Fluorine doped tin oxide (FTO) is a transparent conducting oxide which is widely used in different applications ranging from sensors, digital displays, smart window coatings, catalysts supports, and electrode substrates for various electrochemical applications. FTO shows higher chemical and thermal resistance and better mechanical properties than that of ITO. FTO has a (rutile) tetragonal structure with fluorine incorporated as a donor with a direct bandgap of 3.6 eV and an optical bandgap of ~5 eV. If the wave vector (k) of conduction band minimum (CBM) aligns with the wave vector of valence band maximum (VBM) in the energy (E) versus crystal momentum plot of a semiconductor material, then it is considered a direct bandgap material because the electron transition occurs by conserving momentum and no energy is dissipated by phonon or photon emissions. It is generally considered that fluorine occupies the oxygen site as a singly charged donor because of its similar atomic radius to that of O2− and similar bonding energies of Sn-O and Sn-F. Fluorine doping of SnO2 results in low electrical resistivity of FTO (< 4 x 10−4 Ω cm), and interstitial fluorine displaces the oxygen in the lattice structure. Fluorine on an oxygen site is considered to act as a shallow donor. It is reported that an increased level of F doping increases the resistivity which could be due to compensation of donors. Oxygen vacancies (V0) participate in the charge transfer reaction of SnO2 and the conductivity varies inversely with pO2.

Since FTO is used as an electrode as well as a catalyst in various electrochemical applications, stability against corrosion is an important issue. FTO is considered to have a chemical stability greater than SnO2 due to fluorine doping which results in ionic type bonding. However, theoretical calculations based on density functional theory indicated that the cohesive energy decreased with the incorporation of fluorine in the SnO2 lattice. A finite amount of electron density of states (DOS) at the Fermi level has been reported for the F doped and Sb SnO2 that resulted in a better electrical conductivity. On the other hand, this finite DOS at the Fermi level may be detrimental to the chemical stability of the material because it is widely reported that materials having a clear separation between completely filled bonding state and empty antibonding states will have a high melting point and good chemical stability. These observations indicate that FTO may not be as stable as it is perceived to be.

An overview of the literature on the corrosion behavior of FTO showed mixed results on its stability. Corrosion of SnO2 at anodic potentials in LiClO4 solution was reported by Cachet et al. Corrosion reportedly occurred in a narrow potential range of 0.8 to 1.2 V SCE at pH 8. A current peak was observed at 1.1 V SCE. The corrosion products observed in pH 11 solution were Sn4(OH)6Cl2 and Sn3O(OH)2Cl2. The anodic corrosion process was attributed to the reaction of OH− and Cl− radicals with the oxide surface that captured the electrons causing breaking of the surface bonds. The building up of the corrosion intermediates shifted the band edges of SnO2 to more positive potentials.

In pH 8 buffer solution with 0.04 M chloride ions, the corrosion of SnO2 with F and Sb doping was observed at a narrow potential window of 0.9−1.3 V SCE. This potential window was in the vicinity of chloride oxidation potential. FTO was coated on the austenitic stainless steel bipolar plates of fuel cells to improve the corrosion resistance. The SnO2:F coating reduced the dissolution rate of 316L stainless steel in 1 M H2SO4 + 2 ppm F− solution at 70 °C by half of that observed on the uncoated 316L. When cathodically polarized, FTO showed monotonous increase in cathodic current in 0.3 M Na2SO4 (un-adjusted pH) when the potential went more negative to −1.4 V SCE and was attributed to hydrogen evolution. When the potentials were scanned in the anodic direction, two oxidation peaks were noted at −0.94 and −0.28 V SCE possibly linked to hydrous tin oxide/tin hydroxide. Electrochemical etching of FTO in 2 M HCl + 0.03 M zinc acetate at 0.03 V using a two-electrode configuration was reported by Bae et al. Benck et al. evaluated different substrates including ITO and FTO for electrochemical electrode applications and observed the FTO substrate to be stable in three different electrolytes (sulfuric acid, sodium acetate, and sodium hydroxide). The overview of the literature showed mixed results on the stability of the FTO.

The main objective of this investigation was to evaluate the electrochemical conditions that may cause degradation of the FTO, and understand the underlying mechanism of such degradation. In order to accomplish this objective, potentiodynamic polarization and cyclic voltammetry studies were carried out in different pH conditions using commercial FTO substrates. Electrochemical impedance spectroscopy, UV-Vis photo absorbance spectroscopy, electron microscopy, and Raman spectroscopy were employed for understanding the electrochemical degradation process.

**Experimental**

FTO coated glass slides (size: 100 mm × 100mm) were obtained from a commercial supplier (TechInstro, India). These were 1.1 mm thick clear soda lime glass plates coated with 180–200 nm thick fluorine doped tin oxide by the spray pyrolysis method. There was no passivation layer applied either to the coating or glass. The specific resistivity of the FTO glass was 9–11 ohm/sq and transmittance at 550 nm was ~79%. 10 mm wide 20 mm long specimens were cut from the coupons, cleaned with soap water, rinsed in deionized water, ultrasonicated in acetone, and dried in air before electrochemical testing. The exposed area in all the tests was 1.35 cm². The test
electrolytes were 0.1 M HCl (pH: 1.05), 0.1 M HNO₃ (pH: 1.1), 0.1 M NaCl (pH: 6.2), 0.1 M NaOH (pH: 13.1), and 0.1 M NaOH + 0.1 M NaCl (pH: 13.1).

Prior to starting each electrochemical experiment, the FTO specimen was immersed in the test solution for 600 seconds at the open circuit condition. The electrolyte was not purged with air or inert gas. The electrolyte was exposed to ambient air. The electrochemical cell consisted of a platinum counter electrode, FTO working electrode, and an Ag/AgCl reference electrode in saturated KCl. All the potentials indicated in this work were measured with reference to Ag/AgCl in saturated KCl which is +197 mV versus a standard hydrogen electrode (SHE). Anodic and cathodic polarization measurements were carried out separately on two different specimens in each electrolyte using a potentiostat (Gamry Instruments). Cathodic polarization across all solutions ranged from 0 V vs open circuit potential (OCP) to −2 V vs Ag/AgCl. The anodic polarization potentials ranged from 0 V vs OCP to +3 V vs Ag/AgCl. Potentiodynamic polarization measurements were carried out at a scan rate of 0.5 mV/s. Electrochemical impedance spectroscopy was carried out at the open circuit condition before and after potentiodynamic polarizations by scanning the frequency from 10 kHz to 0.1 Hz. Mott-Schottky analysis was carried out by measuring the imaginary impedance at 1000 Hz and every 50 mV intervals by scanning the potential from positive to negative values. The FTO samples were cleaned with DI water and acetone after the corrosion testing.

In order to understand the surface chemistry of the FTO during electrochemical conditioning, in-situ UV-Vis photo absorbance spectroscopy was carried out (Spectro 115E, 350–1050 nm, Gamry Instruments). The electrochemical cell consisted of 0.8 cm wide FTO as the working electrode, a Pt-wire loop counter electrode, and a miniature Ag/AgCl reference electrode. These electrodes were assembled in a 1 cm square quartz cuvette having a volume of 10 ml. The photo absorbance spectra were collected by conditioning the FTO at different potentials determined from the cyclic voltammetry (CV). During the CV, first the potential was scanned in the cathodic direction from OCP to −2.0 VAg/AgCl (pH 1.1) or −2.8 VAg/AgCl (pH 13.1) at a scan rate of 10 mV/s. After reaching the cathodic potential limit, the potential scanning continued in the anodic direction to a maximum potential of 2.5 VAg/AgCl (pH 1.1), or 1.8 VAg/AgCl (pH 13.1). The cyclic voltammetry data allowed us to gather information regarding potential windows and polarization potentials for the potentiostatic in-situ UV-Vis experiments. The potentials of potentiostatic (PS) experiments were determined from the cyclic voltammetry (CV) peak currents and shoulders. The in-situ UV-Vis absorbance spectra were collected by conditioning the FTO specimen at different constant potentials. Each experiment started by applying the highest cathodic potential and moving to the next desired potential in the anodic direction. Each potential was applied for 120 s and optical absorbance spectra were collected at every 50 s. The average of four spectra is reported.

Cyclic stability of the FTO was evaluated by carrying out cyclic voltammetry from −2 to 2 VAg/AgCl in 0.1 M HCl and 0.1 M NaOH electrolytes at a scan rate of 1 V/s. The number of CV cycles continued until the recorded peak current density was less than 10 μA/cm². This type of test is referred to as accelerated stress test. All electrochemical tests were either duplicated or triplicated to verify reproducibility, and only the repeatable results are presented in this report.

After electrochemical tests, the FTO specimens were analyzed ex-situ using a scanning electron microscope (ZEISS LEO SUPRA 35 VP), and a Raman spectrometer. Raman spectra obtained with a Thermo Fischer DXR Raman microscope operating with a 10 mW, 532 nm wavelength laser. A pair of spectra points taken for samples collected in each reaction. The scattering volume is approximated to be 2 μm² and spectra were collected in the range 10 - 4000 cm⁻¹ with a spectral resolution of 2 cm⁻¹.

**Results and Discussion**

Figures 1a and 1b show the SEM micrograph and XRD profile of the as-received FTO specimen. The FTO coatings show faceted grains with sizes ranging from 120 to 200 nm. The XRD peaks indicated a tetragonal lattice structure (cassiterite SnO₂ according to JCPDS file # 00-005-0467) with a preferred growth orientation along (200) planes.

**Anodic polarization.**—Figure 2a shows the anodic polarization behavior of FTO in different pH conditions. The anodic polarization started from the open circuit potential without any prior cathodic polarization. The OCP values in different electrolytes are summarized in Table I. The OCP values of FTO shifted in the negative direction as the pH of the electrolytes increased. The OCP was more positive in the nitric acid solution and more negative in the NaOH solutions. The anodic polarization behavior of FTO was influenced more by the pH of the electrolytes than by the anions of the solution. For example, similar anodic polarization behaviors were noted between nitric acid and hydrochloric acid (pH ∼ 1) solutions, as well as between NaOH, and NaOH + NaCl (pH ∼ 13) solutions. Monotonic increase in the current density was noted with increase in the anodic potential in the pH ∼ 1 solutions, without a well-defined transition to passive state. On the other hand, a passive-like behavior was observed in high pH solutions, especially in the 0.1 M NaCl. The Sn was fully oxidized in the FTO. Therefore, the observed anodic current is attributed neither to oxidation of FTO nor to other significant faradaic reactions. The anodic current could be associated either with the charging and discharging of surface states present in the semiconductor electrode,24 or with formation of an electron depleted region at the surface by band bending during anodic polarization that supplied electrons to the bulk which in turn flowed through the potentiostatic circuit causing an anodic current.25 The band bending increased with an increase in the anodic polarization. Therefore, the monotonic increase in the current density observed in pH ∼ 1 solutions at potentials below 1.5 VAg/AgCl could be associated with the electron flow due to band bending, and ionization of deep donor levels such as oxygen vacancies (V'O).26 When the semiconductor electrode has a low level of doping, electron tunneling is considered to be the main mechanism of anodic current density.27 The observed anodic current density at potentials below 1.2 VAg/AgCl in acidic and near-neutral electrolytes was less than 0.2 μA/cm².
The anodic current density increased significantly at potentials more positive than 1.5 V Ag/AgCl. Cachet et al. proposed a corrosion mechanism based on the adsorption and oxidation of Cl ion. Adsorption of Cl ions on the SnO2 surface has been supported by carrying out a sequence of electrochemical experiments by Laitinen et al. Cachet et al. estimated the adsorbed layers to be one or two monolayers based on the electrochemical quartz crystal microbalance studies. The adsorption induced corrosion reactions were based on the Volmer-Tafel-Heyrovsky mechanisms given as:

\[ M + X^- \leftrightarrow M \cdots X^+ + e^- \quad \text{(Volmer step)} \]  
\[ M \cdots X^+ \leftrightarrow M-X \quad \text{(radical formation step)} \]

Where \( M \) denotes an active metal site in the FTO, \( X^- \) denotes Cl or OH, and \( X^+ \) denotes the radical. The release of electron flowed through the potentiostat recording an anodic current. This radical formation step is followed by formation of an adsorbed layer:

\[ M \cdots X^+ \leftrightarrow M-X \quad \text{(radical formation step)} \]

At this stage, two possible reactions could occur such as: i) evolution of chlorine or oxygen and (ii) a chemical reaction that breaks the Sn-O bond and forms corrosion products such as \( SnCl_2^{2-}, SnOCl_2 \).

The gas evolution reaction is given by either Tafel or Heyrovsky step:

\[ M-Cl \leftrightarrow M + Cl_2 \quad \text{(Tafel)} \]  
\[ M-Cl \leftrightarrow M + Cl_2 \quad \text{(Heyrovsky)} \]

It is well documented that very large overpotential is required for oxygen evolution on the SnO2 electrode. Cachet et al. reported higher activity of Sb doped SnO2 toward the chlorine evolution reaction than that of fluorine doped SnO2. The chlorine evolution wave was reported to initiate at 2.7 V vs. SCE. In this investigation, FTO specimens showed similar current densities in 0.1 M HCl and 0.1 M HNO3 solutions up to 2 V Ag/AgCl. The increase in the current density above 2 V Ag/AgCl could be attributed to the oxygen evolution reaction (OER) in the nitric acid solution, and both oxygen and chlorine evolutions in the HCl and NaCl solutions as seen in Figure 2a. The overpotential for OER in 0.1 M HNO3 at a current density of 1 mA/cm² was about 1.4 V. Since both oxygen and chlorine evolution reactions are possible in 0.1 M HCl solution, the overpotential for OER cannot be estimated unambiguously. Chlorine evolution is not expected in alkaline solution due to formation of stable ClO4 ions. Therefore, the anodic current recorded at potentials > 0.6 V vs. Ag/AgCl in NaOH + NaCl electrolyte could solely be attributed to the OER. The overpotential at 1 mA/cm² for OER in pH 13 solutions was about 1.2 V. It is noted that addition of chloride decreased the OER activity of FTO in the alkaline solution. This is an expected result because both OH⁻ and Cl⁻ will compete for adsorption sites and the reaction kinetics could be slowed down. Overall, the anodic polarization studies on the FTO in different pH electrolytes indicated the recorded anodic current was predominantly due to oxygen or chlorine evolution depending on the electrolyte, and not to dissolution of FTO. However, the oxygen evolution reaction could involve removal of the oxygen in the oxide lattice by the Reaction 5 and by the Volmer-Heyrovsky steps:

\[ SnO_2 \rightarrow Sn^{4+} + O_2 + 4e^- \]

It should also be noted that such dissolution reactions depend on how the diffusivity of oxygen is affected by the defect structures present in the material. Fluorine doping could help improve the stability under OER condition.

Table I summarizes the ranges of Tafel slopes and exchange current densities for OER on FTO in different electrolytes. The anodic Tafel slope was calculated by considering the linear portion of the anodic polarization plot closer to the corrosion potential. The Tafel slope of the OER was calculated by considering the linear portion of the anodic polarization between 1.23 V vs. SHE and ~600–900 mV positive to 1.23 V vs. SHE. The OER equilibrium potentials at pH: 1.1, 6.2, and 13.1 are 0.97, 0.67, and 0.26 V vs. Ag/AgCl, respectively. The Tafel slope for a single electron step for OER (\( b_{OER} \)) is given as:

\[ b_{OER} = \frac{\partial \alpha}{\partial \log j} = \frac{2.3RT}{a_dF} \]

Where \( \varepsilon \) = overpotential, \( j \) = current density, \( a_d \) = transfer coefficient, and other symbols have the usual meanings.

### Table I. Summary of anodic polarization of FTO in different electrolytes.

| Test condition | Range of open circuit potential, V Ag/AgCl | Range of anodic Tafel slope, V/decade | Range of OER – Tafel slope, V/decade | Range of OER exchange current density, A/cm² |
|----------------|------------------------------------------|--------------------------------------|--------------------------------------|-----------------------------------------------|
| 0.1 M HNO₃     | 0.44 to 0.48                             | 0.46 to 0.50                         | 0.37 to 0.42                         | \( 9.62 \times 10^{-8} \) to \( 6.2 \times 10^{-7} \) |
| 0.1 M HCl      | 0.39 to 0.42                             | 0.48 to 0.51                         | 0.24 to 0.25                         | \( 5.8 \times 10^{-8} \) to \( 7.7 \times 10^{-9} \) |
| 0.1 M NaOH     | −0.132 to −0.138                        | 0.38 to 0.48                         | 0.068 to 0.08                        | \( 2.2 \times 10^{-12} \) to \( 7.6 \times 10^{-12} \) |
| 0.1 M NaOH + 0.1 M NaCl | −0.14 to −0.143                        | 0.30 to 0.36                         | 0.12                                | \( 3.7 \times 10^{-11} \) |
| 0.1 M NaCl     | 0.20 to 0.23                             | 1.36 to 1.42                         | 0.125 to 0.2                         | \( 7.2 \times 10^{-12} \) to \( 1.1 \times 10^{-11} \) |

Figure 2. Polarization behavior of FTO in different electrolytes: (a) anodic polarization, and (b) cathodic polarization.
There are several possible reaction steps for OER on the oxide surface. It is well documented that FTO contains a significant concentration of oxygen vacancies that results in good electrical conductivity. Also, it is well documented that oxygen vacancies (denoted as \( V_0 \) in Equation 7) are active sites for water dissociation. Therefore, the OER steps in the acidic or neutral media considered here are based on the original work proposed by Bockris and coworkers.

\[
\text{VO}_x\text{M-O} + \text{H}_2\text{O} \rightarrow \text{O-M-OH} + \text{H}^+ + e^- \tag{7}
\]

O-M-OH + O-M-OH \rightarrow 2 M-O + O_2 + 2H^+ + 2e^- \tag{8}

If the reaction 7 is the rate limiting step for OER, then the current is given by the relation:

\[
I = \frac{nFk_{OH}^0 a_{OH}}{RT} \exp\left(-\frac{\alpha_7 F\varepsilon_7}{RT}\right) \tag{9}
\]

Where, \( n \) = number of electrons, \( F \) = Faraday’s constant, \( A = \text{area} \), \( k_7 = \text{rate constant of Reaction 7 in the forward direction which is given by the relation} \)

\[
\theta_1 = \frac{k_7^0 a_{OH} \exp\left(\frac{F\varepsilon_7}{RT}\right)}{K_7^0 a_{OH}^2 + K_7^0 a_{M}^2 \exp\left(\frac{F\varepsilon_7}{RT}\right)} \tag{10}
\]

Where, \( K_7^0 \) = the ratio of forward and reverse reaction rate constants, \( \theta_1 = \text{surface coverage,} \ a_{OH} = \text{activity of water,} \ e = \text{potential} \). The current involved in the reaction 8 can be estimated from the relation:

\[
I = \frac{nFk_{OH}^0 \theta_{12}^2 \exp\left(1 - \alpha_{12}\right) F\varepsilon_{13}}{RT} \tag{11}
\]

Where \( \theta_{12} \) is given by the relation 10.

The OER kinetics in the alkaline solutions could occur by the following steps:

\[
\text{VO}_x\text{M-O} + \text{OH}^- \rightarrow \text{OH-M-O} + e^- \tag{12}
\]

\[
\text{OH-M-O} + \text{OH}^- \rightarrow \text{MOO}^- + \text{H}_2\text{O} \tag{13}
\]

\[
\text{MOO}^- + \text{MOO}^- \rightarrow 2 \text{MO} + \text{O}_2 + 2e^- \tag{14}
\]

If Reaction 12 is the rate limiting step for OER, then the current is given by:

\[
I = \frac{nFk_{OH}^0 a_{OH} \exp\left(1 - \alpha_{12}\right) F\varepsilon_{13}}{RT} \tag{15}
\]

When the rate limiting step is Reaction 13, equilibrium condition is assumed for Reaction 12, and the surface coverage of MOOH, \( \theta_{12} \) may be approximated by the reaction:

\[
\theta_{12} = \frac{k_{12}^0 \exp\left(\frac{F\varepsilon_{12}}{RT}\right)}{k_{12}^0 + K_{12}^0 \exp\left(\frac{F\varepsilon_{12}}{RT}\right)} \tag{16}
\]

The current associated with Reaction 13 is given by the relation:

\[
I = \frac{nFk_{OH}^0 \theta_{12}^2 a_{OH} \exp\left(1 - \alpha_{13}\right) F\varepsilon_{14}}{RT} \tag{17}
\]

When Reaction 14 is rate limiting, the OER current could be expressed as:

\[
I = \frac{nFk_{OH}^0 \theta_{14}^2 \exp\left(1 - \alpha_{14}\right) F\varepsilon_{14}}{RT} \tag{18}
\]

Where \( \theta_{14} \) is written as:

\[
\theta_{14} = \frac{k_{14}^0 a_{OH} \exp\left(\frac{F\varepsilon_{14}}{RT}\right)}{k_{14}^0 + K_{14}^0 \exp\left(\frac{F\varepsilon_{14}}{RT}\right)} \tag{19}
\]

The Tafel slopes of 120 mV/dec, 40 mV/dec, and 30 mV/dec are widely associated with Volmer, Heyrovsky, and Tafel type rate determining steps, respectively. In this investigation, the Tafel slope of OER in 0.1 M NaOH + 0.1 M NaCl was 120 mV/dec, which suggests Volmer step given in Reaction 11 to be the rate limiting step. A similar mechanism could be suggested for OER in the 0.1 M NaCl solution. The Tafel slope of the 0.1 M NaOH did not align well with any one particular mechanism. It could be suggested that depending on the surface coverage, and availability of active sites, both Volmer (Reaction 12), and Heyrovsky (Reaction 13) could be operative. The Tafel slopes observed in acidic solutions were much higher than those observed in neutral or alkaline solutions. A Tafel slope of 393 mV/dec was reported for NiCoO₂ nanosheets in 0.1 M KOH. The exchange current density for OER on FTO was in the range of \( 2 \times 10^{-12} \) to \( 3.7 \times 10^{-11} \) A/cm² in neutral and alkaline solutions. Acidic solutions showed exchange current densities in the order of \( 10^{-9} \) to \( 10^{-7} \) A/cm² for OER on FTO.

Table II summarizes the range of linear polarization resistance values calculated during anodic polarization of FTO in different pH electrolytes. The resistance was calculated by polarizing the specimens \( \pm 25 \) mV versus their open circuit potentials. The resistance before conducting the potential dependent polarization experiment did not vary with the pH of the electrolyte. However, the linear polarization resistance decreased considerably when tested on the specimens that were polarized to \( 3 \) V Ag/AgCl except for the specimens polarized in the 0.1 M NaOH solution. The increase in the resistance could be attributed to formation of a possible corrosion product layer in the NaOH solution. Such a protective layer may not be stable in the NaOH + NaCl solution, and in the acidic solutions as well.

**Cathodic polarization**—Figure 2b shows the cathodic polarization plots for FTO in different pH conditions. Here, depending on the open circuit potentials two different cathodic reactions are considered viz., 1) oxygen reduction reaction (ORR), and 2) hydrogen evolution reaction (HER). Table III summarizes the cathodic polarization results in terms of Tafel slopes of these two reactions and their estimated exchange current densities. The Tafel slope of ORR was calculated from the linear portion of cathodic polarization plot between 0.5 V and 0.1 V Ag/AgCl for pH 1 solutions, and between −0.3 and −0.6 V Ag/AgCl for pH 13 solutions. It is noted that the Tafel slopes of ORR were similar to those observed for OER. This indicates that the ORR (\( O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \)) is also controlled by the presence of oxygen vacancies of FTO. Oxygen vacancies show good affinity to oxygen adsorption and the strong binding between these two lowered the activation energy for the ORR. The exchange current densities of the ORR are summarized in Table III which ranged from \( 1.0 \times 10^{-12} \) A/cm² (in 0.1 M NaCl) to \( 4.6 \times 10^{-10} \) A/cm² (in 0.1 M HNO₃). The cathodic polarization plots revealed distinguishable regions of active and concentration polarizations for both ORR and HER. The limiting current density of ORR was in the order of \( 10^{-4} \) A/cm². The cathodic polarization of FTO was pH specific and identical behaviors were observed in acidic solutions (0.1 M HNO₃ and 0.1 M HCl), and alkaline solutions (0.1 M NaOH, and 0.1 M NaOH + 0.1 M NaCl). The HER equilibrium potentials at pH: 1.1, 6.2, and 13.1 are \(-0.26, -0.56 \) and \(-0.97 \) V Ag/AgCl, respectively. The Tafel slopes of the HER were calculated by considering the linear portion of the cathodic polarization plot between \(-0.75 \) and \(-1.0 \) VAg/AgCl for the pH 1.1 solutions, and between \(-1.56 \) and \(-1.78 \) VAg/AgCl for the pH 13.1 solutions. The Tafel slopes for HER on FTO ranged from \(-0.17 \) to \(-0.22 \) V/dec. The exchange current densities of HER ranged from \( 1.2 \times 10^{-8} \) to \( 9 \times 10^{-7} \) A/cm². The cathodic polarization behavior is important to understand the corrosion rate of FTO in the open circuit conditions. According to the mixed potential theory, both the corrosion potential, and corrosion current are determined by the Tafel slopes and exchange current.
differences of the anodic and cathodic reactions. Higher exchange current density and shallower Tafel slope of the cathodic reactions may result in more noble corrosion potential and higher corrosion current density ($i_{corr}$). This line of reasoning indicates that the corrosion rate of FTO will be higher in the acidic solutions than in the alkaline solutions.

The cathodic polarization could also result in the reduction of Sn$^4+$ either to a lower valence state or to elemental form by the reaction:

$$\text{SnO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{Sn}^{(4-a)+} + 2\text{H}_2\text{O} \quad [20]$$

Formation of SnH$_4$ is possible at low potential by following the reaction:

$$\text{Sn} + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{SnH}_4 (g) \quad E^0 = -1.074 - 0.059\text{pH} -0.0148\log p_{\text{SnH}_4} \quad [21]$$

Since SnH$_4$ is a gaseous phase, cathodic corrosion will occur at potentials more negative to the redox potential of Reaction 21. Placid et al. observed that FTO was stable when cathodically polarized to potentials more negative to the redox potential of Reaction 21. However, these authors observed two oxidation peaks during the reverse scan that corresponded to hydrous tin oxide/hydroxide though post-test surface analyses did not show formation of new phases. Our investigation indicated a change in the surface morphology of the FTO after cathodic polarization in the 0.1 HCl solution.

Figure 3a shows the morphology of the FTO grains after anodic polarization in the 0.1 M HCl solution. No significant amount of dissolution after anodic polarization was observed. On the other hand, the specimen cathodically polarized in 0.1 M HCl showed significant change in the morphology (Fig. 3b) as compared to that of pristine FTO. The change in morphology could be attributed to reduction of SnO$_2$ and formation of new phases such as SnO, Sn(OH)$_2$, Sn(0), or SnH$_4$. Since the formation of gaseous SnH$_4$ results in cathodic corrosion, this reaction could lead to a significant change in the morphology. Figures 4a–4f show the morphologies of the post tested FTO specimens after anodic and cathodic polarizations. It was observed that anodic polarization of FTO in 0.1 M HNO$_3$ did not result in any noticeable amount of dissolution. Similar conclusion cannot be drawn for the specimens polarized in neutral and alkaline pH electrolytes because the sharp faceted grains of FTO appeared to be rounded after anodic polarization as seen in Figures 4c and 4e. This could be attributed to the breaking of Sn-O bonds during oxygen evolution by removal of lattice oxygen as given in the Reactions 3 and 5. In contrast to the cathodically polarized specimen in the 0.1 M HCl, the specimen cathodically polarized in the 0.1 M HNO$_3$ showed no noticeable change in the morphology. This indicated stability of the FTO in the nitric acid solution was attributed to the presence of NO$_3^-$/NO$_2^-$ as active redox species instead of Sn$^+/\text{Sn}^{2+}$. The possible redox reactions are listed as:

$$\text{NO}_3^- + 2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{NO}_2^- + \text{H}_2\text{O} \quad [22]$$

$$\text{NO}_2^- + 7\text{H}^+ + 6\text{e}^- \leftrightarrow \text{NH}_3\text{OH} + \text{H}_2\text{O} \quad [23]$$

It is possible that during cathodic polarization a monolayer of SnO$_2$ transformed to Sn which catalyzed the nitrate reduction reactions. The
surface of FTO was protected by the localized formation of NH4OH. Similar observation was reported by Lee and Lu.41

Figures 4d and 4f show the morphologies of the FTO after cathodic polarization in NaCl and NaOH solutions, respectively. A noticeable change in the morphology of these post-test specimens could be observed which indicated reduction of SnO2 at the surface level and possible formation of new surface layers. In this work, the dissolution products in the electrolytes were not analyzed. Recently, Geiger et al.42 investigated the stability of tin based electrocatalyst supports in 0.1 M H2SO4 by polarizing at a potential window of −0.6 to 3.2 VRHE. The dissolution products were analyzed in-situ using inductively coupled plasma-mass spectroscopy. These authors42 observed significant reductive dissolution of Sn during cathodic polarization and the dissolution charge was 5.6% of the total cathodic charge. However, no measurable dissolution was reported when the FTO was polarized between −0.34 VRHE and 2.7 VRHE. Anodic dissolution was observed when the potential was increased to 3.2 VRHE. Similar type of dissolution could be expected in the present work.

**Electrochemical impedance spectroscopy (EIS).**—Figures 5a–5f illustrate the Nyquist plots of FTO specimens in different electrolytes before and after potentiodynamic polarization studies. The Nyquist plots essentially showed one time constant. Therefore, the EIS data were fitted with a simple Randle’s type circuit as shown in Table IV. The values of the circuit components are summarized in Table IV for various test conditions. In the equivalent circuit, Rs and Rp represent the electrolyte resistance and resistance to charge transfer, respectively. Qf represents interfacial leaky capacitance whose impedance (Z) is given by the relation: $Z = 1/((jω)^m Q_f)$ where $j = \sqrt{-1}$, $ω$ = frequency, and the exponent ‘m’ represents the surface heterogeneity or continuously distributed time constants for charge transfer when $m < 1$.43 Since the Nyquist plots predominantly revealed one semicircle implying a single time constant, the impedance behavior is represented by a single R-C loop. Both the FTO coating and faradaic processes occurring at the FTO/electrolyte are represented by a constant phase element (Qf) connected in parallel with a resistor (Rp). The resistance of the electrolyte is represented by the resistor Rs which is in series with the charge transfer resistance of the FTO and electrolyte interface. The impedance responses associated with the FTO coating and the electrolyte interface could not be resolved individually because of the observed single time constant. Similar type of equivalent circuit was reported for the FTO in dilute acidic and basic solutions.44 The increase in the Rp and decrease in the values of Qf indicated increased corrosion resistance.

Figure 5a shows the EIS of FTO in 0.1 M HCl solution before and after anodic polarization. The equivalent circuit values summarized in Table IV indicate that the Rp value increased and the Qf value decreased after anodic polarization, indicating good corrosion resistance of FTO in the HCl solution under anodic bias conditions. After cathodic polarization, the values of both Rp and Qf. The decrease in
the $R_F$ value could be attributed to cathodic reduction of SnO$_2$ and cathodic corrosion. The decreased $Q_F$ could be associated with decrease in the electrochemically active area due to cathodic corrosion. Figure 5b shows the Nyquist plots of FTO before and after anodic polarization in nitric acid solution. After anodic polarization, the $R_F$ value decreased and the $Q_F$ increased by about 7% which indicated a decrease in the corrosion resistance of FTO in the nitric acid solution. Similar observation was made after cathodic polarization in the nitric acid solution. Figure 5c shows the EIS in NaCl before and after cathodic polarization. The impedance values considerably decreased after cathodic polarization in the NaCl solution. Figure 5d shows the impedance spectra of FTO in NaOH solution before and after anodic polarization. Both anodic and cathodic polarization in NaCl solution decreased the corrosion resistance of the FTO as seen from the EIS data summarized in Table IV. Figures 5e and 5f show the impedance spectra before and after anodic and cathodic polarization in the 0.1 M NaOH + 0.1 M NaCl solution.
NaOH + 0.1 M NaCl, respectively. The corrosion resistance of FTO was observed to increase after polarization in either direction in alkaline chloride solution.

Figures 6a–6f show the Mott-Schottky (M-S) plots of FTO before and after potentiodynamic polarizations in different pH conditions. The M-S plots showed positive slope at potentials < 1.5 VAg/AgCl, indicating n-type conductivity. At potentials between 1.5 and 2.0 VAg/AgCl a negative slope was observed, indicating p-type conductivity. The charge carrier density corresponding to the n-type conductivity is summarized in Table V. The charge carrier density may correspond to oxygen vacancies. Formation of one oxygen vacancy may release two electrons. When fluorine occupies the oxygen vacancy, only one electron would be released.5,7,8 Table V summarizes the n-type charge carrier densities calculated under different polarized conditions. It is observed that the charge carrier density did not vary significantly after anodic polarization in the high pH electrolytes. On the other hand, ~100% increase in the charge carrier density was observed after anodic polarization in acidic solutions. An order of magnitude increase in the charge carrier density was noted after cathodic polarization in the alkaline and neutral solutions, whereas an order of magnitude decrease of the charge carrier density was noted in HCl solution. This could be attributed to the reduction of SnO₂ to Sn in the HCl solution.

At high anodic potentials, a negative slope was observed in the M-S plots of FTO before and after potentiodynamic polarizations in different pH conditions. A negative slope was observed, indicating a negative polarization in the alkaline and neutral solutions, whereas an order of magnitude increase of the charge carrier density was observed after anodic polarization in the HCl solutions. These observations indicated that SnO₂ was not significant during cathodic polarizations in these solutions.

Table IV. Equivalent electrical circuit and summary of the values of circuit components that fitted with the electrochemical impedance spectroscopy data of FTO before and after potentiodynamic polarization.

| Test Condition | Rs ohm | Rp ohm | Qt S cm⁻¹ | n | χ² |
|----------------|--------|--------|------------|---|----|
| 0.1 M HNO₃, pre-cathodic | 58.76 | 1.4 × 10⁹ | 13.8 × 10⁻⁶ | 0.982 | 5.2 × 10⁻³ |
| 0.1 M HNO₃, post-cathodic | 57.8 | 1.2 × 10⁹ | 17.5 × 10⁻⁶ | 0.971 | 2.3 × 10⁻³ |
| 0.1 M HNO₃, pre-anodic | 48.14 | 1.07 × 10⁹ | 16.8 × 10⁻⁶ | 0.983 | 5.3 × 10⁻³ |
| 0.1 M HNO₃, post-anodic | 46.27 | 0.675 × 10⁶ | 18 × 10⁻⁶ | 0.975 | 0.5 × 10⁻³ |
| 0.1 M HCl, pre-anodic | 43.71 | 6.5 × 10⁶ | 22.4 × 10⁻⁶ | 0.982 | 0.24 × 10⁻³ |
| 0.1 M HCl, post-anodic | 43.59 | 12.6 × 10⁶ | 12.6 × 10⁻⁶ | 0.988 | 0.1 × 10⁻³ |
| 0.1 M HCl, pre-cathodic | 41.86 | 1.63 × 10⁶ | 12.9 × 10⁻⁶ | 0.969 | 4 × 10⁻³ |
| 0.1 M HCl, post-cathodic | 40.3 | 0.55 × 10⁶ | 1.85 × 10⁻⁶ | 0.89 | 25 × 10⁻³ |
| 0.1 M NaOH, pre-cathodic | 62.73 | 146.9 | 26.5 × 10⁻⁶ | 0.857 | 3.3 × 10⁻³ |
| 0.1 M NaOH, post-cathodic | 67.66 | 266.9 | 42.3 × 10⁻⁶ | 0.958 | 0.19 × 10⁻³ |
| 0.1 M NaOH, pre-anodic | 59.6 | 174.6 | 15.6 × 10⁻⁶ | 0.927 | 2 × 10⁻³ |
| 0.1 M NaOH, post-anodic | 61.15 | 128.3 | 16.9 × 10⁻⁶ | 0.924 | 1.6 × 10⁻³ |
| 0.1 M NaOH + 0.1 M NaCl, pre-anodic | 49.33 | 612.2 | 39.8 × 10⁻⁶ | 0.734 | 29 × 10⁻³ |
| 0.1 M NaOH + 0.1 M NaCl, post-anodic | 54.17 | 788.9 | 15 × 10⁻⁶ | 0.92 | 12 × 10⁻³ |
| 0.1 M NaOH + 0.1 M NaCl, pre-cathodic | 62.4 | 261.6 | 16.9 × 10⁻⁶ | 0.875 | 7.3 × 10⁻³ |
| 0.1 M NaOH + 0.1 M NaCl, post-cathodic | 65.93 | 353.1 | 5.5 × 10⁻⁶ | 0.93 | 1.43 × 10⁻³ |
| 0.1 M NaCl, pre-anodic | 72.56 | 3.65 × 10⁶ | 10.1 × 10⁻⁶ | 0.976 | 1.38 × 10⁻³ |
| 0.1 M NaCl, post-anodic | 69.5 | 4.68 × 10⁶ | 12.2 × 10⁻⁶ | 0.963 | 15.7 × 10⁻³ |
| 0.1 M NaCl, pre-cathodic | 86.4 | 1.6 × 10⁶ | 10.6 × 10⁻⁶ | 0.96 | 6 × 10⁻³ |
| 0.1 M NaCl, post-cathodic | 58.6 | 0.118 × 10⁶ | 99.7 × 10⁻⁶ | 0.852 | 0.108 |

Table V. Charge carrier density (n-type) based on Mott-Schottky analyses (cm⁻³).

| Solution            | Pre-anodic          | Post-anodic         | Pre-cathodic        | Post-cathodic       |
|---------------------|---------------------|---------------------|---------------------|---------------------|
| 0.1 M HCl           | 0.87 × 10⁻¹ – 1.12 × 10¹ | 1.60 × 10⁻¹ – 1.73 × 10¹ | 0.22 × 10⁻¹ – 0.28 × 10¹ | 0.62 × 10⁻⁹ – 0.86 × 10⁻⁸ |
| 0.1 M HNO₃          | 1.22 × 10⁻¹ – 1.45 × 10¹ | 2.05 × 10⁻¹ – 3.15 × 10¹ | 2.4 × 10⁻¹ – 3.1 × 10⁻¹ | 2.0 × 10⁻² – 2.3 × 10⁻¹ |
| 0.1 M NaOH          | 1.04 × 10⁻¹ – 1.22 × 10¹ | 1.28 × 10⁻¹ – 1.43 × 10¹ | 1.02 × 10⁻¹ – 1.45 × 10⁻¹ | 1.07 × 10⁻² – 1.25 × 10⁻² |
| 0.1 M NaOH + 0.1 M NaCl | 0.47 × 10⁻¹ – 0.72 × 10² | 0.54 × 10⁻¹ – 0.82 × 10² | 0.44 × 10⁻¹ – 0.60 × 10⁻¹ | 1.19 × 10⁻² – 1.26 × 10⁻² |
| 0.1 M NaCl          | 0.68 × 10⁻¹ – 0.82 × 10² | 0.84 × 10⁻¹ – 0.93 × 10² | 0.42 × 10⁻¹ – 0.62 × 10⁻¹ | 0.82 × 10⁻² – 1.05 × 10⁻² |
Figure 6. Mott-Schottky plots of FTO in different electrolytes before and after polarization: (a) 0.1 M HNO$_3$, (b) 0.1 M NaCl before and after anodic polarization, (c) 0.1 M NaOH + 0.1 M NaCl before and after anodic polarization, (d) 0.1 M NaOH + 0.1 M NaCl before and after cathodic polarization, (e) 0.1 M NaOH before and after anodic polarization, and (f) 0.1 M NaOH before and after cathodic polarization.

| Solution              | Range of p-type charge carrier density ($\text{cm}^{-3}$) |
|-----------------------|-----------------------------------------------------|
| Pre-anodic ($\text{cm}^{-3}$) | Post-anodic ($\text{cm}^{-3}$)                      |
| 0.1 M HCl             | $1.73 \times 10^{20}$ - $1.92 \times 10^{20}$     | $0.45 \times 10^{21}$ - $0.56 \times 10^{21}$ |
| 0.1 M HNO$_3$         | $1.88 \times 10^{20}$ - $2.03 \times 10^{20}$     | $0.34 \times 10^{21}$ - $0.52 \times 10^{21}$ |
| 0.1 M NaOH            | $1.80 \times 10^{20}$ - $1.93 \times 10^{20}$     | $2.34 \times 10^{20}$ - $2.63 \times 10^{20}$ |
| 0.1 M NaOH + 0.1 M NaCl | $1.62 \times 10^{20}$ - $1.73 \times 10^{20}$     | $2.68 \times 10^{20}$ - $2.83 \times 10^{20}$ |
| 0.1 M NaCl            | $1.70 \times 10^{20}$ - $1.83 \times 10^{20}$     | $1.94 \times 10^{20}$ - $2.03 \times 10^{20}$ |

Table VI. p-type charge carrier density ($\text{cm}^{-3}$) based on Mott-Schottky analyses at high anodic potentials.
Figure 7. UV-Vis photo absorption spectra of FTO after electrochemical polarization at different potentials in different electrolytes: (a) Cyclic voltammograms of FTO in different electrolytes; (b) during polarization in 0.1 M HCl; (c) during polarization in 0.1 M HNO₃; (d) during polarization in 0.1 M NaCl; (e) during polarization in 0.1 M NaOH; (f) during polarization in 0.1 M NaOH + 0.1 NaCl.

UV-Vis absorbance occurs by excitation of bonding electrons. Absorption of photons could result in different types of electron transitions such as bonding to antibonding orbital (σ → σ*), nonbonding (unshared electron pairs) to antibonding (n → σ*), π → π*, transition of d and f electrons, and charge transfer electrons. Functional groups in a molecule can be identified from the wavelengths of absorption peaks by correlating with the type of bond. In this investigation, the optical path includes the electrolyte, FTO/electrolyte interface, and the bulk of FTO. The absorption spectra contain information of all these components. However, the variation in the spectra between different potentiostatic conditions of a given electrolyte system could be attributed to the changes occurring at the FTO/electrolyte interface. Fig. 7b shows the absorption spectra of FTO in 0.1 M HCl at different potentials. The spectrum at −1.6 V_Ag/AgCl was obtained under reducing condition. The optical absorbance decreased as the wavelength of light increased. The UV absorbance peaks of SnCl₂ were reported to occur at 236 and 323 nm with a shoulder tapering off at around 350 nm. Since the absorbance spectra were recorded at wavelengths longer than 350 nm, the presence of SnCl₂ as a corrosion product could not be confirmed. The lower absorbance than that observed in other potential conditions (except for 2.5 V_Ag/AgCl) could be associated with cathodic dissolution of the FTO that resulted in a porous film as seen in Fig. 3b. The absorbance increased when the potential was 2.5 V_Ag/AgCl, which could be attributed to oxidation of Sn back to SnO₂. At 2.0 V_Ag/AgCl, the absorbance started at about 510 nm, indicating presence of a low bandgap layer, possibly SnO type, on the
specimen. At 2.5 V_{Ag/AgCl}, the absorbance decreased possibly due to anodic dissolution or formation of oxygen vacancies that resulted in porous structure.

Fig. 7c shows the UV-Vis absorbance spectra at different potentials in the range of −2.0 to 2.5 V_{Ag/AgCl} in nitric acid solution. These potentials are associated with different positions at either cathodic or anodic current waves. Irrespective of the applied potential, the absorbance spectra showed more or less a similar trend. The absorbance of FTO in nitric acid solution was similar to that observed in the HCl solution at −1.6 V or 2.5 V_{Ag/AgCl}. This result suggests that polarization of FTO in cathodic and anodic directions in the nitric acide solution caused significant dissolution. The UV absorption of NO_3^− ion occurs at 200 nm (owing to π → π* transition) and near 300 nm (n → π* transition). These absorption peaks are not shown here due to limitation of the instrument used in this study. Fig. 7d shows the absorbance spectra collected in NaCl solution at different applied potentials starting at the most cathodic condition and moving in the anodic direction. The results are similar to those observed in the nitric acid solution.

Fig. 7e shows the absorbance spectra collected in 0.1 M NaOH solution. The highest absorbance was noted during the initial potential-tostatic conditioning at −2.7 V_{Ag/AgCl}. At this potential a significant reduction current was recorded in the CV. The reduction of SnO_2 could occur in two steps: first step as Sn(IV) → Sn(II); and second step Sn(II) → Sn(0). Conversion of Sn to SnH_4 could occur at low potentials. The high absorbance observed at this potential indicates that no significant change occurred with the specimen in 120 s. When the potential moved to −1.9 V_{Ag/AgCl} (shoulder of the cathodic wave) a significant reduction in the absorbance was observed implying degradation of the specimen. Application of anodic potentials did not change the absorbance behavior significantly from that observed in −1.9 V_{Ag/AgCl}. The UV-Vis absorbance peak for SnO in alcohol solutions was reported at around 330 nm. In this investigation, the absorbance data were recorded for wavelengths > 350 nm. Therefore, it is not possible to assign the absorbance peaks unequivocally to SnO. However, presence of SnO after electrochemical conditioning could not be ruled out. Fig. 7f illustrates the absorbance results of FTO tested in 0.1 M NaOH +0.1 M NaCl solution at different potentials starting from the cathodic potential and moving toward anodic direction. The results are similar to those observed in the NaOH solution.

**Raman spectroscopy of Post-CV tested FTO.**—Figures 8a–8e show the Raman spectra of FTO samples after anodic polarization in different electrolytes. The Raman spectroscopy was carried out in ambient condition. It should be noted that the specimens could oxidize in air after electrochemical experiments. Raman shift is the difference between the wavelengths of incident and scattered radiation caused by the change in polarizability during vibration of the atoms in the lattice. The tetragonal unit cell of SnO_2 has two formula units and as given in Table IV. Table VII summarizes the values of equivalent circuit components. It was observed that the Q_1 increased during the first 150 cycles which could be attributed to roughening of the surface due to reduction of SnO_2 and associated cathodic corrosion. This argument is supported by the morphological changes observed on the tested FTO surface. The charge transfer resistance (R_T) decreased with increase in the number of CV cycles until 150 cycles. The impedance of FTO increased at high frequencies with the number of CV cycles in the 0.1 M NaOH solution, as seen in Figure 9d. When the interfacial capacitance was determined at a fixed frequency of 1000 Hz from the imaginary impedance, a decreasing trend was noted as the CV cycles increased. Figure 9e shows the Mott-Schottky plots of FTO in the 0.1 M HCl after 50 and 100 cycles in comparison with that prior to CV tests. An n-type behavior was observed at potentials below 2 V_{Ag/AgCl} and a p-type behavior was noted at higher anodic potentials than 2.4 V. The n-type charge carrier densities were about 8 × 10^{20}, 6 × 10^{20}, and 5 × 10^{20} cm^{-3} after 0.5, 50, and 100 CV cycles, respectively. The flatband potentials shifted to more negative potentials from 0.15 to −0.1 V_{Ag/AgCl} and to −0.45 V_{Ag/AgCl} for 50, and 100 cycles, respectively. The Fermi energy levels of the FTO can be determined with the E_F (v_{TO}) Raman vibration of non-stoichiometric SnO_2. The broad peaks observed around 955, and 1090 cm^{-1} could be assigned to the glass substrate. Overall, the Raman spectroscopy results indicated that the FTO specimens tested in extreme pH conditions showed formation of surface oxygen vacancies; whereas, specimens exposed to 0.1 M NaCl showed only minor peaks associated with oxygen vacancies. Huang et al. analyzed the corrosion products of tin using Raman spectroscopy and observed peaks at 760, and 470 cm^{-1} for SnO; 904, 752, and 470 cm^{-1} for Sn(OH)_2; and 750, and 580 cm^{-1} for Sn(OH)_4. The Raman spectra of this investigation did not clearly reveal the presence of such corrosion products. Eifert et al. identified intermediate tin oxides such as SnO_2 and SnO using Raman spectroscopy. None of the intermediate oxide phases could be observed on the post-CV tested FTO specimens of this investigation.

**Cyclic stability studies.**—Cyclic stability or accelerated stress test results are presented in Figure 9. The specimens lost electrical connectivity after about 215 cycles in the 0.1 HCl solution. On the other hand, the peak current values in the 0.1 NaOH solution deteriorated significantly only after 500 cycles, as seen in Figure 9b, but the electrical connectivity was not lost even after 3500 cycles as seen from the EIS results presented in Figure 9d. The CV results in Figure 9a indicated that the cathodic and anodic peak current densities started to decrease considerably after 100 cycles. Figure 9c shows the impedance behavior as a function of number of CV cycles. The EIS data could be fitted with an equivalent electrical circuit similar to the one discussed earlier and as given in Table IV. Table VIII summarizes the values of equivalent circuit components. It was observed that the Q_1 increased during the first 150 cycles which could be attributed to roughening of the surface due to reduction of SnO_2 and associated cathodic corrosion. This argument is supported by the morphological changes observed on the tested FTO surface. The charge transfer resistance (R_T) decreased with increase in the number of CV cycles until 150 cycles. The impedance of FTO increased at high frequencies with the number of CV cycles in the 0.1 M NaOH solution, as seen in Figure 9d. When the interfacial capacitance was determined at a fixed frequency of 1000 Hz from the imaginary impedance, a decreasing trend was noted as the CV cycles increased. Figure 9e shows the Mott-Schottky plots of FTO in the 0.1 M HCl after 50 and 100 cycles in comparison with that prior to CV tests. An n-type behavior was observed at potentials below 2 V_{Ag/AgCl} and a p-type behavior was noted at higher anodic potentials than 2.4 V. The n-type charge carrier densities were about 8 × 10^{20}, 6 × 10^{20}, and 5 × 10^{20} cm^{-3} after 0.5, 50, and 100 CV cycles, respectively. The flatband potentials shifted to more negative potentials from 0.15 to −0.1 V_{Ag/AgCl} and to −0.45 V_{Ag/AgCl} for 50, and 100 cycles, respectively. The Fermi energy levels of the FTO can be determined

| Sample tested in | Sharp/strong peaks | Weak peaks | Broad peaks | Shoulder |
|------------------|--------------------|------------|-------------|----------|
| 0.1 M HCl        | 630                | 784        | 300         | 1090     | 952      |
|                  | 243                | 606        | 283         | 483      |          |
| 0.1 M NaCl       | 1099               | 244        | 772         | 482      | 955      |
|                  | 124                | 562        | 196         |          |          |
| 0.1 M HNO_3      | 1089               | 123        | 565         | 283      | 610      |
| 0.1 M NaOH       | 629                |            |             |          |          |
|                  | 630                | 778        | 1093        | 477      | 606      |
|                  | 243                | 567        | 477         | 606      |          |
| 0.1 M NaCl       | 132                |            | 283         |          |          |
| 0.1 M NaCl       | 1104               | 242        | 628         | 198      |          |
| 0.1 M NaCl       | 1062               | 123        | 283         |          |          |
| 0.1 M NaCl       | 630                | 606        | 123         | 1093     | 955      |
| 0.1 M NaCl       | 243                | 566        | 766         | 482      | 173      |
Figure 8. Raman spectra of FTO after electrochemical polarization in different electrolytes: (a) after anodic polarization in 0.1 M HCl; (b) after anodic polarization in 0.1 M HNO$_3$; (c) after anodic polarization in 0.1 M NaCl; (d) after anodic polarization in 0.1 M NaOH; (e) after anodic polarization in 0.1 M NaOH + 0.1 NaCl.

based on the flatband potential values. The conduction band minimum energy levels can be calculated using standard solid state physics expressions and the charge carrier density data obtained for different experimental conditions. The effective density of states ($N_C$) in the conduction band of pristine FTO was calculated as $5.14 \times 10^{24}$ m$^{-3}$ by considering the effective mass of an electron ($m^*$) as $0.27m_e$, where $m_e$ is the standard mass of electron. These calculations showed that the energy gap between the conduction band minimum (CBM) and Fermi level to be 0.129, 0.122, and 0.118 eV for the specimens of 0, 50, and 100 cycles, respectively. These results are summarized in Figure 11.
Figure 9. Cyclic stability testing of FTO: (a) Cyclic voltammetry of FTO in 0.1 M HCl; (b) Cyclic voltammetry of FTO in 0.1 M NaOH; (c) Bode plots at 0 and 200 cycles of CV in 0.1 M HCl; (d) Bode plots at 0 and 3500 cycles of CV in 0.1 M NaOH; (e) Mott-Schottky of FTO after 0, 50 and 100 cycles of CV in 0.1 M HCl.

as a schematic illustration to analyze the energetics of charge transfer. The band edge positions of the FTO are given in Fig. 10 as a function of number of cycles. The initial Fermi level of FTO was located at 0.4 V_{RHE}. The Fermi level was determined from the flatband potential data derived from the Mott-Schottky analyses. After 50, and 100 CV cycles, the Fermi level moved to 0.15 V_{RHE}, and $-0.194$ V_{RHE} respectively. The conduction band minimum (CBM) also moved with the movement of the Fermi level. As schematically illustrated in Fig. 10, it is seen that after 100 cycles the CBM is positioned above the energy level of H$_2$/H$^+$. The Fermi level shift after 100 CV cycles could help ease charge transfer for hydrogen reduction and possibly easy reduction of SnO$_2$ to Sn that lead to instability.

The surface morphology of the FTO specimens after stability tests are given in Figures 11a–11d. The images were acquired specifically at two locations viz 1) at the air/electrolyte interface where the failure was considered to initiate that caused loss of electrical connectivity, especially in the 0.1 M HCl solution, and 2) at the center of the area immersed in the electrolyte. The air/electrolyte interface region looked similar in both the electrolyte as seen in Figures 11a and 11c. The original faceted grains of FTO underwent significant dissolution at the grain boundaries and finer dissolution of the grain faces. It is believed that this intergranular type corrosion led to loss of electrical connectivity. On the other hand, different modes of degradation were observed at the center of the specimen depending on the environmental condition. In HCl solution, the faceted grains were still visible after 215 cycles of CV, but additional globular particles- possibly reduced Sn- were present as seen in Figure 11b. Figure 11d shows a complete intergranular type corrosion of FTO in the NaOH solution. The reduction of SnO$_2$ to Sn globular particles were not seen in this electrolyte, even though the cyclic voltammetry suggested a reduction of
Table VIII. Equivalent circuit values fitted with EIS data of FTO in HCl during stability tests.

| Number of CV cycles | $R_S$ (ohm) | $R_F$ (ohm) | $Q_F$ (S.s) | $\chi^2$ | $n$  |
|---------------------|-------------|-------------|-------------|---------|------|
| 0                   | 71.6        | $3.74 \times 10^6$ | $16.7 \times 10^{-6}$ | 0.992   | $30.2 \times 10^{-6}$ |
| 50                  | 74.51       | $14 \times 10^3$   | $50.2 \times 10^{-6}$ | 0.948   | $3.2 \times 10^{-3}$  |
| 100                 | 150         | $11.9 \times 10^3$ | $59.3 \times 10^{-6}$ | 0.898   | $1.2 \times 10^{-3}$  |
| 150                 | 651         | $2.14 \times 10^6$ | $74.5 \times 10^{-9}$ | 0.821   | $19 \times 10^{-3}$   |
| 200                 | 201         | $9.2 \times 10^6$  | $232 \times 10^{-9}$ | 0.952   | $18 \times 10^{-3}$   |

SnO$_2$ during the cathodic sweep and oxidation of Sn during the reverse sweep.

Fig. 12 illustrates the XRD patterns of FTO specimens after cyclic voltammetry in different electrolytes. Only the specimen tested in nitric acid solution showed additional XRD peaks as compared to the as-received FTO. The specimens tested in other electrolytes did not show any significant change in the XRD pattern. However, a decrease in intensity was observed in (110) and (310) planes after CV testing in HCl and NaOH+NaCl solutions. The specimen tested in the nitric acid solution showed a minor peak at 30.45° which could be associated with (101) plane of tetragonal SnO phase (PDF # 6-0395). The tetragonal SnO is considered a thermodynamically unstable phase. Additional peak at 28.55° could not be assigned to any known tin oxide phases. Similar observation was reported by Dai et al. during thermal annealing of SnO diskettes in oxygen atmosphere at 500°C. This unidentified peak was attributed to an intermediate or transitional phase between SnO-Sn$_2$O$_3$-SnO$_2$. Deng et al. also reported similar unassigned peaks during synthesis of nanocrystalline tin oxide from Sn(II) halide precursors. Presence of the XRD peaks associated with SnO and other transitional phase clearly indicated that the FTO specimen was not stable when cycled between $-2.0$ and $2.5$ V$_{Ag/AgCl}$ in 0.1 M HNO$_3$.

In general, the FTO substrate is considered to have better chemical and thermal stability than indium tin oxide (ITO) coated glass substrate. FTO is used in various applications such as light-emitting diodes (LEDs), touch panels, flexible electronics, dye sensitized and perovskite solar cells, and other optoelectronics where patterning of electrode is required. Chemical etching is one of the cost effective methods for making patterns on the FTO. Because of its chemical inertness, chemical etching of FTO is not an easy process and

![Figure 10. Schematic illustration of shift in the Fermi levels of FTO with the number of CV cycles in 0.1 M HCl. The energy levels are with reference to vacuum level, and the standard hydrogen electrode potential is at $-4.5$ eV. The figure is not to scale.](image)

![Figure 11. Surface morphology of cyclic stability tested FTO: (a) at the solution/air interface of FTO after 215 cycles in 0.1 M HCl; (b) at the center of exposed area after 215 cycles in 0.1 M HCl; (c) at the solution/air interface of FTO after 4500 cycles of CV in 0.1 M NaOH; (d) at the center of exposed area after 4500 cycles of CV in 0.1 M NaOH.](image)
recently an electrochemical method has been proposed that requires application of high potentials between 3–9 V using a two-electrode configuration. Due its high chemical stability, FTO finds application as an electrode in electrochemical devices such as water electrolyzers, fuel cells, and sensors. Therefore, it is important to understand the electrochemical behavior of FTO at different pH conditions. In this study, the stability of FTO was found to be influenced by the pH, potential window, and the direction or sequence of polarization.

The polarization results as shown in Figs. 2a and 2b and the surface morphologies after polarizations indicated that cathodic polarization at low potentials where the formation of gaseous SnH4 phase was expected. No significant current was recorded during the anodic polarization from the corrosion potential up to the oxygen evolution potential mainly because the Sn was in its fully oxidized state in the FTO. The EIS results after polarization in either direction showed significant changes in the impedance characteristics indicating that the corrosion resistance of the FTO decreased after polarization in the potential window of −2 V vs Ag/AgCl to 3 V vs Ag/AgCl. The charge transfer resistance values decreased, and the leaky capacitance values increased after polarization. The decrease in the impedance after anodic polarization was attributed to the increase in the concentration of oxygen vacancies because of oxygen evolution by removal of oxygen from the FTO lattice. Increase in the charge carrier concentration after anodic polarization as determined from the Mott-Schottky results (Table V) supports this observation. Raman spectroscopic results also support the formation of increased oxygen vacancies after anodic polarization in acidic and basic solutions as seen in Fig. 8. The XRD result indicated formation of additional phases such as SnO, and intermediate Sn₂O₅ phases after cyclic voltammetry test in 0.1 M HNO₃ as shown in Fig. 12. The accelerated stress test or cyclic stability test results indicated that when polarized both in the cathodic and the anodic directions at a very fast scan rate of 1 V/s, the stability of FTO was impaired more rapidly in the 0.1 M HCl solution than in the 0.1 M NaOH solution. The degradation of the FTO in HCl solution was attributed to the change in the electronic property of the material that resulted in upward shift of the conduction band minimum which in turn facilitated easy hydrogen evolution that led to reduction of SnO₂. All these results point out that the FTO may not be as chemically inert as perceived it would be under different electrochemical polarization conditions and care should be taken when used as an electrode.

Conclusions

Electrochemical polarizations studies were carried out on commercial FTO specimens in different pH conditions such as 0.1 M HCl, 0.1 M HNO₃, 0.1 M NaCl, 0.1 M NaOH, and 0.1 M NaOH + 0.1 M NaCl solutions at room temperature. Based on the experimental results, the following conclusion could be drawn:

Oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER) were the cathodic reactions observed during cathodic polarization of the FTO. The activity of FTO for HER was higher in the acidic solutions than that in the neutral or alkaline solutions. The reduction of SnO₂ occurred during the cathodic polarization in the HCl solution and alkaline solutions but not in the nitric acid solution. Oxygen evolution reaction (OER) occurred at high anodic potentials in all the solutions. The Tafel slope of OER increased following the order: NaOH < NaOH+NaCl < NaCl < HCl < HNO₃.

Accelerated stress tests were carried out in 0.1 M HCl and 0.1 M NaOH solutions by scanning the potential from −2 V to 2 V_RHE at a scan rate of 1 V/s. Intergranular corrosion leading to loss of electrical connectivity was observed after 215 CV cycles in the 0.1 M HCl solution. The stability of FTO was better in the 0.1 NaOH solution; even though the catalytic activity was lost after 500 cycles, no loss of electrical connectivity was observed even after 4500 cycles.

The FTO was observed to be more stable in NaCl and HNO₃ solutions than in HCl or NaOH solutions.

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