Anodic dissolution of Zr in acidic fluoride media was investigated using potentiodynamic polarization and electrochemical impedance spectroscopy. The surface state of the electrode was analyzed using X-ray photon spectroscopy, and the surface morphology was characterized using atomic force microscopy. EIS data acquired at multiple dc potentials were subjected to mechanistic analysis. Reaction mechanism analysis approach reveals that at least four intermediates are required to describe the observed results. The intermediates are likely to be Zr sub-oxides, oxyfluorides and ZrO2. The proposed mechanism successfully predicts the major features observed in polarization and impedance spectra. At low overpotentials, the fractional surface coverage of Zr3+ species is higher than that of Zr4+ species, and the electrochemical dissolution rate is higher than the chemical dissolution rate. As the overpotential increases, the surface is covered with Zr4+ species and chemical dissolution rate becomes comparable to electrochemical dissolution rate. Although the surface is covered with Zr4+ species at higher overpotentials, significant chemical and electrochemical dissolution processes continue to occur and hence Zr is not protected in acidic fluoride media under anodic conditions.

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Surface characterization—The morphology of the surface held in the active and passive regions was analyzed using AFM (Bruker). The surface state of the electrode held in the active dissolution region was also analyzed using XPS. A SPECS Surface Nano Analysis GmbH spectrometer was used to acquire XPS data and the X-ray source was Al Kα. Analysis of the XPS data along with impedance spectra, were subjected to mechanistic modeling, as described in the later part of this paper.

Results and Discussion

Potentiodynamic polarization—Figure 1 shows the potentiodynamic polarization curve of Zr RDE immersed in 10 mM HF solution. An active region of dissolution was observed up to 0.2 V vs. OCP where the current increases rapidly with the overpotential. The current shows a decreasing trend between 0.2–0.5 V vs. OCP, and slight increase near 0.5 V vs. OCP. At potentials above 0.6 V vs. OCP, a slight decrease in the current values corresponding to the passive region of dissolution was observed. The region above 0.2 V vs OCP can be considered as passive, although strictly speaking the surface is not well protected in this region. The current values are high and a significant dissolution continues to occur. For other valve metals such as Ti, Nb, and Ta, a rapid decrease in current density is reported at potentials beyond the transition potential. Zr metal shows unusual behavior in the passive region compared to the other valve metals. However, since the current decreases at least slightly with potential, this region is termed as passive. The data shows significant fluctuations in the current values in the passive region, which was found to be the case in all repeat runs. These fluctuations are likely due to continuous oxide formation and destruction. The polarization data along with impedance spectra, were subjected to mechanistic modeling, as described in the later part of this paper.

Surface characterization—The surface morphology of the Zr electrode dissolving in the 10 mM HF solution in the active and passive regions was studied using AFM. The active region topography due to the active dissolution of the metal. AFM image in the passive region was obtained by holding the electrode at 0.2 V vs. OCP for 1 hour in 10 mM HF solution. The electrode was then rinsed with water and dried in N2 stream, and the surface was analyzed using XPS. The binding energy values were corrected using the peak of the adventitious carbon, which is expected to be present at 284.8 eV. The data were analyzed using XPS Peak 4.1 software (R.W.M. Kwok).

The XPS spectra of Zr 3d, F 1s and O 1s are presented in Fig. 3. The experimental data are shown as filled circles, whereas the model results are presented as a continuous line. The de-convoluted peaks are shown as dashed lines. In Figs. 3a, three peaks at 177.93, 182.12, and 182.66 eV corresponding to Zr 3d5/2 levels were resolved. These were attributed to Zr-metallic (3d5/2), Zr4+ (3d5/2), and Zr3+ (3d5/2) respectively. Three peaks at 180.33, 184.52, and 185.06 eV corresponding to Zr-metallic (3d5/2), Zr4+ (3d5/2), and Zr3+ (3d5/2) respectively, were also resolved. The energy difference of the doublet peaks of Zr 3d5/2 and Zr 3d3/2 was 2.4 eV, which matches well with the literature reports. The charged species of Zr can be an oxide or oxyfluoride or fluoride. In earlier publications, the binding energy of Zr-oxide (ZrO2-3d5/2) was reported to be present at 182.6 eV and that of zirconium oxyfluoride (ZrO2F-(3d5/2) was reported at 182.5 eV. These values are close to the binding energy values (182.66 eV) obtained for Zr3+ (3d5/2) in this study. Hence the observed peaks for Zr3+ in these samples can arise from Zr sub-oxide and Zr-oxo fluoride. Literature indicates that the peaks corresponding to Zr4+ (3d5/2) in the oxide form (ZrO2) would be present at about 182.0 eV and this is close to the value observed (182.12 eV) in this work. The other possible forms of ZrF4 in this case are fluorides and oxyfluorides. ZrF4 and ZrOF2 are reported to show 3d5/2 peaks at 185.4, 186.5 and 186.8 eV respectively. Analysis of the XPS data reported here does not show any evidence for the presence of ZrF4 or ZrOF2 on the sample surface.

Figures 3b and 3c show the F 1s and O 1s spectra of the sample surface respectively. The F 1s spectra shows two peaks at 684.44 and 685.29 eV. The peak at 684.44 eV correspond to zirconium oxyfluoride, and the peak at 685.29 eV can be attributed to the F 1s of NaF. Since Na2SO4 was used as the supporting electrolyte, traces of NaF could be present on the surface. The O 1s spectra show two peaks at 529.86 and 532.04 eV. The peak near 529.86 eV is attributed to metal oxides, and that near 532.04 eV corresponds to the adsorbed oxygen. The XPS data can be used to identify the species present on
Figure 3. XPS spectra and deconvoluted peaks of Zr electrode held at 0.2 V vs. OCP (in the active region) for 1 hour in a solution containing 10 mM HF and 100 mM Na₂SO₄ (a) Zr 3d (b) F 1s (c) O 1s. Points represent the experimental data and the dashed lines are the deconvoluted peaks.

Electrochemical impedance spectroscopy.—Markers A, B, and C in Fig. 1 correspond to three dc potentials in the active region of dissolution, which are 0.075, 0.1, and 0.15 V vs. OCP, respectively. Markers D and E correspond to 0.5 and 0.8 V vs. OCP in the passive region of dissolution. EIS data were measured at these five dc potentials. Figure 4 shows the complex plane plots of the EIS data of Zr in 10 mM HF solution in both active and passive regions. The experimental EIS data were tested using linear KKT, and the validation results are shown as lines in Fig. 4. Since the EIS data in the passive region show negative resistance, KKT transformation was performed in the admittance mode. It is seen that the spectra are KKT compliant, and the residual errors were found to be less than 2%.

Figure 4a shows that the impedance spectra in the active region exhibit two capacitive loops in the high and mid frequency ranges and a pseudo-inductive loop in the low frequency range. The high frequency loop can be attributed to the double layer and the charge transfer resistance (which is the high frequency limit of the faradaic impedance). The mid and low frequency loops can be attributed to the response of the faradaic process, which are described in the following section, to potential perturbations at these frequencies, since the contribution of double layer current to the total current will be very small at these frequencies. Figure 4b shows that the EIS spectra in the passive region exhibit a pseudo-inductive loop in the mid frequency region and an apparent negative resistance and capacitance at low
Figure 4. Complex plane plots of EIS data of Zr dissolution in 10 mM HF solution at different dc potentials in the (a) active region (b) passive region. Inset shows the data at mid-frequencies, expanded for clarity. Note that, in the inset, the arrow shows the direction of experimental data points. Filled circles represent the experimental data and the lines represent the linear KKT model fit.

In this work, Zr anodic dissolution in active and passive regions are analyzed and a single mechanism is proposed to explain the observed results.

Reaction mechanism analysis (RMA).—Visual inspection of the complex plane plots of the passive region in Fig. 4b shows two capacitive loops and a pseudo-inductive loop in the passive region in addition to the double layer capacitance at high frequencies. This suggests that at least three time constants are required to model the faradaic processes. Although it is possible to model the impedance spectra using equivalent electrical circuits (EEC), better insights of the anodic dissolution can be obtained using mechanistic analysis and hence EEC results are not presented. Earlier, by analyzing the polarization data in HF solutions, we proposed a four step mechanism with two adsorbed intermediates to describe Zr anodic dissolution.17

In this work, a careful inspection of Fig. 4b shows that, post inductive loop at slightly lower frequencies, a capacitive arc is exhibited, i.e. as frequency decreases, the data points in the complex plane plot move toward larger $Z_{\text{dc}}$ values, as indicated by the arrow in the inset of Fig. 4b. At even lower frequencies, a negative resistance is exhibited. This low frequency negative resistance is also seen in EIS spectra acquired in the passive region for other valve metals like Ti, Nb and Ta dissolution in HF.18,20,27,28 Earlier, Cattarin et al.27 studied the anodic dissolution of Nb in HF and the data acquired in the passive region exhibited a pseudo inductive loop at mid frequencies and a negative differential resistance at low frequencies. The spectra in the transpassive dissolution region were modeled using an equivalent electrical circuit which accounts for the film present on the surface.
Analyzing the potentiodynamic polarization data along with the EIS data acquired at multiple dc potentials is challenging, but offers more information about the system investigated.

Initially, the mechanism described in Eq. 1 was evaluated to model the experimentally observed features in the impedance spectra of anodic dissolution of Zr in HF based solutions.\textsuperscript{45} In the active region, the model could predict two capacitive loops in the high and mid frequency regions, but the pseudo-inductive loop at low frequencies was not predicted by the model.\textsuperscript{46} It is to be noted that if an impedance spectrum at one dc potential were modeled, then all the features, including the low frequency inductive loop can be predicted by the mechanism given in Eq. 1. However when all the spectra and the polarization data were modeled together, the mechanism shown in Eq. 1 could not predict all the major features. In the passive region, the model captures the high frequency capacitive loop, mid-frequency pseudo-inductive loop and low frequency negative resistance but failed to predict the positive capacitive arc observed in the intermediate frequencies. Earlier, it was assumed that all Zr(III) species, whether they are oxides or oxyfluorides or fluorides, can be represented by a single species viz. Zr\textsuperscript{3+}, and likewise, all Zr(IV) species can be represented by Zr\textsuperscript{4+} regardless of the associated anions. It appears that a new mechanism, which distinguishes between sub-oxides and oxyfluorides with the same state of charge of the cation, is necessary to satisfactorily explain the EIS results. Therefore, a more detailed reaction mechanism (Fig. 5), which is a superset of the mechanism proposed in the earlier work, was evaluated. The impedance was calculated using the circuit given in Fig. 6, where the faradaic impedance (Z_F) is estimated using the mechanism given in Fig. 5.

In the mechanism described in Fig. 5, the number of intermediate species is four and the overall mechanism is similar to the one proposed in Eq. 1. It must be noted that multi-electron transfer, such as the first step in Fig. 5, is unlikely to occur in an elementary step. Thus, the first step can be regarded as an overall representation of three elementary steps, viz. Zr\textsuperscript{3+} \( \xrightarrow{k_1} \) Zr\textsuperscript{4+} + e\textsuperscript{-}, Zr\textsuperscript{4+} \( \xrightarrow{k_2} \) Zr\textsuperscript{5+} + e\textsuperscript{-} and Zr\textsuperscript{5+} \( \xrightarrow{k_3} \) Zr\textsuperscript{6+} + e\textsuperscript{-}. Earlier publications have also employed such multi electron steps in mechanistic analysis.\textsuperscript{41–43} The kinetics of the multi electron steps is given by an equation analogous to the Butler-Volmer equation.\textsuperscript{44} The fractional surface coverage values of the intermediate species Zr\textsuperscript{3+} \( \xrightarrow{k_1} \) Zr\textsuperscript{4+}, Zr\textsuperscript{4+} \( \xrightarrow{k_2} \) Zr\textsuperscript{5+}, and Zr\textsuperscript{5+} \( \xrightarrow{k_3} \) Zr\textsuperscript{6+} are denoted by \( \theta_1 \), \( \theta_2 \), \( \theta_3 \) and \( \theta_4 \) respectively.

In this mechanism, the rate constants \( k_1 \) and \( k_2 \) are independent of the potential as they do not involve any electron transfer. All other rate constants are assumed to vary with potential in an exponential manner as \( k_i = k_{o,i}e^{\beta_iE} \), where \( k_{o,i} \) is the pre-exponent, and \( E \) is the potential measured with respect to OCP. Here, \( \Gamma \) denotes the total number of sites per unit area and ‘t’ denotes the time. The methodology followed for the derivation of the current and impedance expressions is given in the literature in detail.\textsuperscript{44–46} Langmuir adsorption isotherm model is employed. The mass balance equations corresponding to the adsorbed species are given in Eq. 2.

\[
\Gamma \frac{di_F}{dt} = k_1(1 - \theta_2 - \theta_3 - \theta_4) - k_2 \theta_1 - k_3 \theta_2 + k_4 \theta_3 - k_5 \theta_1
\]

\[
\Gamma \frac{di_F}{dt} = k_2(1 - \theta_2 - \theta_3 - \theta_4) - k_2 \theta_1 + k_4 \theta_2
\]

\[
\Gamma \frac{di_F}{dt} = k_3 \theta_1 - k_3 \theta_2 - k_5 \theta_1
\]

\[
\Gamma \frac{di_F}{dt} = k_4 \theta_2 - k_4 \theta_4 - k_6 \theta_4
\]

At steady-state conditions, Eq. 2 can be set to zero to calculate the corresponding fractional surface coverage values of the intermediates (appendix A). The expression for faradaic current is given by

\[
i_F = F \int \left(3 \times \left(k_1(1 - \theta_2 - \theta_3 - \theta_4) - k_2 \theta_1 + k_4 \theta_2\right) + \left(k_3 \theta_1 - k_3 \theta_2 + k_5 \theta_1 + k_5 \theta_2\right)\right)
\]

and the steady-state current is given by

\[
i_{F,SS} = F \left[4 \times (k_5 \theta_1SS + k_4 \theta_2SS) + k_6 \theta_4SS + k_6 \theta_4SS\right].
\]

Here, \( F \) is the Faraday constant. The expressions of rate constant and surface coverage terms can be expanded using the Taylor series, and linearized by neglecting the higher order terms.

\[
k_i = k_{o,i}e^{\beta_iE_{ac}} \approx k_{o,i}e^{\beta_iE_{ac}} (1 + b_iE_{ac})
\]

\[
\theta_i = \theta_{i,SS} + \frac{d\theta_i}{dE}E_{ac}
\]

After linearization of Eqs. 3 and 4, the faradaic impedance can be written as:\textsuperscript{44–46}

\[
Z_F^{-1} = \Delta i_F \frac{\Delta E}{E}
\]

\[
= F \left[(-3k_{id,c} - 3k_{id,e} - 3k_{id,e} + k_{id,e} + k_{id,c}) \frac{d\theta_i}{dE} + (-3k_{id,c} - 3k_{id,e} - 3k_{id,e} + k_{id,e} + k_{id,c}) \frac{d\theta_i}{dE} + (-3k_{id,c} - 3k_{id,e} - k_{id,c} + k_{id,c} + k_{id,c}) \frac{d\theta_i}{dE} + R_{ct}^{-1}\right]
\]

where \( R_{ct}^{-1} \) is

\[
R_{ct}^{-1} = \left[3[b_1k_{id,c}(1 - \theta_{i,SS} - \theta_{i,SS} - \theta_{i,SS} - \theta_{i,SS} - b_{-3}k_{id,c}\theta_{i,SS}] + 3[b_1k_{id,c}(1 - \theta_{i,SS} - \theta_{i,SS} - \theta_{i,SS} - \theta_{i,SS}) - b_{-2}k_{id,c}\theta_{i,SS}] + (b_1k_{id,c}\theta_{i,SS} - b_{-3}k_{id,c}\theta_{i,SS}) + (b_1k_{id,c}\theta_{i,SS} - b_{-4}k_{id,c}\theta_{i,SS}) + b_1k_{id,c} + b_1k_{id,c}\theta_{i,SS} + b_1k_{id,c}\theta_{i,SS} + b_1k_{id,c}\theta_{i,SS} + b_1k_{id,c}\theta_{i,SS}\right]
\]

\[
\approx F \left[\begin{array}{c}
3[b_1k_{id,c}(1 - \theta_{i,SS} - \theta_{i,SS} - \theta_{i,SS} - \theta_{i,SS} - b_{-3}k_{id,c}\theta_{i,SS}] + 3[b_1k_{id,c}(1 - \theta_{i,SS} - \theta_{i,SS} - \theta_{i,SS} - \theta_{i,SS}) - b_{-2}k_{id,c}\theta_{i,SS}] + (b_1k_{id,c}\theta_{i,SS} - b_{-3}k_{id,c}\theta_{i,SS}) + (b_1k_{id,c}\theta_{i,SS} - b_{-4}k_{id,c}\theta_{i,SS}) + b_1k_{id,c} + b_1k_{id,c}\theta_{i,SS} + b_1k_{id,c}\theta_{i,SS} + b_1k_{id,c}\theta_{i,SS} + b_1k_{id,c}\theta_{i,SS}\end{array}\right]
\]

\[
\approx F \left[\begin{array}{c}
3[b_1k_{id,c}(1 - \theta_{i,SS} - \theta_{i,SS} - \theta_{i,SS} - \theta_{i,SS} - b_{-3}k_{id,c}\theta_{i,SS}] + 3[b_1k_{id,c}(1 - \theta_{i,SS} - \theta_{i,SS} - \theta_{i,SS} - \theta_{i,SS}) - b_{-2}k_{id,c}\theta_{i,SS}] + (b_1k_{id,c}\theta_{i,SS} - b_{-3}k_{id,c}\theta_{i,SS}) + (b_1k_{id,c}\theta_{i,SS} - b_{-4}k_{id,c}\theta_{i,SS}) + b_1k_{id,c} + b_1k_{id,c}\theta_{i,SS} + b_1k_{id,c}\theta_{i,SS} + b_1k_{id,c}\theta_{i,SS} + b_1k_{id,c}\theta_{i,SS}\end{array}\right]
\]
Table I. Solution resistance (Rsol) and double layer CPE parameters used in model fits. The data shown in Fig. 4 were modeled using the circuit given in Fig. 6. Faradaic impedance was calculated for the reaction shown in Figs. 5.

| Potential (V vs. OCP) | Rsol (Ω cm²) | Y0 (× 10⁻⁵ Ω⁻¹ S⁰ cm²) | n |
|-----------------------|--------------|--------------------------|---|
| 0.075                 | 9.75         | 12.3                     | 0.89 |
| 0.1                   | 9.11         | 6.44                     | 0.93 |
| 0.15                  | 10.37        | 4.65                     | 0.93 |
| 0.5                   | 10.49        | 1.23                     | 0.96 |
| 0.8                   | 10.15        | 2.16                     | 0.92 |

The total impedance, Zₜ can be written as

\[ Zₜ = R_{sol} + \left( Z_{CPE}^{-1} + Z_{r}^{-1}\right)^{-1} \]  

where ZCPE is the impedance of the constant phase element, given by

\[ Z_{CPE} = \left[ Y_0 (j\omega)^n \right]^{-1} \]  

The expressions for \( \frac{\partial n}{\partial E} \), \( \frac{\partial m}{\partial E} \), and \( \frac{\partial n}{\partial F} \) are presented in Appendix A. The model impedance was calculated using Eq. 8 and the model steady-state current was calculated using Eq. 4. The Matlab program used to calculate the impedance can be obtained by contacting the corresponding author. The solution resistance and CPE parameter values are listed in Table I. The values of solution resistance are close to 10 Ω·cm² at all dc potentials. The values of constant phase exponent vary between 0.89 and 0.96, which indicates that the surface is heterogeneous in nature. 50-52 This is also evident from the AFM images (Fig. 2). The best fit kinetic parameters, estimated using an optimization program written in Matlab, are shown in Table II.

The rate constant values at two dc potentials each in the active and passive regions are listed in Table III. In the passive region, the forward rate constants \( k_{1,dc} \), \( k_{2,dc} \), \( k_{3,dc} \), and \( k_{4,dc} \) are significantly larger than the respective reverse rate constants \( k_{1,dc}^{-1} \), \( k_{2,dc}^{-1} \), \( k_{3,dc}^{-1} \), and \( k_{4,dc}^{-1} \), indicating that the reaction can be considered irreversible in the passive region. However, in the active region, the reverse reactions cannot be neglected. A comparison of the chemical dissolution steps by the two pathways shows that \( k_5 \) is significantly larger than \( k_6 \) and that the chemical dissolution rate via \( Zr^{4+}_{ads(1)} \) intermediate species will be more than the corresponding dissolution rate via \( Zr^{4+}_{ads(2)} \) species. On the other hand, \( k_{8,dc} \) is almost two orders of magnitude less than \( k_{7,dc} \) and hence electrochemical dissolution \( Zr^{3+}_{ads(2)} \) intermediate species will be much less than the electrochemical dissolution via \( Zr^{3+}_{ads(1)} \) species.

Figures 7 shows the dc current predicted by the model (dashed line), along with the experimental data (continuous line). The model predictions for the anodic polarization data matches well with the experimental data. The model captures the transition from active to passive region. Previous model prediction could only identify the increase in the current in the active region and the continuous decrease in current in the passive region. 40-42 The present detailed model also captures the slight increase in current increase near 0.5 V vs. OCP in the passive region. The model predictions for the EIS data in both active

| Parameter | Value |
|-----------|-------|
| \( k_{10} \) (mol cm⁻² s⁻¹) | \( 1.86 \times 10^{-6} \) |
| \( k_{20} \) | \( 5.99 \times 10^{-7} \) |
| \( k_{30} \) | \( 1.56 \times 10^{-7} \) |
| \( k_{40} \) | \( 1.32 \times 10^{-9} \) |
| \( k_{50} \) | \( 2.08 \times 10^{-9} \) |
| \( k_{60} \) | \( 9.31 \times 10^{-9} \) |
| \( k_{70} \) | \( 2.75 \times 10^{-8} \) |
| \( k_{80} \) | \( 1.64 \times 10^{-11} \) |
| \( k_{90} \) | \( 8.81 \times 10^{-7} \) |
| \( k_{100} \) | \( 1.49 \times 10^{-8} \) |
| \( k_{110} \) | \( 6.76 \times 10^{-7} \) |
| \( k_{120} \) | \( 1.05 \times 10^{-6} \) |

Table II. Optimized parameters used to simulate the model fit in Figs. 7 and 8 using the mechanism shown in Fig. 5.

| Parameter | Value |
|-----------|-------|
| \( b_1 \) (V⁻¹) | \( 0.16 \) |
| \( b_2 \) | \( 1.22 \) |
| \( b_3 \) | \( 0.05 \) |
| \( b_4 \) | \( 4.75 \) |
| \( b_5 \) | \( 2.41 \) |
| \( b_6 \) | \( 7.48 \) |
| \( b_7 \) | \( 28.96 \) |
| \( b_8 \) | \( -3.91 \) |
| \( b_9 \) | \( -4.96 \) |
| \( b_{10} \) | \( -29.20 \) |
| \( \gamma \) (mol cm⁻²) | \( 3.03 \times 10^{-8} \) |

Figure 7. Experimental and model polarization data for the Zr RDE dissolving in 10 mM HF solution. The continuous lines represent the experimental data and the dashed line represent the model prediction.

Table III. Comparison of kinetic rate constant values of the mechanism shown in Fig. 5, in the active and passive regions.

| Rate constants (mol cm⁻² s⁻¹) | 0.1 | 0.15 | 0.5 | 0.8 |
|-------------------------------|-----|-----|-----|-----|
| \( k_{1,dc} \) | \( 1.87 \times 10^{-6} \) | \( 1.91 \times 10^{-6} \) | \( 2.01 \times 10^{-6} \) | \( 2.11 \times 10^{-6} \) |
| \( k_{2,dc} \) | \( 6.07 \times 10^{-7} \) | \( 7.20 \times 10^{-7} \) | \( 1.10 \times 10^{-6} \) | \( 1.59 \times 10^{-6} \) |
| \( k_{3,dc} \) | \( 1.56 \times 10^{-7} \) | \( 1.57 \times 10^{-7} \) | \( 1.60 \times 10^{-7} \) | \( 1.62 \times 10^{-7} \) |
| \( k_{4,dc} \) | \( 1.38 \times 10^{-9} \) | \( 2.69 \times 10^{-9} \) | \( 1.42 \times 10^{-8} \) | \( 5.90 \times 10^{-8} \) |
| \( k_{5} \) | \( 2.08 \times 10^{-9} \) | \( 2.08 \times 10^{-9} \) | \( 2.08 \times 10^{-9} \) | \( 2.08 \times 10^{-9} \) |
| \( k_{6} \) | \( 9.31 \times 10^{-9} \) | \( 9.31 \times 10^{-9} \) | \( 9.31 \times 10^{-9} \) | \( 9.31 \times 10^{-9} \) |
| \( k_{7,dc} \) | \( 2.82 \times 10^{-8} \) | \( 3.95 \times 10^{-8} \) | \( 9.18 \times 10^{-8} \) | \( 1.89 \times 10^{-7} \) |
| \( k_{8,dc} \) | \( 1.76 \times 10^{-11} \) | \( 5.02 \times 10^{-11} \) | \( 6.87 \times 10^{-10} \) | \( 6.47 \times 10^{-9} \) |
| \( k_{9,dc} \) | \( 6.60 \times 10^{-7} \) | \( 1.14 \times 10^{-8} \) | \( 4.53 \times 10^{-13} \) | \( 7.63 \times 10^{-17} \) |
| \( k_{10,dc} \) | \( 1.43 \times 10^{-8} \) | \( 8.27 \times 10^{-9} \) | \( 2.11 \times 10^{-9} \) | \( 6.53 \times 10^{-10} \) |
| \( k_{11,dc} \) | \( 6.43 \times 10^{-7} \) | \( 3.22 \times 10^{-7} \) | \( 5.68 \times 10^{-8} \) | \( 1.28 \times 10^{-8} \) |
| \( k_{12,dc} \) | \( 7.81 \times 10^{-7} \) | \( 1.31 \times 10^{-8} \) | \( 4.78 \times 10^{-13} \) | \( 7.50 \times 10^{-17} \) |
Figure 8. Complex plane plots of experimental and model EIS data of Zr dissolving in 10 mM HF solution at different dc potentials. (a) 0.075 V vs. OCP, (b) 0.1 V vs. OCP, (c) 0.15 V vs. OCP, (d) 0.5 V vs. OCP, and (e) 0.8 V vs. OCP. Filled circles are the experimental data and filled squares with lines are the mechanistic model fit.

Figure 9. Variation of steady state surface coverage of the adsorbed species and the bare metal with respect to the overpotential, based on the proposed mechanism.
and \( Zr^{3+}_{ads(1)} \). The electrochemical dissolution is a function of the rate constants \( k_7 \) and \( k_8 \) as well as the surface coverage of \( Zr^{3+}_{ads(1)} \) and \( Zr^{3+}_{ads(1)} \). The rate constant \( k_7 \) is three orders of magnitude smaller than \( k_8 \) and the total electrochemical dissolution rate is determined by the dissolution step involving \( k_7 \) and \( Zr^{3+}_{ads(1)} \). This electrochemical dissolution rate increases with overpotential due to the increase in \( k_7 \) and \( Zr^{3+}_{ads(1)} \), until about 0.18 V vs. OCP. Further increase in the overpotential reduces the electrochemical dissolution, since the decrease in \( Zr^{3+}_{ads(1)} \) surface coverage is more than the increase in rate constant \( k_7 \). The initial increase and the further decrease in electrochemical dissolution rate is the combined effect of the change in these two variables with overpotential. In the passive region, both dissolution rates are significant, leading to insufficient passivation of Zr metal in acidic fluoride media.

**Conclusions**

The detailed mechanism of Zr anodic dissolution in acidic fluoride media was identified using mechanistic analysis of potentiodynamic polarization and EIS data acquired at multiple dc potentials in both active and passive regions. XPS results provide evidence for the presence of Zr(III) and Zr(IV) species, as well as oxides, and oxyfluorides on the electrode surface. The proposed mechanism contains four adsorbed intermediates, which are likely to be oxides, sub-oxides and oxyfluorides of Zr. The changes in the fractional surface coverage of the intermediates with respect to potential was estimated. The model predicts that, at large overpotentials, although the surface is covered with Zr(IV) species, both chemical and electrochemical dissolution rates are insignificant, leading to insufficient passivation of Zr.

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**Appendix A**

The expressions for steady-state surface coverage of various species are shown in Eqs. A1–A4. Here the subscript “dc” represents the rate constant is evaluated at \( \Delta E \).

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**References**

1. J. Ai, Y. Chen, M. Urquidi-Macdonald, and D. D. Macdonald, *J. Electrochem. Soc.*, 154, C43 (2007).
2. Y. Chen, M. Urquidi-Macdonald, and D. D. Macdonald, *J. Nucl. Mater.*, 348, 133 (2006).
3. F. Rosalbino, D. Maccio, A. Saccone, E. Angelini, and S. Delfino, *J. Solid State Electrochem.*, 14, 1451 (2010).
