Effect of HF Concentration on Anodic Dissolution of Titanium

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Anodic dissolution of Ti metal in varying concentrations of hydrofluoric acid (10–100 mM HF) was investigated using potentiodynamic polarization and electrochemical impedance spectroscopy. Polarization curves obtained at all concentrations of HF solution showed that current initially rises with potential, and decreases at higher potentials. Complex plane plot of the impedance spectra of Ti dissolution in 25 and 50 mM HF solutions exhibited three capacitive loops in the active region and a capacitive behavior with negative resistance in the passive region. The surface was characterized using X-ray photoelectron spectroscopy. A four step mechanism with chemical and electrochemical dissolution steps was employed to model Ti dissolution. The analysis shows that the simulated results match the polarization trends satisfactorily in all the solutions investigated. The model predicts that HF₂⁻ and remaining HF are the species that influence chemical and electrochemical dissolution steps respectively. The estimates of surface coverage values of the adsorbed species showed that with increasing over potential, the metal surface was progressively covered with oxide film, while an increase in nominal HF concentration leads to a decrease in fractional surface coverage.

Titanium is used as engineering material in medical implants, aerospace applications, and in industrial applications by virtue of its low density, high strength and high corrosion resistance.1 Due to the presence of a tenacious passive oxide layer on its surface, Ti is highly corrosion resistant in most of the harsh chemical environments.2,3 However, the oxide layer readily dissolves in acidic fluoride medium. The anodic dissolution phenomena of Ti in fluoride media is important not only in corrosion but also in several technologies and industrial applications such as pickling of Ti,4 manufacture of Ti based automobile parts,5 and formation of self-organized TiO₂ nano tubes.2,3,6 Ti dissolution in fluoride medium has been studied extensively, and its dissolution in acidic fluoride media depends mainly on the concentrations of various species formed by HF dissolution, pH of the solution and temperature.6,8–10 Straumanis and Chen measured the volume of hydrogen produced during Ti dissolution in HF and proposed that the reaction order is 0.66 when the HF concentration is below 0.2 N and unity when it is more than 0.2 N.8 Ti dissolution in a solution of 0.1 N HF + 1 M HCl was measured at various temperatures, and the order was reported to be 0.76 while the activation energy was 6.9 kcal/mol.8,10 HF, in combination with HNO₃ and a few other additives such as acetic acid, H₂PO₄, dodecyl benzene sulfonic acid, carbamide, sodium benzoate or sodium nitrate, have been used for chemical milling of Ti.11–15 In Ti pickling, addition of nitric acid is used to prevent hydride formation at the metal surface, which can lead to hydrogen embrittlement.16 Ti dissolution in HF + HNO₃ solution is modeled using a mechanistic approach with Ti₃⁺ and TiO₂ as intermediate species.16

The effect of pH on Ti dissolution, mainly in the passive region, has been published in the literature.15–17 Recently, Wang et al. have reported the effect of dissolved oxygen (DO) on the corrosion of pure Ti in acidic fluoride medium using electrochemical methods.18 They have observed that DO content decreased the anodic current density and showed negligible effect on the cathodic current. Previous studies on potentiodynamic polarization of Ti dissolution in acidic fluoride media indicate the existence of three regimes of dissolution viz., active, passive and transpassive.6,8,19 Active region occurs at low overpotential where the current increases with potential. In the passive region, the current decreases steeply with potential due to surface passivation. This is followed by the transpassive region where the current shows a slight increase with potential due to dissolution of Ti through the passive film. EIS analysis of Ti dissolution kinetics in media containing fluoride ions in the transpassive region have been reported previously.6,8,12,17,21–23 In the active and passive regions, the dissolution kinetics of Ti in 100 mM HF was described by Fasmin et al.24 However the impedance measurement and analysis were performed at a fixed concentration (100 mM) of HF.24 One of the limitations of the earlier studies is that the species attacking the metal surface is not clearly identified and only the overall reaction kinetics with respect to nominal HF concentration is reported, with limited information on the detailed mechanism. HF, being a weak acid, dissociates only slightly and forms multiple species in the aqueous medium. It is important to identify the species that impact the individual steps of the dissolution mechanism. In this study the effect of changing HF concentrations on Ti dissolution mechanism in the active and passive regions has been investigated. Potentiodynamic polarization data were acquired at different HF concentrations, while EIS data were acquired at different dc potentials as well. The oxidation state of Ti was determined using X-ray photoelectron spectroscopy (XPS). The results were analyzed to determine the species that impact the rate constants in the dissolution mechanism.

Experimental

Ti electrode was purchased from Sigma Aldrich (99%) and they were cut into 5 mm × 4 mm metals discs. The discs were mounted into the teflon head of a rotating disc electrode (RDE) and used as the working electrode in the electrochemical experiments. A conventional three electrode cell was used for the experiments with platinum wire as counter electrode and Ag/AgCl (in 3.5 M KCl) as reference electrode. The electrode was polished mechanically using successively finer grades of sand paper (400, 800, 1000, 1200) and ultrasonicated in ethanol medium. The electrode was rinsed in Milli-Q water and immersed into the solution containing HF and supporting electrolyte. 1 M Na₂SO₄ was used as the supporting electrolyte to reduce the solution resistance. The concentration of HF was varied from 10 to 1000 mM. All solutions were made using the Milli-Q water (18.2 MΩ-cm). PARSTAT 2263 (AMETEK) work station along with Pine Instruments MSR speed rotator, which controls the speed was used to conduct the experiments. The electrode was rotated at 900 rpm to enhance the mass transfer and higher rotational speeds yielded overlapping results. Potentiodynamic experiments were conducted by varying the potential from open circuit potential (OCP) to 1000 mV above OCP in different concentrations of HF solutions. The electrode potential was scanned at 20 mV/s during potentiodynamic polarization experiments. A lower scan rate (2 mV/s) also resulted in practically same polarization data, which indicates that the contribution of the double layer capacitance toward the total current was negligible. The
Impedance data was acquired at different potential, and the frequency was varied from 100 kHz to 100 mHz. The maximum current represents the transition from active to passive region and the corresponding value of potential is the transition potential. In 1000 mM HF solution, a sudden drop in current in the passive region shows the results of the potentiodynamic polarization experiments of Ti in solutions of various concentrations of HF and 1 M Na$_2$SO$_4$. A wide range of HF concentration was employed in this study, starting from low concentration of 10 mM to a higher concentration of 1000 mM. Inset shows the patterns observed at lower concentrations (10 and 25 mM), expanded for clarity. In all the curves, initially the current value increases rapidly with potential up to a maximum value, and thereafter decreases with potential. The increase in initial the current value increases and the transition potential value shifts toward more anodic values. Figure 2 shows the transition current as a function of nominal HF concentration, and based on the correlation the overall reaction can be deemed to be first order with respect to HF. Although the correlation is good, it is desirable to employ all the information contained in the polarization curve to understand the detailed mechanism of the reaction and identify the species involved in the steps.

Similar polarization curves were observed for anodic dissolution of other valve metals like Nb and Ta, which are group 5 elements in periodic table. On the other hand, Zr, which is a group 4 element like Ti, exhibits a different trend. The polarization curves of Zr in HF show an active region followed by a limited passivation with the current decreasing only slightly with potential. The low passivation current in Ti shows that its ability to withstand attack by HF is significantly better than that of Zr.

HF, at low to moderate concentrations, forms many species in aqueous medium as showed in Eq. 1.

\[
\begin{align*}
HF & \xrightleftharpoons[K_1]{K_2} H^+ + F^- \\
HF + F^- & \xrightleftharpoons[K_3]{K_4} HF_2^- \\
HF + HF_2^- & \xrightleftharpoons[K_5]{K_6} H_2F_3^- 
\end{align*}
\]

The equilibrium constants are $K_1 = 6.84 \times 10^{-4}$, $K_2 = 5$ and $K_3 = 0.5$, as reported in the literature.28 The values of the remaining species such as H$^+$, F$^-$, HF$^-$, HF$_2^-$, and remaining HF are calculated by solving the species mass balance equations. The calculated values of solutions compositions at various nominal HF concentrations are shown in Table I. In moderate HF concentrations, the concentrations of H$^+$ and F$^-$ are very low compared to that of remaining HF. The concentrations of all the species, except F$^-$ ions, increase with nominal HF concentration. In case of F$^-$ ion concentration, it increases up to 500 mM nominal HF and remains roughly the same at 1 M nominal HF. An analysis of characteristic values such as transition current and transition location shows a moderate level of correlation with all the species. This imposes a difficulty in identifying the species responsible for the dissolution using the data acquired in only HF solutions. In order to distinguish the contribution of species formed due to the HF dissociation on the anodic dissolution, the equilibrium concentrations were altered with the addition of F$^-$ and H$^+$ ions into the HF solutions. Experiments were conducted with the addition of 50 mM KF and 50 mM H$_2$SO$_4$ to 100 mM HF solution. With the addition of KF, the remaining F$^-$ ions increase and with H$_2$SO$_4$ addition, the remaining H$^+$ ions increase drastically. The species concentrations

![Figure 1. Potentiodynamic polarization curves of Ti in solutions with 1 M Na$_2$SO$_4$ supporting electrolyte and HF concentration of (a) 10 mM (b) 25 mM (c) 50 mM (d) 100 mM (e) 250 mM (f) 500 mM (g) 1000 mM. The inset shows the plots at low HF concentrations, expanded for clarity.](image1)

![Figure 2. Transition current obtained from Fig. 1 as a function of nominal HF concentration.](image2)
in these solutions are presented in Table I. Figure 3 shows the polarization curves of Ti dissolution in HF solutions containing KF or H2SO4. The polarization curves show active-passive regions similar to those in pure HF solutions. The transition current value increases with the addition of KF and decreases slightly with the addition of H2SO4. The observed points of transition in Fig. 1 and Fig. 3, in terms of current and potential, are summarized in Table II. The addition of KF shifts the transition potential to a more anodic value whereas the addition of H2SO4 shifts it to a more cathodic value.

Impedance spectra.—The impedance spectra of Ti dissolution in 25 and 50 mM HF solutions were obtained at various dc potentials in quasi potentiostatic mode, where a sinusoidal potential perturbation is superimposed on dc potential. The dc potentials were chosen such that two are in the active region and two in the passive region and the results are presented as complex plane plots in Fig. 4. The experimental data are shown as points, while equivalent electrical circuit model results, described in the later section, are shown as lines. It is seen from Fig. 4a that for Ti dissolving in 25 mM HF, the complex plane plot in the active region exhibit three capacitive loops, although the two loops in the mid and low frequency ranges are not well separated. The double layer would contribute to the high frequency loop while the faradaic process would yield the low frequency loops. In all the impedance data, low frequency points have more noise, probably due to the long acquisition time needed. When impedance data is available in limited frequency range, direct integration of KKT can be applied only with extrapolation. Alternatively, measurement model approach can be employed wherein the data can be fitted to a circuit with increasing number of Voigt elements until there is no further decrease in the residues. A variation of the measurement model approach is the linear KKT which employs Voigt elements with well-defined time constants, which leads to a set of linear equations to be solved. The impedance data were subjected to linear KKT validation, and an example is presented in Fig. 5. It is seen that the experimental data and linear KKT model match reasonably well. Figure 4a shows that the magnitude of low frequency impedance increases with over potential in the active region. The same trend is seen in Fig. 4b, where the results of Ti dissolving in 50 mM HF in the active region are show. A comparison of Figs. 4a and 4b shows that the magnitude of the impedance, in mid and low frequencies, is lower in solutions with 50 mM HF concentration. This is along the expected lines since the slope of polarization curve is more at higher HF concentration.

Figures 4c and 4d show the complex plane plots of EIS for Ti dissolving in 25 and 50 mM HF respectively, in the passive region. At high frequencies, a capacitive loop is seen, while at mid and low frequencies, a capacitive loop with a negative resistance is seen. The data at low frequency end could be modeled adequately only when a pseudo inductance is employed, as described in detail in the equivalent circuit analysis section. In the passive region, the magnitude of the low frequency impedance decreases with an increase in potential at both concentrations employed. In the polarization plot, the slope of the current potential result at the earlier potential is larger than the slope at the later potential, and the low frequency impedance is inversely related to the slope of the polarization curve. In the passive region, at the earlier potential, an increase in potential leads to a larger surface coverage of passivating film and a decrease in current. At later potential, the surface is already covered to a large extent by the film and further increase will lead to a relatively smaller decrease in current, thus resulting in a smaller slope of current potential curve and a larger low frequency impedance. The presence of large dc current at these potentials will contribute to the noise in the spectrum, especially at low frequencies. Repeat runs were performed to verify that the data is reproducible, and slight variations were observed mainly in low frequency data. Nevertheless, even in systems with large dc current, EIS acquired at various potentials help identify the mechanisms and hence they were employed in literature and in this study.

Surface characterization.—Figure 6 shows the XPS results of the surface held in the passive region for 1 h, with the open squares

| Nominal [HF] (mM) | Added KF (mM) | Added H2SO4 (mM) | Transition Current (mA/cm²) | Transition Potential (mV vs. OCP) |
|------------------|---------------|------------------|----------------------------|-------------------------------|
| 10               | 0             | 0                | 2.3                        | 235                           |
| 25               | 0             | 0                | 6.5                        | 292                           |
| 50               | 0             | 0                | 14.4                       | 312                           |
| 100              | 0             | 0                | 35.2                       | 389                           |
| 250              | 0             | 0                | 64.3                       | 444                           |
| 500              | 0             | 0                | 103.2                      | 528                           |
| 1000             | 0             | 50               | 202.7                      | 724                           |
| 100              | 50            | 0                | 41.2                       | 411                           |
| 100              | 0             | 50               | 33.8                       | 348                           |

Figure 3. Potentiodynamic polarization curves of Ti in solutions with 1 M Na2SO4 supporting electrolyte and 100 mM HF with and without additive.

Table I. Concentration of various species in HF solutions, estimated from the reactions given in Eq. 1.

| Nominal [HF] (mM) | Added KF (mM) | Added H2SO4 (mM) | Added [KF] (mM) | Added [H2SO4] (mM) | Actual [HF] (mM) | [H+] (mM) | [F−] (mM) | [HF2−] (mM) | [H2F3−] (mM) |
|------------------|---------------|------------------|-----------------|--------------------|-----------------|-----------|-----------|-------------|-------------|
| 10               | 0             | 0                | 0               | 0                  | 7.59            | 2.32      | 2.236     | 0.085       | 0           |
| 25               | 0             | 0                | 0               | 0                  | 20.67           | 3.95      | 3.578     | 0.370       | 0.004       |
| 50               | 0             | 0                | 0               | 0                  | 42.91           | 5.98      | 4.905     | 1.052       | 0.026       |
| 100              | 0             | 0                | 0               | 0                  | 87.56           | 9.35      | 6.405     | 2.804       | 0.142       |
| 250              | 0             | 0                | 0               | 0                  | 220.28          | 18.38     | 8.198     | 9.029       | 1.154       |
| 500              | 0             | 0                | 0               | 0                  | 437.11          | 33.44     | 8.941     | 19.541      | 4.954       |
| 1000             | 0             | 0                | 0               | 0                  | 857.91          | 66.00     | 8.891     | 38.138      | 18.977      |
| 100              | 50            | 0                | 0               | 0                  | 82.21           | 1.56      | 36.042    | 14.815      | 0.706       |
| 100              | 0             | 50               | 0               | 0                  | 97.36           | 51.94     | 1.282     | 0.624       | 0.035       |
Figure 4. Complex plane plots of impedance spectra of Ti dissolving in HF solutions at different dc potentials. (a) 25 mM HF - active region (b) 50 mM HF - active region (c) 25 mM HF - passive region (d) 50 mM HF - passive region. Equivalent circuit model fit was performed with the circuit shown in Fig. 7. The points show the experimental data and the dashed lines show the model fit.

Figure 5. Experimental data and linear KKT results of impedance spectra of Ti dissolution 25 mM HF solutions at 0.1 V vs. OCP, shown as complex plane plot. Symbols are the experimental points and the dashed lines are the linear KKT results.

Figure 6. XPS data of Ti 2p, along with the de-convoluted peaks. Open squares are the raw data, continuous black line is the model data and dashed lines are individual peaks. The electrode was maintained at 0.6 V vs. OCP for 1 h in 100 mM HF solution.

Figure 7. Equivalent electrical circuit used to model the spectra of Ti dissolution in active and passive regions.

The XPS results show that the Ti atoms on the surface can be at an oxidation state of 0 or 3 or 4. This information can assist in selecting suitable intermediate species while formulating a mechanism to explain the electrochemical results.

EEC modeling.—The circuit shown in Fig. 7 was used to model the impedance spectra in the active and passive regimes. In all cases, a constant phase element (CPE) was used to simulate the depressed depicting the experimental data and continuous line showing the model fit. The individual de-convoluted peaks are represented by the dashed lines. Two peaks at 458.1 eV and 463.8 eV respectively correspond to Ti 2p_3/2 and Ti 2p_1/2 binding energy levels of TiO_2. 6,39–42 On the other hand, two peaks at 453.1 eV and 459.1 eV respectively can be assigned to Ti 2p_3/2 and Ti 2p_1/2 binding energy levels of metallic Ti. 39–42 The peaks at 457.1 eV and 462.9 eV would be assigned to Ti 2p_3/2 and Ti 2p_1/2 of Ti_3O_5. 6,39–43 The spin orbit splitting is 5.7 eV for Ti^{3+} and Ti^{4+}, while it is 6.0 eV for metallic Ti, which match well with the published reports. 42–44 The XPS results show that the Ti atoms on
semicircle in the high frequency range. Two Maxwell elements (R1, C1 and R2, C2) were employed to represent the faradic process. The values of resistances and capacitances were maintained positive in the active region. In the passive region data analysis, one resistance (R2) and capacitance (C2) and the polarization resistance (Rcol) were allowed to hold negative values to capture mid and low frequency trends. The lines in Fig. 4a and Fig. 4b show EEC fitting of the active and passive region for Ti dissolving in 25 and 50 mM HF. The low frequency data is noisy and the EEC fit shows some deviation from experimental points. Nevertheless, EEC model fits capture all the major features in the active region, viz. three capacitance loops at a given potential and concentration, and a decrease in polarization resistance with nominal HF concentration, and the negative resistance in the passive region in both solutions.

Table III shows the best fit parameters obtained for EIS data in all dc potentials in both solutions. The standard error in each parameter is given in the parenthesis. It is seen that the standard error is low in case of solution resistance, CPE exponent and polarization resistance, and is high in case of Maxwell elements. The CPE exponent values are less than unity which indicates that the surface is rough. A variety of factors such as surface disorder, chemical or structure non uniformity, porosity of electrode, variation of surface film properties can result in CPE behavior. In this case, CPE behavior is likely due to surface roughness and accompanying heterogeneity. The solution resistance (Rcol) is more or less a constant (varying from 1.57 to 1.9 Ω cm²). The polarization resistance (Rp) is the value of faradaic impedance at the limit of zero frequency and can be easily identified in the Maxwell circuit representation. The values obtained (Table III) are along the expected lines. The polarization resistance increases with over potential in both active and passive regions. It should be noted that the polarization resistance is negative in the passive region and hence a decrease in its magnitude corresponds to an increase in the actual value. The values of polarization resistance decrease with concentration in the active region and increase with concentration in the passive region. In EIS, the differential impedance of the system is measured. In the polarization curves, it is seen that the slope is negative at higher potentials and that an increase in potential leads to a decrease in current. Polarization curves can be viewed as the low frequency limit of the impedance analysis. Thus at a potential where the slope of polarization curve exhibits a negative slope, a sinusoidal potential at low frequencies will lead to a sinusoidal current with 180° phase offset. Low frequency inductive loops can be modeled using a pair of inductance and resistance, or a pair of capacitance and resistance but with negative values. There are mathematically equivalent, and each Maxwell pair is related to the relaxation of adsorbed intermediate species. The standard error in the Maxwell elements are quite high and in some cases more than 100%. The large standard error is the result of large dc current, and corresponding scatter in the data. In addition, the average values do not show a monotonic trend. It is not possible to draw strong conclusions with confidence from the trends in these values. Besides even if the equivalent circuit element values are acquired with low standard errors, obtaining physical insights from these values is quite challenging. In particular, the negative capacitance or resistance values of C2 and R2 cannot be directly related to the physical processes. Besides, the polarization data cannot be analyzed using EEC with constant element values. Hence, mechanistic analysis of the potentiodynamic polarization data is employed to model the system and predict the impedance patterns.

**Reaction mechanism analysis.**—Ti metal dissolution in 100 mM HF has been investigated using potentiodynamic polarization and electrochemical impedance spectroscopy. A four step mechanism was proposed to explain the observed data, measured at one HF concentration. Recently, the zirconium dissolution kinetics in solutions containing different concentrations of HF was determined by modeling the polarization data measured in multiple HF concentrations. It is important to note that more than one model can easily provide excellent model fits when data from only pure HF solutions are analyzed, since the individual species concentrations are correlated. However, when results of Ti dissolving in solutions containing HF as well as KF or H2SO4 are included in the analysis, the predictor correlations are broken and many mechanisms would fail to predict the trends correctly, enabling identification of the appropriate mechanism. It is evident from the impedance spectra in the active region, that a minimum of two adsorbed species are involved in the reaction mechanism which results in two capacitive loops in the mid and low frequency regions. Four different mechanisms were evaluated for identifying the mechanism which can best explain the electrochemical experimental results of Ti dissolution in acidic fluoride media. Initially, a three step mechanism was evaluated for modeling the polarization data (Eq. 2).

\[
Ti \xrightarrow{k_1} Ti^{+4}_{ads} + 3e^- \\
\ xrightarrow{k_2} Ti^{+3}_{ads} + e^- \\
\ xrightarrow{k_3} Ti^{+2}_{ads} + e^- 
\]

Here \(k_1, k_{-1}, k_2, k_{-2}, k_3\) are the rate constants and \(\theta_1\) and \(\theta_2\) are the surface coverage values of \(Ti^{+4}_{ads}\) and \(Ti^{+3}_{ads}\), species respectively. A mechanism, in the strictest sense, must contain only elementary reaction steps, and an elementary reaction step cannot have multi electron transfer. However, a multi electron transfer step can be considered as a pseudo elementary step if one of the steps is rate limiting, and the term mechanism used here includes the pseudo elementary steps. It is assumed that the rate constants (except \(k_1\)) vary exponentially with potential. Since the third step is chemical dissolution, \(k_3\) is not expected to depend on potential. The adsorption process was assumed to follow the Langmuir isotherm. The adsorbed species may be oxides or fluorides or oxy-fluorides of Ti and it is further presumed that the rate constants \(k_1, k_{-1}, k_2, k_{-2}\) will not be impacted by the concentrations of \(H^+\) and \(F^-\) ions. Only the rate constant corresponding to the dissolution step, viz. \(k_3\), is expected to be influenced by the concentration of various species. For the mechanistic modeling \(k_3\) was written as a function of species concentration as \(k_3 = k_{30} [X]\). Each of the species, viz. \(H^+, F^-\), remaining HF, HF₂, and H₂F₂ were evaluated as possible candidate. The difference between the model and experimental current values was minimized, after normalizing
the current with the transition current. However this mechanism was rejected since it could not model the current decrease in the passive region.\(^{56}\)

Next, a mechanism proposed by Fasmin et al.\(^{24}\) which contains an additional electrochemical dissolution step (Eq. 3) was evaluated.

\[
T_i \xrightarrow{k_1} Ti^{3+}_{ads} + 3e^- \\
T_i^{3+}_{ads} \xrightarrow{k_2} T_i^{4+}_{ads} + e^- \tag{3}
\]

In this mechanism only \(k_3\) and \(k_4\) are presumed to depend on the concentration of HF dissociation species. Furthermore, since the last step involves electron transfer, \(k_4\) is allowed to vary with potential. These rate constants are represented as given by Eq. 4a and Eq. 4b.

\[
k_{30} = k_{30}^0[X]^0 \\
k_{40} = k_{40}^0[Y]^0 \tag{4b}
\]

The optimized parameters obtained from the Matlab program are given in Table IV. The experimental and model predictions for the EIS data were compared with the experimental data. The faradaic impedance was obtained by solving the mass balance equations and the faradaic current expressions.

\[
\theta_{1SS} = \frac{k_{1dc}(k_{2dc} + k_3)}{(k_{1dc} + k_{1dc} + k_{2dc} + k_{3dc})(k_{2dc} + k_3) + k_{3dc}(k_{1dc} - k_{2dc})} \\
\theta_{2SS} = \frac{k_{2dc}}{k_{2dc} + k_{3dc}} + k_{1SS} \\
\]

where the subscript ‘SS’ refers to steady state conditions. The best fit results were obtained when \(k_3\) and \(k_4\) are represented as the functions of HF\(^{-}\) and HF\(^{+}\) respectively. These relations are given by Eq. 9a and 9b.

\[
k_{30} = k_{30}^0[HF^{-}]^{α} \times 54 \\
k_{40} = k_{40}^0[HF^{+}]^{β} \times 22 \tag{9b}
\]

The model predictions for the EIS data were compared with the experimental data. The faradaic impedance was obtained by solving the mass balance equations and the faradaic current expressions.

Two other mechanisms, one where the last step of Eq. 3 was replaced by a direct dissolution step and the second where the last step was a catalytic reaction, were also evaluated. However, the match was poorer and hence the models were rejected. Although the match is semi-quantitative, it must be remarked that the model matches the experimental data even better when the analysis was limited to polarization curves obtained for Ti dissolving in pure HF solutions. In fact, all mechanisms with four step which were evaluated in this study were able to match the polarization results up to 100 mM HF concentrations (results not shown). The deviations increase to the level shown in Fig. 9 when the data set analyzed includes the polarization curves obtained with the addition of KF and H\(_2\)SO\(_4\). Figure 10 shows both the experimental and model predicted polarization curves when KF/H\(_2\)SO\(_4\) is added to HF solution. With the addition of KF to HF solution, the model successfully predicts that the transition current would be higher and with the addition of H\(_2\)SO\(_4\) to HF solution, the transition current would be lower. Besides, the model predicts that, with the addition of KF, transition potential will be more anodic and will the addition of H\(_2\)SO\(_4\), it would be less, as seen in the experimental results.

The model predictions for the EIS data were compared with the experimental data. The faradaic impedance was obtained by solving the mass balance equations and the faradaic current expressions.

Table IV. Best fit parameters for the polarization curves of Ti dissolving in acidic fluoride media, using the mechanism shown in Eq. 3.

| Parameter   | Value         |
|-------------|---------------|
| \(k_{10}\)  | \(7.09 \times 10^{-8}\) |
| \(k_{20}\)  | \(1.00 \times 10^{-12}\) |
| \(k_{10}\)  | \(6.36 \times 10^{-7}\) |
| \(k_{20}\)  | \(2.45 \times 10^{-11}\) |
| \(b_1\)     | 3.80          |
| \(b_2\)     | 12.00         |
| \(b_3\)     | 5.50          |
| \(b_4\)     | -37.70        |
| \(k_{10}\)  | \(4.77 \times 10^{-10}\) |
| \(k_{20}\)  | \(9.29 \times 10^{-7}\) |
| \(\alpha\)  | 0.54          |
| \(\beta\)   | 1.22          |
| \(\Gamma\)  | \(4.00 \times 10^{-11}\) |
the charge balance and the mass balance equations, as described in earlier study.24 The expression for the faradaic impedance $Z_F$ can be written as

$$Z_F = \frac{\Delta i_F}{\Delta E} = (R_{ct})^{-1} - F \left\{ \left[ 3(k_{1dc} + k_{-1dc}) - (k_{2dc} + k_{4dc}) \right] \frac{d\theta_1}{dE} ight. \\
\left. + \left[ 3k_{1dc} + k_{-2dc} \right] \frac{d\theta_2}{dE} \right\} \quad [10]$$

where $(R_{ct})^{-1}$ is given by

$$(R_{ct})^{-1} = F \left\{ \left[ 3b_1k_{1dc}(1 - \theta_{1SS} - \theta_{2SS}) \right] - \left[ b_{-1}k_{-1dc}\theta_{1SS} \right] \\
+ \left[ b_2k_{2dc}\theta_{1SS} \right] - \left[ b_{-2}k_{-2dc}\theta_{2SS} \right] + \left[ b_4k_{4dc}\theta_{1SS} \right] \right\} \quad [11]$$

The mass balance equations (Eq. 10, Eq. 11) can be linearized using Taylor’s approximation,24 to estimate the values of $\frac{d\theta_1}{dE}$ and $\frac{d\theta_2}{dE}$. The experimental data and the model predictions for the EIS at different dc potentials for Ti dissolving in 25 and 50 mM HF solutions are shown as 3D plots in Fig. 11 and Fig. 12 respectively. The EIS model data shows qualitative match with the experimental data. The model shows two loops in the active region, with a small loop in the low frequency end. A mechanism with two adsorbed intermediates can result in an impedance spectrum with up to 3 loops in the complex plane plot. However, if two of the time constants are close, or if the frequency range of data acquisition is not very wide, then the number of loops can be fewer, and this may explain the observed results. In the passive
Figure 12. Impedance data and model fits, as three dimensional plots, for Ti dissolving in HF in the passive region (a) 25 mM HF at 0.35 V vs. OCP (b) 25 mM HF at 0.45 V vs. OCP (c) 50 mM HF at 0.45 V vs. OCP (d) 50 mM HF at 0.55 V vs. OCP. The points show the experimental results and the continuous lines show the model fit.

region, model captures the first capacitive loop and the second loop with negative resistance and capacitive behavior in the low frequency end. Although the match is not quantitative, the overall patterns are reproduced by the model. The parameter values are different from the values proposed in the earlier study, but the trends predicted are very similar. The equations relating the kinetic parameters to the impedance are nonlinear and it is possible that more than one set of kinetic parameters can match the experimental data to a similar level. EIS contains information at many frequencies whereas polarization data correspond to a part of it, i.e. at the dc limit. Even a minor side reaction can modify the EIS without changing the polarization data much. The fact that the order of chemical dissolution step is 0.5 clearly suggests that the step is not elementary. Thus the dominant reaction pathway along with the dissolved species which impact the rate constants can be identified by analyzing the polarization data, while a comparison of EIS data can ensure that the proposed mechanism can simulate the pertinent features.

Figure 13 shows the variation of surface coverage of the Ti\textsuperscript{3+} ads with respect to potential under steady state conditions as predicted by the mechanism in Eq. 3. Initially the surface coverage of Ti\textsuperscript{3+} ads shows a rapid increase with potential, and then it gradually decreases with potential. Figure 14 shows the variation of surface coverage of the Ti\textsuperscript{4+} ads with respect to potential. The surface coverage of Ti\textsuperscript{4+} ads increases gradually, and value approaches unity at higher potentials. The surface coverage of the bare metal decreases and at higher potential it becomes zero (not shown). With an increase in nominal HF concentration, the surface coverage of the Ti\textsuperscript{4+} ads and Ti\textsuperscript{3+} ads decreases whereas the fractional surface coverage of the bare metal increases.

The effect of potential and HF concentrations on the chemical dissolution rates were estimated and are presented in Fig. 15. Chemical dissolution rate is proportional to the fractional surface coverage of the Ti\textsuperscript{4+} ads and k\textsubscript{3}, which in turn depends on HF\textsubscript{2} concentration. As the potential increases, the chemical dissolution rate increases and reaches a saturation value following the trend of Ti\textsuperscript{4+} ads fractional surface coverage. With increase in nominal HF concentration, at higher...
over potentials, the chemical dissolution rate increases, since the fractional surface coverage of $Ti^{4+}_{ads}$ is almost a constant in this region, and $k_3$ increases with HF$_2^-$ concentration. At lower over potentials, the predictions can be explained as follows. The chemical dissolution rate depends on both $k_3$ and $\theta_2$ values. While $k_3$ increases with HF$_2^-$ species concentration, $\theta_2$ decreases (at a given potential) with HF$_2^-$ species concentration. The resulting effect appears in the dissolution rates shown in Fig. 15.

Electrochemical dissolution rate is proportional to the fractional surface coverage of $Ti^{4+}_{ads}$ and $k_3$, which in turn depends on the concentration of remaining HF. The effect of potential and HF concentration on electrochemical dissolution is shown in Fig. 16. Initially, the electrochemical dissolution rate increases and at high overpotentials, the dissolution rate decreases. This is because of the combined effect of the rate constant $k_3$ and the surface coverage values of $Ti^{4+}_{ads}$. At low overpotentials, the increase in the $k_3$ has major contribution while at high overpotentials the decrease in $\theta_2$ value dominates and results in a decrease in the electrochemical dissolution. At a given potential, as the HF concentration increases, the electrochemical dissolution increases.

The model predicts that remaining HF and HF$_2^-$ impact the chemical and electrochemical dissolution steps respectively, but reasons for this behavior are not clear. Investigating the interactions between the various solution species and the surface, for example by density functional theory, might throw light on the nature and strengths of these interactions.

**Conclusions**

Anodic dissolution of Ti in solutions with varying HF concentrations was investigated using potentiodynamic polarization and impedance spectroscopic experiments. Polarization results showed clear active and passive regions, with increasing current at higher HF concentrations. Experiments were also conducted with addition of KF or H$_2$SO$_4$ to break the correlation between the concentrations of various species of HF dissociation. XPS analysis identified Ti in oxidation state of 3 and 4 in the passive region. A four step mechanism with a chemical and an electrochemical dissolution steps occurring in parallel was proposed to explain the observed results in the active and passive region. The model was able to capture all the salient features of the observed polarization curves all solutions. The predicted impedance spectra captured the overall trends qualitatively. According to the proposed mechanism, HF$_2^-$ is the key species controlling the electrochemical step and remaining HF affects the chemical dissolution step.

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**Figure 15.** Variation of chemical dissolution rate with potential and nominal HF concentration (a) 10 mM (b) 25 mM (c) 50 mM (d) 100 mM (e) 250 mM (f) 500 mM (g) 1000 mM.

**Figure 16.** Variation of electrochemical dissolution rate with potential and nominal HF concentration (a) 10 mM (b) 25 mM (c) 50 mM (d) 100 mM (e) 250 mM (f) 500 mM (g) 1000 mM.
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