fleury, “Corrosion properties of Ni-Nb & Ni-Nb-M (M = Zr, Mo, Ta & Pd) metallic glasses in simulated PEMFC conditions.”
X-ray photo-electron spectral analyses were accomplished with a Physical Electronics (PHI) 5800 spectrometer, Al Kα excitation (hν = 1486.6 eV).

3. Results and Discussion

3.1. Potentiodynamic polarization

The potentiodynamic polarization curves of the Ni60Nb40, (Ni60Nb40)97Ta5, (Ni60Nb40)97Mo3, (Ni60Nb40)75Zr25 and (Ni60Nb40)90Pd10 ribbons investigated in 1M H2SO4 + F⁻ solution are shown in figure 1a and figure 1b for, respectively, air and hydrogen bubbling conditions. For all alloy systems, the potential scans started below Ecorr, and the current densities observed in these regions could be due to the hydrogen evolution in 1M H2SO4 solution. At Ecorr, the current densities decreased and then increased linearly due to the metal dissolution from the alloy surfaces. These active dissolution regions were followed by constant current densities regions called passive ranges. At potentials greater than 1600 mV (vs. Ag/AgCl), the current densities increased significantly due to O2 evolution, dissolution of the passive film and transpassivation phenomena. The corrosion current density (icorr) was estimated from the intersection of anodic and cathodic polarization curves, and the polarization resistance (Rp) was calculated from the equation Rp = 2.303 \[ \frac{ba \cdot bc}{(ba + bc)} \] / icorr, where ba and bc are the anodic and cathodic slopes, respectively.

The results indicate that the alloying of the Ni60Nb40 alloy with Ta, Mo and Pd decreased the values of icorr and ipass with no appreciable change in the Ecorr. Particularly, the addition of Ta and Mo promoted the spontaneous passivation and thereby reduced the icorr by one order, whereas the addition of Zr increased the values of both icorr and ipass by three orders. The (Ni60Nb40)90Pd10 alloy also exhibited similar adverse effect in H2 atmosphere.

3.2. Potentiostatic polarization

The potentiostatic experiments were carried out in PEMFC cathodic conditions at 0.6 V for 2 hours.
As shown in figure 2, a similar behaviour under potentiostatic condition can be observed for the binary and ternary alloys, except for the (Ni₆₀Nb₄₀)₇₅Zr₂₅ alloy composition. The decrease of the current density indicated the tendency to spontaneously passivate and the stabilization was achieved in a shorter period (15 min) for the ternary alloys in comparison to the Ni₆₀Nb₄₀ binary alloy (40 min). In contrast, the current density for the (Ni₆₀Nb₄₀)₇₅Zr₂₅ alloy was found to increase continuously to reach a high value, thus confirming the tendency observed from the potentiodynamic polarization analyses.

3.3 Chemical Immersion Test

The weights of the specimens were measured before and after immersion. Table 1 summarizes the important corrosion parameters obtained from the above three methods. The addition of Ta element reduced the weight loss of Ni₆₀Nb₄₀ alloy appreciably whereas Mo addition showed a marginal effect.

| Alloy                  | icorr (A/cm²) | Ecorr (V) | Rp (ohm) | Wt loss (mg/cm²) | ipass (0.6V) (A/cm²) |
|------------------------|---------------|-----------|----------|------------------|----------------------|
| Ni₆₀Nb₄₀               | 4.708×10⁻⁶    | -0.015    | 4.200×10⁴ | 0.142            | 14.8×10⁻⁶            |
| (Ni₆₀Nb₄₀)₉₀Pd₁₀      | 4.260×10⁻⁶    | 0.041     | 2.703×10⁴ | 0.217            | 9.75×10⁻⁶            |
| (Ni₆₀Nb₄₀)₉₀Ta₅       | 5.416×10⁻⁷    | -0.035    | 5.255×10⁴ | 0.0055           | 3.75×10⁻⁶            |
| (Ni₆₀Nb₄₀)₉₀Mo₃       | 3.582×10⁻⁶    | -0.04     | 1.328×10⁴ | 0.136            | 2.15×10⁻⁶            |
| (Ni₆₀Nb₄₀)₇₅Zr₂₅      | 5.582×10⁻²    | 0.093     | 3.141×10³ | 0.475            | 278×10⁻⁶             |

In overview, it was understood that Ni₆₀Nb₄₀ alloy exhibited good corrosion resistant owing to the formation of Nb₂O₅ oxide layer [4]. However, the addition of easily passivating metals such as Ta, and Mo, in to Ni₆₀Nb₄₀ alloy markedly improved its icorr, Rp, and ipass. The passivating capability of Ta can be attributed to the easy formation of highly stable and uniform TaO₂(OH) film even in highly aggressive medium [6]. Whereas Mo, due its very low ionization energy (651 KJ/mol), could immediately formed a thin temporary film which acted as diffusion barrier, thus assisted the accumulation of passivating species of the alloy, with subsequent dissolution of Mo (VI) [7]. However, the (Ni₆₀Nb₄₀)₉₀Pd₁₀ alloy exhibited spontaneous passivation with a slight increase in ipass and Ecorr values in comparison to the Ni₆₀Nb₄₀ alloy. It implies that the dissolution of active Ni should have been increased by the presence of noble Pd, leading to Nb enrichment near the surface. However, the barrier effect of this alloy is not comparable with that of (Ni₆₀Nb₄₀)₉₀Ta₅ and (Ni₆₀Nb₄₀)₉₀Mo₃ systems. Meanwhile, the addition of Zr led to adverse effect, which was attributing to the formation of small volume of heterogeneity on the free surface of the ribbon during melt spinning that resulted in an unusual increase of ipass in the passivation region. Matsuura [8] reported that for certain alloy compositions, thin crystalline layers were formed on the free surface of amorphous Fe-rich Fe-Zr alloys during melt spinning. Yoshioka et al. [9] suggested that small crystals undetected by X-ray diffraction could be associated with the high anodic current density in the passivation region in Ni-Cr-P-B alloy system.

3.4 XPS analysis

XPS analyses were carried out before and after immersion to study the composition and thickness of the passive oxide layers. Figure 3 depicts the cationic contents in the surface film of Ni₆₀Nb₄₀ and (Ni₆₀Nb₄₀)₇₅Zr₂₅ alloys before and after corrosion. The XPS spectra exhibited peaks for the Ni, Nb, Zr, and oxygen. O₁s peaks originate from oxygen in metal-O-metal bond and metal –OH bond. The peaks of Ni 2p, Nb 3d and Zr 3d were corresponding to the species in the oxidized state of the surface film and the metallic states in the underlying alloy surfaces. After air exposure, (figure 3 a) the film formed on Ni₆₀Nb₄₀ alloy was found to be enriched with Nb, Ni and O. However, after the immersion test, the surface of the alloy was enriched only with Nb and O, while Ni was almost depleted due to its active dissolution. These trends were also observed in all above alloys except for the (Ni₆₀Nb₄₀)₇₅Zr₂₅.
Consequently, the oxide layer thickness was increased from 18 to 65 nm after immersion. After exposure to air, the surface oxide thickness of the (Ni$_{60}$Nb$_{40}$)$_{75}$Zr$_{25}$ alloy system was found to be 60 nm; however, after immersions test it was slightly decreased (50 nm). This behaviour could be attributed to the presence of surface heterogeneities which could increase the active dissolution, leading to a decrease in the oxide layer thickness with Ni ions enrichment on the surface.

![Figure 3](image)

**Figure 3** Cationic concentrations on the surfaces of the amorphous alloys (a) Ni$_{60}$Nb$_{40}$ before corrosion (b) Ni$_{60}$Nb$_{40}$ after corrosion (c) (Ni$_{60}$Nb$_{40}$)$_{75}$Zr$_{25}$ before corrosion and (d) (Ni$_{60}$Nb$_{40}$)$_{75}$Zr$_{25}$ after corrosion.

4. Conclusion

The corrosion and passivation current densities of Ni$_{60}$Nb$_{40}$ alloy were significantly decreased by the addition of Ta and Mo, whereas the Pd addition improved its corrosion current density only. The (Ni$_{60}$Nb$_{40}$)$_{75}$Ta$_{5}$ amorphous alloy was found to be the best candidate among the studied alloys in terms of corrosion while the alloying of Zr led to adverse effect.

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