Journal of Fluorine Chemistry, 68 (1994) 121–129

The effect of water and triethylamine on the anodic dissolution of Ni in the acetonitrile anhydrous HF system

M. Noel* and S. Chidambaram
Central Electrochemical Research Institute, Karaikudi-623 006, Tamil Nadu (India)

(Received April 22, 1993; accepted November 12, 1993)

Abstract

In general, the anodic dissolution of Ni in a 2.0 M HF solution in an acetonitrile/water mixture decreases with increasing acetonitrile content, as indicated by the increasing passivation potential, decreasing dissolution charge and decreasing reactivation potential in the reverse sweep in cyclic voltammetric measurements. However, in mixtures containing up to 90% acetonitrile content, the salt film formed on Ni readily dissolves in the electrolyte and the electrode continues to dissolve during multi-sweep cycling. In acetonitrile/anhydrous HF (AHF) media, however, the passive NiF_2 film formed is highly stable. With increasing HF content, a significantly increased quantity of water is required to dissolve the NiF_2 layer and thus reactivate dissolution of the Ni substrate. The observed current–time transients correspond to a typical salt film dissolution. In the acetonitrile/AHF/triethylamine system however, the anodic process is significantly different. These studies suggest that acidity is an important factor in fluoride attack on the Ni substrate and even causes a change in the mechanism of attack.

Introduction

Pure nickel is one of the metals which is least corroding in anhydrous hydrogen fluoride (AHF) [1]. To date, nickel is the only commercially viable anode for the electrochemical perfluorination (ECPF) of organic compounds in AHF [2, 3]. These factors have led to only a few serious attempts to evaluate the anodic polarisation of Ni in AHF. The stability of Ni in AHF has been attributed to the high heat of formation of the NiF_2 film [4] and its low solubility in AHF [5]. In voltammetric studies, a distinct anodic peak corresponding to NiF_2 film formation has been noted although not confirmed in all subsequent studies [6]. Above 3.0 V, the anodic current increases with potential with a Tafel slope of 0.4–0.5 V per decade [7]. It is still difficult to ascertain whether NiF_2 film growth or F_2 evolution proceeds in the potential region beyond 3.0 V.

Even trace levels of water were found to enhance the passivity of Ni in AHF [8]. The electrocatalytic properties of Ni towards F_2 generation and electrochemical fluorination were also found to improve in the presence of trace levels of water [9, 10]. ESCA studies under these conditions have confirmed the presence of a thin oxide layer in between the Ni substrate and the NiF_2 film [11]. At *c.* 2.0% H_2O, anodic polarisation of Ni in AHF leads to the formation of OF_2 [12, 13].

From the other end of the concentration scale, aqueous HF solutions are highly corrosive towards Ni in general. The addition of HF to H_2SO_4 media was found to lead to attack on the passive oxide layer and to Ni dissolution [14, 15]. Alkali metal cations further enhance fluoride attack [14, 15]. In addition, in aqueous media dissolution, passivation and NiF_2 film growth proceed only on a thin inner layer of nickel oxide [16, 17].

Until quite recently a wide gap existed between anodic dissolution studies in anhydrous HF containing small concentrations of water [8–13] and studies with aqueous solutions containing up to 1.0 M HF [14–17]. In a recent study from this laboratory [18], an attempt was made to study the anodic dissolution of Ni in 1.0–20.0 M HF in aqueous solution. It has been established from these studies that two distinct dissolution pathways exist for Ni dissolution, viz. direct dissolution of Ni substrate followed by precipitation of the NiF_2 film [eqns. (1) and (2)]

$$Ni_x \rightleftharpoons Ni_{x-1} + Ni^{2+} + 2e \qquad (1)$$

$$Ni_{x-1} + Ni^{2+} + 2F^- \rightleftharpoons Ni_{x-1}NiF_2 \qquad (2)$$

accompanied by the dissolution pathway through a thin oxide layer proposed by earlier workers [16, 17], which may be represented by eqns. (3) and (4):

---

*Author to whom correspondence should be addressed.

0022-1139/94/$07.00
SSDI 0022-1139(93)03046-O

$$\mathrm{Ni}_x(\mathrm{NiO})_n \rightleftharpoons \mathrm{Ni}_{x-1}(\mathrm{NiO})_n + \mathrm{Ni}^{2+} + 2e \qquad (3)$$

$$\mathrm{Ni}_{x-1}(\mathrm{NiO})_n + \mathrm{Ni}^{2+} + 2\mathrm{F}^- \rightleftharpoons \mathrm{Ni}_{x-1}(\mathrm{NiO})_n\mathrm{NiF}_2 \qquad (4)$$

The direct dissolution pathway apparently occurs from 0.5 M HF onwards and is further enhanced with increasing HF content [18].

In aprotic solvents like acetonitrile, Ni shows considerable passivity in acidic as well as neutral media [19–21]. The activity of the fluoride ion is fairly high in acetonitrile [22, 23] as well as in acetonitrile/water mixtures [24]. Acetonitrile is also one of the organic compounds which undergoes ECPF on Ni electrodes in AHF [25, 26]. The acetonitrile/triethylamine/HF system is a convenient medium for mild and selective electrofluorination [27] in which Pt rather than Ni is the anode of choice. However, no report of the anodic dissolution of Ni in the presence of fluoride in acetonitrile or acetonitrile/water mixtures has been reported to date. In the present work, which is a continuation of our earlier report [18], attempts have been made to evaluate the effect of water and triethylamine on the anodic dissolution of Ni in acetonitrile media.

Experimental

Freshly distilled AR grade acetonitrile (CH_3CN) and standardised 20.0 M aqueous HF solutions were used for the preparation of acetonitrile/water mixtures. Preparation of 2.0 M and 5.0 M AHF in acetonitrile medium required the addition of a quantity of AHF (containing <1 ppm water; TANFAC, India) to acetonitrile under low temperature conditions, due care being taken to avoid moisture absorption. The content of HF, which was always taken in slight excess during AHF transfer, was later determined and standardised by adding the required quantity of solvent. Acetonitrile/AHF/triethylamine solutions were also prepared by this method [28].

The Ni working electrode was polished to a mirror finish and washed well with triply distilled water and then with trichloroethylene before use. Since an insoluble passive NiF_2 film is formed on the Ni electrode during each potential cycle, especially when the water content is low, the electrode had to be repeatedly cleaned and polished after each CV experiment in order to obtain reproducible results.

Other experimental details include the use of a Pt foil counter-electrode, Pd–H_2 reference electrode, an all-polypropylene cell assembly and FEP tubing to avoid HF–glass contact [18, 28, 29]. The experiments were carried out at 30±1 °C.

Results

Anodic dissolution in acetonitrile/water media containing 2.0 M HF

Figures 1(a) and (b) depict the typical cyclic voltammetric (CV) responses obtained for 2.0 M HF in H_2O and CH_3CN/H_2O media containing 20% CH_3CN, respectively. At such low concentration of CH_3CN, the CV responses are very similar qualitatively. However, the forward and reverse peak potential values (E_{pf} and E_{pr}, respectively) in 20% CH_3CN solution shift to slightly more positive and more negative potentials, respectively (Table 1). The forward and reverse peak current (i_{pf}, i_{pr}) and anodic dissolution charge in the forward and reverse sweep (Q_f, Q_r) decrease in the presence of acetonitrile. However, in addition, in 20% CH_3CN solution the NiF_2 film formed on the Ni is soluble in the electrolyte medium. In the multiple sweep CV for example [Fig. 1(c)], the entire CV responses due to anodic dissolution, passivation and the reactivated dissolution during the reverse sweep are completely reproducible. In this medium, a significant increase in the background current occurs only beyond the E_{pf} value which itself lies quite close to 1.3 V.

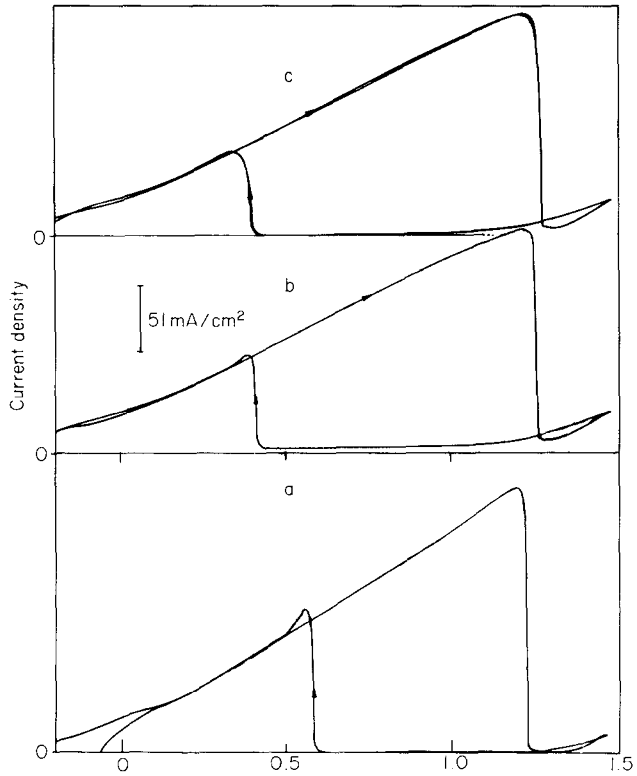

Fig. 1. Cyclic voltammetry of Ni in (a) H_2O and (b) 20% CH_3CN/H_2O media containing 2 M AHF at the same sweep velocity, i.e. 10 mV s^{-1}, and (c) the effect of repeat sweeps on the CV in (b) at a sweep velocity of 30 mV s^{-1}.

TABLE 1. Voltammetric features of Ni in CH_3CN/H_2O media containing 2 M aqueous HF at a sweep velocity of 10 mV s^{-1}

Conc. of CH_3CN (%)	E_{pf} (V)	E_{pr} (V)	i_{pf} (mA cm^{-2})	i_{pr} (mA cm^{-2})	Q_f (C cm^{-2})	Q_r (C cm^{-2})	Anodic potential limit[a] (V)
0	1.19	0.56	206	112	13.8	4.2	1.5
20	1.22	0.38	170	74	13.5	3.4	1.5
40	1.62	0.40	125	38	7.2	2.4	2.1
60	2.40	0.42	82	15	5.9	2.2	2.7
80	3.60	0.45	45	7	2.0	1.2	4.7
90	4.30	0.30	30	3	2.1	1.3	5.7

[a] For obtaining Q_f and Q_r values.

In 2.0 M aqueous HF solutions containing 40% CH_3CN, in addition to a further decrease in the i_p and Q values (Table 1), the passivation potential moves to 1.62 V [Fig. 2(a)]. The background current is itself significant at this potential and hence, in the reverse sweep, the current–potential curve contains a linear slope before the zero level passivation current arises at c. 1.0 V. The reactivation potential E_{pr}, however, remains virtually unchanged [Fig. 2(a)]. Further decreases in the i_p and Q_f values are noted when the acetonitrile content is increased to 60% [Fig. 2(b)]. Another interesting observation arises with both solutions in multi-sweep experiments [Figs. 2(c) and (d)]. Although anodic dissolution proceeds at about the same rate as noted in the first sweep, the passivation potential moves to more positive values in subsequent sweeps [Figs. 2(c) and (d)]. The same trend was also maintained in acetonitrile/water media containing 80% and 90% acetonitrile (Table 1).

Variations in the sweep rate have no significant effect on the qualitative features in the cyclic voltammograms in acetonitrile/water media. Typical voltammetric features at 30 mV s^{-1} and 50 mV s^{-1} in different water/acetonitrile compositions are summarised in Table 2. The peak potentials are not significantly affected by the sweep rate although the i_{pf} and i_{pr} values decrease slightly. The Q_f and Q_r values decrease significantly with the sweep rate (Table 2).

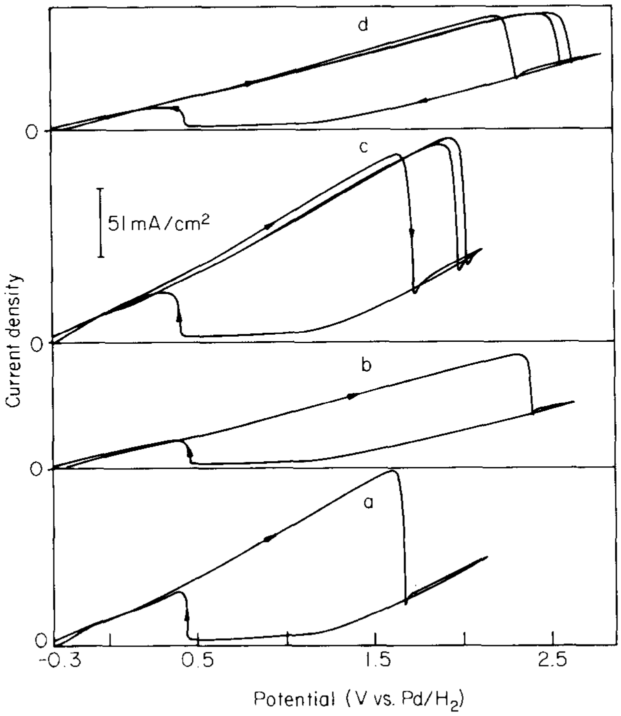

Fig. 2. Cyclic voltammetry of Ni in CH_3CN/H_2O media containing 2 M AHF: (a) 40% CH_3CN; (b) 60% CH_3CN at the same sweep velocity, i.e. 10 mV s^{-1}; (c) and (d) the effect of three repeat sweeps on the CV in (a) and (b), respectively, at a sweep velocity of 30 mV s^{-1}.

Anodic dissolution in acetonitrile/AHF media

As far as the first voltammetric sweep is concerned, there is qualitative similarity between the responses of the CH_3CN/2 M AHF system (Fig. 3) and the CH_3CN/2 M AHF/H_2O systems presented above (Figs. 1 and 2). The i_{pf} value decreases further, but the E_{pf} value remains at c. 4.0–4.5 V [Fig. 3(a)]. However, during the reverse sweep the current reaches a minimum level of c. 3.0 V rather than the 1–1.5 V level observed in mixed solvent systems. Another interesting feature is the complete absence of a reactivated dissolution current during the reverse sweep. In multi-sweep experiments, no dissolution peak was noted after the first anodic sweep [Fig. 3(a)]. The voltammetric responses were also quite similar at higher sweep rates, provided a freshly polished electrode was taken for each voltammetric recording [Fig. 3(b)]. However it was found that even if the electrode is kept under open circuit conditions for 3 min with stirring in the same medium and the CV recorded later, no anodic dissolution peak is noted [Fig. 3(c)] and the passive layer formed on the electrode is not found to be removed. A linear increase in the current with potential is noted beyond 3.0 V [Fig. 3(c)]. The quantitative voltammetric features are summarised in Table 3.

Addition of water to acetonitrile/2.0 M AHF led to some interesting transitions in the voltammetric

TABLE 2. Voltammetric features of Ni in CH_3CN/H_2O media containing 2 M aqueous HF at sweep voltages of 30 and 100 mV s^{-1}

Conc. of CH_3CN (%)	Sweep rate (mV s^{-1})	E_{pf} (V)	E_{pr} (V)	i_{pf} (mA cm^{-2})	i_{pr} (mA cm^{-2})	Q_f[a] (C cm^{-2})	Q_r[a] (C cm^{-2})
0	30	1.17	0.51	201	97	4.47	1.17
	100	1.18	0.42	194	61	1.35	0.27
20	30	1.22	0.33	173	66	4.61	1.06
	100	1.23	0.28	147	43	1.05	0.26
40	30	1.68	0.36	135	36	2.46	0.85
	100	1.72	0.28	127	26	0.81	0.25
60	30	2.28	0.42	82	15	1.95	0.70
	100	2.24	0.32	75	10	0.57	0.20
80	30	3.4	0.40	41	6	0.76	0.43
	100	3.2	0.30	40	4	0.23	0.14
90	30	4.2	0.30	44	3	0.83	0.45
	100	4.2	–	42	–	0.25	0.16

[a] Anodic potential limits as presented in Table 1 for corresponding acetonitrile concentrations.

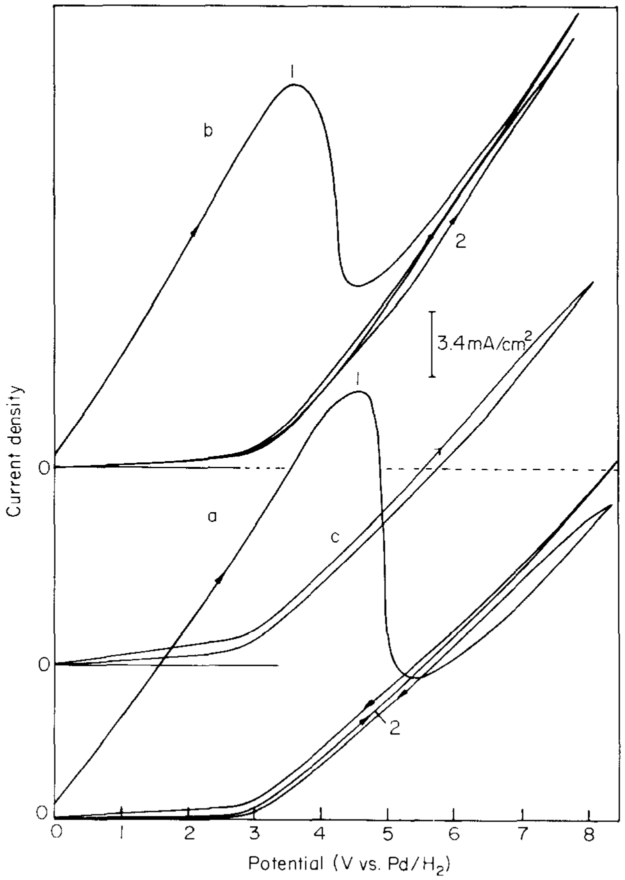

Fig. 3. Cyclic voltammetry of Ni in CH_3CN medium containing 2 M AHF at sweep velocity (mV s^{-1}) of (a) 50 and (b) 150 where two repeat sweeps are depicted. (c) Repeat sweep at 150 mV s^{-1} in the same medium after stirring for 3 min.

behaviour. Addition of 0.5 M H_2O (0.9–10 ml of electrolyte) did not influence the voltammetric response. However, when the molar concentration of water was close to the molar concentration of HF, significant film dissolution leading to smaller anodic peaks in the subsequent sweeps were noted. Typical responses in the presence of 3.0 M H_2O in a multi-sweep experiment are presented in Fig. 4(a). It should be noted that the value of i_{pf} decreases in subsequent sweeps and that E_{pf} shifts in the negative direction with sweep number. On further increasing the water content beyond the 5.0 M level, the voltammetric features become similar to those presented in Fig. 2. If the electrode is kept under open circuit conditions, the NiF_2 film dissolves to a significant extent in the presence of 3.0 M H_2O. This may be seen from Fig. 4(b) which was recorded after maintaining the electrode in solution with stirring for 3 min.

The voltammetric response in acetonitrile containing 5.0 M AHF was similar qualitatively to that in acetonitrile/2.0 M AHF medium. However, the dissolution peak current increased with AHF concentration (Table 3) and, once again, the passive NiF_2 layer did not dissolve significantly during multi-sweep experiments or under open circuit conditions in the same solution.

The effect of addition of water to the acetonitrile/5.0 M AHF system is, however, quite different when compared with that in the acetonitrile/2.0 M AHF system. At a constant sweep rate, E_{pf} shifts to less positive potentials with increasing amounts of water and i_{pf} increases slightly (Table 3). However, the Q_f values remain more or less unchanged at a constant sweep rate up to a 3 M addition of water (Table 3). In the multi-sweep experiments, no dissolution effect was noted in subsequent sweeps even in the presence of 6 M water. Under open circuit conditions, the NiF_2 film remained intact in this medium, as indicated by the subsequent voltammetric response.

Typical i versus t transient responses obtained for Ni in acetonitrile/5.0 M HF solutions are presented in Fig. 5. The potentials selected are indicated in the

TABLE 3. Voltammetric features of Ni in CH_3CN medium containing 2 and 5 M AHF and the effect of water addition in this medium

Conc. of AHF (M)	Conc. of water added (M)	Sweep rate (mV s^{-1})	E_{pf} (V)	i_{pf} (mA cm^{-2})	Q_f (C cm^{-2})	Q_r (C cm^{-2})	Anodic potential limit (V)
2	0	50	3.70	20	2.11	1.15	8
2	0	150	4.60	22	0.55	0.20	8
2	1	150	4.50	21	0.59	0.36	8
2	3	150	4.30	22	0.66	0.36	7
5	0	50	4.15	57	3.90	1.55	8
5	0	150	4.75	67	1.78	0.57	8
5	1	150	3.75	69	1.81	0.65	8
5	3	150	3.40	75	1.78	0.78	8
5	6	150	2.70	82	2.06	0.99	6.5

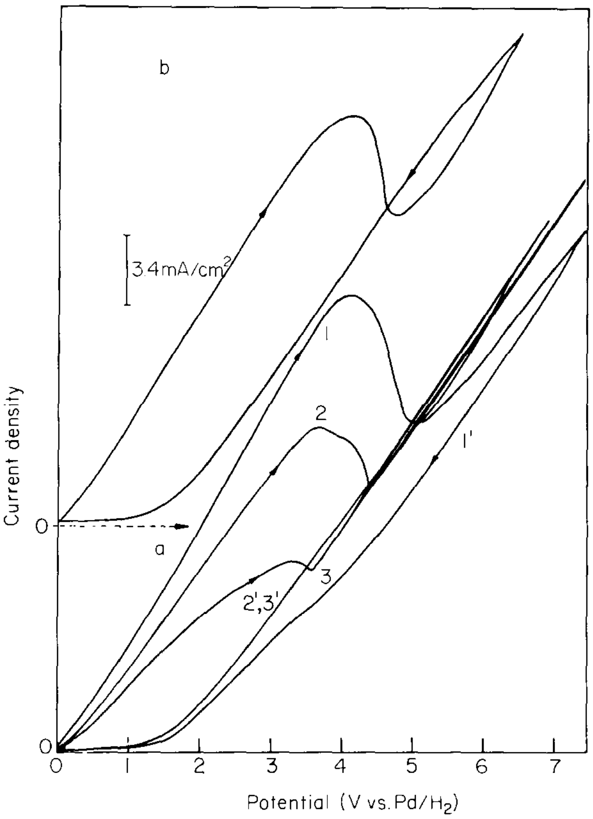

Fig. 4. Cyclic voltammetry of Ni in CH_3CN medium containing 2 M AHF and 3 M water at a sweep velocity of 150 mV s^{-1}: (a) effect of three repeated sweeps on the CV; (b) repeat sweep after stirring for 3 min.

linear sweep voltammetric response depicted in Fig. 5(A). In the active dissolution region [a in Fig. 5(B)], a significant anodic dissolution current was noted even over long periods of time. However, near the E_{pf} region the current rose sharply and then fell to significantly lower levels [b in Fig. 5(B)]. At 6.5 V, i.e. in the linearly rising portion beyond E_{pf}, the i versus t response shows

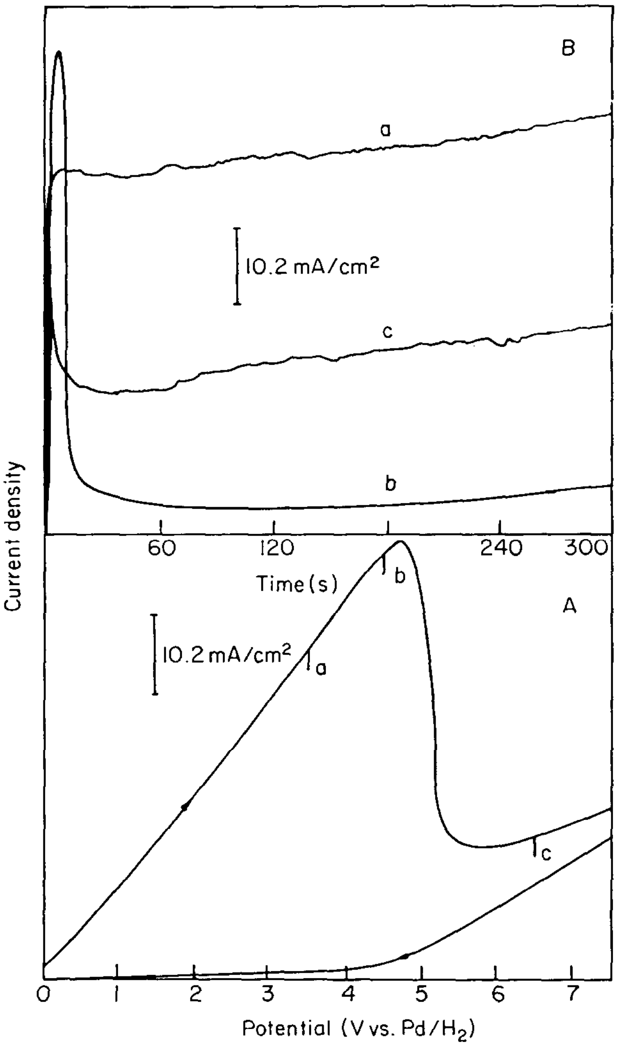

Fig. 5. (A) Linear sweep voltammetry of Ni in CH_3CN containing 5 M AHF at a sweep velocity of 150 mV s^{-1}; a, b and c depict the potentials selected for transient response experiments shown in (B). (B) Plots of i versus t transients in CH_3CN containing 5 M AHF at step potentials (V) from 0.0 to (a) 3.5, (b) 4.5 and (c) 6.5.

a significant increase with time once more [c in Fig. 5(B)].

Anodic dissolution in acetonitrile/HF/triethylamine media

Both the acetonitrile/AHF system and the acetonitrile/AHF/H_2O system considered above are acidic in nature. To evaluate the acidity effect in the acetonitrile environment, a number of experiments were also carried out in acetonitrile/AHF/triethylamine media. The voltammetric response in this system is drastically different from the responses presented above. This is true even if the molar concentration of AHF employed is higher than that of triethylamine. Typical cyclic voltammograms for Ni in acetonitrile containing 3.0 M HF and 2.0 M triethylamine at different sweep rates are presented in Fig. 6. During the first anodic sweep, a significant anodic current was noted only beyond 4.5 V at all sweep rates employed. This is in contrast to the increase in the anodic current at 0.0 V itself for more acidic systems (Figs. 1–4). The rise in current is, however, quite sharp and the peak potential is attained at *c*. 5.5 V. The value of i_{pf} increases directly with sweep rate (Table 4) but Q_f does not decrease with the sweep rate. At higher sweep rates a distinct second anodic peak may also be noted. No reactivated dissolution was noted in the reverse sweep at any sweep rate. In multi-sweep experiments, a significant anodic current was noted only beyond 6.5 V [Figs. 6(b) and (c)]. Once again, under open circuit conditions the film formed during the first sweep was not removed in this medium.

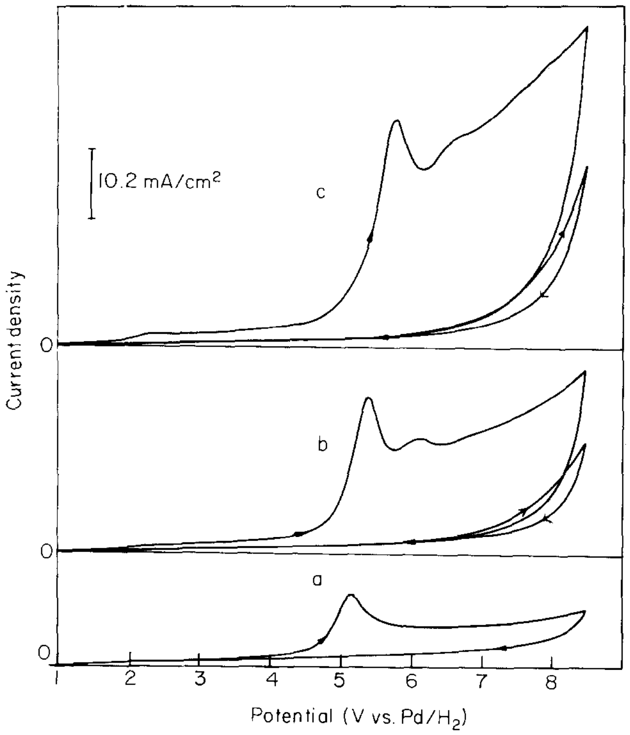

Fig. 6. Cyclic voltammetry of Ni in CH_3CN medium containing 3 M AHF and 2 M triethylamine at a sweep velocity (mV s^{-1}) of (a) 50, (b) 100 and (c) 150, with two repeat sweeps for (b) and (c).

TABLE 4. Voltammetric features of Ni in CH_3CN medium containing 3 M AHF and 2 M triethylamine

Sweep rate (mV s^{-1})	E_{pf} (V)	i_{pf} (mA cm^{-2})	Q_f (C cm^{-2})	Q_r (C cm^{-2})	Anodic potential limit (V)
50	5.30	11	0.61	0.28	8.5
100	5.40	23	0.72	0.18	8.5
150	5.75	33	0.70	0.22	8.5

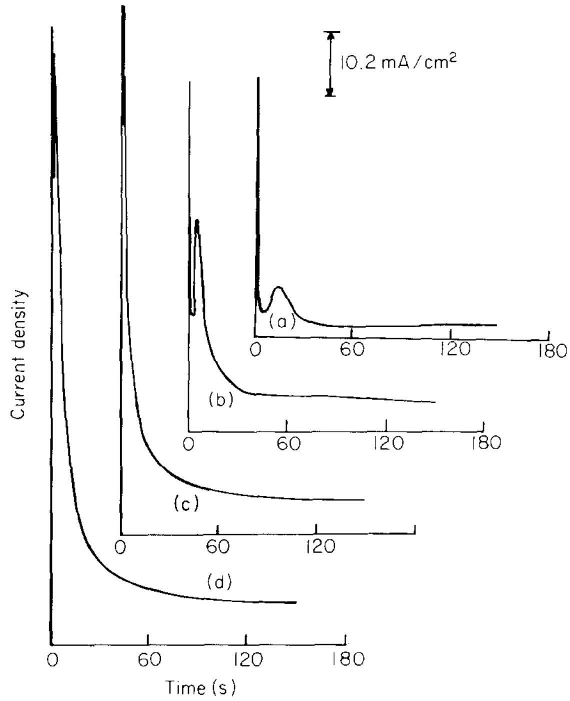

Fig. 7. Plots of *i* versus *t* transients in CH_3CN medium containing 3 M AHF and 2 M trimethylamine at step potentials (V) from 0.0 to (a) 5, (b) 5.5, (c) 6.5 and (d) 7.5.

The potentiostatic *i* versus *t* transient response in the presence of triethylamine (Fig. 7) is also different from that in acetonitrile/5.0 M HF medium [Fig. 5(B)]. In general, the anodic current in this medium (Fig. 7) is considerably less than in more acidic media. The *i* versus *t* response always exhibits a peak before sustaining a sharp fall. The time necessary for the maximum current to be attained generally decreases with anodic potential limit. Over long periods, a small but noticeable increase in the anodic current also occurs with the anodic potential limit.

Discussion

Most of the anodic polarisation experiments in the present work were carried out in 2.0 M HF solutions. From previous results [18], it is quite clear that at such low acid concentrations the anodic dissolution proceeds through a thin oxide layer involving reactions of the type depicted in eqns. (3) and (4) above.

Water and other solvents seem to influence the anodic dissolution in at least two ways. The first effect, of course, is the ability to dissolve the NiF_2 salt film. In the second subtle way, water acts as a base and thus enhances the acidity of the medium. This appears to be absolutely essential for anodic dissolution of Ni below 3.0 V. These aspects and the possible electrode processes through the passive NiO/NiF_2 layer are considered here in the light of the present experimental results.

Solvent effects on film solubility

With decreasing water content, the anodic dissolution current (i_{pr}) as well as the dissolution charge (Q_f) decrease significantly at all sweep rates (Tables 1 and 2). With increasing acetonitrile content, the reactivated dissolution charge and current (Q_r and i_{pr}) decrease even more significantly (Tables 1 and 2). This means that the anodic dissolution or solubility of NiF_2 becomes even more difficult once a compact NiF_2 passive layer has been formed.

The voltammetric responses also show that E_{pf} is primarily controlled by the chemical rate of film formation, rather than by the electrochemical reaction rate. With a decreasing dissolution rate of Ni at higher acetonitrile concentrations (40%), the value of E_{pf} shifts well beyond 1.2 V and reaches values close to 4.3 V in 90% acetonitrile. With decreasing dissolution of Ni, the rate of NiF_2 salt formation also decreases and hence compact passive layer formation is delayed until further dissolution occurs at more positive potentials.

In the multi-sweep experiments, the E_{pf} values were found to increase with sweep number when the CH_3CN concentration exceeded 40% [Figs. 2(c) and (d)]. This is again due to insufficient Ni^{2+} dissolution to allow compact NiF_2 film formation with increasing acetonitrile concentration. The NiF_2 film formed in previous sweeps may also remain undissolved on the electrode surface, leading to a non-uniform surface and uneven anodic dissolution and film formation.

In water-free acetonitrile medium in which the NiF_2 salt is practically insoluble, passive film formation is quite complete even during the first sweep. Hence, in subsequent sweeps, a significant anodic current is not noted at all in this medium below 3.0 V. Further decreases in the anodic dissolution current and dissolution charge relative to the 90% acetonitrile/water system may be noted (Table 3). However, the anodic dissolution charge values of 2–4 C cm^{-2} still appear to be quite high for monolayer formation involving a two-electron process (normally, a monolayer film would require *c.* 300–400 $\mu C\ cm^{-2}$ of charge). Hence the NiF_2 film must be formed as a porous three-dimensional arrangement, containing at least 10 stacks of NiF_2 monolayers.

In the acetonitrile/AHF system, the electrolytic conductivity is achieved primarily by self-ionization of HF [22–24].

$$3HF \rightleftharpoons H_2F^+ + HF_2^- \tag{5}$$

When small quantities of water are added, this acts like a base in this medium.

$$H_2O + 2HF \rightleftharpoons H_3O^+ + HF_2^- \tag{6}$$

Trace amounts of water present in the acetonitrile/AHF mixture may be protonated according to the above reaction. Hence free H_2O molecules are not available for dissolving the NiF_2 film in acetonitrile/HF systems provided the concentration of H_2O (in molar terms) does not significantly exceed the concentration of AHF. In 2.0 M AHF, for example, 3.0 M H_2O is required for generating a significant anodic dissolution current in the second and subsequent sweeps (Fig. 4). In 5.0 M HF solution, even the presence of 6.0 M H_2O does not induce anodic dissolution in subsequent sweeps.

Medium acidity and film dissolution

As discussed above, many of the present experimental observations may be understood in terms of the ability of the solvent to dissolve the NiF_2 salt layer. However, it appears that the acidity of the medium is also important for ensuring anodic dissolution. In CH_3CN/HF media, the acidity of the medium is ensured by the self-ionisation of HF [eqn. (5)]. In the presence of water, the acidity is enhanced by the protonation of H_2O by HF [eqn. (6)]. The acidity of the solvent probably assists dissolution by chemically reacting with the oxide or hydroxide layer present on the nickel surface through reactions such as:

$$Ni(OH)_2 + H_2F^+ \rightleftharpoons Ni(OH)F + H_3O^+ \tag{7}$$

$$Ni(OH)_2 + H_3O^+ + HF_2^- \rightleftharpoons Ni(OH)F + 2H_2O + HF \tag{8}$$

$$Ni(OH)F + H_2F^+ \rightleftharpoons NiF_2 + H_3O^+ \tag{9}$$

$$Ni(OH)F + H_3O^+ + HF_2^- \rightleftharpoons NiF_2 + 2H_2O + HF \tag{10}$$

Such chemical reactions probably enhance the anodic dissolution of Ni either by reducing the thickness of the oxide layer or enhancing its porosity. Such reactions cannot occur in alkaline solutions and hence the Ni surface exhibits passivity towards fluoride attack.

The present experimental results also indicate that the acidity is important in effecting anodic dissolution in the CH_3CN/HF system. In the presence of triethylamine (Et_3N), the following acid–base reaction would dominate over the ionisation process depicted in eqns. (5) and (6).

$$Et_3N + 2HF \rightleftharpoons Et_3NH^+ + HF_2^- \tag{11}$$

Because of the decreased acidity of the medium, the anodic dissolution currents noted from 0.0 V in CH_3CN/HF media (Figs. 3 and 4) are completely absent in $Et_3N/CH_3CN/HF$ media (Fig. 6). In the latter solutions, a significant anodic current is noted only beyond 4.0 V.

The voltammetric features are also quite different. The voltammograms in the CH_3CN/HF and $CH_3CN/HF/H_2O$ systems (Figs. 3 and 4) are similar to those predicted by a dissolution–precipitation [30] mechanistic pathway [31–34] as represented in eqns. (3) and (4). The voltammetric peak currents in the $Et_3N/CH_3CN/HF$ systems (Fig. 6), however, increase linearly with sweep rate (Table 4) which is characteristic of an adsorptive reaction pathway [34]. Hence, an entirely new mechanistic pathway may need to be invoked in order to understand the anodic reactions occurring beyond 4.0 V in $Et_3N/CH_3CN/HF$ media (see later).

Anodic processes on passive layers

In CH_3CN/HF as well as in $CH_3CN/HF/H_2O$ media, a linear current potential response is noted beyond the anodic dissolution peak, in both the forward and reverse sweeps (Figs. 1–4). This type of i versus E response suggests that the overall electron transfer rate is controlled by the resistivity of the passive film. The control of the actual electrode process taking place in such a system by the passive film can only be speculated upon. However, one further difference is worth noting. In $CH_3CN/HF/H_2O$ systems (Figs. 1, 2 and 4), the linear plot of i versus E on the reverse sweep cuts the background level to around 1.2 V. In this case, it appears that oxide growth facilitates further fluoride film growth and oxygen evolution on the passive layer. In CH_3CN/HF media in the absence of water, the cut-off potential is at *c.* 3.0 V (Fig. 3). Electron transfer through the passive layer occurs only beyond this potential region, with fluoride film growth and evolution of F_2 gas being the likely competitive electrode processes occurring. The i versus t transient plots (Fig. 5) also indicate considerable potential-dependent anodic currents except in the passivation potential region, suggesting that the rate of the overall process depends directly on the resistivity of the film.

In $Et_3N/CH_3CN/HF$ media, the oxide layer itself remains intact and exhibits passivity, since the anodic current is noted only beyond 4.5 V. It is tempting to speculate that F^- ion discharge leading to film growth or F_2 evolution occurs on this passive layer in this case:

$$NiO + F^- \longrightarrow NiOF + e \tag{12}$$

$$NiOF + F^- \longrightarrow NiO + F_2 + e \tag{13}$$

The observation of current maxima in the i versus t transient plots (Fig. 7) and the dependence of the maximum current (i_m), as well as the maximum current time (t_m) on the potential, suggests that film growth via a nucleative process [34, 35] occurs before significant F_2 evolution. These aspects, as well as the dissolution behaviour of Ni in media such as $CH_3CN/KF/HF$, require more detailed investigation. Some work is in progress in this direction.

Conclusions

The voltammetric response of Ni in CH_3CN/H_2O media containing HF are similar qualitatively to those observed earlier in aqueous HF solutions [9, 10]. However, anodic dissolution in the forward sweep and reactivated dissolution in the reverse sweep continuously decrease with increasing acetonitrile content. In acetonitrile media alone, the NiF_2 film becomes extremely stable and further polarisation proceeds only through this passive layer at more positive potentials. Trace levels of water have no noticeable effect on the voltammetric response. Reasonable NiF_2 solubility and remarkable anodic dissolution are noted only when the molar concentration of water exceeds that of HF.

In the acetonitrile/triethylamine/AHF system, anodic dissolution starts only beyond 4.5 V. In this medium, the experimental results obtained indicate an entirely different mechanism for film formation through nucleative growth.

The present results in the acetonitrile/AHF system clearly open up considerable scope for further studies.

References

1 N. Hackerman, E.S. Snavely and L.D. Fiel, *Corros. Sci.*, *7* (1967) 39.
2 J. Burdon and J.C. Tatlow, *Adv. Fluorine Chem.*, *1* (1960) 129.
3 S. Nagase, *Fluorine Chem. Rev.*, *1* (1967) 77.
4 A.K. Vijh, *J. Electrochem. Soc.*, *115* (1968) 1096.
5 A.K. Vijh, *J. Electrochem. Soc.*, *119* (1972) 1187.
6 A.G. Doughly, M. Fleischmann and D. Pletcher, *J. Electroanal. Chem.*, *51* (1974) 456.
7 J.S. Clarke and A.T. Kuhn, *J. Electroanal. Chem.*, *85* (1977) 299.

8 N. Hackerman, E.S. Snavely and L.D. Fiel, *Electrochim. Acta, 12* (1967) 535.
9 N. Watanabe, B. Chang and M. Haruta, *Electrochim. Acta, 16* (1971) 1179.
10 B. Chang, N. Watanabe and K. Nakanishi, *Electrochim. Acta, 17* (1972) 1317.
11 N. Watanabe and M. Haruta, *Electrochim. Acta, 25* (1980) 461.
12 J.A. Dunhue and A. Zletz, *J. Electrochem. Soc., 115* (1968) 1039.
13 D. Hass and P. Wolter, *Z. Anorg. Allg. Chem., 463* (1980) 91.
14 J. Osterwald and H. Trunk, *Werkst. Korros., 28* (1977) 321.
15 M. Cid, A. Jouanneau, D. Nganga and M.C. Petit, *Electrochim. Acta, 23* (1978) 945.
16 B. Löchel, H.H. Strehblow and M. Sakashita, *J. Electrochem. Soc., 131* (1984) 522.
17 B.P. Löchel and H.H. Strehblow, *J. Electrochem. Soc., 131* (1984) 713.
18 M. Noel and S. Chidambaram, *J. Electroanal. Chem.*, in press.
19 R.G. Kelly and P.J. Moran, *Corros. Sci., 30* (1990) 495.
20 Z.Y. Lu, D.M. Muir and I.M. Ritchie, *J. Electroanal. Chem., 168* (1984) 163.
21 V.V. Ekilik, E.N. Balakshina and V.P. Grigorjev, *Bull. Electrochem., 7* (1991) 254.
22 G.T. Hefter and P.J. McLay, *J. Solution Chem., 17* (1988) 535.
23 J. Bessiere and F. Bazine, *J. Fluorine Chem., 44* (1989) 45.
24 J. Bessiere and F. Bazine, *Electrochim. Acta, 35* (1990) 1885.
25 A. Haruta and N. Watanabe, *J. Fluorine Chem., 7* (1976) 159.
26 N. Watanabe and M. Haruta, *Asahi Garasu Kogyo Gijutsu Shoreikai Kenkyu Hokoku, 27* (1975) 1; [*Chem. Abs., 86* (1977) 48 465].
27 I.N. Rozhkov, in M. Baizer and H. Lund (eds.), *Organic Electrochemistry. An Introduction and Guide*, 2nd edn., Marcel Dekker, New York, 1983, p. 805.
28 R.S.S. Guzman, J.R. Vilche and A.J. Arvia, *J. Appl. Electrochem., 8* (1978) 67.
29 H.H. Strehblow, B. Titze and B. Löchel, *Corros. Sci., 19* (1979) 1047.
30 W.J. Mueller, *Trans. Faraday Soc., 27* (1931) 737.
31 A.J. Calandra, N.R. de Tacconi, R. Perevio and A.J. Arvia, *Electrochim. Acta, 19* (1974) 901.
32 V.I. Birss and C.A. Wright, *Electrochim. Acta, 27* (1982) 1429.
33 S.K. Poznyak and A.I. Kulak, *J. Electroanal. Chem., 278* (1990) 227.
34 M. Noel and K.I. Vasu, *Cyclic Voltammetry and the Frontiers of Electrochemistry*, Oxford IBH, New Delhi, 1990, Chap. 8.
35 J.A. Harrison and H.R. Thirsk, in A.J. Bard (ed.), *Electroanalytical Chemistry*, Marcel Dekker, New York, 1971, Vol. 5, p. 67.