

Electrolytic Hydrogen Penetration through the Native Oxide on Pure Ti

Y. Zeng,¹ J.J. Noël,¹ Z. Tun,² and D.W. Shoemith¹

¹ Dept. of Chemistry, The University of Western Ontario, London, Ontario, Canada N6A 5B7

² Canadian Neutron Beam Centre, National Research Council Canada, Chalk River Laboratories, Chalk River, ON, Canada K0J 1J0

Titanium and its alloys are rendered highly corrosion resistant by the presence of a passive oxide layer that spontaneously forms on the metal surface on exposure to the environment. Another protective feature of this oxide layer is that it acts as a barrier to hydrogen atoms (a by-product of the corrosion reaction) that would otherwise be readily absorbed by the metallic Ti, leading to formation of brittle hydride phases.

Despite the role of the oxide in controlling H ingress into titanium, hydrogen absorption into and through the oxide has not been thoroughly studied. In previous neutron reflectometry experiments, Wiesler and Majkrzak [1, 2] studied the growth of the passive oxide on titanium at $3 V_{SCE}$ and its hydrogen loading at $-2 V_{SCE}$ in $0.05 M H_2SO_4$. They demonstrated that the passive oxide was permeable to hydrogen during cathodic polarization. Tun, Noël, and Shoemith [3, 4] observed the progressive ingress of hydrogen atoms through an anodic oxide film on titanium under cathodic polarization. They found that, while the oxide acted as a barrier to hydrogen ingress into the metal, some of the hydrogen produced on the surface during cathodic polarization was absorbed into the oxide. However, neither of these studies clarified the threshold potential at which hydrogen absorption into the passive oxide can occur. Moreover, the native (air-formed) oxide on pure Ti may be different from that formed on α -Ti alloys, and from the oxide formed at high potentials in aqueous solution (the cited works all involved anodically grown oxide films), or oxides carefully formed in a vacuum chamber.

Our approach was to take advantage of the large contrast between Ti and deuterium (D) to help determine whether or not changes observed during in situ electrochemistry/neutron reflectometry experiments can be ascribed to hydrogen absorption into the oxide during cathodic polarization and to establish the potential value of the hydrogen absorption threshold on the native oxide on pure Ti.

To investigate hydrogen absorption into the oxide on pure titanium, a pure titanium layer was first deposited on a Si wafer by magnetron sputter deposition in a vacuum chamber. We deposited ~ 25 nm thick Ti films on the polished (111) face of single-crystal, atomically flat, silicon disks, 10 cm in diameter. The sputter-deposition was carried out in an Ar atmosphere (pressure 3×10^{-3} Torr) at a rate of ~ 0.08 nm/second. The native oxide layer spontaneously formed when the fresh Ti film was removed from the vacuum chamber and exposed to the ambient air. Neutron reflectometry measurements of the as-prepared sample were made with the beam incident from the air and Si sides of the film.

Neutron reflectometry measurements were then performed using 2.37 \AA neutrons on the D3 reflectometer, with the sample mounted on a custom-made electrochemical cell, first dry, then later filled with deaerated H_2O or D_2O containing $0.27 M NaCl$. The cell and electrochemical instrumentation have been described previously [3, 4]. When the sample was mounted on the electrochemical cell it yielded an electrode with a surface area of 64 cm^2 exposed to the solution. Starting from the open circuit potential and headed toward increasingly cathodic polarizations, a series of fixed potentials was applied to the oxide-covered Ti film, and at each potential, neutron reflectometry measurements were performed with repeated scans, concurrent with amperometric and electrochemical impedance spectroscopy (EIS) measurements of electrochemical properties.

The variation of current density with time in deaerated $0.27 M NaCl$ in D_2O is shown in Figure 1. For potentials $< -0.1 V$, cathodic currents were observed, indicating water reduction to deuterium (hydrogen). Substantial increases in the current magnitude were observed for potentials below $-0.4 V$.

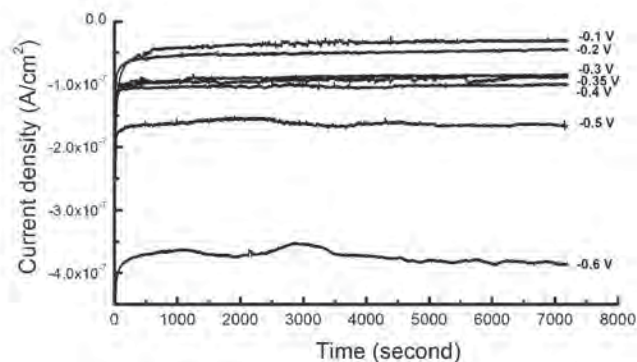


Fig 1. Variation of current density with time recorded on an oxide-covered Ti electrode in deaerated $0.27 M NaCl$ in D_2O during cathodic polarization.

EIS spectra were recorded after the amperometric measurements, once the current had stabilized. A parallel RC equivalent circuit with a single time constant was fitted to the impedance data to determine the solution resistance and the resistance and capacitance of the oxide layer. The oxide film resistance and capacitance values in D_2O solution obtained from these fits are shown in Figure 2. The oxide capacitance was observed to increase gradually as the potential decreased. The oxide resistance decreased only slightly from the open circuit potential to $-0.4 V$; below that potential the resistance decreased much more substantially.

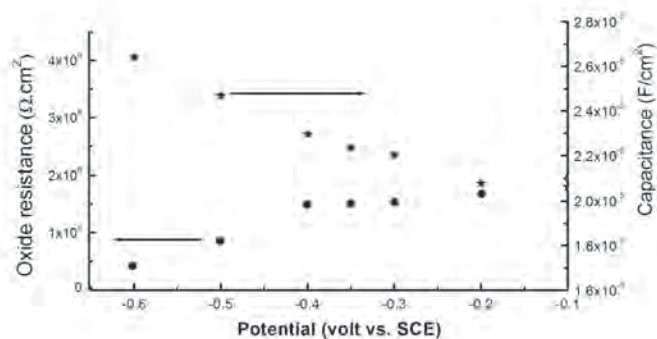


Fig 2. Variation of oxide capacitance and resistance with potential in 0.27 M NaCl in D_2O , as determined from in situ electrochemical impedance spectroscopy.

The normalized intensity profiles of neutrons reflected from the oxide-covered Ti electrode recorded during cathodic polarization in deaerated D_2O containing 0.27 M NaCl are shown in Figure 3. The reflectivity signal in the Q_z range $0.13 \sim 0.15 \text{ \AA}^{-1}$ is indistinguishable from the background noise and was given zero weight in the fitting process. At potentials $\geq -0.2 \text{ V}$, the intensity profile recorded on the as-prepared sample did not change with potential, indicating no change in the composition and thickness of the sample. However, when the potential was decreased to -0.3 V , noticeable changes of the normalized intensity profile were observed. Further decreases in potential resulted in a continuous and gradual change in the intensity profiles.

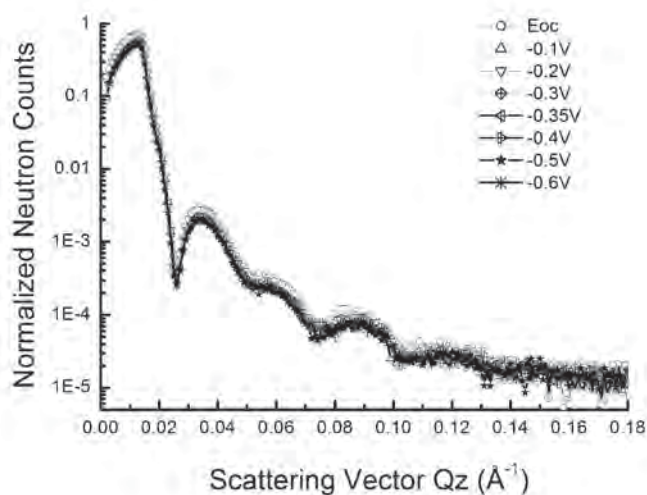


Fig 3. Normalized intensity profiles of reflected neutrons from an oxide-covered Ti film electrode during cathodic polarization in deaerated D_2O containing 0.27 M NaCl.

The two structural models found to best fit the data using Parratt 3.2 software are shown in Figure 4. From the open circuit potential to -0.2 V , no changes in the intensity profiles, and therefore no detectable deuterium absorption were observed; the sample surface composition is suggested to be the sequence of layers Si/SiO₂/Ti/TiO₂/D₂O. At potentials of -0.3 V and lower, the reduction of heavy water to produce deuterium at the TiO₂ surface, and the adsorption of the deuterium atoms

can provide a reasonable explanation for the change in the intensity profiles observed. Therefore, a deuterium-containing surface layer was included in the sample structure (Figure 4).

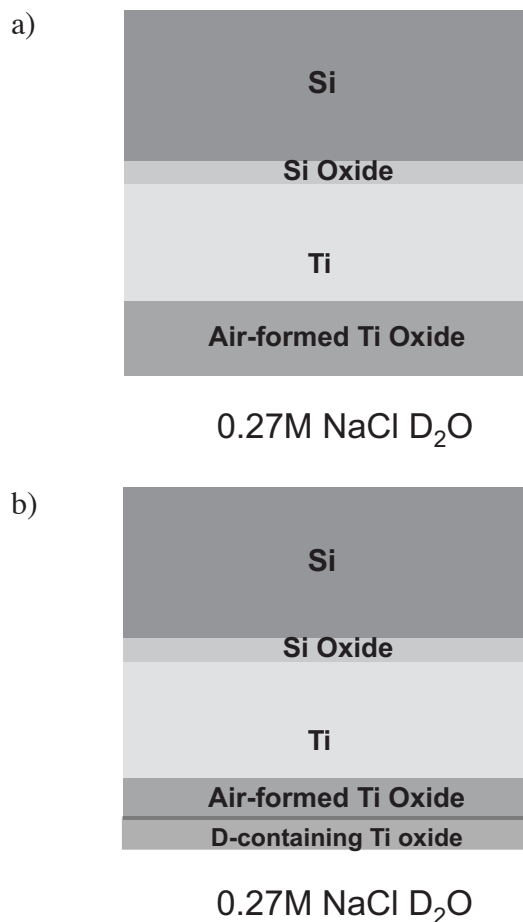


Fig 4. Schematic showing surface structural models fit to the normalized intensity profiles for cathodic polarization in D_2O containing 0.27 M NaCl. (a) Model for the sample surface from the open circuit potential to -0.2 V . (b) Model for the sample surface at potentials $\leq -0.3 \text{ V}$.

Figure 5 shows example fits of these two models to the experimental results acquired at open circuit potential and -0.3 V (Figure 3). Least-squares fitting to the normalized data yielded the layer profiles shown in Figure 6.

The SLD of the Ti film at open circuit was $-6.10 \times 10^{-7} \text{ \AA}^{-2}$, which is somewhat positive of that of bulk Ti ($-1.95 \times 10^{-6} \text{ \AA}^{-2}$), possibly due to oxygen absorption into the metal, as was previously observed [3]. The thickness of the air-formed oxide is about 7.63 nm, in agreement with early optical polarization observations by Andreeva [5]. The model SLD value of the oxide increased gradually from the oxide/Ti interface to the oxide/solution interface, which is an unexpected outcome and gives us some concerns about the validity of our model or fitting process. Except for the region close to the oxide/solution interface, the oxide has a lower SLD value than that of titanium oxide crystals (rutile or anatase), implying that the air-formed oxide may have an amorphous structure, or again that the model is not correct.

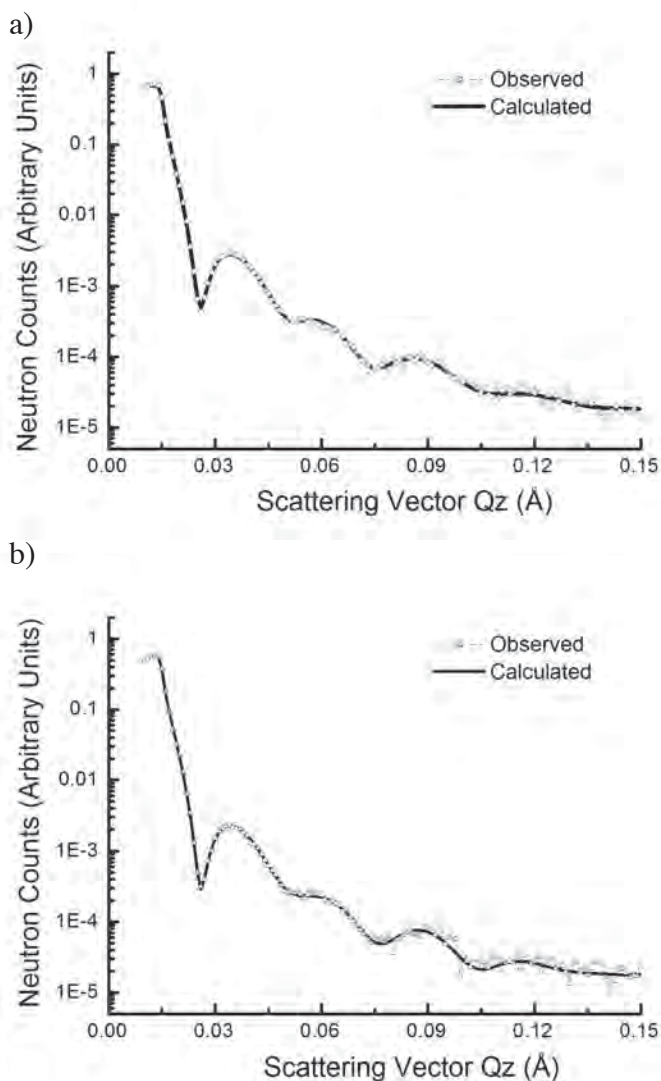


Fig 5. Normalized plots of measured reflected neutron intensity profiles fitted by (a) the model in Figure 4a and (b) the model in Figure 4b. (a) Open Circuit Potential. (b) -0.3V.

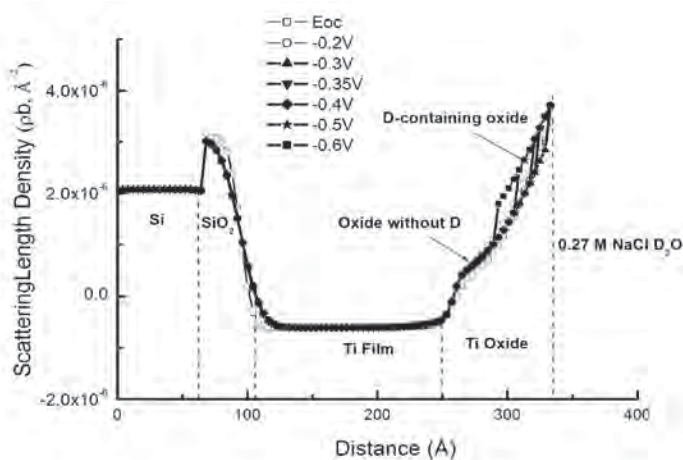


Fig 6. Layer profiles for the Ti film electrode after polarization to different potentials in deaerated D_2O containing 0.27 M NaCl.

At potentials < -0.3 V, a higher SLD region in the oxide layer developed at the oxide-solution interface, growing in thickness inward toward the metal-oxide interface as the applied potential decreased. Deuterium has a high scattering length (6.671 fm) and its adsorption on, or incorporation into the oxide would result in an increase of SLD. The behaviour is similar to that observed for progressive hydrogen penetration through the anodic oxide into anodized Ti [3].

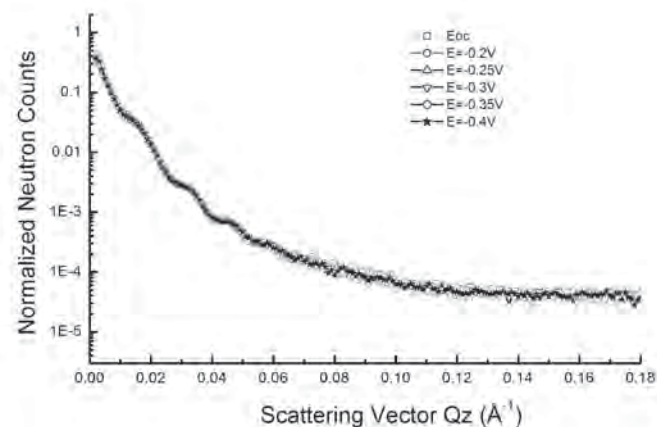


Fig 7. Normalized intensity profiles of reflected neutrons from an oxide-covered Ti-Si wafer electrode during cathodic polarization in deaerated H_2O containing 0.27 M NaCl.

Figure 7 shows the normalized intensity profiles of reflected neutrons for the equivalent set of experiments in deaerated H_2O containing 0.27 M NaCl. The interference pattern in the intensity profiles was much weaker than for the film used for the D_2O experiments, suggesting that the specimen did not possess clearly defined layers and interfaces and was therefore not useful for neutron reflectometry measurements. During cathodic polarization, no significant changes in the intensity profiles were observed at potentials ≥ -0.4 V, as would be expected based on the potentiostatic and EIS measurements, which yielded similar results to those in the D_2O experiments above. Fitting efforts have not yet generated any useful information from this data set.

References

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