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The influence of monovalent cations on the stability of electrochemically formed nickel fluoride films

Abstract The stability of electrochemically formed NiF_2 film in 1.0 M perchloric acid containing monovalent fluorides namely, NH_4F, HF, NaF, KF and LiF, is investigated using cyclic voltammetry, chronoamperometry, atomic absorption spectroscopy and scanning electron microscopy. In addition to direct dissolution of nickel and dissolution through the oxide layer, a new mode of dissolution of NiF_2 film as NiF_3^- and NiF_4^{2-} through complex formation is proposed. This process is significantly influenced by the alkali metal fluorides. On a comparative basis the stability of NiF_2 decreases in the order $NH_4F > HF > KF > LiF$.

Key words NiF_2 layer · Nickel dissolution Monovalent fluorides

Introduction

Nickel is one of the least corroding metals in fluoride environments, primarily owing to the formation of an insoluble nickel fluoride film [1, 2]. The anodic dissolution and passivation behaviour of this metal has been evaluated in F_2, HF and different metal fluoride environments in connection with a variety of industrial applications [3]. Alkali metal fluorides, which are added to improve the conductivity of the medium in the electrochemical fluorination of hydrocarbons in liquid HF, also cause enhanced corrosion [4, 5]. High temperature corrosion of Ni in $NH_4^+HF_2^-$ and related fluoride salts assumes significance in nuclear fuel reprocessing technology [6] as well as in production of high purity nitrogen trifluoride [7–9]. The electrochemical behaviour

has also been investigated in a KF/2HF melt in connection with fluorine generation [10]. The corrosion resistance of Ni in a LiOH/LiF melt has been evaluated for potential use as a container in thermal storage systems [11]. In aqueous media, significantly higher anodic dissolution of Ni is noticed in the presence of HF and a number of alkali metal fluorides [12–17]. In some of these investigations involving HF, NH_4F, NaF, KF and LiF, it is implicitly assumed that the cationic species does not influence the anodic dissolution of Ni significantly. The present study clearly invalidates this implicit assumption and suggests at least three different ways in which the cationic species can influence the stability of the nickel fluoride film.

Experimental

High purity Ni rod (99.99% pure, Johnson Matthey) of 5 mm diameter, tight-fitted into a Teflon rod, was used as the working electrode. A Pt counter electrode and Pd-H_2 reference electrode were used. Polypropylene was found to be stable towards fluoride attack under the present experimental conditions. Hence a single compartment polypropylene cell was used for voltammetric measurements. The voltammetric and chronoamperometric measurements were carried out at 298 K. Surface characterization was carried out with a JEOL (Model 35CF) scanning electron microscope. The amount of Ni^{2+} species dissolved in the electrolyte was estimated using atomic absorption spectroscopy (GBC 906AA, Australia).

All other experimental details including instrumental set up and electrode pre-treatment procedures have already been described [18, 19].

Results

Cyclic voltammetric studies

Even in strong acidic media, the Ni electrode surface has a uniform oxide layer. As long as the electrode is not polarized in the cathodic hydrogen evolution region, the oxide layer does not show any anodic dissolution peak

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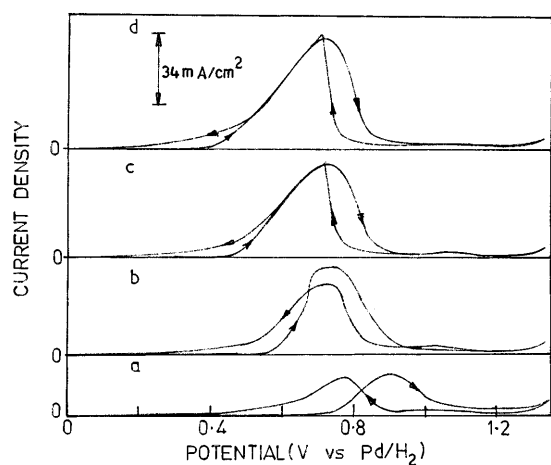Tel.: +91-4565-2322
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in the absence of fluoride ions. This is true even when the electrode is kept in the acidic medium under open circuit conditions for a few hours.

Typical cyclic voltammetric (CV) curves of Ni in 1.0 M $HClO_4$ containing 2–15 mM HF at a constant sweep rate (v) of 10 mV s^{-1} are presented in Fig. 1. In the forward sweep a distinct anodic peak (E_{pf2}), which increases with HF concentration, is noticed (a small peak, E_{pf1}, around 0.5 V is not noticed in this media, however; see later). Beyond the peak potential region the current drops to zero level, which is typical of a passivation process. The onset of another anodic peak (E_{pr2}) during the reverse sweep, which is a characteristic feature of reactivated dissolution, is also noticed in these CV curves. The onset of the anodic dissolution process occurs at less positive potentials with increasing fluoride concentrations (Fig. 1).

The CV responses of Ni in the presence of NH_4F in the same concentration range of HF are qualitatively quite similar to those of Fig. 1. The peak potential and peak current values are also only slightly different at all concentrations. Typical peak potential and peak current values at 15 mM and 100 mM fluoride concentrations for all the fluorides investigated are presented in Tables 1 and 2, respectively, for quantitative comparison.

At identical concentration ranges, noticeably higher anodic currents are obtained in the presence of NaF (Fig. 2). In addition to the main anodic peak (E_{pf2}) noticed for HF and NH_4F, two new peaks tend to appear in NaF. A small peak noticed around 0.5 V is termed the first peak (E_{pf1}). No distinct peak is noticed beyond 0.9 V in the forward sweep, but in the reverse sweep a distinct dissolution peak is noticed in this potential region. This peak is denoted as E_{pr3} (Fig. 2 and Tables 1 and 2).

All three dissolution processes become distinctly visible in the presence of 4–15 mM KF in 1.0 M $HClO_4$ (Fig. 3). The dissolution currents in all three dissolution peak potential regions are distinctly higher for this flu-

Table 1 Effect of HF, NH_4F, NaF, KF and LiF (15 mM and 100 mM) on the anodic peak potential characteristics of Ni in 1 M $HClO_4$ medium at $v = 10$ mV s^{-1} 100 mV s^{-1}

Nature of F⁻	Conc. of F⁻ (mM)	Sweep rate (mV s⁻¹)	E_{pf1} (V)	E_{pf2} (V)	E_{pr3} (V)	E_{pr2} (V)
HF	15	10	–	0.72	–	0.71
	100	10	–	0.69	–	0.68
NH_4F	15	10	0.44	0.75	–	0.72
	100	10	0.57	–	–	–
NaF	15	10	0.56	0.75	–	0.67
	100	10	0.63	0.94	1.11	0.88
KF	15	10	0.62	0.90	1.09	0.89
LiF	15	10	0.73	0.97	–	0.86
	100	10	–	0.98	1.20	0.98
HF	15	100	–	0.88	–	0.53
	100	100	–	0.67	–	0.37
NH_4F	15	100	–	0.82	–	–
	100	100	–	0.90	1.20	0.66
NaF	15	100	–	–	–	0.58
	100	100	–	0.86	–	0.69
KF	15	100	–	0.94	–	0.81
LiF	15	100	–	–	–	0.75
	100	100	–	0.95	1.10	0.95

oride when compared to the other three discussed above (Tables 1 and 2). At low concentrations of KF (Fig. 3a) the reactivated dissolution is not noticed in the reverse sweep. However, this process increases significantly at higher KF concentrations (Fig. 3b and c) and E_{pr3} beyond 1.0 V becomes distinctly visible. In $HClO_4$ medium, KF concentrations beyond 15 mM could not be employed owing to solubility limitations.

Maximum anodic dissolution currents for Ni in 1.0 M $HClO_4$ media, however, are noticed in the presence of LiF, in the same concentration range (Fig. 4). The dissolution peaks are shifted to more positive potentials in this medium. The reactivated dissolution peak beyond 1.0 V (E_{pr3}), distinctly noticed in the presence of KF, is not noticed in this medium (Fig. 4).

Above 15 mM, the anodic dissolution continues to increase with concentration for all the fluorides. On a comparative basis, all the monovalent fluorides exhibited the same dissolution trends. In 100 mM, for example, HF addition led to only one anodic dissolution peak (E_{pf2}). The first and third peaks were absent . The CV responses of the same 100 mM concentration of NH_4F, NaF and LiF are compared in Fig. 5 at 10 mV s^{-1}. The dissolution rate in the presence of LiF is indeed significantly higher (Fig. 5c). The single dissolution peak in this case covers a wider potential range and passivation in the forward sweep sets in only around 1.3 V. The reactivated dissolution in the reverse sweep also covers the whole potential range.

The dissolution charges obtained by integrating the area under the voltammogram during forward (Q_f) and reverse (Q_r) sweeps are also summarized in Table 2. The general trend noted in the peak currents also prevails in the case of dissolution charges.

The dissolution-passivation responses also exhibit some interesting time dependences. CV responses of

Fig. 1 Cyclic voltammetry (cv) of Ni in 1.0 M $HClO_4$ containing HF of conc. (mM) *a* 2, *b* 4, *c* 8, *d* 15 at 10 mV s^{-1}

Table 2 Effect of HF, NH$_4$F, NaF, KF and LiF (15 mM and 100 mM) on the anodic peak current and charge density characteristics of Ni in 1 M HClO$_4$ medium at $v = 10$ mV s^{-1} and 100 mV s^{-1}

Nature of F$^-$	Conc. of F$^-$ (mM)	Sweep rate (mV s^{-1})	i_{pf1} (mA cm^{-2})	i_{pf2} (mA cm^{-2})	i_{pr3} (mA cm^{-2})	i_{pr2} (mA cm^{-2})	Q_f (C cm^{-2})	Q_r (C cm^{-2})
HF	15	10	–	51	–	51	1.25	0.99
	100	10	–	102	–	131	3.12	2.58
NH$_4$F	15	10	9	55	–	58	1.36	1.02
	100	10	19	87	20	68	2.04	1.84
NaF	15	10	27	62	–	52	1.41	1.20
	100	10	22	105	48	105	3.24	2.97
KF	15	10	25	112	66	110	3.54	4.02
LiF	15	10	69	122	–	119	3.26	1.39
	100	10	–	171	–	171	7.85	7.92
HF	15	100	–	6	–	10	0.02	0.03
	100	100	–	112	–	7	0.38	0.02
NH$_4$F	15	100	–	38	–	–	0.07	–
	100	100	–	31	–	39	0.03	0.10
NaF	15	100	–	–	–	34	0.01	0.09
	100	100	–	55	–	80	0.11	0.18
KF	15	100	–	34	–	95	0.07	0.27
LiF	100	100	–	178	212	180	0.80	0.84

100 mM HF in 1.0 M HClO$_4$ media at different sweep rates (v) show that the anodic dissolution rate during the forward sweep does not increase significantly with v. The reactivated dissolution rate during the reverse sweep significantly decreases with v. At lower HF concentrations, the peaks in the forward as well as reverse sweeps decrease with v. Around 200 mV s^{-1} in 15 mM HF, for example, both the dissolution peaks completely disappear. The effects of v on NH$_4$F solutions were also quite similar to those of HF solutions.

In the case of NaF and KF, the forward dissolution peak decreases with increasing v while the reactivated dissolution peak in the reverse sweep increases with increasing v. Typical CV responses for 15 mM KF in 1.0 M HClO$_4$ at different sweep rates are presented in Fig. 6. Similar trends were noticed in the presence of NaF.

In the case of LiF, the dissolution peaks in the forward as well as reverse sweeps decrease slightly with v, but both dissolution processes remain unaffected even at high sweep rates. The dissolution charges, however, decrease slightly with v (Table 2).

Other techniques

Further investigations on the anodic dissolution were carried out in NaF, KF and LiF solutions, where all the three dissolution processes are noticed. Chromoamperometric responses at different potential regions were re-
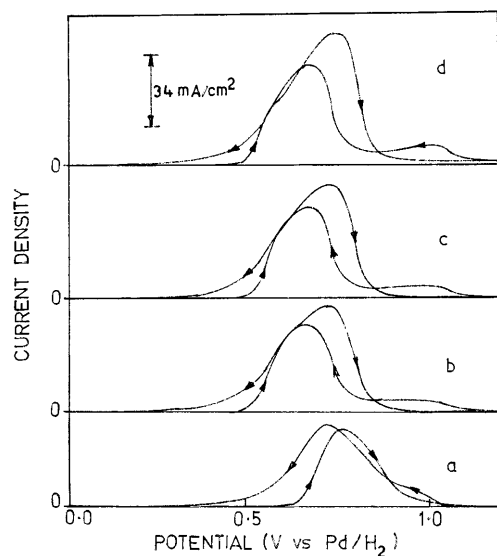
Fig. 2 CV of Ni in 1.0 M HClO$_4$ containing NaF of conc. (mM) a 4, b 8, c 10, d 15 at 10 mV s^{-1}
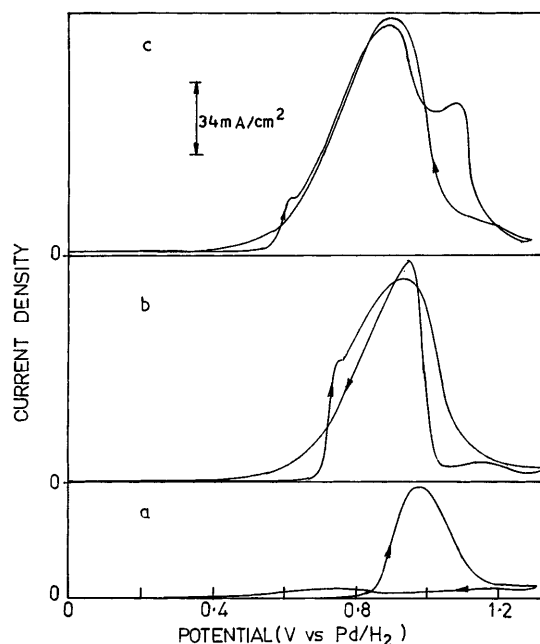
Fig. 3 CV of Ni in 1.0 M HClO$_4$ containing KF of conc. (mM) a 4, b 8, c 15 at 10 mV s^{-1}

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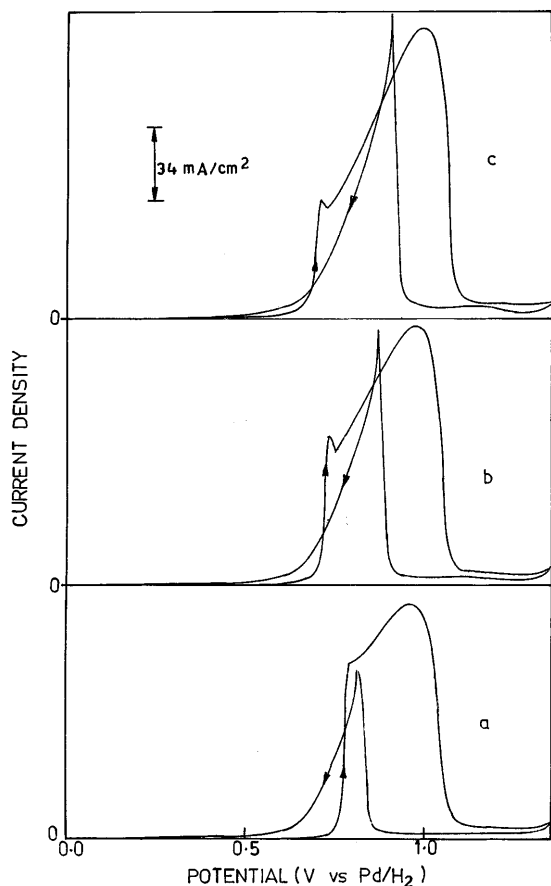
Fig. 4 CV of Ni in 1.0 M HClO$_4$ containing LiF of conc. (mM) a 6, b 10, c 15 at 10 mV s^{-1}
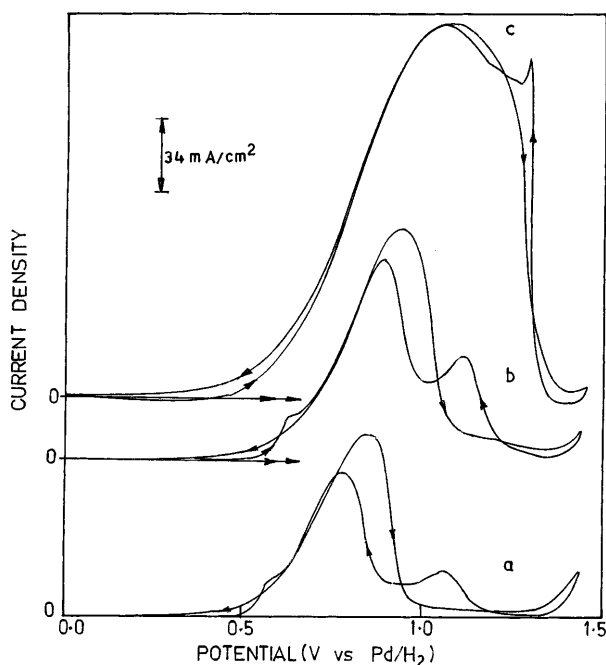
Fig. 5 CV of Ni in 1.0 M HClO$_4$ containing 100 mM of a NH$_4$F, b NaF, c LiF at 10 mV s^{-1}
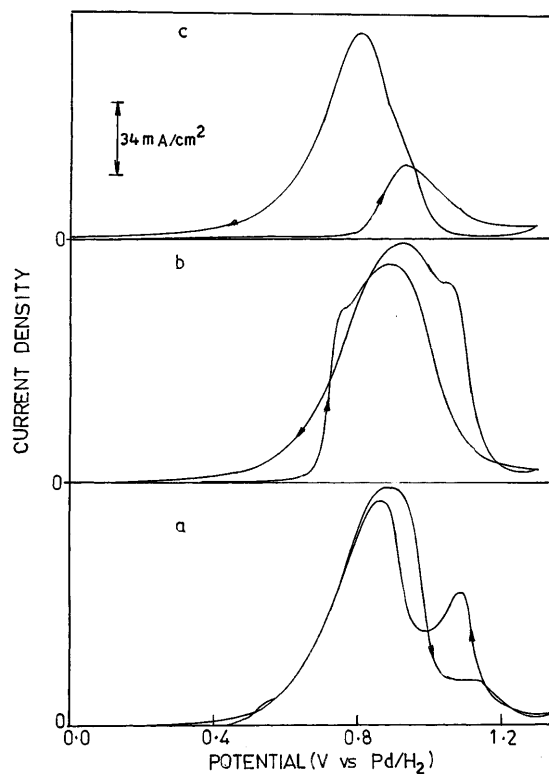
Fig. 6 CV of Ni in 1.0 M HClO$_4$ containing 15 mM KF at a 4, b 30, c 100 mV s^{-1}

corded and the total dissolution charges were also calculated (Table 3). In the active dissolution region, the anodic dissolution charges increase with increasing anodic potential in all the three cases. Typical chronoamperometric responses in the peak potential region for NaF and LiF are compared in Fig. 7a and b, respectively. In the third peak potential region (E_{pr3}), however, the current-time curve shows a sharp fall in the case of NaF (Fig. 7c), while the current-time response actually remains high and even increases with time in the case of LiF solutions (Fig. 7d). The anodic dissolution charges for LiF also remain high (Table 3). Despite limited solubility of KF, the chronoamperometric responses are quite similar to those in LiF solutions (Table 3). In the potential region corresponding to E_{pr3} the anodic dissolution charges are indeed found to be considerably higher.

All these results confirm the existence of three distinct dissolution processes and also considerably higher dissolution rates in LiF and KF solutions.

Atomic absorption spectroscopy (AAS) was employed to estimate the amount of Ni^{2+} species dissolved. The total anodic charge passed during current-time transients (for 300 s in the present experiment) gives the estimate of total Ni^{2+} species formed electrochemically. The difference between these two values thus gives a broad estimate of the percentage of NiF$_2$ remaining on the electrode surface after the anodic polarization process.

These data are presented in Table 4 for anodic polarization of nickel in LiF, NaF and KF media at their corresponding dissolution peak potentials. These data

Table 3 Current density values, Q, from i-t transients recorded for 300 s for the anodic polarization of nickel in 1.0 M $HClO_4$ medium

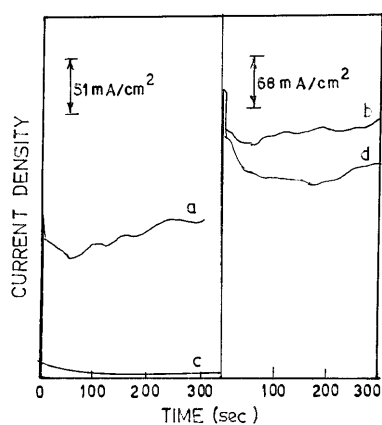| Nature of F^- ion	Concentration (mM)	Potential (V)	Q (C cm^{-2})
NaF	100	0.70	18.7
		0.80	25.4
		0.95	38.7
		1.10	1.3
KF	15	0.70	8.6
		0.80	22.9
		0.90	44.5
		1.10	72.4
LiF	100	0.70	31.6
		0.90	81.4
		1.10	91.6
		1.20	78.0

Table 4 AAS data of nickel dissolved for 300 s in 1.0 M $HClO_4$ medium containing different fluoride salts

Nature of F^- ion	100 mM NaF	15 mM KF	100 mM LiF
Number of moles of nickel dissolved $\times 10^{-3}$ M (from i-t)	4.00	4.60	9.20
Number of moles of nickel in solution $\times 10^{-5}$ M (from AAS)	0.15	1.05	2.60
Number of moles of NiF_2 on the nickel surface $\times 10^{-5}$ M	3.85	3.55	6.60
Thickness of NiF_2 film (μm)	67	66	125

suggest that in all cases the Ni^{2+} species going into solution is only a small fraction of the total anodic charge passed. In the case of NaF, which does not activate a dissolution process, over 96% of the Ni^{2+} species formed during anodic polarization remains on the electrode surface. In the case of 100 mM LiF and 15 mM KF the NiF_2 fraction remaining on the surface is much lower, about 77%.

If one assumes that the NiF_2 film formed is uniform, the surface concentration of NiF_2 obtained in these experiments may be used to calculate the thickness of the NiF_2 film using the density of NiF_2 (2.6 g/cm^2). The NiF_2 film thickness turns out to be 67, 66 and 125 μm in NaF, KF and LiF solutions respectively (Table 4).

However, scanning electron microscopy (SEM) clearly suggests that the dissolution process proceeds rather non-uniformly through the generation of circular pits. SEM micrographs obtained after anodic polarization of nickel in aqueous KF and LiF indicated that the pitted surface layer formed from KF solutions is rougher when compared to the surface formed from dissolution in LiF solution. In KF solutions the width of the circular pits were found to vary between 50 μm and 500 μm. In LiF solutions the width of the pits were more uniform


Fig. 7 i-t transients in 1.0 M $HClO_4$ containing 100 mM (a, c) NaF at step potentials of 0.95 and 1.1 V and (b, d) LiF at step potentials of 1.1 and 1.2 V, respectively

and vary between 300 μm and 600 μm. The pit density was found to be considerably higher in KF solutions when compared to those in LiF solutions. The apparent depth of the pits (>200 μm) in the SEM micrographs was also considerably larger than the thickness of the NiF_2 film calculated above, under the assumption of uniform dissolution.

Discussion

In earlier work from this laboratory [18], two distinct pathways for the anodic dissolution of Ni in HF media were identified, depending on acid concentration. At lower acid concentrations the anodic dissolution proceeds through the oxide layer:

$$Ni_x(NiO)_n \rightarrow Ni_{x-1}(NiO)_n + Ni^{2+} + 2e^- \qquad (1)$$
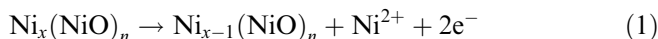
This is followed by the formation of a NiF_2 passive layer by a chemical precipitation reaction.

$$Ni_{x-1}(NiO)_n + Ni^{2+} + 2F^- \rightarrow Ni_{x-1}(NiO)_nNiF_2 \qquad (2)$$
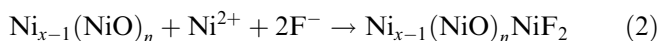
This is the process that is responsible for the second anodic peak in the present work. During the reverse sweep, the oxide or fluoride layer is partially reduced at active sites and this reactivates the anodic dissolution process [18].

At high HF concentrations a distinct anodic dissolution process was noticed below 0.5 V [18]. This was shown to be due to direct dissolution of Ni through the pits in the oxide layer. The dissolution precipitation on the oxide free sites of Ni may be represented as follows:

$$Ni_x \rightarrow Ni_{x-1} + Ni^{2+} + 2e^- \qquad (3)$$

$$Ni_{x-1} + Ni^{2+} + 2F^- \rightarrow Ni_{x-1}NiF_2 \qquad (4)$$
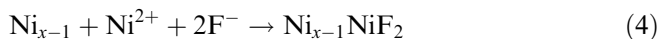
With small quantities (<100 mM) of alkali fluorides, the localized oxide-free pits may be formed only to a small extent and hence the first anodic peak appears as a knee at the foot of the second peak in the present work.

In alkali metal fluorides, the NiF_2 layer may also dissolve by a third pathway, namely through complex formation:

$$Ni_{x-1}(NiO)_nNiF_2 + K^+ + F^-$$
$$\rightarrow Ni_{x-1}(NiO)_n + K^+ + NiF_3^- \qquad (5)$$

$$Ni_{x-1}(NiO)_n NiF_2 + 2K^+ + 2F^-$$
$$\rightarrow Ni_{x-1}(NiO)_n + 2K^+ + NiF_4^{2-} \quad (6)$$
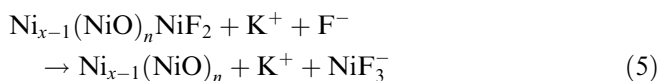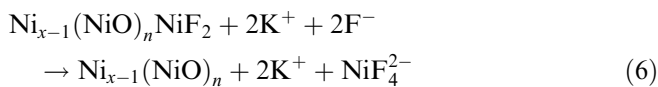
This dissolution through the formation of complex ionic species probably takes place at a relatively faster rate when compared to the formation of Ni_{aq}^{2+} and F_{aq}^- species through chemical dissolution. This process is responsible for the third anodic peak beyond 1.0 V. Since this dissolution process is also time dependent, the dissolution peak is predominent in the reverse sweep alone (Figs. 2, 3, 6).

The stability of electrochemically formed NiF_2 film is influenced by all the monovalent fluorides in all the three modes, namely direct dissolution (first anodic peak region), dissolution through the oxide layer (second anodic peak region) and dissolution of NiF_2 film through complex formation (third anodic peak region). The relative influence, however, varies for different monovalent fluorides in 1.0 M $HClO_4$.

Among the monovalent fluorides, NH_4F and HF show the least effect on the stability of the NiF_2 layer. During the forward sweep they show a small dissolution current in the second anodic peak region. Dissolution through complex formation is not at all noticed. During reverse sweep, little reactivated dissolution is noticed especially at high sweep rates.

Even with NH_4F and HF the dissolution rate in HF is slightly higher. This is due to the acidity influence of H^+ and NH_4^+ in enhancing the solubility of Ni^{2+}.

Among the three alkali metal fluorides investigated, NaF is least effective in influencing the dissolution of the NiF_2 layer. Under identical conditions the dissolution currents in NaF solutions are considerably lower (Tables 1 and 2). The dissolution charges from current-time transients are also lower. The chemical dissolution through complex formation in the third anodic potential region is also quite small. AAS studies also confirm very little chemical dissolution of Ni^{2+} species.

KF is only slightly soluble in $HClO_4$; however, it exerts considerable influence on the dissolution of NiF_2 even at 15 mM. All three dissolution processes occur significantly in this medium, as confirmed by CV (Tables 1 and 2) and chronoamperometry (Table 3). AAS studies also show that about 20% of the total NiF_2 formed goes into solution owing to complex formation (Table 4). After polarization the surface layer is quite rough, with circular pits .

LiF dissolves in $HClO_4$ to a greater extent. It also influences the dissolution of the NiF_2 layer through all three dissolution pathways. One additional influence of aqueous LiF solutions should also be considered. The acidity of proton solvated water molecules of the Li^+ ion would be high [20, 21]. This would enhance the dissolution rate of nickel over the entire potential region. This is the cause of the higher dissolution rate with LiF, noticed in CV (Fig. 5), chronoamperometry (Fig. 7) and SEM. AAS also indicates a much higher dissolution rate as well as a fairly thick NiF_2 film in 0.1 M LiF solutions.

Conclusions

The present investigation suggests that monovalent cations can influence anodic dissolution of metals in at least three distinct ways. The cationic species can significantly influence the formation of complex cationic species at the interface and its subsequent dissolution. The Lewis acidity or the solvation free energy of the cationic species may also have a profound effect on anodic dissolution. All these factors influence the direct anodic dissolution of Ni, dissolution through the oxide layer and finally the dissolution through complex formation. Among the monovalent fluorides considered in this work, the overall stability of NiF_2 decreases in the order $NH_4F > HF > KF > LiF$.

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