

Electrolytic hydrogen penetration through the native oxide on zirconium: Part II

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If absorbed into Zr metal, hydrogen (or deuterium) can lead to hydrogen-induced cracking. Fortunately, the passive oxide layer that affords Zr materials their superb corrosion resistance is also a very good barrier to hydrogen ingress under most service conditions; however, much room remains to further our understanding of the mechanism of hydrogen absorption by Zr and its alloys and the conditions under which the barrier properties of the ubiquitous surface oxide can be defeated. Previously, we used in situ neutron reflectometry and electrochemistry to study anodic oxide growth on Zr and the response of the anodized Zr to cathodic polarization [1,2], and this work allowed us to conclude that the anodic oxide on Zr prevents hydrogen ingress into Zr during cathodic polarization to potentials as low as $-3 V_{SCE}$ in neutral or near-neutral pH solution at room temperature. In this experiment we used in situ neutron reflectometry to detect and quantify hydrogen and deuterium absorbed into zirconium during cathodic charging in aqueous solution at different pH and applied potentials to explore the protectiveness of the native oxide (i.e., the un-anodized surface) against hydrogen absorption.

The sample of interest was a thin film of Zr (nominally ~50 nm thick) deposited onto a polished Si(111) substrate by magnetron sputtering from target-grade Zr. The quality of the sample and its suitability for neutron reflectometry experiments (flatness, uniformity, reflectivity, etc.) were verified by X-ray reflectometry at CNBC before neutron reflectometry was attempted. Neutron reflectometry measurements were taken on the D3 reflectometer with the sample mounted on an electrochemical cell, which was either empty or filled with electrolyte solution. For electrochemical experiments, the electrochemical cell, with the Zr thin-film as working electrode, was filled with 0.1 M Na₂SO₄ solution, made with either H₂O or D₂O. Initially, open circuit potential (E_{oc}) measurements were recorded, followed by electrochemical impedance spectroscopy (EIS) at the steady-state open circuit potential value (about 30 mV_{SCE}). Subsequently, potentiostatic polarization in the cathodic sense was applied to the working electrode, current measurements then alternating with EIS. Neutron reflectometry scans were taken simultaneously with electrochemical measurements, with the sample at ambient temperature. Measurements at E_{oc} and a series of potentiostatic steps at increasingly negative potentials were made in the Na₂SO₄ solution at its original (as-prepared) pH (5.6), before the pH was decreased by adding H₂SO₄, and a series of neutron and EIS scans performed at a polarization of $-1.6 V_{SCE}$ at pH 3.0 and pH 2.0.

The reflectometry results showed the oxide and metal layers of the sample to maintain stable dimensions at all pH values during the experiments (see Figure 1). The barrier quality of the native oxide film on zirconium was found to be strongly dependent on the pH of the solution in which it was polarized. Hydrogen absorption was not observed during cathodic polarization in near-neutral pH solution, however increasing amounts of hydrogen were absorbed during cathodic polarization as the pH was lowered, as evidenced by the decreasing scattering length density (SLD) of both the metallic Zr and native Zr oxide layers seen in Figure 1 (experiment performed in H₂O solution). The hydrogen

concentration in the oxide layer was higher than that in the metallic layer, by nearly a factor of 2. At pH 2, the hydrogen content of the oxide reached 13.5 atoms/nm³ and that of the metallic layer was 7 atoms/nm³; for comparison, there are 27.8 Zr atoms/nm³ in ZrO₂ and 42.9 Zr atoms/nm³ in Zr metal. These numbers represent very high concentrations of absorbed hydrogen, in both cases. An additional very unusual and unexpected observation was that after we stopped applying cathodic polarization at the end of the experiment, the hydrogen content of oxide and metal dropped significantly (to 6.4 and 4.8 hydrogen atoms/nm³, respectively).

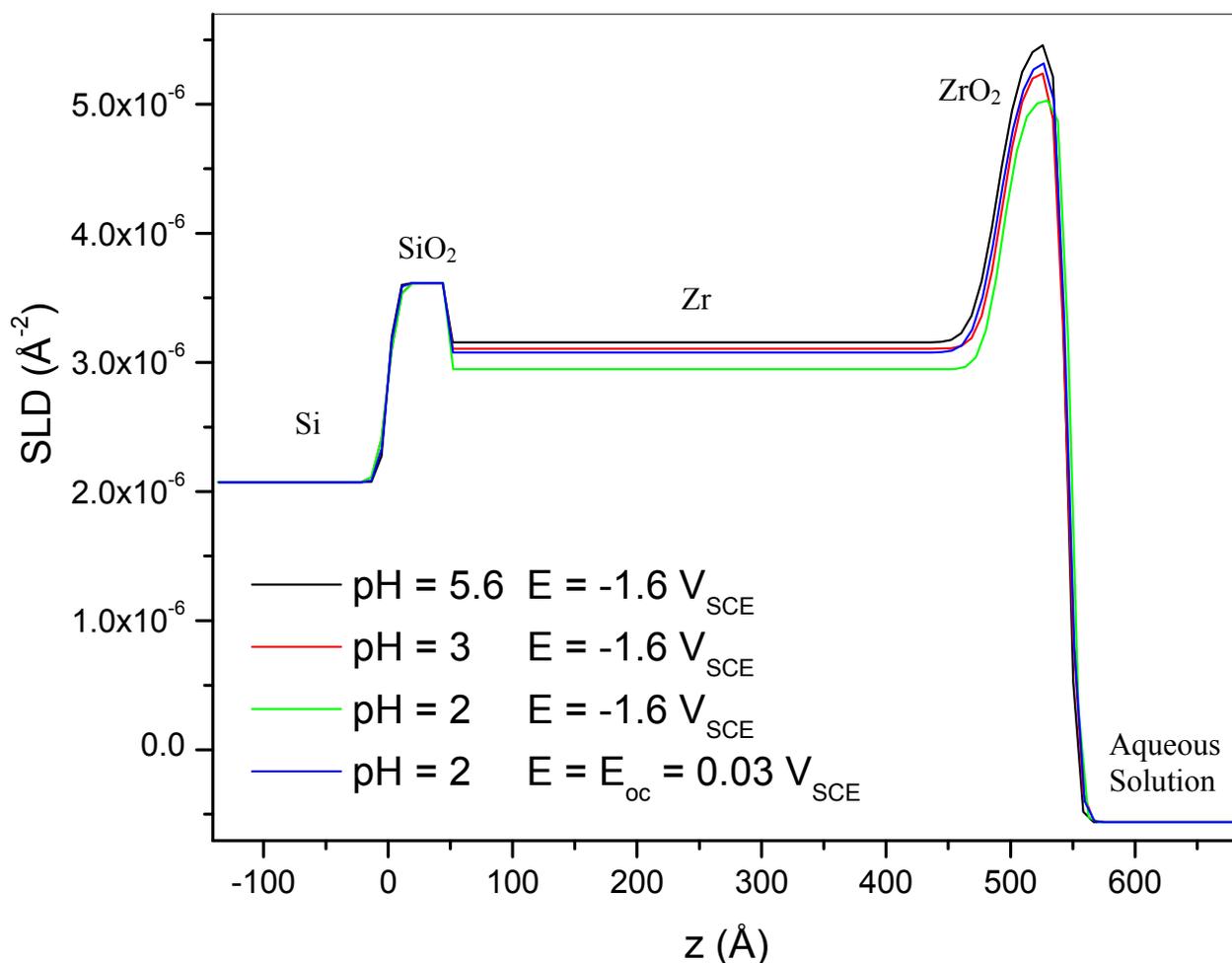


Figure 1. Real space profiles determined from in situ neutron reflectometry scans of a Zr thin film on a Si substrate in 0.1 M Na₂SO₄ in H₂O, with pH as indicated in the legend. The applied polarization during the scans was -1.6 V_{SCE}, except for the final scan at pH 2, which was recorded with the sample at its open circuit potential. The nominal composition of each layer is noted as an aid to viewing.

Support for these observations was obtained from similarly performed experiments in D_2O solution, although in these experiments we do not obtain useable data concerning the oxide layer in situ because the large positive-going swing in SLD from metal to D_2O obscures the oxide when we work in D_2O -based solution. Therefore we alternated in situ (cell filled with solution) and ex situ (cell drained) reflectometry scans, and obtained the results shown in Figure 2 for the deuterium content of the metal layer. In this case, the deuterium content of the metal layer increased with time under polarization, and jumped to a lower value in the ex situ scans after polarization was ceased. The overall deuterium content of the metal observed under polarization in these scans was lower than the hydrogen content of the metal under polarization in the H_2O experiments, but that may have been a consequence of the losses during the ex situ periods between cathodic charging steps; given sufficient time, the deuterium may eventually have achieved similar levels.

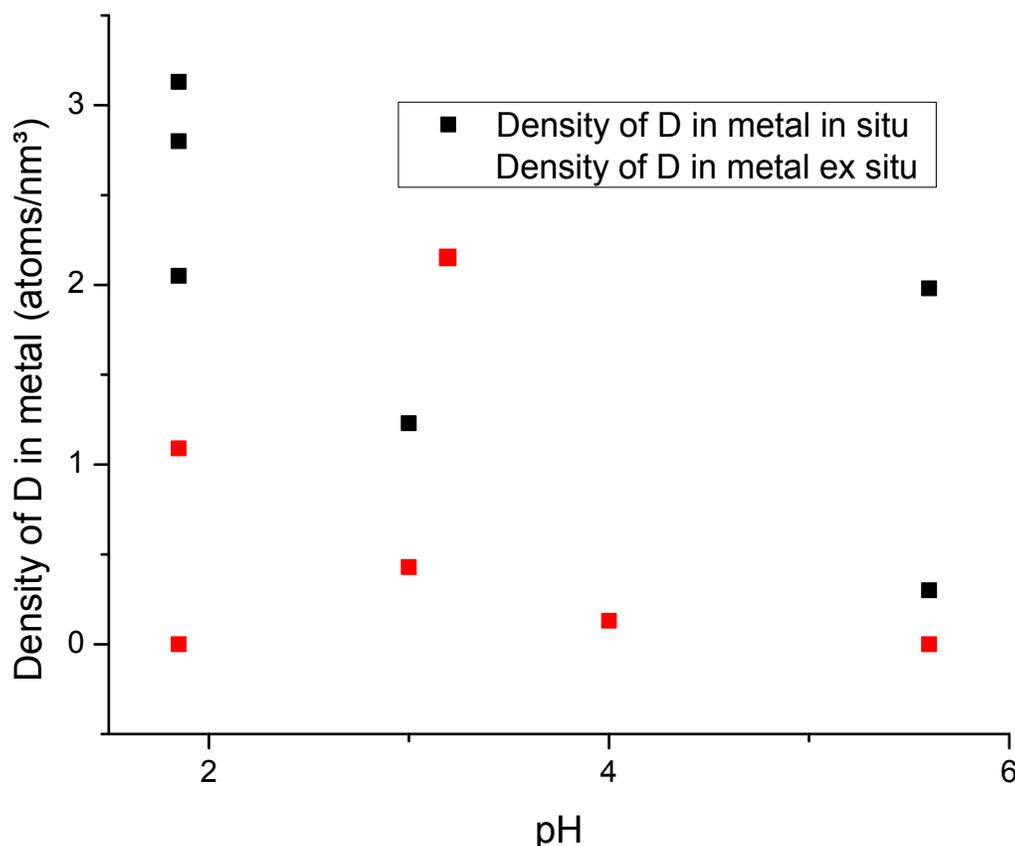


Figure 2. Deuterium content of metallic Zr layer of a thin film electrode polarized at -1.6 V vs a saturated calomel reference electrode (black symbols) and ex situ immediately after polarization (red symbols). Multiple symbols at a single pH value show the deuterium content increasing with time during polarization and decreasing with time ex situ.

References

- [1] Z. Tun, J.J. Noël, and D.W. Shoesmith, "[Anodic oxide growth on Zr in neutral aqueous solution](#)" *Pramana - Journal of Physics*, Vol. 71, No. 4, 2008, pp. 769-776.
- [2] J.J. Noël, D.W. Shoesmith, and Z. Tun, "Anodic oxide growth and hydrogen absorption on Zr in neutral aqueous solution – A comparison to Ti", *Journal of the Electrochemical Society*, Vol. 155, No. 8, 2008, pp. C444-C454.