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Interaction between organic molecules and electrogenerated nickel fluoride films: the choice of organic reactants for electrochemical perfluorination

N. Suriyanarayanan · M. Noel

Abstract The interactions of organic molecules such as acetonitrile, propylene carbonate, and sulfolane on the electrogenerated nickel fluoride films were investigated using cyclic voltammetry and scanning electron microscopy. The effect of water, alkali metal fluorides, fluoride content, and acidity are also reported. Based on these studies, the potential effect of these factors on electrochemical perfluorination processes are projected. Water and alkali metal fluorides would enhance the dissolution of nickel fluoride film. Organic molecules like acetonitrile dissolve nickel fluoride film, while propylene carbonate forms thick polymeric layers on nickel surface. Higher acidity and fluoride ion content enhance the stability of a thin, catalytically active nickel fluoride film. Organic reactants like sulfolane form a composite film with nickel fluoride and, thus, enhance the long-term stability and electrocatalytic activity.

Keywords Nickel fluoride film · Organic molecules film interactions · Electrochemical perfluorination · Surface effects

Introduction

Electrochemical perfluorination is one of the well-established processes whose mechanism remains a debatable issue even after five decades of consistent industrial success [1–5]. Any mechanistic debate must account for the following two key features of the process. Nickel is the only successful anode material employed in this process. Moreover, only a few classes of organic compounds, namely carboxylic acid chlorides, sulfonic acid fluorides, trialkyl amines, and heterocyclic compounds containing N and O atoms, have been successfully perfluorinated with reasonably high yield and selectivity.

Recent mechanistic studies [6–9] and reviews [9, 10] have clearly brought out the catalytic role of the redox active NiF_2/NiF_3 film in the electrochemical fluorination processes. The loosely held fluorine-free radical present in the electrogenerated NiF_3 film sustains the free radical mechanistic pathway [6–10]. The chemical oxidative fluorination of organic compounds by high-valence nickel fluorides in the hydrogen fluoride (HF) media [11, 12] also lends support to this mechanism. The carbon chain isomerization process which was considered to occur through an alternative carbocation mechanism has also been explained through the formation of an adsorbed cyclopropane intermediate on the electrogenerated NiF_3 layer [13, 14].

The second issue, namely, the specific structural requirements of the organic molecules for successful perfluorination on electrogenerated NiF_3, still remains largely unanswered. The chemisorption of reactant molecule on electrode surface until complete replacement of hydrogen atoms by fluorine atoms in the carbon chain was proposed earlier. This mechanism was commonly termed as zipper mechanism. However, many recent investigations do not support this mechanistic pathway [6–16]. It is true that all the reactants, which lead to successful perfluorination, can also undergo protonation and, thus, ensure electrolytic conductivity in anhydrous hydrogen fluoride (AHF) medium. But why is it that conducting additives such as alkali metal

N. Suriyanarayanan
Department of Physics, Government College of Technology,
Coimbatore 641 013, India

M. Noel (✉)
Central Electrochemical Research Institute,
Karaikudi 630 006, India
e-mail: yemenoel@yahoo.co.in

fluorides are not successful? Why it is that some common solvents such as sulfolane undergo facile electrochemical fluorination, while other solvents such as acetonitrile and propylene carbonate (PC) fail? What is the role of the reactant–HF ratio or the medium acidity on the electrochemical behavior of nickel fluoride films? These are some of the issues that deserve further attention.

To answer some of these questions, the electrochemical behavior of nickel in water, acetonitrile, propylene carbonate, and sulfolane media containing alkali metal fluorides and triethylamine-tris-hydrogen fluoride (TEA.3HF) were investigated. The effect of TEA–HF ratio on the electrogenerated nickel fluoride was also investigated in sulfolane medium. Apart from the effect of electrolytic conductivity, these studies have thrown some further light on other effects of organic molecules on nickel fluoride film stability and electrochemical activity.

Materials and methods

TEA.3HF was prepared by mixing TEA with freshly distilled AHF (TANFAC, India) at the temperature range of freezing mixture, evaluating the HF content by titration and adjusting the TEA.3HF ratio accordingly [15]. Ni ($0.196 \, cm^2$) rod tight-fitted into Teflon served as the working electrode. A Pt foil ($3 \, cm^2$) served as the counter electrode. Although neat TEA.3HF and other fluoride media employed in the present work are not aggressive towards glass, a polypropylene undivided cell was used throughout. The choice of reference electrode posed some problems. The palladium (Pd/H_2) electrode showed instability, especially in TEA.3HF in which Pd dissolution was noticed. Hence, a Pt wire was used as a quasi reference electrode in TEA.3HF. The measurements suggested that the Pt quasi reference potential in TEA.3HF is always close to the Pd/H_2 reference electrode within the limit of ± 20 to ± 30 mV. The reference potential, however, was compared from time to time externally against a saturated calomel electrode.

MeCN (high-performance liquid chromatography), propylene carbonate (analytical reagent (AR) grade), sulfolane (AR grade), and triply distilled water were used as solvents. The alkali metal fluorides employed (KF, NaF, NH_4F, LiF) were also of AR grade. The working electrode was polished to a mirror finish and washed repeatedly with triply distilled water and then with trichloroethylene before use. As an insoluble fluoride film is formed on Ni electrodes during each potential cycle, these electrodes had to be repeatedly cleaned and polished after each cyclic voltammetric (CV) experiment to obtain reproducible results.

A Wenking potentiostat (model VSG 72) was used for potential control and programming, and a Rikadenki (model

NP-0363) was used to record the results. Scanning electron microscopy (SEM) was performed with JEOL (model 30CF) scanning electron microscope. All of the experiments were carried out at 303 ± 1 K.

Results and discussion

### Organic additive and electrolytic conductivity

Nickel fluoride films are highly insoluble in anhydrous hydrogen fluoride. However, AHF possesses very low electrolytic conductivity. Organic reactants that undergo facile electrochemical fluorination contain carbonyl groups, sulfonyl groups, or N, O, or S heteroatoms that can be protonated by anhydrous HF resulting in good electrolytic conductivity required for electrochemical fluorination. For example, RCOF can be protonated by HF, leading to ionic species and thus enhancing conductivity.

$$RCOF + HF \rightarrow [RCOHF]^+ + F^- \tag{1}$$
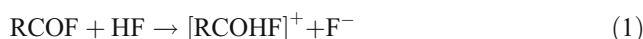
Water can also act as a base in HF media and enhance conductivity.

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

Excess water can act as a solvent and dissolve the NiF_2 film. Typical cyclic voltammograms recorded in 1.0 M $HClO_4$ (Fig. 1a) indicates the dissolution and precipitation process occurring on Ni electrode.

$$Ni \rightarrow Ni^{2+} + 2e \tag{3}$$

$$Ni^{2+} + 2HF_{aq} \rightleftharpoons NiF_2 + 2H^+aq \tag{4}$$
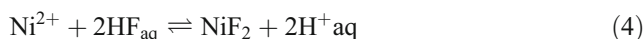
The above dissolution process increases significantly in the presence of KF (Fig. 1b). The peak current values in Fig. 1a and b are quite similar. However, the overall dissolution charge (as measured by the area under the anodic dissolution region) is substantially higher in the presence of KF. In addition to the direct dissolution precipitation process (Eqs. 3 and 4), KF also enhances the dissolution of NiF_2 salt layer through reactions 5 and 6 [17]:

$$NiF_2 + KF \rightarrow KNiF_3 \tag{5}$$

$$NiF_2 + 2KF \rightarrow K_2NiF_4 \tag{6}$$

The anodic dissolution rate also depends on the nature of the cation. For example, Fig. 2 indicates that, for the identical fluoride salt concentration, the anodic dissolution rate or anodic dissolution current increases in the order $NH_4F < NaF < LiF$. In all these cases, reactivated dissolution
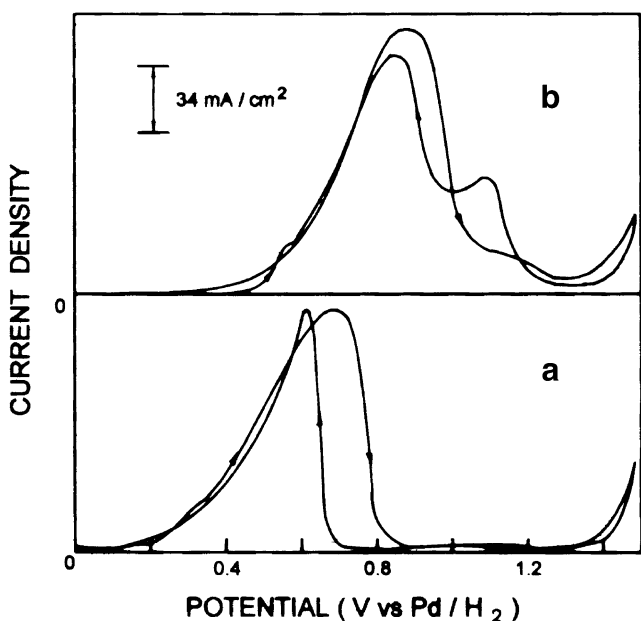
Fig. 1 Cyclic voltammograms of Ni in 1.0 M $HClO_4$ containing **a** 100 mM HF and **b** 20 mM KF at $v = 10$ (mV s^{-1})

is noticed during the reverse sweep in the presence of HF as well as other fluoride salts. (Figs. 1 and 2), suggesting the highly unstable nature of electrochemically formed NiF_2 salt layers in these media [17].

In some earlier perfluorination studies involving hydrocarbon, attempts were made to add salts such as KF, LiF, and NaF to improve the conductivity of the electrolyte [5].
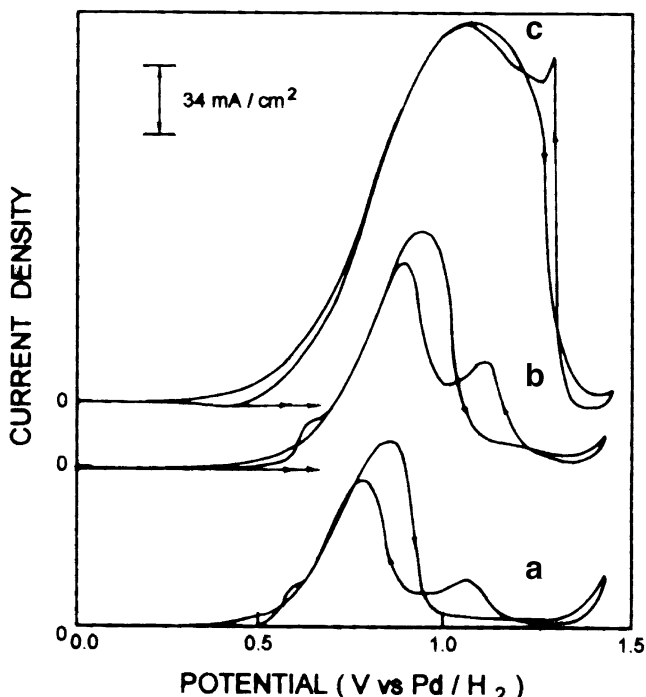
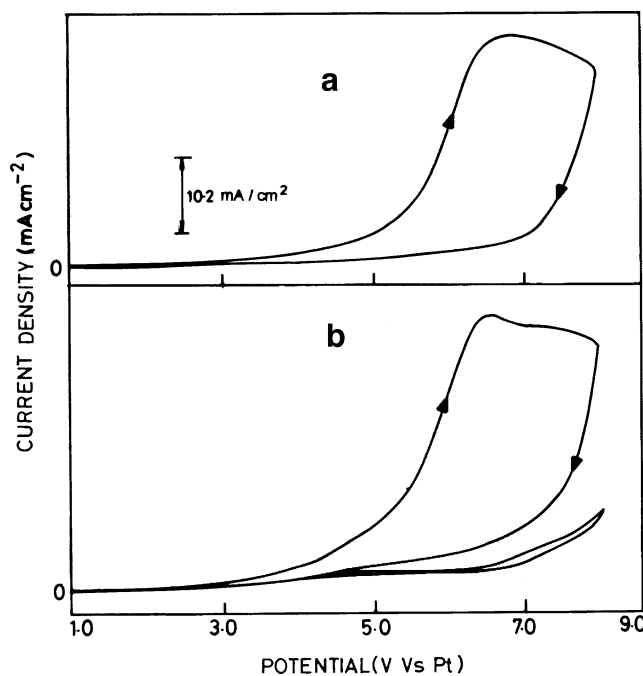Fig. 2 CV of Ni in 100 mM $HClO_4$ containing 100 mM of *a* NH_4F, *b* NaF, *c* LiF at $v = 10$ (mV s^{-1})

Fig. 3 CVs of Ni in CH_3CN containing **a** 0.1 M TEA.3HF, **b** 0.2 M TEA.3HF at 40 mVs^{-1}

The excessive dissolution of Ni was observed in these studies. The NiF_2 film dissolution mechanism presented here (Eqs. 5 and 6) should be the cause for such anodic dissolution and complex sludge formation ($KNiF_3$ and K_2NiF_4 are similar alkali metal fluoride salts).

Dissolution of anodic film due to organic reactant

Typical CV curves obtained during the anodic polarization of Ni in acetonitrile containing 0.1 and 0.2 M TEA.3HF at 40 mV s^{-1} are shown in Fig. 3a and b, respectively. The anodic oxidation process in this medium starts only beyond 3.5 V. The anodic dissolution current increases with the concentration of TEA.3HF. In the second and subsequent sweeps, anodic oxidation process is initiated only beyond 7.0 V, suggesting the formation of a passive layer (Fig. 3b).

The anodic dissolution charge obtained by integrating the cyclic voltammogram in this medium, however, is greater than 1,000 mC cm^{-2} (Table 1). For a monolayer of NiF_2 formation on planer Ni surface by 2e oxidation

Table 1 Voltammetric features of Ni in CH_3CN, PC, and sulfolane containing 0.1 M TEA.3HF at 40 mV s^{-1}

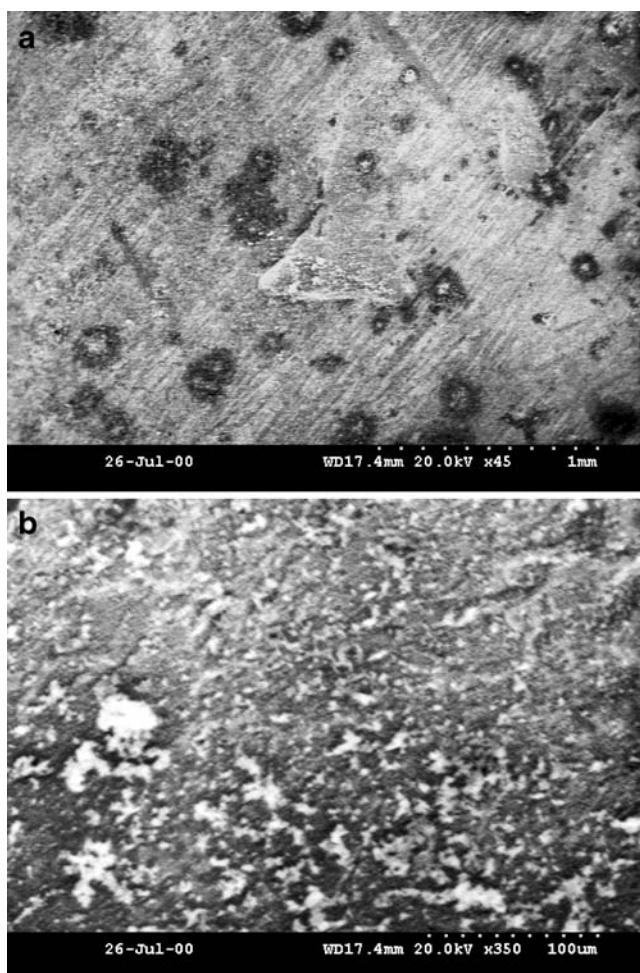| Sl no.	Solvent	Anodic potential range (V)	E_{pa} (V)	I_{pa} (mA cm^{-2})	Q (mC cm^{-2})
1	CH_3CN	1.0 to 8.0	6.75	29.07	1,013
2	PC	−0.8 to 8.0	–	–	487.70
3	Sulfolane	−1.0 to 8.0	–	–	78.28

Fig. 4 SEM images of Ni in CH$_3$CN containing 0.2 M TEA.3HF after five cycles between 1.0 and 8.0 V at 40 mV s^{-1}: **a** ×45, **b** ×350

process, the actual anodic charge required was calculated to be around 400 μC cm^{-2} [17].

$$Ni + 2F^- \rightarrow NiF_2 \qquad (7)$$

The anodic dissolution charge noticed in the present work is substantially greater than the 400 μC cm^{-2} required for a monolayer of NiF$_2$ film formation. This suggests substantially higher film dissolution. The SEM pictures of nickel surface obtained after five potential cycles under identical conditions are shown in Fig. 4. These pictures clearly indicate substantial roughness and fairly large-sized pits on the electrode surface. These features suggest substantial NiF$_2$ film dissolution in this medium.

Earlier work from this laboratory on the anodic behavior of Ni in TEA.3HF medium also indicated enhanced film dissolution in the presence of trace levels of water as well as acetonitrile [15]. All these experimental results suggest that organic compounds like acetonitrile can also dissolve the NiF$_2$ film like water and, hence, these would not undergo direct electrochemical fluorination.

Polymer film formation on the electrode

Propylene carbonate containing fluoroanion salts are commonly employed as electrolytes in lithium ion batteries. Hence, the effect of this solvent on the anodic behavior of nickel was also investigated. Typical CV curves obtained in PC containing 0.1 M TEA.3HF at different sweep rates are presented in Fig. 5a and b, respectively. Significant anodic current is noticed beyond 3.0 V; however, no distinct anodic peak is observed. The anodic current at each potential increases with sweep rate. In the second and subsequent sweeps, substantial anodic current is also observed beyond 4.0 to 5.0 V.

The anodic charge obtained by integrating the CV curve was found to be 500 mC cm^{-2} (Table 1). While this value is lower than that observed in acetonitrile, the charge is still substantially higher than the monolayer coverage. SEM picture (Fig. 6) shows substantially thick and non-uniform polymer film formation on the electrode surface. This is another possible competitive process for electrochemical fluorination.
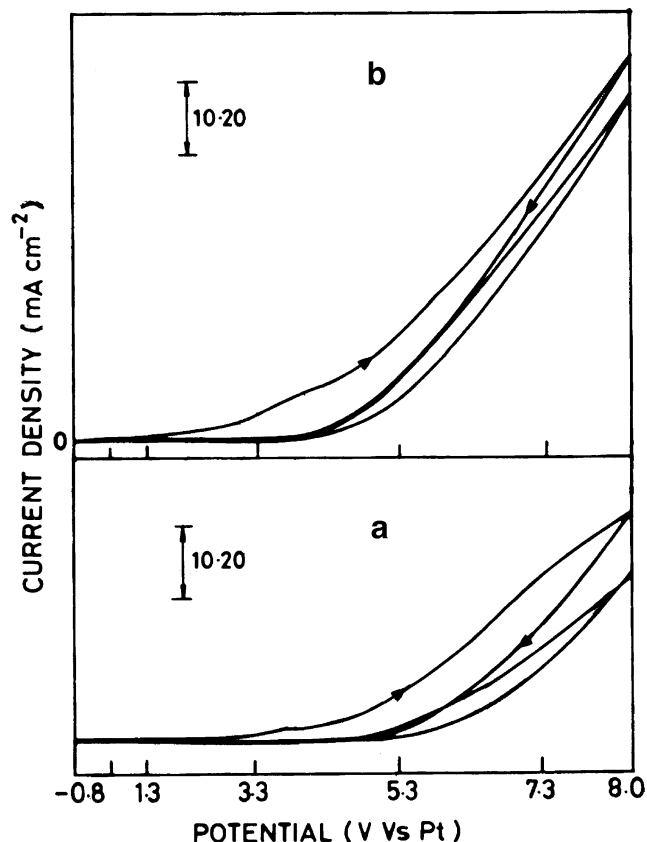

Fig. 5 Multisweep CVs of Ni in PC containing 0.1 M TEA.3HF at different sweep rates v (mVs^{-1}): **a** 40, **b** 320
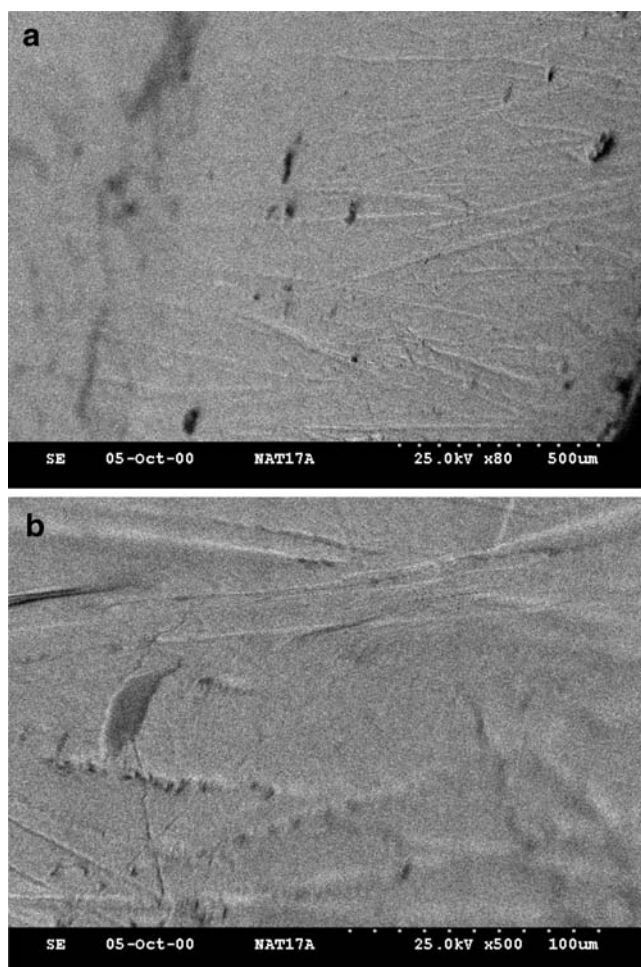
Fig. 6 SEM images of Ni in PC containing 0.2 M TEA.3HF after five cycles between −0.8 and 8.0 V at 40 mVs⁻¹: **a** ×50, **b** ×500

Compact conductive film formation

Sulfolane is another convenient solvent used in electrosynthesis. It is also a reactant commonly employed in electrochemical perfluorination for the synthesis of perfluoro butane sulfonyl fluoride. Hence, the anodic behavior of Ni in this media was also investigated.

Typical multisweep CV curves obtained during the anodic polarization of Ni in sulfolane containing 0.1M TEA.3HF at 40 and 320 mV s⁻¹ are shown in Fig. 7a and b, respectively. The voltammograms are similar to those obtained in PC medium (Fig. 5a and b); however, the anodic current values are substantially smaller in sulfolane medium (compare the Y-axis scale in Figs. 5 and 7). The anodic charge is close to 80 mC cm⁻² (Table 1).

The SEM pictures (Fig. 8) indicate a uniform and compact film formation on the electrode surface during anodic polarization. If 400 μC cm⁻² is assumed to be the charge required for a monolayer of nickel fluoride, the anodic film may be approximately 20 monolayers thick. The anodic film may be an insoluble composite one con-

taining nickel fluoride and organic reactant or its partially fluorinated intermediates. Such a composite nickel fluoride film indeed is proposed to be an ideal catalyst layer for electrochemical fluorination [5].

The CV curves shown in Fig. 7 also indicate steady current–potential values during the forward as well as reverse sweeps except for the first anodic sweep. This anodic process is initiated beyond 3.0 V (Fig. 7). This anodic process is probably related to the formation of high-valence nickel fluoride, which then acts as the redox catalyst in electrochemical fluorination reaction, as shown below.

$$NiF_2 + HF \rightarrow NiF_3 + H^+ + e \qquad (8)$$

$$2NiF_3 + RH \rightarrow 2NiF_2 + RF + HF \qquad (9)$$
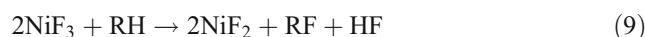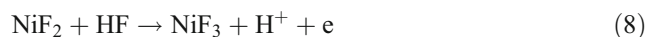
Acidity of the electrolyte

In electrochemical fluorination process, the anhydrous HF content usually tends to be more than 90%. Hence, a few more experiments were carried out to evaluate the effect of higher concentration of HF and acidity in sulfolane medium. Typical multisweep CV curves obtained in sulfolane containing 3 and 5 M AHF for nickel electrode in sulfolane
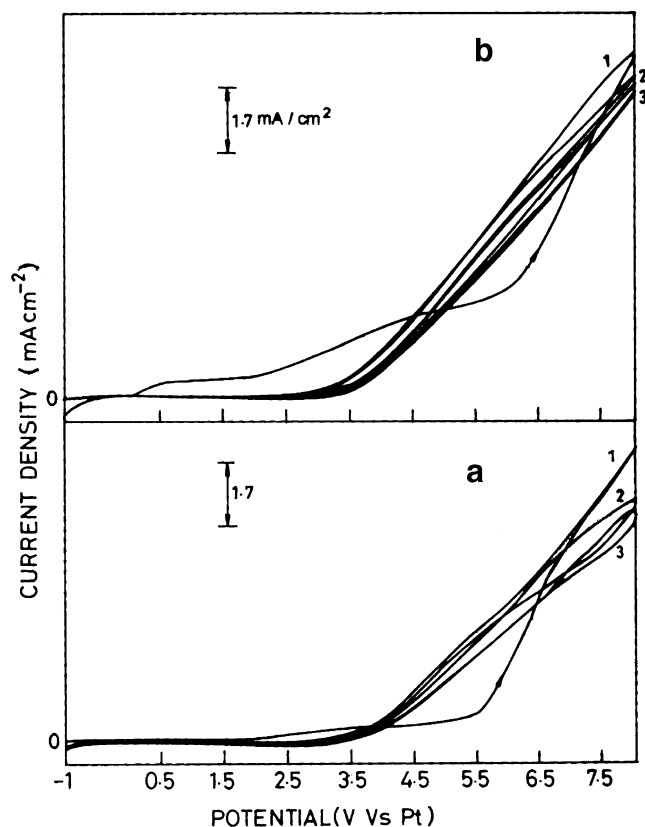

Fig. 7 Multisweep CVs of Ni in sulfolane containing 0.1 M TEA.3HF at different sweep rates v (mVs⁻¹): **a** 40, **b** 320
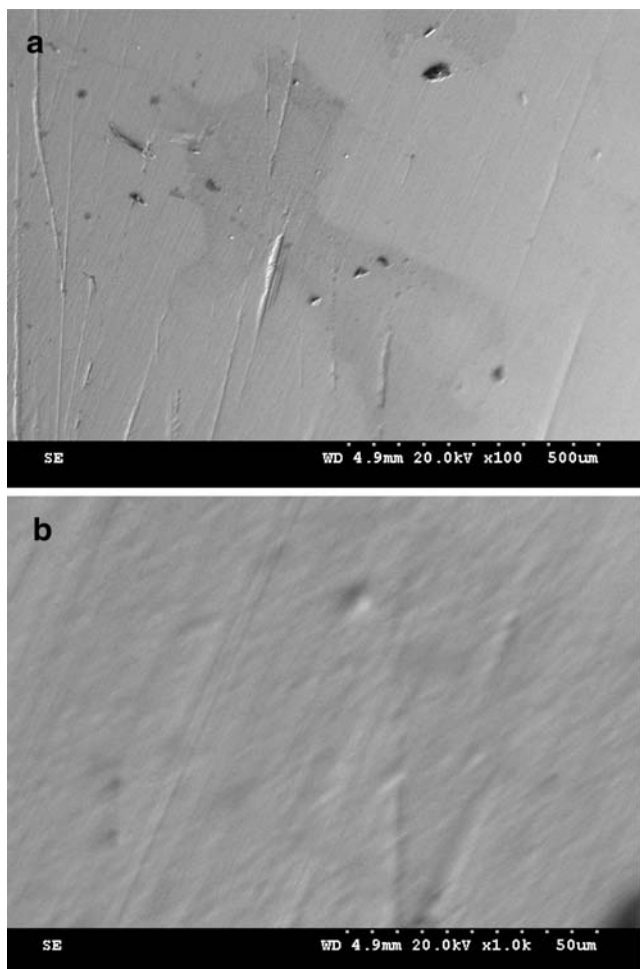
Fig. 8 SEM images of Ni in sulfolane containing 0.2 M TEA.3HF after five cycles between −1.0 and 8.0 V at 40 mVs^{-1}: **a** ×100, **b** ×1.0K

Fig. 9 Multisweep CVs of Ni in sulfolane containing **a** 3.0 M AHF, **b** 5.0 M AHF at 40 mVs^{-1}

medium are shown in Fig. 9a and b, respectively. In this acidic medium, the anodic dissolution process starts at around 0.0 V itself during the first anodic sweep. The anodic current also increases with increasing HF content (Fig. 9a and b). This anodic film formation process by dissolution–precipitation mechanism, however, occurs only during the first anodic polarization sweep. In all subsequent sweeps, significant anodic current due to NiF_3 film growth occurs only beyond 2.5 V. The film growth potential region in acidic sulfolane medium (2.5 V) is, however, lower than the 3.5 V region observed in TEA.3HF medium (compare Figs. 7 and 9). The anodic dissolution charge was also found to be substantially lower (Table 2).

To evaluate the effect of medium acidity, triethylamine in incremental mole ratios was added to 3 M AHF–sulfolane solution, and the voltammetric responses were recorded. Typical voltammograms obtained under these conditions are shown in Fig. 10. In the presence of TEA, the anodic dissolution process initiates only beyond 1.0 V. The shapes of the voltammograms are also different (compare Figs. 9 and 10); with increasing amine content, the anodic
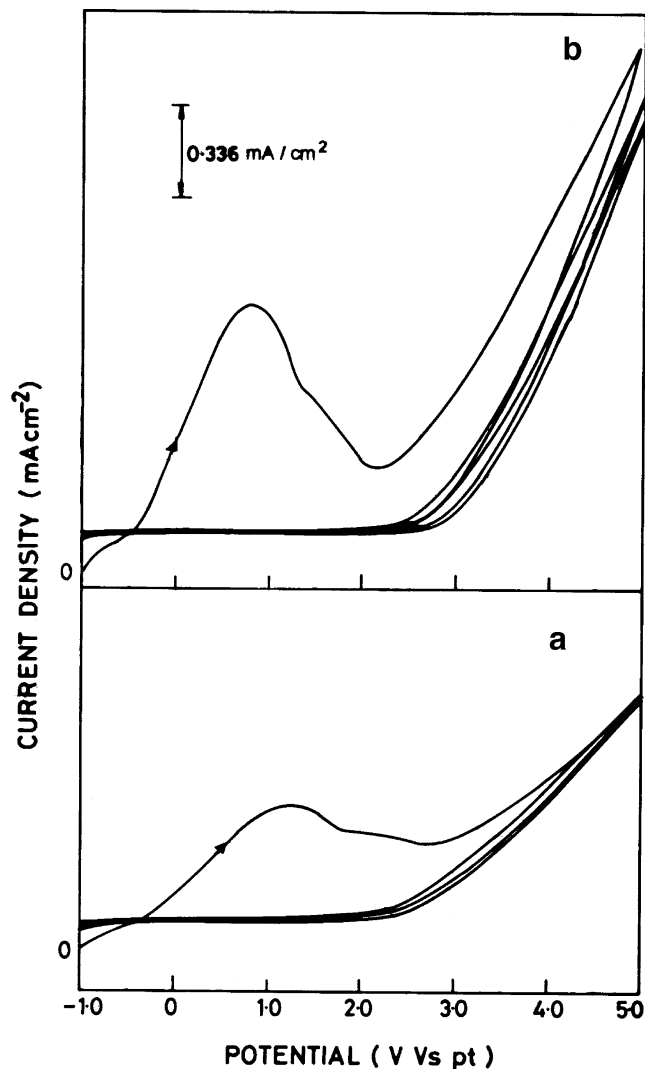
peak current also increased (Fig. 10). The dissolution charge Q obtained under these conditions (Table 2) were, however, substantially lower than the dissolution charges obtained with higher HF content. In general, the solubility of NiF_2

Table 2 Voltametric features of Ni in sulfolane containing 3.0 M AHF and various concentrations of TEA, at 40 mV s^{-1}

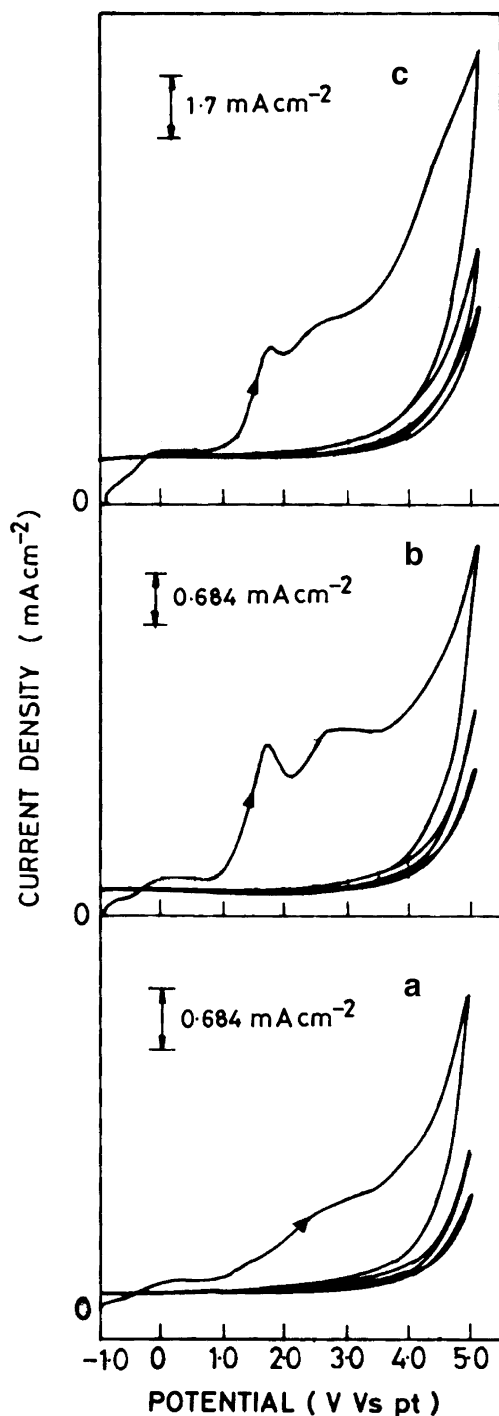| Sl no.	Concentration of TEA (M)	E_{pa} (V)	I_{pa} (mA cm^{-2})	Q (mC cm^{-2})
1	0	1.25	0.42	19.93
2	1.0	3.35	0.62	10.40
3	1.5	1.45	0.34	26.52
		2.50	0.92	
4	3.0	1.65	1.57	49.16
		2.65	1.81	
5	4.5	1.65	3.24	66.07
		2.65	4.26	

Potential range=−1.0 to 5.0 V

Fig. 10 Multisweep CVs of Ni in sulfolane containing 3.0 M AHF and different concentrations of TEA: **a** 1.5 M TEA, **b** 3.0 M TEA, **c** 4.5 M TEA at 40 mVs^{-1}

nucleation growth process. Typical crystal structures obtained during the anodic polarization of Ni in 3 M AHF containing 4.5 M TEA are shown in Fig. 11. Thus, the medium acidity can influence not only the rate of film growth but also the mechanism of film growth.

Conclusions

The present studies indeed shed some light on the possible factors that can positively or negatively influence the electrochemical process. They are of the following:

1. Alkali metal fluorides can enhance the dissolution of electrogenerated NiF$_2$ film and, hence, may not be suitable for enhancing the conductivity of AHF during electrochemical fluorination. For similar reasons, water also cannot be used as conductive additive.
2. All organic molecules that can form conducting electrolyte solutions with AHF may not be suitable for
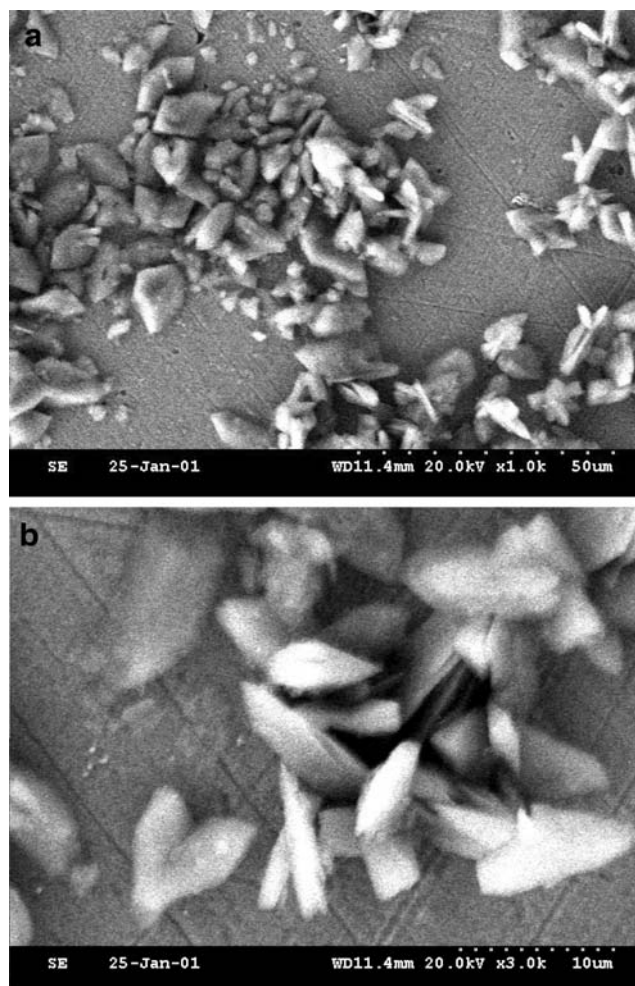

Fig. 11 SEM images of Ni in sulfolane containing 3.0 M AHF and 4.5 M TEA after five cycles between −1.0 and 5.0 V at 40 mVs^{-1}: **a** ×1K, **b** ×3.0K

film decreases with increasing fluoride content in the electrolyte.

SEM revealed another interesting feature of the effect of TEA.HF ratio. When the mole ratio of TEA exceeds that of AHF, the NiF$_2$ formation does not follow the dissolution–precipitation mechanism suggested by Eqs. 1 and 2 above. NiF$_2$ rather grows as well-defined crystals through a

electrochemical perfluorination. Some organic molecules can either dissolve the nickel fluoride film or form thick polymeric layers on nickel electrodes, thus preventing electrochemical perfluorination process.

3. Stronger acidity and higher fluoride ion content in the electrolyte favor formation of a thin compact, stable, and catalytic nickel fluoride film for electrochemical fluorination.

4. Organic compounds such as sulfolane which undergo facile electrochemical fluorination may also be incorporated on the nickel fluoride film, which ensure long-term stability coupled with sustained electrocatalytic activity.

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