JOURNAL OF APPLIED ELECTROCHEMISTRY **28** (1998) 889–894

Hydrogen permeation inhibition by thin layer Zn–Ni alloy electrodeposition

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Received 11 November 1996; revised 22 August 1997

The inhibition of hydrogen permeation by zinc-nickel electrodeposited alloy was investigated using the Devanathan–Stachurski permeation technique. The hydrogen evolution and hydrogen permeation rates for the zinc–nickel alloy electrodeposits on iron are compared with the rates for bare iron, zinc electroplated on iron, and nickel electroplated on iron. Hydrogen evolution rates and hydrogen permeation rates were followed as functions of time at different applied potentials. The hydrogen permeation inhibition for thin zinc–nickel electroplates (20 s at 10 mA cm^{-2} and 10 s at 20 mA cm^{-2}) averaged 80% and intermediate to that of nickel and zinc. This inhibition was considered to be mostly due to kinetic effects. Zinc–nickel electroplated for 20 and 40 min. at 10 mA cm^{-2} inhibited the hydrogen permeation greater than 95% as compared to bare iron. This inhibition was due to both kinetics and the barrier effect caused by the diffusion resistance of the membrane.

Keywords: *zinc*, *zinc-nickel*, *hydrogen*, *permeation*, *inhibition*

1. Introduction

Zinc–nickel alloy has received considerable interest recently as a possible sacrificial coating replacement for zinc and cadmium electrodeposits. Studies of the electroplate have been carried out for many years [1–3], but a renewed interest may partially be due to heightened environmental awareness and hence greater interest in finding a replacement for cadmium. In 1966, Davis and Gray [4] reported on the hydrogen permeation inhibition by some electrodeposited coatings including Zn–Ni; however, most studies have been concerned with the electroplating process or the corrosion characteristics of the Zn–Ni alloy and have not focused on the hydrogen permeation characteristics of the alloy.

Corrosion studies have also indicated that the Zn–Ni alloys may be useful as a substitute for cadmium deposits in marine environments [5]. Zn–Ni alloy may also be useful in galvanizing or in more corrosive environments. Nickel is well known for its stability in corrosive alkaline environments, such as exist in many cement stabilized applications. Since the open circuit potential of Zn–Ni alloy is more noble than that of pure zinc, the mixed potential of Zn–Ni coupled to iron or steel (as in galvanizing) would be less anodic than that of pure Zn. Zn–Ni coatings been found to corrode more slowly than Zn coatings [5].

In addition to determining the corrosion characteristics for a potential protective or sacrificial coating, the hydrogen permeation characteristics are also important. Hydrogen permeation can cause embrittlement of metals and alloys during electroplating, cathodic protection, and corrosion of metals. Hydrogen evolution is an undesirable additional reaction in all of these processes. Therefore, a coating which minimizes the permeation of hydrogen into the substrate metal is desirable.

Researchers have used several metals as surface treatment for the inhibition of hydrogen permeation [6–13]. Surface electroplates may decrease hydrogen permeation by one or more of several mechanisms. The modified surface can act as a physical barrier to hydrogen diffusion due to the low diffusion rate of hydrogen through the electroplate. The discharge kinetics of the hydrogen evolution reaction can be inhibited. Finally, the absorption of hydrogen into the modified surface can be decreased compared to the unmodified surface. More hydrogen will then recombine to form hydrogen molecules which subsequently move away from the surface as hydrogen gas. The latter two mechanisms (reaction kinetics changes rather than diffusion kinetics changes) are thought to be most important for thin electroplates.

In addition to the sacrificial coating providing protection itself for hydrogen permeation into the substrate steel, the smaller difference in potentials between the substrate and galvanizing coating for Zn–Ni may be useful for hydrogen permeation inhibition. The cathodic sites on a protected steel substrate would have a smaller cathodic overpotential than when galvanically coupled with zinc. Less hydrogen would be generated, especially in the presence of oxygen which could be reduced rather than reducing water (in alkaline environments) or protons (in acidic environments) to form hydrogen.

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The anomalous codeposition of Zn–Ni has been studied by many researchers [14, 15]. It has been found that the concentration of zinc in the alloy is strongly dependent on the current density of the plating process. The higher the current density, the greater the zinc content of the electrodeposit. In addition to current density, the plating bath temperature, bath composition, and bath pH play important roles in the composition and quality of the electrodeposit [15].

The objective of this study was to investigate the effect of electrodeposition of Zn–Ni alloy on hydrogen permeation inhibition, as compared to plating pure Ni or pure Zn. The results presented here focus on the permeation inhibition effect of the Zn–Ni coating itself and not on any possible changes in hydrogen evolution or permeation that might occur on exposed substrate sites.

2. Experimental details

The permeation experiments were carried out in a two compartment system separated with a bipolar iron membrane, shown schematically in Fig. 1. The hydrogen evolution current and hydrogen permeation current were measured continuously as functions of time. On the anodic side of the membrane, the potential was held constant at −0.3 V vs a Hg/HgO reference electrode. This potential corresponds to a practically zero concentration of absorbed atomic hydrogen on the surface [3]. 0.1 mm thick iron membranes 99.5% purity were used. Prior to the experiments the membranes were prepared by polishing with 600 grade sandpaper and cleaning in an ultrasonic cleaning bath.

To avoid oxidation of the Fe membrane surface on the anodic side, a thin layer of palladium was electroplated on this surface. The electrodeposition of palladium was carried out using a solution of 2.2×10^{-5} M $K_2Pd(NO_2)_4$ and 0.2 M NaOH at a current density of 200 μA cm^{-2} for 4 h with the membrane in the permeation cell. The anodic compartment was then drained, rinsed with deionized water, and refilled with fresh 0.2 M NaOH. Both the anodic and cathodic solutions were pre-electrolyzed for 24 h in separate electrolytic cells prior to the experiments to remove any impurities in the solutions. After plating the palladium on the anodic side, the cathodic side was filled with 1.0 M H_3BO_3, 1.0 M Na_2SO_4, 0.4 M NaCl. Nitrogen gas was bubbled through both compartments during the experiments to remove any dissolved oxygen.

Prior to electrodepositing metals on the bare Fe membrane, the membrane was first saturated with hydrogen to fill any irreversible trapping sites by holding the Fe foil on the cathodic side at $E_c = -1.3$ V vs SCE for one hour. The applied potential was then reduced to $E_c = -1.15$ V and held for approximately one hour. Permeation rates were subsequently measured on the bare Fe at several applied cathodic potentials, to insure that each membrane had similar permeation behavior before the electrodeposits.

Zinc–nickel alloy electroplates were electrodeposited galvanostatically from: 0.5 M $NiSO_4$, 0.20 M $ZnSO_4$, 0.50 M Na_2SO_4 at either 10 mA cm^{-2} for 20 s or 20 mA cm^{-2}for 10 s.

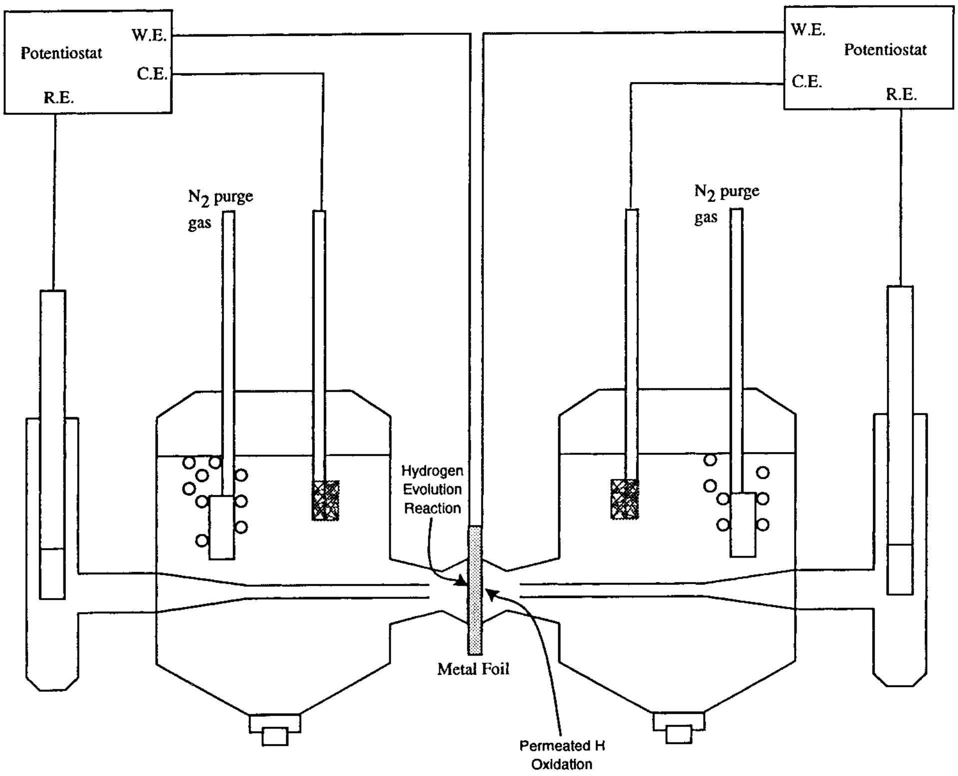

Fig. 1. Schematic diagram of permeation cell.

Zinc electroplates were plated from an acid zinc bath [16]: 0.56 M $ZnSO_4$, 0.63 M Na_2SO_4, 0.51 M NaCl, 0.32 M H_3BO_3 at 10 mA cm^{-2} for 20 s.

Nickel electroplates were plated from a hard nickel bath: 0.68 M $NiSO_4$, 0.47 M NaH_4Cl, 0.49 M H_3BO_3 at 10 mA cm^{-2} for 20 s.

Immediately after plating *in situ*, the plating bath was drained, the cell rinsed with DI water, and fresh cathodic solution added. Permeation experiments were carried out subsequently. Similar to the bare iron, the permeation measurements on the plated iron were carried out after holding E_c at −1.3 V (vs SCE) for one hour and then reducing E_c to −1.15 V for approximately one hour. The electroplates were kept at $E_c = -1.15$ V or more negative to prevent zinc oxidation during the experiments. All the electroplates were treated in the same way to reduce differences in permeation inhibition due to the surface changes over long periods of time.

3. Results and discussion

Figure 2 shows the cathodic current density, i_c, during the hydrogen permeation studies against the applied cell potential, E_c, for the electroplates. At lower cathodic potentials, the cathodic current for the zinc–nickel electroplates is intermediate to zinc and nickel, whereas at higher cathodic potentials (E_c more negative), the cathodic currents for the zinc–nickel electroplates is similar to that of the pure nickel plate. The slope of the Zn–Ni curves indicates that the transfer coefficient for the hydrogen discharge reaction for these electroplates was different than that of either pure Zn or pure Ni electroplates.

Figure 3 shows the permeation current density, j_∞ against the applied cell potential E_c for the electroplates. The Zn–Ni electroplates showed permeation current densities between those of zinc and nickel, while the permeation current densities of all the electroplates are much reduced compared to bare iron. Table 1 shows the average percent decrease in the hydrogen evolution current and the permeation current over all the potentials studied for each electroplate relative to bare iron. The −88% i_c reduction for nickel indicates an 88% increase in cathodic current density for the nickel electroplate as compared to bare iron. The present zinc composition of the electroplates as measured by energy dispersion spectroscopy (EDS) is also shown in Table 1.

Figure 4 shows the effect of multiple Zn–Ni electroplates on the permeation rate. Each Zn–Ni electroplate was carried out for 20 s and the permeation rate measured at different applied potentials between successive electroplates. After the first electroplate there is no significant decrease in permeation rate for these then electroplates. This indicates that for these very thin electroplates, the hydrogen permeation inhibition is due mostly to changes in hydrogen discharge and reaction kinetics rather than to a diffusion barrier effect.

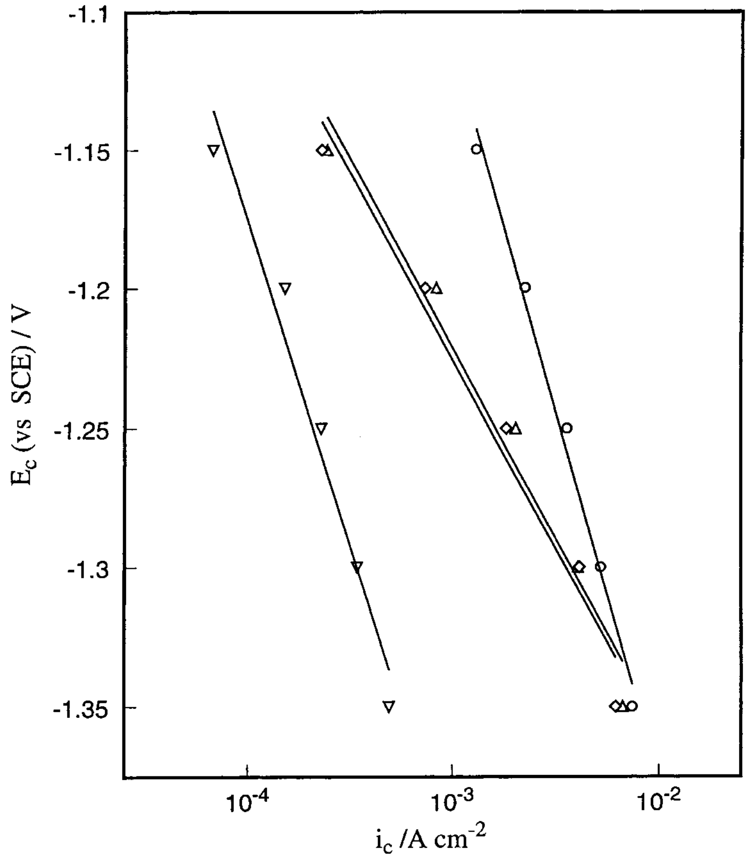

Fig. 2. Cathodic current, i_c, against applied potential, E_c. Key: (○) Ni, 10 mA cm^{-2}; (△) Ni–Zn, 10 mA cm^{-2}; (◇) Ni–Zn, 20 mA cm^{-2}; (▽) Zn, 10 mA cm^{-2}.

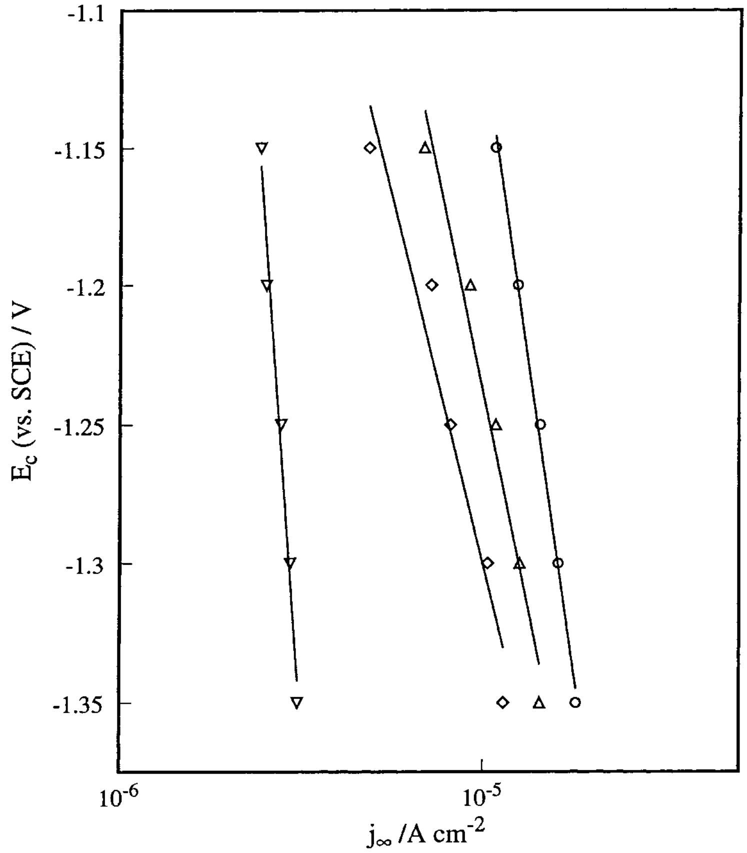

Fig. 3. Permeation current, j_∞, against applied potential, E_c. Key: (○) Ni, 10 mA cm^{-2}; (△) Ni–Zn, 10 mA cm^{-2}; (◇) Ni–Zn, 20 mA cm^{-2}; (▽) Zn, 10 mA cm^{-2}.

Permeation rate measurements at $E_c = -1.15$ V vs SCE over long time periods for bare iron and thick zinc and zinc–nickel electrodeposits on iron are shown in Figs. 5 and 6. The hydrogen permeation rate through iron increased over time and finally levelled off after approximately 40 h. It should be noted that this change over time is not the same as a diffusion controlled permeation transient that occurs when the applied potential or current is suddenly changed. Such transients are two or three orders of magnitude faster. The changes seen in Fig. 5 over a long time period are thought to be due to the many possible changes occurring on the surface of iron including localized corrosion sites or surface cracking. This type of response is not seen with the zinc–nickel nor zinc electroplates (Fig. 6). Zinc–nickel and zinc electroplates showed very stable small hydrogen permeation rates. Figure 6 compares these hydrogen permeation rates through Zn–Ni on iron with those of Zn electroplates on iron. As can be seen, the permeation inhibition of these thicker Zn–Ni deposits is nearly the same as those for zinc. The permeation inhibition for these 'thick' deposits was due to both kinetic effects and the diffusion barrier effect. Permeation transients were substantially delayed with these coatings compared to bare substrate. The hydrogen permeation transients were of the order of 30 or more minutes for these coatings, as compared to approximately 4 min for bare substrate or very thin zinc–nickel electroplates.

Table 1. Average percent decrease in i_c and j_∞ against bare iron

	i_c reduction /%	j_∞ reduction /%	*Zn* content /%
Ni	−88	70	0
Ni–Zn 10 mA cm^{-2}	17	78	65
Ni–Zn 20 mA cm^{-2}	21	83	75
Zn	88	94	100

4. Conclusions

Zinc–nickel alloy electroplates showed hydrogen discharge kinetics substantially different than those of either Zn or Ni electroplates. The permeation inhibition of thin Zn–Ni electroplates when the diffusion resistance of the electroplate was negligible compared to the substrate was approximately 80%, while the average cathodic current inhibition was only 19%.

Zinc–nickel electroplated for 20 and 40 min at 10 mA cm^{-2}, inhibited the hydrogen permeation greater than 95% as compared to bare iron. For the thicker electroplates, however, the inhibition was due to both kinetics and the barrier effect caused by the diffusion resistance of the membrane.

The possibility of using Zn–Ni for a corrosion and hydrogen permeation inhibition coating seems promising. If the corrosion rate can be reduced as compared to zinc sacrificial coatings, the hydrogen

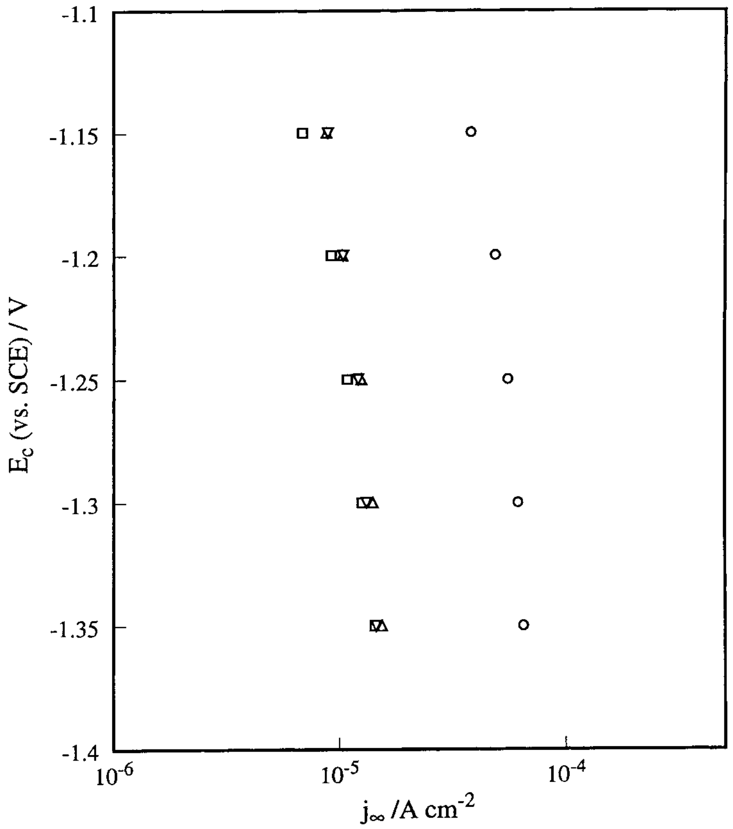

Fig. 4. Effect of successive Zn–Ni electroplates on permeation current density, j_∞, at different applied potentials, E_c. Key: (○) bare Fe; (□) Ni–Zn, 20 s at 10 mA cm^{-2}; (◇) Ni–Zn, 40 s at 10 mA cm^{-2}; (▽) Ni–Zn, 60 s at 10 mA cm^{-2}.

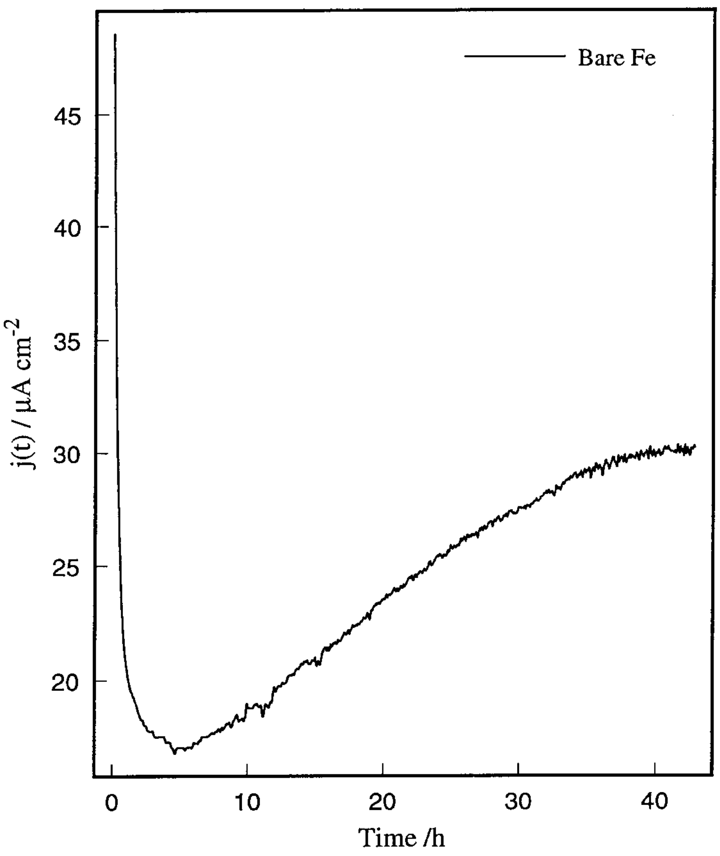

Fig. 5. Permeation current density over long time period for bare iron.

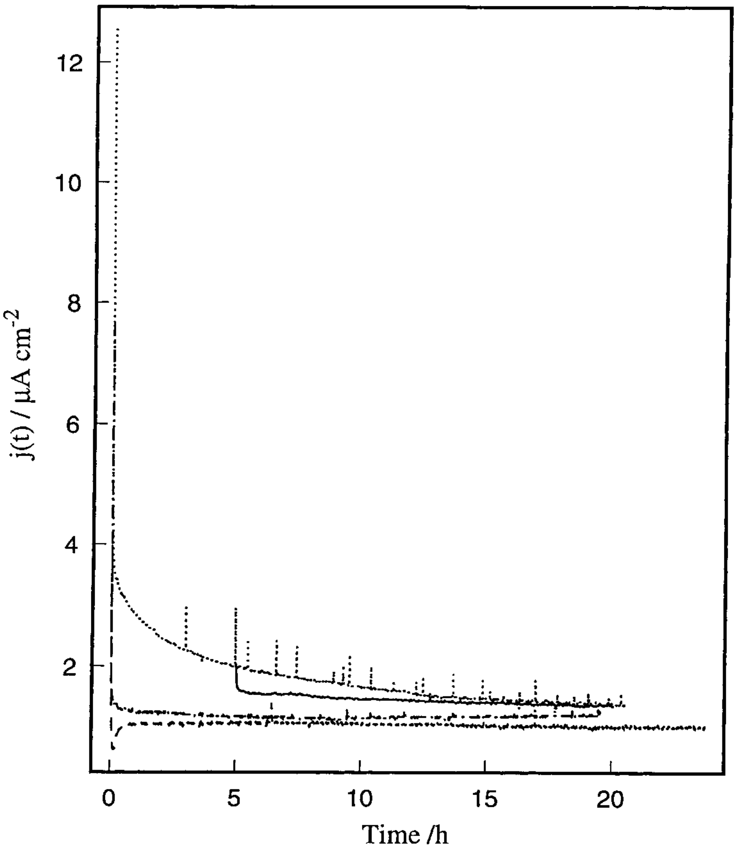

Fig. 6. Effect of zinc and zinc–nickel electroplates on permeation current density over long time period. Key: (—) Zn, 20 min at 10 mA cm^{-2}; (- - - -) Zn, 40 min at 10 mA cm^{-2}; (······) Zn–Ni, 20 min at 10 mA cm^{-2}; (-····-) Zn–Ni, 40 min at 10 mA cm^{-2}.

evolution rate will also be reduced during the corrosion process. The hydrogen produced would either be produced on exposed cathodic substrate (steel) sites or possibly at cathodic sites (Ni sites) on the coating. If the hydrogen is produced at the Ni sites, the permeation rate may be inhibited compared to that of hydrogen produced on the substrate metal. In addition, since the mixed potential between the substrate metal and the Zn–Ni coating is less cathodic for the substrate than if zinc and the substrate were coupled [5], the overpotential for the hydrogen discharge reaction will be less on exposed substrate sites. Other cathodic reactions such as oxygen reduction may occur in preference to hydrogen discharge, further reducing the amount of hydrogen introduced into the metal at any exposed substrate sites.

Acknowledgements

Technical assistance and financial support by A. John Sedriks, Office of Naval Research, under grant number AAESRT N000014-93-1-1094, are gratefully acknowledged.

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