

# Electrolytic Hydrogen Penetration through Native Oxide on Pure Ti

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Titanium corrosion processes are often accompanied by hydrogen production. Crevice corrosion is also supported by the reduction of protons inside the crevice, leading to the absorption of atomic hydrogen to produce extensive hydride formation [1]. Cathodic polarization and galvanic coupling with other metals also cause hydrogen evolution on and its penetration into Ti. Hydrogen must pass through the TiO<sub>2</sub> film before absorption into the underlying titanium alloy to cause hydrogen-induced cracking (HIC). For absorption to proceed, redox transformation (Ti<sup>4+</sup> → Ti<sup>3+</sup>) in the oxide film is necessary [2,3]. This requires significant cathodic polarization of the metal, generally only achievable by galvanic coupling to active materials, such as carbon steel, or the application of a cathodic protection potential. Given these complexities and the absence of experimental data for aqueous solutions, it is difficult to predict the cathodic potential at which hydrogen transported through the oxide and what fraction of the hydrogen atoms generated on the oxide surface will reach the Ti substrate. We herein employed in situ NR method coupled with EIS technique to address two main curiosities:

- 1) The cathodic potential at which hydrogen atoms begin to penetrate into the metal and,
- 2) Critical hydrogen concentration in Titanium thin film after that hydride begins to form.

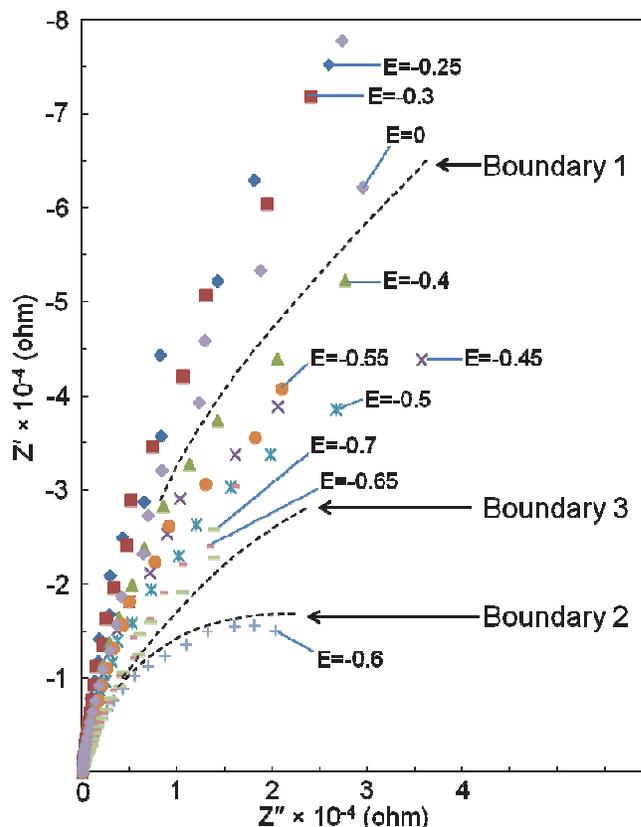
From the Nyquist diagrams of the EIS data (Figure 1), the overall picture of the stages the sample went through as the cathodic potential was increased fall into four groups between 3 boundaries:

Group 1: Data collected from E = 0 to -0.35 V<sub>SCE</sub> (above Boundary 1).

Group 2: Data collected from E = -0.40 to -0.55 V<sub>SCE</sub>.

Group 3: Data collected at E = -0.60 V<sub>SCE</sub> (below Boundary 2) with low |Z| value.

Group 4: Data collected at E = -0.65 V<sub>SCE</sub> and -0.70 V<sub>SCE</sub> where |Z| increased again, but remained lower than the original value.



**Figure 1** Nyquist diagrams of EIS data carried out simultaneously with NR during the different Cathodic polarizations. Four distinctive regions with three potential boundaries were observed.

On the other hand, squared fitted in-situ NR data were measured simultaneously under the same cathodic potential and shown in Figure 2 where the SLD versus thickness is plotted. The separations between the aforementioned boundaries can be seen in the SLD of the titanium metal. We see that the most pronounced effect of the cathodic polarization is to increase of SLD of the Ti layer without affecting the thickness much. The vastly expanded vertical scale of the inset shows that the SLD increased monotonically as the potential became more negative. This increase is most certainly due to absorption of D into the Ti layer. Horizontal bars in the inset show that SLD demarcates cathodic polarization into the same four groups as seen in the EIS

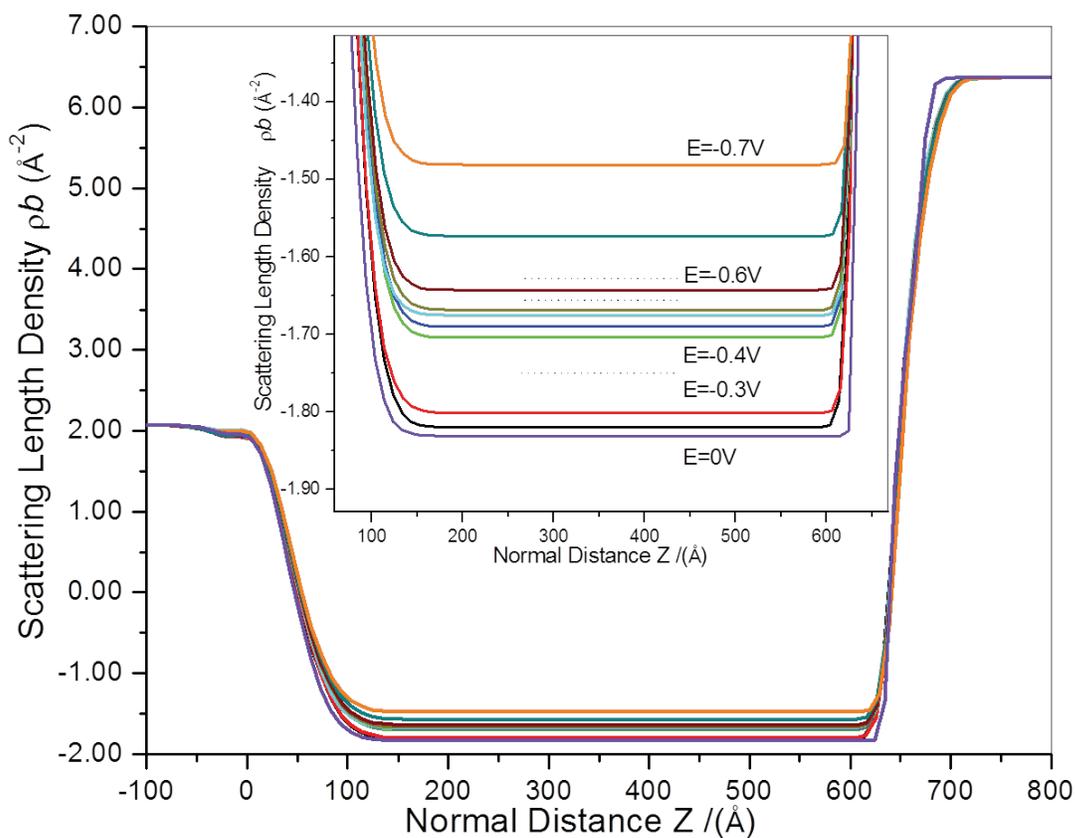
(Figures 1). This consistency between two entirely independent techniques is the strongest possible endorsement for our results.

The results obtained from the combined techniques of electrochemistry and NR (Figure 1, 2), lead to Figure 3 where the SLD(Ti) and molar ratio of the Deuterium penetrated into the Titanium metal are plotted as functions of the applied potential. Error bars in both are given according to the uncertainties estimated by comparing the models obtained for the as-prepared sample as it was investigated in various geometries. At small cathodic polarizations (up to about  $-0.35 V_{SCE}$ ) no significant current was observed and the changes in SLD (Ti) was small. At about  $-0.37V$  a jump in current and

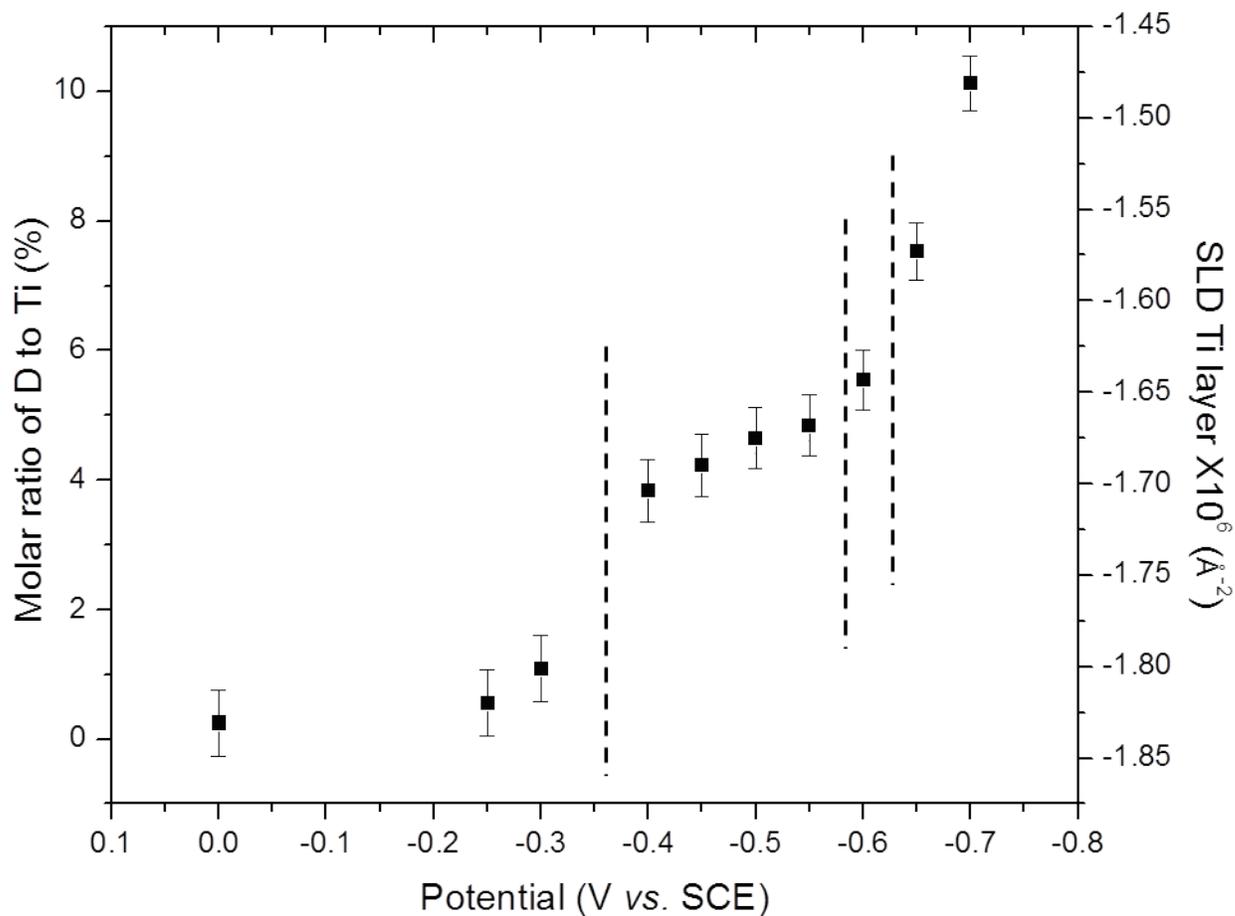
SLD(Ti) can be attributed to the starting point cathodic polarizations for Hydrogen ingress into the Ti metal. At lower cathodic polarizations, both EIS and NR (Figure 3) show  $-0.6 V_{SCE}$  as the onset of the next level of H ingress.

#### References

- [1] D.W. Shoesmith et al., *Hydrogen Absorption and the Lifetime Performance of Titanium Waste Containers*. AECL-11770 (Pinawa, Manitoba, Canada: Atomic Energy of Canada Limited, 1997).
- [2] M. A. Gaudett and J. R. Scully, *Metall. Mater. Trans. A*, **30**, 65 (1999).
- [3] J.J. Noël, M.G. Bailey, J.P. Crosthwaite, B.M. Ikeda, S.R. Ryan, D.W. Shoesmith, Atomic Energy of Canada Ltd., Report, AECL-11608, COG-96-249, (1996).



**Figure 2** The SLD profiles of the Si/Ti/TiO<sub>2</sub>/D<sub>2</sub>O system at different applied potentials. The inset is the closer look at the SLD values of Ti metal layer which are categorized at different voltages. The electrolyte was 0.27M of NaCl in D<sub>2</sub>O.



**Figure 3** The SLD change for titanium metal which is used to evaluate the molar ratio of deuterium penetrated into the titanium film. Both SLD and Moles of D are plotted as a function of applied potential. The measurements were done at potentiostatic polarization in 0.27 M NaCl in D<sub>2</sub>O.