THE RELATIVE INFLUENCE OF ACETONITRILE AND WATER ON THE ANODIC DISSOLUTION OF NICKEL IN FLUORIDE MEDIUM

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The anodic polarization behavior of nickel electrode was studied in fluoride ions containing acetonitrile medium. In the voltammetric study, a distinct anodic peak was noticed which corresponds to the formation of nickel fluoride (NiF_2) film. The film formed during the first potential polarization is stable in the absence of water. With the addition of water, the solubility of NiF_2 layer enhances anodic dissolution. However, the film formed in high concentration of fluoride ion is fairly stable even in presence of equi-molar quantities of water. The addition of water after or before polarization has only little influence on the anodic behavior. The competitive influence of fluoride ion and water on the stability of NiF_2 film and the resistivity of this film towards interfacial electron transfer are also studied.
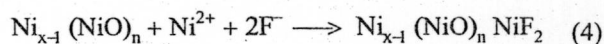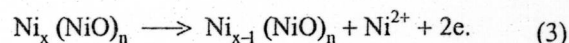
INTRODUCTION

Pure nickel is one of the least corroding metals in anhydrous hydrogen fluoride (AHF) [1]. Till 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 few serious efforts to evaluate the anodic polarization of nickel in AHF. The stability of nickel in AHF was attributed to the high heat of formation of NiF_2 film [4] and its low solubility in AHF [5]. In voltammetric studies, a distinct anodic peak corresponding to NiF_2 film formation was noticed in the first sweep which disappeared in all subsequent sweeps [6]. Beyond 3 V, the anodic current increased with potentials with a Tafel slope of 0.4 to 0.5 V per decade [7]. It is still difficult to ascertain whether NiF_2 film growth or fluorine evolution proceeds in the potential region beyond 3 V.

Even trace level of water was found to enhance the passivity of nickel in AHF [8]. The electrocatalytic properties of nickel towards fluorine generation and electrochemical fluorination were also found to improve in presence of trace level water [9-10]. Electron Spectroscopy for Chemical Analysis (ESCA) studies in these conditions have confirmed the presence of a thin oxide layer in between the nickel substrates

and NiF_2 film [11]. At about 2.0% level of H_2O, anodic polarization of nickel in AHF leads to fluorine formation [12,13]. Anodic dissolution of nickel in 1 M to 20 M HF in aqueous solutions showed that two distinct dissolution pathways exist for nickel dissolution of nickel substrate followed by precipitation of NiF_2 films (equations 1 and 2).

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

$$Ni_{x-1} + Ni^{2+} + 2F^- \longrightarrow Ni_{x-1} NiF_2 \qquad (2)$$
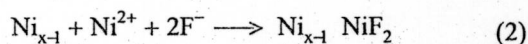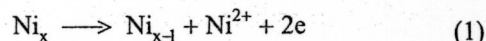
and the dissolution pathway through a thin oxide layer proposed by earlier workers [15,16] which may be represented by equations 3 and 4.

$$Ni_x (NiO)_n \longrightarrow Ni_{x-1} (NiO)_n + Ni^{2+} + 2e. \qquad (3)$$

$$Ni_{x-1} (NiO)_n + Ni^{2+} + 2F^- \longrightarrow Ni_{x-1} (NiO)_n NiF_2 \qquad (4)$$

The direct dissolution pathway is noticed from 5 M concentration of HF onwards which enhances further with increase of H_2O content [14].

In aprotic solvents like acetonitrile, nickel shows considerable passivity in acidic as well as neutral media [17-19]. Fluoride ion activity is fairly high in acetonitrile [20,21] as well as acetonitrile-water mixtures [22]. Acetonitrile is also one of the organic compounds, which undergoes electrochemical perfluorination on nickel electrodes

in AHF. [23]. Acetonitrile- triethylamine-HF system (Et$_3$N.nHF/CH$_3$CN) is a convenient medium for mild electrofluorination [24] in which Pt rather than nickel is the electrode of choice. The anodic behavior of nickel in the absence and presence of Et$_3$N was also studied in anhydrous HF/ CH$_3$CN supporting electrolyte system with different concentrations of Et$_3$N [25]. In our laboratory, some voltammetric experiments on the anodic dissolution of nickel in CH$_3$CN/ HF in presence and absence of water were reported [26].

In this work, the voltammetric behavior of nickel is extensively investigated in CH$_3$CN media containing 2 *M*, 4 *M* and 6 *M* AHF solutions. The effect of water on the film formation and the growth processes are also reported. Polarization studies were also carried to find out if the nickel electrode in CH$_3$CN/ HF system is electrochemically active enough to oxidize or reduce other organic compounds.

EXPERIMENTAL DETAILS

To prepare 2 *M*, 4 *M* and 6 *M* AHF in acetonitrile medium, required quantity of AHF (with < 1 ppm level of water content, TANFAC, India) was added to acetonitrile under low temperature conditions, with due care to avoid moisture absorption. The HF content, which was always taken in slight excess during AHF transfer was later determined and standardized by adding required quantity of solvent.

Nickel working electrode was polished to the 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 nickel electrode during each potential cycle, especially when water content is low, the electrode had to be cleaned and polished after each cyclic voltammetric experiment to get reproducible results.

Polypropylene undivided cell was used throughout the experiments with FEP tubing to avoid HF glass content. Pt foil was used as counter electrode and Pd/ H$_2$ as the reference electrode. If the concentration of HF is very high, Pd/ H$_2$ shows some instability as a result of the dissolution of Pd itself in the medium. In such cases, the experiment was continued with new Pd foil. The reference potential however, was compared from time to time externally against saturated calomel electrode (SCE) [14].

CH$_3$CN (HPLC) and triply distilled water were used as solvents. Nitrobenzene, anthracene and methyl phenyl sulfide (AR, Ranbaxy) was used without purification. A Wenking potentiostat and scan generator (model VSG 72) was used for potential control and programming and Rikandenki (model NP-0363) was used to record the results. All the experiments were carried out at 303 ± 1 K.

RESULTS AND DISCUSSION

Voltammetric studies in CH$_3$CN-HF medium

Typical cyclic voltammograms of nickel in CH$_3$CN medium having different concentrations of AHF at constant sweep rate of 120 mVs^{-1} are presented in Fig. 1. The current-potential curve shows a linear increase initially followed by anodic peak and a subsequent linearly increasing portion beyond the anodic peak potential region (Fig. 1). A direct comparison of voltammetric data in all the three concentration ranges at a constant
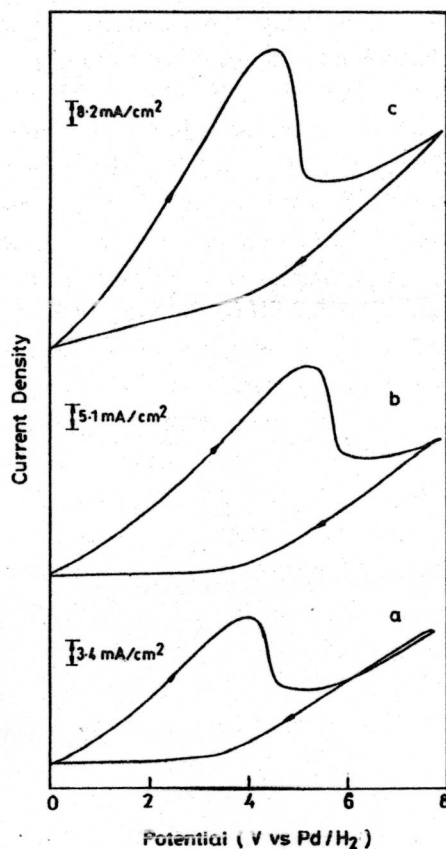

Fig. 1: CV of Ni in CH$_3$CN containing AHF Conc, (*M*) a) 2 b) 4 c) 6 at v 120 mVs^{-1}

sweep rate of 60 mVs^{-1} is presented in Table I. The anodic dissolution peak current (i_p) and peak potential (E_p) increase with HF concentration and sweep rate where as the charge (Q) decreases with sweep rate. Fig. 1 indicates two linear regions in the voltammograms, one before the peak potential and another after the peak potential. The slopes of the regions as measured by evaluating $\Delta E / \Delta i$ is very high in both the linear potential region and also vary significantly.

The dissolution curves obtained in the present case essentially correspond to the dissolution-precipitation model of resistive film formation or more commonly known as Muller's passivation model. The voltammetric characteristics corresponding to this model have been derived and experimentally verified earlier [27- 28]. The model as well as the cyclic voltammetric method corresponding to such dissolution-precipitation processes, have also been discussed [29].

The linear current-potential region in these voltammetric curves essentially corresponds to the resistivity to charge transfer. In the potential region prior to the peak potential, the resistivity essentially corresponds to the pore resistance of the Muller's passivation model. The linear region beyond the peak potential is due to resistivity offered by the NiF$_2$ film formed on the electrode surface. Hence, $\Delta E / \Delta i$ in these two regions are different.

The NiF$_2$ film formed during the first anodic sweep is fairly stable and hence in subsequent sweeps, the dissolution charge and the anodic peaks are completely absent. This is found to be the case for all concentrations of HF. These responses are also quite insensitive to changes in sweep rate. This clearly suggests that in CH$_3$CN containing anhydrous HF, NiF$_2$ passive film formed on nickel electrodes are highly insoluble and fairly stable.

Voltammetric studies in CH$_3$CN-HF-H$_2$O medium

Some detailed investigations were carried out to find out the effect of water on the solubility of passive NiF$_2$ films. It was found out that the fluoride ion concentration and water have diagonally opposite effect on NiF$_2$ film stability. With increase in HF content, film stability increases and with increase in water content, the film solubility increases. Typical cyclic voltammogram of nickel in CH$_3$CN containing 2 M AHF and 3 M-water at 120 mVs^{-1} is presented in Fig. 2(a). Typical dissolution peak is noticed in the first sweep. In this case, significant anodic dissolution is noticed in subsequent sweep as well (Fig. 2 curves b to c). This clearly indicates that NiF$_2$ film undergoes dissolution in this medium.

Keeping the water content at 3 M level, if the concentration of HF is increased to 4 M in the same medium, the cyclic voltammogram is presented in Fig. 3. In the multisweep cyclic voltammograms, no anodic dissolution is noticed in the second and subsequent sweeps (Fig. 3a). In 4 M HF-CH$_3$CN solution itself if the water content is further increased to 6 M level, significant anodic dissolution is noticed in all subsequent sweeps (Fig. 3b). The anodic dissolution also increases in the first sweep. The

TABLE I: Voltammetric features of nickel in CH$_3$CN containing 2 M, 4 M and 6 M AHF and the effect of addition of water at constant sweep rate (60 mVs^{-1})

Conc of AHF added (M)	Conc of water added (M)	E_p (V)	I_p (mA . cm^{-2})	Q (C.cm^{-2})	$\Delta E_1 / \Delta i_1$ (VmA^{-1})	$\Delta E_2 / \Delta i_2$ (VmA^{-1})
2	0	3.7	20.40	0.90	0.97	1.50
4	0	4.7	33.80	1.10	0.90	1.60
6	0	4.8	61.85	2.40	0.30	0.50
2	3	3.6	21.40	0.98	0.75	0.75
4	3	3.9	45.10	1.74	0.30	0.40
6	3	3.3	79.40	2.50	0.40	0.30
2	6	3.4	30.60	1.20	0.50	0.50
4	6	2.8	60.60	1.91	0.20	0.20
6	6	2.6	91.80	2.60	0.20	0.20

resistivity of the film (as measured by $\Delta E/\Delta i$ value), also changes with sweep number both before the peak potential region and after the peak potential region. Similar responses were also obtained in these solutions when each cyclic voltammogram was recorded after the regular time interval.

At still higher HF concentration level (6 *M*), NiF_2 film dissolution effects are not at all noticed in CH_3CN-HF solutions containing 3 *M*-water as well as 6 *M*-water. In this medium, it is quite interesting to note that even 6 *M*-water is not able to affect the solubility of NiF_2 layer. Some experiments were also carried out to find the effect of addition of water on a previously polarized nickel electrode in AHF-CH_3CN system. The results obtained in 2 *M* AHF-CH_3CN solution under these conditions are presented in Fig. 4. These multisweep cyclic voltammograms indeed indicate that the addition of water after the NiF_2 film formation also has only marginal effect on the film solubility. With increase in water content, however, the anodic dissolution increases significantly (Figs. 4a to c). Similar effects were also noticed in 4 *M* AHF solutions. Significant anodic dissolution in subsequent sweep was noticed, only when water content reaches 7 *M* level in this medium.

Comparison of the two sets of experiments (Figs. 2 and 4), clearly indicates that the addition of water after polarization or before polarization does not influence the dissolution of NiF_2 film significantly. The net results of cyclic voltammetric curves are quite similar in both the cases. Quantitatively, however, slight decrease in the solubility of NiF_2 film is noticed if the water is added after the formation of the NiF_2 film.

Direct comparison of effect of water addition in all the three AHF media is made in Table I. From the Table, it may be noted that the dissolution current increases with water content and decrease with sweep rate. One interesting observation deserves the special mention. The $\Delta E/\Delta i$, which is indeed a measure of resistivity of the anodic processes, is found to be highly sensitive to both HF content and water content (Table I). At high HF and water content, the value decreases significantly. The slope values before and after the peak potential region also become quite identical. These data indicate that at-least in high HF and high water content situations the same type of surface film offers the observed resistivity to the anodic reaction on nickel electrode.
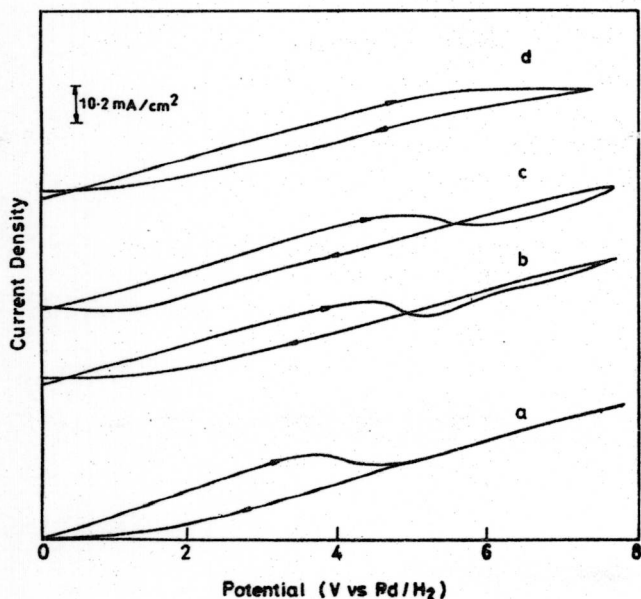

Fig.2 CV of Ni in CH_3CN containing AHF (2 *M*) and H_2O (3 *M*) ν (mVs^{-1}) 120 for
a) subsequent CV at ν (mVs^{-1}) b) 60 c) 120 d) 240
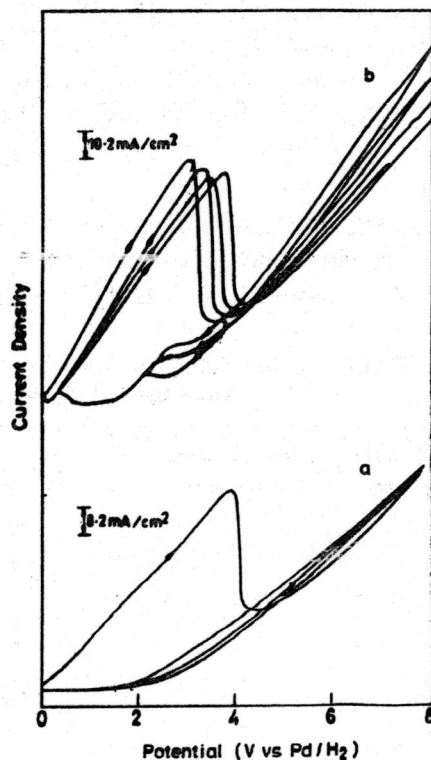
Fig. 3: Effect of H_2O on the multisweep CV of Ni in CH_3CN/AHF (4 *M*) ν (mVs^{-1}) 60. Conc. of H_2O (*M*) a) 3 b) 6

Potentiostatic polarization studies in CH₃CN-HF medium

Some potentiostatic polarization studies are also carried out to find out whether significant changes in the current-time response are noticed over longer periods of time. Typical current-time curves obtained in 2 *M* AHF solutions at different step potentials with a regular time interval of 60 seconds are presented in Fig. 5. These current-time curves indicate that the film dissolution in the pre-peak region (Fig. 5a) is almost independent of time. In the peak potential region during the first potential step, the anodic dissolution is significantly higher during the first 20 seconds. Subsequently only very low anodic currents are noticed (Fig. 5b). Beyond the anodic peak region, once again, a linear current-time curve, which increases with the step potentials, is noticed (Fig. 5c). In all these cases, however, the anodic process involved over longer period of time does not show any significant variation with time. Quantitatively, the dissolution charges obtained at each potential at regular intervals are summarized in Table II. These data also quantitatively support the above conclusion.

Polarization studies in presence of organic compounds

Some polarization studies were also carried to find out the electrochemical activity of nickel electrode to oxidize or reduce simple organic compounds in the non-aqueous fluoride medium. For this, both methyl phenyl sulfide and anthracene were tried to see any increasing current in the voltammetric responses in the anodic region. nickel electrode was initially polarized in 2 *M* AHF-CH₃CN media and cyclic voltammogram was recorded. Both these organic compounds did not bring out any noticeable change in the voltammetric features. No distinct oxidation peak for the organic compound is visible. Hence, the organic compounds do not undergo direct oxidation on this pre- polarised electrode surface. However, in the linear potential region beyond 3 V oxidizing reagents such as active fluorine or high valent nickel fluorides may be formed, which may subsequently oxidize organic compound. However, these aspects require further investigation.

Nickel electrode in CH₃CN-HF medium is passive to direct electron-transfer even when polarized in the cathodic directions. This is apparent from the cyclic voltammetric curve recorded for reduction of nitrobenzene on nickel in this medium. No distinct voltammetric features are noticed in presence of this compound as well.
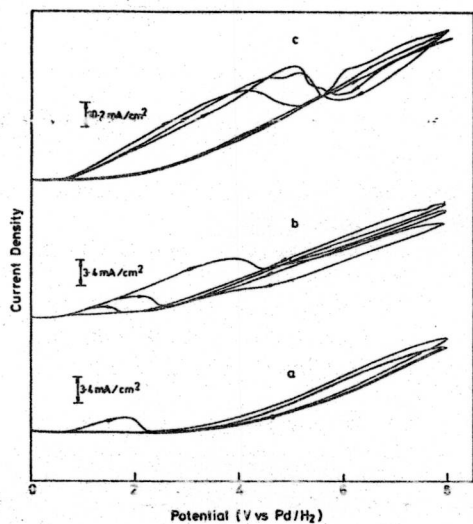

Fig. 4: Effect of addition of water on the CV of previously polarized Ni electrode in CH₃CN/AHF (2*M*) ν (mVs⁻¹) 60, Conc of H₂O (*M*) a) 1 b) 2 and c) 3
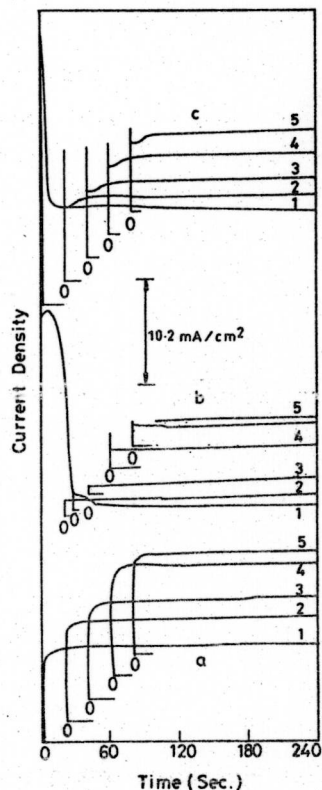

Fig. 5: Current time curves of Ni in CH₃CN/AHF (2 *M*) at step potentials (V) from 0.0 to a) 2 b) 3.4 and c) 4.5 each curve recorded after a time interval of 60 seconds

TABLE II: Charge density (Q) and current density values (i_p) from current time curves recorded for 100 seconds for the anodic polarization of nickel in CH_3CN containing 2 *M* AHF

Curve No	Step potentials	i_{pf} of 100 sec (mA.cm^{-2})	Q_f of 100 sec (Ccm^{-2})
1	2.0	14.2	1.43
2	2.0	15.1	1.48
3	2.0	14.8	1.43
4	2.0	15.1	1.48
5	2.0	14.8	1.43
1	3.4	4.7	0.86
2	3.4	2.0	0.20
3	3.4	1.0	0.09
4	3.4	1.5	0.12
5	3.4	—	—
1	4.5	15.0	1.48
2	4.5	12.0	1.21
3	4.5	11.0	1.09
4	4.5	11.4	1.16
5	4.5	11.0	1.09

CONCLUSION

The present investigations clearly indicate the role of solvent (water and acetonitrile) on the voltammetric behaviour of nickel in fluoride media. In anhydrous HF medium, the anodic dissolution increases with HF concentration. The film formed during the first polarization is fairly stable in the absence of water. The solubility of NiF_2 layer in water naturally enhances anodic dissolution. However, this is not true in the case of NiF_2 film formed in presence of high concentration of fluoride ions. At 6 *M* HF concentration level, film dissolution effects are not at all noticed even with the addition of 6 *M*, water. The addition of water after polarization or before polarization has only little influence on the dissolution of NiF_2 film. The passive layer on nickel does not allow any direct oxidation or reduction of organic compounds.

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