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Electrochemistry of metals and semiconductors in fluoride media

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Abstract

The electrochemical surface transformations and diverse applications of a variety of metals and semiconductors in a wide range of fluoride media such as aqueous, non-aqueous media, liquid HF media, room temperature fluoride melts and molten fluoride media with a melting range covering 50–1000 °C are reviewed. Nickel shows excellent corrosion resistance in the absence of water. The anodic performance of this metal in electrochemical perfluorination and NF_3 production is discussed. Compact carbon materials serve as anodes in fluorine generators. In high temperature melts, they perform as consumable anodes. Graphitic carbon undergoes intercalation/de-intercalation process and related battery applications. Cu/CuF_2 couple is a good reference electrode. Pt and vitreous carbon materials are the inert electrodes of choice for electro analytical applications. Electrodeposition of Lithium as a non-dendritic uniform phase is important in Lithium metal based secondary batteries. High temperature fluoride melts are used in electro-deposition of valve metals such as Nb, Ta, and Ti. The stability and decomposition of fluoride complexes in these media are of interest.

1. Introduction

Electrochemistry has played a crucial role in the development of fluorine chemistry. The generation of fluorine itself is achieved by electrolysing KF–2HF melt [1, 2]. A wide variety of perfluorinated organic compounds are still produced by electrolysis in anhydrous HF using nickel anodes [3–6]. This classical field has been reviewed from time to time [7–11]. It is also possible to achieve selective electrochemical fluorination of aromatic compounds in fluoride containing solvent supporting electrolyte system [12–14]. Molten fluoride media are extensively used for the production of valuable metals like Niobium, Tantalum and Titanium [15]. Fluorochemicals also find an important place in the secondary lithium ion battery [16–18]. Graphite fluoride has been a primary battery material for long time. Fluoride media are generally highly corrosive. Though polymeric materials are employed wherever possible, some critical metallic components are still necessary in handling fluorochemicals. Hence the corrosion behaviour of metals in fluoride media is significant [19, 20]. Fluoride media also play a crucial role in the surface treatment of semiconductor materials especially in silicon [21, 22].

The stability of electrode materials, particularly anode materials in fluoride containing electrolytes, is a crucial factor in different electrochemical processes. In fluorine generators, non-graphitic carbon electrodes are employed. In electrochemical perfluorination, nickel is the only electrode which shows high efficiency. In selective electrochemical fluorination processes, Platinum and glassy carbon find predominant use. In high temperature molten salt electrolysis, carbon anodes are essentially used as consumable materials. New dimensionally stable anodes for such media are under active research. Hence a comprehensive understanding of the electrochemical behaviour of a wide variety of metals and semiconductors in fluoride media assumes significance. This is the primary objective of the review.

Apart from electrode materials, fluorine electrochemistry also covers a wide range of electrolyte media. In this review, electrochemical studies in aqueous media on each electrode are introduced. This is followed by studies in non-aqueous and mixed solvent systems. In systems with considerably higher fluoride content, studies in liquid HF medium are initially treated.

2. Anodic behaviour of nickel

2.1. *Aqueous fluoride media*

It is well known that a nickel surface is always covered by an oxide layer in aqueous environment. The oxide film, which is stable in perchlorate and acetate media, was found to dissolve on addition of fluoride ions [23, 24]. The dissolution and corrosion of nickel oxide is uniform in contrast to that of iron, which proceeds through a pitting mechanism [25]. The nature of the oxyfluoride film formed on nickel has also been well characterised [26, 27]. The dissolution of nickel is found to increase with HF concentration up to 50%. Beyond this point, further dissolution decreases with HF content suggesting the involvement of HF as well as water in dissolving Ni^{2+} species [28]. The fluoride ion induced breakdown of passivity of nickel is found to be substantially different from that of chloride and bromide ions [29].

A careful evaluation of the anodic dissolution behaviour of a freshly generated nickel surface without an oxide layer has also been reported. As expected, the anodic dissolution of an oxide free nickel surface is found to be significantly higher than that of an oxide covered Ni surface [30]. In a recent cyclic voltammetric study, two distinct dissolution processes were observed on nickel [31]. In addition to the first dissolution peak observed at low HF concentrations, a distinct second anodic peak was observed at lower potentials and at higher HF concentrations. These anodic peaks were attributed to the direct dissolution of nickel surface and oxide covered surface fractions Figure 1. In aqueous acidic solutions, alkali metal cations were found to influence the anodic dissolution behaviour to a significant extent. The anodic dissolution of nickel in perchloric acid containing LiF for example was found to be substantially higher, when compared to other alkali metal fluorides [32].

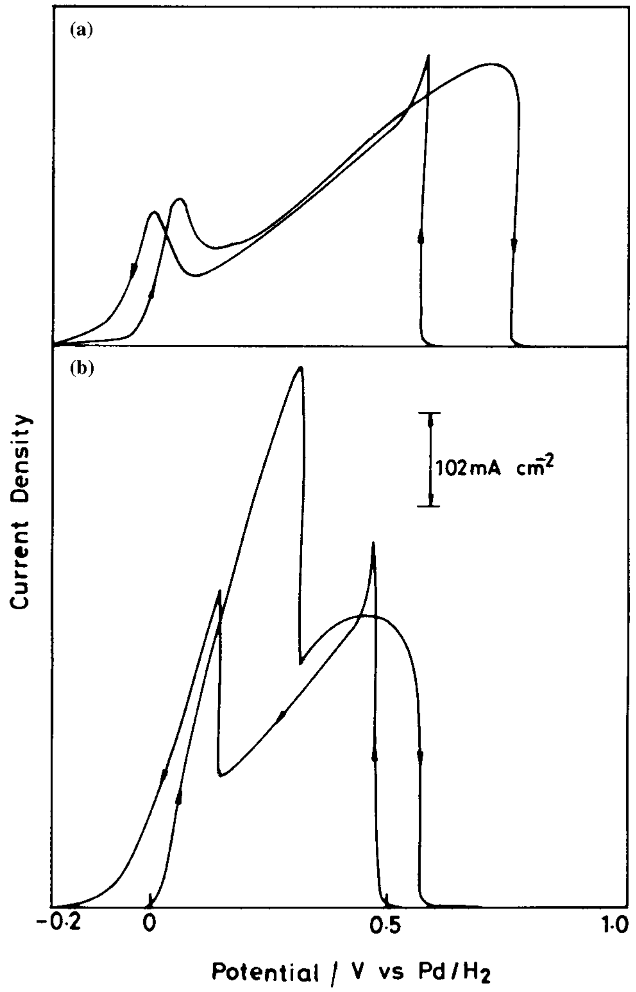

Fig. 1. Cyclic Voltammograms of Ni in HF (a) 10 M (b) 20 M at 10 mV s^{-1}.

2.2. *Non-aqueous fluoride media*

In aprotic solvents like acetonitrile, Ni shows considerable passivity in acidic as well as in neutral media in the absence of fluoride ions [33, 34]. The reactivity of the fluoride ion is fairly high in acetonitrile [35, 36] as well as in acetonitrile-water mixtures [37]. Acetonitrile is also one of the organic compounds, which undergoes electrochemical perfluorination on nickel electrodes in anhydrous hydrogen fluoride (AHF) [38, 39]. Cyclic voltammetric studies in the acetonitrile–HF and acetonitrile–H_2O systems showed the formation of a passive layer and film growth [40, 41].

On adding triethylamine to the acetonitrile–HF system, the voltammetric responses change significantly. In basic fluoride media, anodic dissolution is suppressed and film growth proceeds through a nucleative process [42]. The formation of a passive NiF_2 layer on nickel in acetonitrile indicates that nickel cannot be used for selective electrochemical fluorination, which involves direct oxidation of organic compounds in the lower potential region (<2 V vs SCE).

The anodic behaviour of nickel in propylene carbonate (PC) medium was investigated in connection with the search for cathode grid materials for lithium ion batteries. In perchlorate media, the PC solvent undergoes oxidation on nickel at much lower potentials (4.2 V vs Li/Li^+) due to the catalytic influence of the oxide surface [43]. In the presence of fluoride containing electrolytes such as $LiPF_6$ and $LiASF_6$, the nickel surface is covered with a fluoride layer and hence the oxidation of PC solvent is suppressed [44]. Thus the potential window of the secondary battery is widened.

2.3. *Liquid HF medium*

Pure nickel is one of the least corrosive metals in AHF [45]. Attempts have been made to classify different metals according to their stability in liquid HF [45–47]. Nickel falls among the most stable group of metals. Correlation between physicochemical properties of metal fluorides and their stability in liquid HF has also been attempted [48, 49]. In contrast to Pt and glassy carbon electrodes, the cyclic voltammograms of nickel in liquid HF exhibit a distinct peak around 0.0 V due to the formation of a NiF_2 film [50]. Beyond 3.0 V, a further oxidation current with very high Tafel slope is noticed [51]. It is now generally believed that the oxidation of NiF_2 to high valent nickel fluorides such as NiF_3 and NiF_4 may occur in this potential region.

This film also contains active fluorine [52] which fluorinates the organic compounds [53]. Electrochemical oxidation of organic compounds on these oxidised NiF_2 films is found to be determined by the rate of adsorption/desorption of the organic compound [54, 55].

Even trace levels of water were found to enhance the passivity of Ni in AHF [45, 47]. 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 [45, 47]. ESCA studies under these conditions have confirmed the presence of a thin oxide layer between the Ni substrate and the NiF_2 film [52]. When the H_2O content exceeds 2%, anodic polarisation in AHF leads to the formation of OF_2 [47].

2.4. *Molten fluoride media*

A wide variety of molten fluoride systems with widely different operating temperatures have been employed in fluorine electrochemistry. Organic fluorides such as tetraalkylammoniumfluorides·nHF (TEAF·nHF) systems are essentially room temperature molten electrolytes. Different alkali metal fluorides mixed with HF are used as low temperature melts for F_2 generation and NF_3 production. Melts with still higher operating temperatures are employed in valve metal deposition processes. Cryolite melts (Na_3 AlF_6) are used in aluminium production. A typical set of fluoride melts with their corresponding operating temperatures and applications are summarised in Table 1.

TEAF·nHF and trialkylamine·nHF (TEA·nHF) are the current electrolytes of choice for selective electrochemical fluorination processes. However, very little attention has been paid to the study of the electrochemical behaviour of nickel in this melt. Tasaka et al. have observed similarity between the electrochemical behaviour of this melt with those of other alkali metal fluoride HF melts. Addition of CsF was found to enhance the formation of high valent nickel fluorides [56]. CsF–HF electrolyte can be operated at around 50 °C [57].

The mechanism of formation of NiF_2 film on nickel in KF–2HF was studied using polarisation and impedance measurements [58, 59]. Conway et al have studied the nature and stability of NiF_2 films on nickel electrodes under conditions similar to fluorine generation cells [60]. The anodic polarisation behaviour of steel [61], Cu [60], and monel [62] electrodes has also been compared.

When carbon anodes were employed for the production of NF_3 in molten NH_4F–HF, the NF_3 gas produced was invariably contaminated with CF_4 formed by the decomposition of the carbon anode. Nickel was found to be quite efficient for this process in terms of purity of NF_3 produced [63]. However, considerable loss of the Ni anode due to dissolution in alkali fluoride media is a limitation of the anode materials. Comparison of different metals and alloys indicated that nickel is the best electrode material [64]. Addition of CsF was found to improve the NF_3 yield and reduce the volatility of the electrolyte medium [65]. The composition of nickel oxide, nickel fluoride, high valent nickel oxides and oxy fluorides were also modified by CsF addition [66].

The effect of other alkali metal fluorides [67, 68] and trace level impurities like Ni^{2+} and Fe^{3+} species, which may be generated during electrolysis [69], on the overall efficiency of NF_3 production was also evaluated. Trace level water was also found to influence the composition of oxyfluoride films on nickel and the current efficiency of NF_3 production [70]. The efficiency of nickel was also compared with that of the lithium fluoride impregnated carbon anode [71]. The surface film may also be modified by heat treatment of the electrode material before polarisation [72].

In general, Tasaka et al. characterised four distinct regions in the polarisation curve of Ni in molten ammonium fluoride–HF media. A typical voltammogram is presented in Figure 2. These regions include (a) nickel dissolution region (0.0–1.0 V) (b) nickel oxide based passive region (1.0–4.0 V) (c) high valent nickel oxide and oxyfluoride formation region (4.0–6.0 V) (d) fluorine evolution region (6.0–9.0 V). NF_3 generation proceeds in the oxyfluoride formation region through the intermediates of high valent nickel fluorides.

Table 1. A typical set of fluorine melts with their corresponding operating temperatures/°C

S.No.	Molten media	Operating temperature/°C	Application
1	Trialkylamine.nHF and tetra alkyl ammonium fluoride.nhf	Room temperature	Selective fluorination
2	CsF–HF	50	Basic studies
3	KF–2HF	85	F_2 generation. Electro-chemical fluorination using carbon anodes
4	NH_4F–2HF	100	NF_3 Production
5	KHF_2	250	F_2 generation (old process)
6	LiF–NaF–KF	750	Valve metal deposition
7	LiF–NaF	780	Metal deposition
8	NaF–AlF_3–Al_2O_3	977	Aluminium production
9	NaF	1025	Basic studies

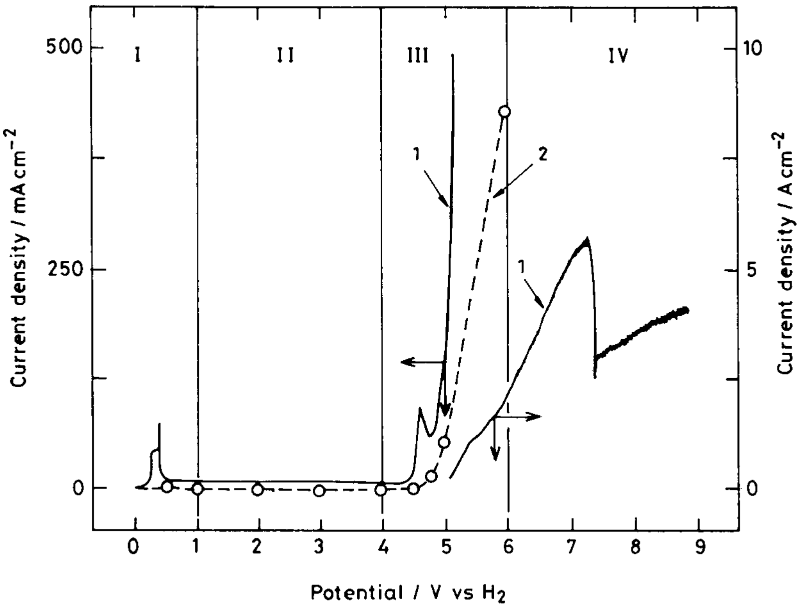

Fig. 2. Polarisation curves of Nickel anode in a well dehydrated melt of NH_4F–2HF at 100 °C. Curve 1=Potential sweep curve at 5 mV s^{-1}; Curve 2=Potentiostatic polarisation curve.

The voltammetric measurements of Ni^{2+} species in LiF–NaF–KF melt eutectic at 600 °C enabled the redox potential of Ni^{2+}/Ni couple to be measured in this fluoride melt [73].

3. Anodic behaviour of carbon

3.1. *Aqueous and non-aqueous fluoride media*

A wide variety of carbon materials such as coke, hard carbon, carbon black, natural graphite, highly oriented pyrolitic graphite and glassy carbon are employed in electrochemistry. For the present purpose, it is worthwhile to broadly classify the carbon anode materials as graphitic and non-graphitic materials.

In aqueous fluoride media, graphite electrodes exhibit anion intercalation during anodic polarisation. The stability and reactivity of such intercalated graphite materials have been studied widely [74].

In 47% HF solutions, covalent graphite fluorides, as well as higher stages of graphite intercalation compounds, have been obtained [75]. In non-aqueous solvents, graphite can also be used for cation intercalation during cathodic polarisation [76]. Surface fluorination of graphite by chemical or electrochemical methods improves the intercalation/de-intercalation behaviour [77, 78]. Fluorinated solvent supporting electrolyte systems are also found to enhance the Li ion intercalation/de-intercalation behaviour [79, 80, 81]. Graphite intercalation chemistry by itself is an extensive area of research. Review papers including its applications in Li ion battery are available [82]. Li ion intercalation is also possible in a wide variety of non-graphitic materials. Among the carbon materials evaluated for Li ion intercalation, graphite materials with relatively high surface area such as graphite fibres and mesocarbon micro beads (MCMB) exhibit excellent intercalation efficiency and life cycle [83].

Glassy carbon electrodes, pyrolitic graphite electrodes and diamond film electrodes are highly stable in fluoride media. Generally, they do not undergo surface damage. Diamond coated electrodes have been shown to exhibit good stability during continuous polarisation in fluoride media [84]. Even glassy carbon and polypropylene composite graphite electrodes (CPP) can be used in voltammetric measurements to study a wide variety of electrochemical processes [85]. The solvent used, however, can influence the quantitative voltammetric responses, the concentration and the nature of fluorine based supporting electrolyte [86]. Hence caution must be exercised when these electrodes are used in aqueous and non-aqueous solvents containing supporting electrolyte anions such as BF_4^-, ASF_6^- and PF_6^-.

3.2. *KF–2HF melts*

Fluorine evolution generally occurs at around 5.0–6.0 V on compact carbon anodes in KF–2HF melts. This implies significantly high over voltage for fluorine evolution. This has been classically attributed to the presence of a fluoride film on the carbon surface under galvanostatic operating conditions. The cell voltage can suddenly rise followed by complete break down of electrolysis. This is conventionally termed the ‘Anode effect’. A summary of early studies on this subject is available [87, 88].

Recent studies have shown that the film formed, especially at high anodic potentials, can be highly inhibiting towards fluorine generation [89]. Two types of fluoride films have long been identified. A thin C–F film formed at low anodic potentials does not inhibit further electron transfer or fluorine evolution to a great extent. A thick passive layer formed on some parts of the electrode surface is mainly responsible for the passivation or anodic effect [90]. Another inhibiting effect in fluorine generation is the formation of fluorine gas bubbles on the hydrophobic C–F layers of carbon electrodes [91, 92]. The three factors namely the C–F film, the passive layer, gas bubbles and their interplay has made the study of these films more challenging.

Early studies indicated only a very small reduction in the electron transfer rate due to the presence of thin C–F surface films. This was confirmed by the voltammetric study of carbon electrodes previously polarised in KF–2HF melt using simple redox systems in aqueous solutions [93, 94].

Very recent investigations using additional surface analytical tools have indicated that under appropriate conditions the surface film mainly consists of graphite intercalation compounds of fluoride, which exhibit good electronic conductivity and, hence, sustain the fluorine evolution reaction. The fraction of surface covered by insulating covalent CF film is low under normal polarisation conditions [95, 96]. However, if water is present in the KF–2HF melt during polarisation, the carbon electrode develops a thick or a passivating film [97].

The hydrophobicity and passive film formation effects can be reduced significantly by impregnating the carbon electrode prior to polarisation with inorganic salts such as AlF_3/NaF mixture [98] or simply AlF_3 itself [99]. Prior chemical fluorination of carbon electrodes with fluorine gas leads to the formation of covalently bonded graphite fluorides, which are highly inhibiting. However, if a nickel-doped carbon is employed, more ionic graphite intercalation compounds are formed. These films, along with NiF_2 layers formed by nickel doping, maintain good conductivity, and the fluorine gas bubbles are also detached easily from the electrode surface [100]. A similar favourable effect is also noticed with aluminium doped carbon electrodes [101]. A novel method of preparation using isotropic carbon with high permeability is also claimed to exhibit high efficiency without anode effects in fluorine cells [102].

3.3. *Other molten fluorides*

Electrochemical behaviour of carbon anodes in other molten fluoride systems has also been investigated. In a comparative study of carbon anodes in different fluoride media, it was found that the activation energy for $(CF)_x$ film decomposition depended on the melt employed. The activation energy in LiF–NaF–KF melt was found to be much higher than in other low temperature melts containing HF. A typical CV obtained under these conditions is presented in Figure 3. The dissolution of carbon in HF containing melts was also found to be higher [103].

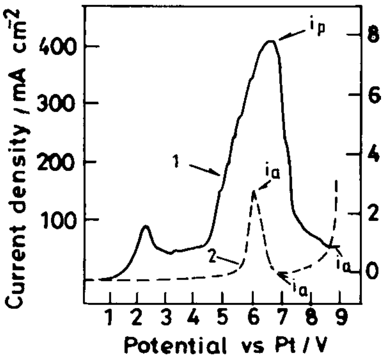

Fig. 3. Typical cyclic voltammograms on carbon in molten fluoride at 200 mV s^{-1}. Electrolyte KF–2HF; temperature 80 °C; anode amorphous carbon. (1) First run and (2) 40th run.

The anodic behaviour of carbon anodes in cryolite melts (Na_3AlF_6) was investigated using cyclic voltammetry [104] and galvanostatic polarisation techniques [105, 106]. Three to four transition times were observed during galvanostatic polarisation which depended on the nature of the carbon material, the electrolyte employed and particularly on the operating temperature of the melt. On porous electrodes, pore flooding is observed at higher current densities.

The anodic processes on both compact and porous graphite materials have been investigated. Again the nature of the electrode material has a significant influence on the type of film formed, their decomposition and the gas evolution reactions [107, 108]. Even in pure LiF electrolyte at 1161 K a graphite electrode exhibits excellent electrochemical stability. The voltammetric behaviour of Lithium sulfide in this medium exhibits a reversible diffusion controlled response [109].

4. Anodic behaviour of other metals

4.1. *Aluminium*

In aqueous chloride solutions, addition of fluoride ions induces aluminium dissolution at substantially lower potentials. In mixed fluoride–chloride electrolytes, the passivation current also depends on the fluoride ion concentration [110]. Fluoride ions are also found to influence porous aluminium oxide formation in organic acid media [111]. The corrosion of aluminium can be substantially suppressed by the addition of imide salts of Li–Tri fluoromethane sulfonate and employing $LiPF_6$ as the additives [112]. Under these conditions aluminium can be used as a cathode grid material in lithium ion batteries.

PC solvent exhibits good stability on aluminium anodes in different supporting electrolytes such as $LiClO_4$, $LiBF_4$ and $LiAsF_6$ [113]. Aluminium dissolution in cryolite–alumina melt has received some attention [114]. A novel ring disc electrode containing a molybdenum disc and a gold ring, which can be operated in cryolite–alumina and other higher temperature melts, has been developed [115].

4.2. *Magnesium*

In aqueous chloride and fluoride media, anodic polarisation of magnesium leads to the formation of chloride and fluoride salt layers on the electrode surface [116]. The properties of chloride and fluoride films are similar [117]. Magnesium also forms a porous structure consisting of a compact oxyhydroxide inner layer and a porous fluoride outer layer. Magnesium shows some similarity to the well-known porous aluminium oxide layers [118].

The anodic behaviour of magnesium in KF–2HF melt has been studied using impedance spectroscopy. The anodic reaction sequence leading to MgF_2 film formation has also been established [119]. A comparative study of the corrosion behaviour of magnesium and copper in KF–2HF shows that magnesium is more stable in low temperature melts with higher HF content. For high temperature melts containing lower concentrations of HF, Cu is found to be less corrosive [120].

4.3. *Copper*

In contrast to the electrode materials discussed so far, the copper fluoride film formed on copper electrode in liquid HF can be reversibly reduced. Hence this electrode is generally recommended as a reference electrode in fluoride media where the solubility of CuF_2 is substantially lower [121]. The Cu/CuF_2 system is also reversible in KF–2HF melt. Typical cyclic voltammograms of Cu obtained in this medium are shown in Figure 4. The reducible CuF_2 film on Cu, a passive NiF_2 film on Ni under identical conditions is also compared. In NH_4HF_2–HF, a Cu surface was found to contain an adsorbed inner oxide layer along with a fluoride film [122].

4.4. *Silver*

The anodic AgF film formed on silver is easily reducible to silver, as in the case of Cu. Recently, this electrochemical process was investigated in TEA·3HF and repeated potential cycling in this medium leads to an increase in the roughness of the Ag surface. Transport properties and decomposition potentials [123, 124] and the anodic behaviour of Ag in this medium are also covered [125]. The high frequency resistivity of the AgF film during potential sweeping was also measured [126]. Other metals such as Zn, Cd, and Hg in the same room temperature system were also studied [127].

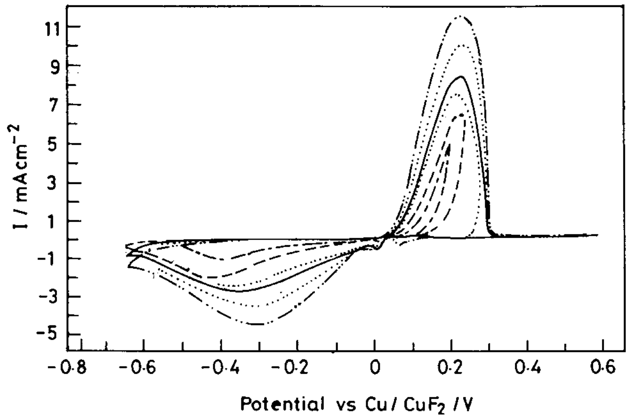

Fig. 4. Cyclic Voltammograms with different anodic limit potentials (E_1) for the Cu in KF–2HF melt at 85 °C. Inset for low limits of 10, 30 and 50 mV s^{-1} vs Cu/CuF_2. E_1: (…_ …_.) 0.200 V; (…) 0.240 V; (…) 0.280 V; (____) 0.340 V; (…) 0.400 V; and (.-.-.-) 0.600 V

4.5. *Platinum*

Platinum serves as an ideal inert electrode in both aqueous and non-aqueous fluoride media. In this respect, Pt is similar to GC [86]. A large number of voltammetric investigations have been carried out in fluoride containing acetonitrile (CH_3CN) medium in early work on selective fluorination [14, 128]. In recent studies, this electrode is also invariably used in $R_4NF.nHF$ [129] as well as in $R_3NF.nHF$ [130]. An interesting voltammetric study of the ferricyanide-ferrocyanide redox couple in solid $R_4NF.nHF$ medium (62–80 K) exhibits a simple diffusion controlled response. The redox reaction proceeds as a simple diffusion controlled process [131]. In liquid HF, Pt also behaves as an inert electrode like glassy carbon, at least well beyond 2.0 V [50]. The fluorine evolution reaction is found to proceed through the oxidative decomposition of Platinum fluoride films [132].

Voltammetric studies of the oxidation of a number of organic compounds in liquid HF have also been reported [133, 134]. The oxidation peak occurs, in general, at significantly lower potentials in liquid HF media. Otherwise, the voltammetric responses on the inert platinum surface are similar to those in other conventional media.

5. Deposition of metals and carbon

Electrodeposition of aluminium and a number of valve metals is a vast field of interest in electrochemistry. Since these processes involve the use of fluoride melts, the role of surface fluoride films on electrodes during electrodeposition is significant. This field has been studied extensively over the past several decades.

5.1. *Lithium*

Electrodeposition of Li from non-aqueous electrolytes like PC assumes great importance from the point of view of Li metal-based secondary batteries. In recent work, Kanamura et al. have found that a small quantity of HF in $PC/LiClO_4$ electrolyte can improve the smoothness of Li deposits significantly. This is probably achieved by selective etching of dendritic Li sites by HF [135]. Similar behaviour was observed in other related carbonate solvents and other supporting electrolyte salts. The prevention of dendritic growth is mainly controlled by the HF content rather than other components [136].

Instead of HF, $(C_2H_5)_4NF(HF)_4$ may also be used as the HF source [137]. This study has also been extended to the evaluation of initial films present on thin Li sheets and the role of HF on their deposition and dissolution behaviour [138, 139]. These studies reveal the presence of 2–5 nm thin Li_2O/LiF bilayer, which ensures better uniformity of Li deposition. Beyond 45 cycles, however, the film thickness increases substantially and the deposit again becomes rough and dendritic.

5.2. *Niobium*

Heavy metals like niobium, titanium, and tantalum are electrodeposited primarily from (LiF–NaF) in the temperature range 700–800 °C.The electrodeposition of niobium, for example, is found to proceed through an instantaneous nucleation growth process. The fluoride complex of niobium NbF_7 undergoes electroreduction in two steps through an Nb^{4+} intermediate stage [140]. Apart from conventional electroanalytical techniques [140], new techniques like square wave voltammetry have also been used for studying this system [141].

The efficiency of electrodeposition of niobium depends very much on the electrolyte purity, especially on complete removal of oxide impurities. The presence of oxide leads to substrate passivation and a drop in overall deposition efficiency [142]. A similar influence of oxide impurities was also observed in K_2NbF_7, NaCl–KCl melts [143].

Nickel–niobium alloy can be obtained by electrodeposition of niobium on nickel in $NaF–CaF_2–K_2NbF_7$ melt. This alloy is of interest as an electrode material in molten carbonate fuel cells [144]. Niobium boride may also be obtained through similar electrodeposition processes using fluoborate salts [145].

5.3. *Titanium*

Electrodeposition of titanium from fluoride media is another process which has received considerable attention. The intermediate complexes involved during the electro reduction of K_2TiF_6 species have been thermodynamically assessed [146]. Electrodeposition using pulsed current leads to more uniform and smooth deposits [147].

Electro-deposition of titanium may also be achieved in chloride melts [148, 149]. However, in fluoride melts containing $NaF–NaBF_4$, it is possible to deposit titanium boride (TiB_2) in a single step [149, 150]. Electrodeposition of titanium boride is carried out at constant potential [150]. Electro-deposition at more negative potential leads to rough deposits. It is also interesting to note that in these melts electrodeposition of Boron from KBF_4 may also be achieved [151].

5.4. *Aluminium*

In cryolite–alumina melts, there has been little work on the cathodic deposition process. Sintered TiB_2 electrodes show good wettability and also some energy saving in the aluminium deposition process [152].

The anodic processes have received slightly greater attention. The dissolved aluminium species seem to form a layer on the carbon anodes, which improves the wettability of the anode surface itself [114, 153].

5.5. *Carbon*

The sequence of complex electrochemical reactions on graphite and other carbon materials has received considerable attention [108, 154, 155] using fast sweep cyclic voltammetry. Amorphous carbon materials may also be electrodeposited from molten LiF–NaF medium. Electro reduction of CO_3^{2-} carbonate ions (as sodium carbonate) in this medium provides very thin amorphous carbon layers on the cathode substrate. Electrochemical and surface analytical techniques have been used to characterise these deposits [156, 157]. Five distinct oxidation peaks corresponding to the formation of different oxidation products namely O_2, CO_2, COF_2, CF_4 and F_2 were identified [158].

6. Anodic behaviour of silicon in fluoride media

Both n-type and p-type silicon undergoes anodic dissolution in fluoride medium through anodic oxidation and photo oxidation respectively, leading to the formation of a porous Si layer. The detailed mechanism of dissolution, formation of Si–H, Si–F and Si–OH bond, pore distribution, film growth and film passivation have been discussed in the early literature [159–162]. In recent times, however, porous silicon promises extensive use in opto-electronics involving photoluminescence and sensor applications. This has led to a surge of interest in this field.

The current status in the mechanism of porous film formation has also been reviewed [163]. Only a brief outline of recent studies is presented [164, 165].

6.1. *Anodic dissolution*

The anodic dissolution of P–Si is similar to the dissolution of titanium metal [166] in aqueous fluoride media. The anodic dissolution, for example, proceeds through chemical dissolution of oxide layers by the complete dissolution of Si atoms in a four-electron oxidation process. However, after removal of one or two electrons, the Si intermediate species can undergo chemical dissolution by reacting with HF, resulting in hydrogen gas evolution. In photo induced dissolution processes, the quantum yield can thus be much greater than one [167]. The detailed sequence of chemical and electrochemical steps leading to such phenomena has received considerable attention.

STM [168] and other *in situ* techniques have been used to identify islands of oxide layers [169]. By tuning the HF content of mixtures containing oxidizing agents such as hydrogen peroxide and nitric oxide, the oxide layer thickness for wafer bonding can be controlled in the region of 1 nm [170].

Two types of oxide layer, namely a porous external layer and a more compact oxide layer at the Si-oxide interface generally exist [171]. At higher anodic potentials, formation and breakdown of thick oxide layers leading to oscillatory phenomena occur [169, 172]. Models for the oxide formation and dissolution have been proposed and verified [173]. The substantial stresses generated during the formation of oxide layers during anodic etching have been measured by *in situ* techniques. The mechanism of stress release during subsequent thermal processing has been correlated with the modifications of hydrogen bonding characteristics of oxide layers [174, 175].

The chemical dissolution of Si in fluoride media is essentially a corrosion process. The corrosion current in the anodic and cathodic polarisation behaviour can be evaluated independently [176]. In dilute HF solutions, uniform etching of p-type, as well as n-type semiconductors, has been achieved [177]. Alkali metal cations can influence the dissolution process significantly [178].

Anodic dissolution of Si may also be achieved in non-aqueous media like CH_3CN–HF. The pore diameter in this medium is generally much larger when compared to aqueous media [179]. The pores are not cross-linked. The anodic dissolution rate and pore structure also depend on the orientation of Si single crystals. In the case of Si (III), only pits are formed exposing the Si (III) plane intact [180].

Apart from CH_3CN, non-aqueous solvents like PC and Dimethylformamide (DMF) have also been employed [181]. HF need not necessarily be the fluoride source. Tetraethylammonium tetra fluoborate and other related fluoride salts such as AsF_6^-, PF_6^- and BF_4^- have also been successfully employed [181, 182]. The significant difference in the porous structures obtained from non-aqueous media may find new applications.

6.2. *Porous structure*

In contrast to the pores formed in non-aqueous media, very fine cross-linked nanopores are generally formed from dilute aqueous fluoride electrolytes [183]. The initially generated pits in the oxide layer form the porous structure. The pits in the form of inverted pyramids proceed into the bulk material and passive Si–H bonds protect the pore walls. The pore formation mechanism on amorphous Si is also similar [184]. Ammonium fluoride solution in the pH range 3.3–3.8 is suitable for nanoporous film formation and other operating parameters such as current density, anodic potential and temperature may also influence the pore density and pore structure [185]. Pulse anodisation of Si has also been reported [186].

Macro porous Si films can be obtained by an appropriate choice of solvent, supporting electrolyte system and doping level of semiconductors. Apart from non-aqueous solvents [179–182], ethanolic HF media can also be used for macropore formation [187]. If the resistivity of Si is very high, the anodic dissolution is mainly controlled by slow carrier diffusion leading to the formation of macropores [188]. The pore size is thus determined by the relative resistivity of the electrode and electrolyte [189]. A pore formation model, based on this observation, has been proposed and experimentally verified [190].

A large number of studies has been attempted to generate evidence for specific mechanisms [163] of porous silicon formation. Evidence for the passivation of pore walls by Si–H bond formation was provided by studies in solutions containing D_2O [191]. The etching rate was found to be directly correlated to the concentration of oxide sites for film growth [192]. On a uniform Si surface nucleation of pores has been shown to be the rate-determining step [193].

The role of carrier diffusion in macropore formation has received attention [194]. Nano-sized Si filaments may also be formed during anodic polarisation of Si. The models for such filament growth by interconnection of pores, along with the experimental conditions for obtaining such filaments, have also been reported [195].

A wide variety of techniques have also been used for characterising the porous Si films. Apart from polarisation measurements [196], a number of other *in situ* spectroscopic methods [197] have been used for characterising such films. At present the most important characteristics is the luminescent property of the porous Si matrix, the nature of wet etching [198, 199] and the type of cationic and anionic surfactants employed [200]. The charge transport and the carrier density in the space charge region of the semiconductor [201] can significantly influence the photo luminescent behaviour of the porous Si. Material characterisation from this angle is of great current interest.

6.3. *Metal deposition*

Just like metal and carbon substrates, semiconductor materials may also be employed as substrates for the electrodeposition of metals. The fundamental principles of electrodeposition, including the thermodynamics and kinetics, however, involve the additional influence of semiconductor properties such as band gap, fermi level, and surface state, space charge and carrier concentration. Brief accounts dealing with these concepts are available [164, 202].

In fluoride media, the deposition of metals on to porous Si surfaces occurs primarily through an electroless deposition process when the aqueous fluoride media contains reducible metal cations like platinum. They accept the electrons released by dissolving Si and are deposited on the porous silicon matrix [202]. Pt deposition, in fact, results in the formation of Pt silicide intermetallic compounds [203]. The porous Si–Pd matrix formed by a similar process can be further employed as a substrate for the electroless deposition of tin. Using this process a thick and stable tin deposits can be obtained [204]. The physicochemical properties of gold deposited on porous Si by a similar procedure have also been described [205]. The pH of the electrolyte medium has a significant effect on the electroless deposition of Ni on porous Si. Though the deposition of Ni was not observed in acidic pH, at a pH around 8.0, the hydroxide or oxide intermediates assist in electroless deposition of Nickel [206].

The potential application of metal deposited on to porous silicon by this procedure, as an electronic contact, is obvious. The widely used electronic contact, namely copper, has naturally received considerable attention in this area. Electroless deposition of Cu on porous Si has been achieved in dilute HF solution containing copper sulfate [207]. Depending on the relative concentration of fluoride ions and Cu^{2+} ions, the electroless deposition of Cu can either enhance Si etching [208] or inhibit further etching of Si by blocking the edge sites [209]. The mechanistic aspects have also received some attention.

7. Conclusions and scope

Despite a wide range of electrolyte media being covered, it is interesting to note that most metals and carbon electrodes behave similarly in different media. For example Ni behaves as a passive electrode in non-aqueous fluoride solutions, liquid HF, molten KF–2HF and molten NH_4HF_2 systems. Cu behaves as a reversible electrode with the Cu/CuF_2 redox film showing stability in a number of electrolyte solutions. Pt serves as an inert electrode in most media. Carbon is an interesting substrate. In fact, compact carbon electrodes serve as inert electrodes at low anodic potentials. Passivity effects predominate at potentials well beyond 4.0 V.

The electrochemistry of many of these metals and carbon electrodes appears to be different in aqueous solutions. Many metals undergo substantial dissolution in aqueous media. In highly concentrated HF aqueous solutions, carbon also undergoes reversible intercalation/de-intercalation processes and irreversible surface damage.

The anodic dissolution of Si in aqueous fluoride media may also be viewed as an extension of such dissolution and instability. However, the dissolution process offers an interesting porous silicon matrix with potential applications in the field of opto-electronics and sensors.

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