

The effect of NaNO₃ on salt films in pitting corrosion of 304 stainless steel using synchrotron X-ray diffraction

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In mixed nitrate/chloride solutions, nitrate can either enhance or inhibit localized corrosion of stainless steel [1]. NO₃²⁻/Cl⁻ ratio is important in determining if the system will experience localized corrosion [2].

When just below the passivation potential, current densities can in fact be exacerbated by the presence of nitrate, with stable current oscillations having been observed in one-dimensional pit systems [3]. It has been suggested that a nitrate-rich salt film develops at the metal interface. By using synchrotron-generated X-ray diffraction, it is possible to analyze the surface of one-dimensional pits *in situ* and characterize salt films during the corrosion process [4].

A one-dimensional pit was grown in 1 M NaCl using 304 stainless steel foils, 50 μm x 3 mm surface area, embedded in amorphous epoxy resin. The pit was grown until a diffusion-limited current was achieved. The cell was held at a range of potentials from 0.3-0.7 V(Ag/AgCl). At each potential, XRD patterns were taken at 2 μm intervals through the salt film. Current and resistance were measured concurrently. The solution was then made up to 1 M NaCl /40 mM NaNO₃, and held at 0.3-0.7 V. The solution was then made up to 1 M NaCl /50 mM NaNO₃ then 1 M NaCl /75 mM NaNO₃, and held at 0.3-0.5 V at each concentration. XRD measurements were made on Beamline I18 at Diamond Light Source using a beam size of 2.5 μm x 20 μm and an energy of 12 keV.

In nitrate-free solutions, a diffusion limited current of ~0.1 mA was observed due to the formation of a resistive salt film on the metal interface. When the nitrate concentration in the solution was increased to 75 mM, a stable diffusion-limited current was seen at 0.3 V (Figure 1). The current observed gradually became more unstable as potential increased. At 0.5 V, strong periodic oscillations in current were seen, reaching 0.18 mA but never dropping below 0.05 mA (Figure 2). The resistance was also seen to oscillate.

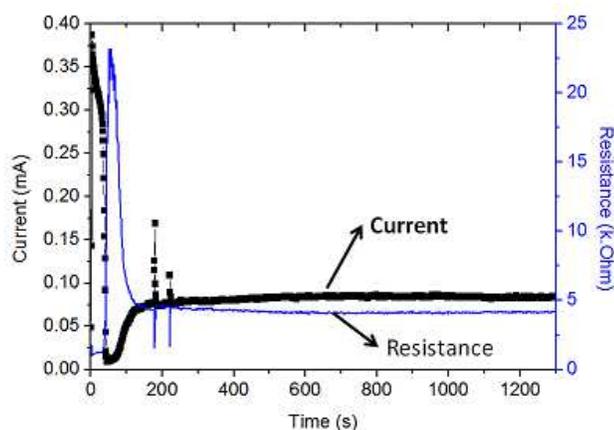


Figure 1 –Current and resistance in 1D pit of 304 stainless steel in 1 M NaCl/75 mM NaNO₃ at 0.3 V(Ag/AgCl)

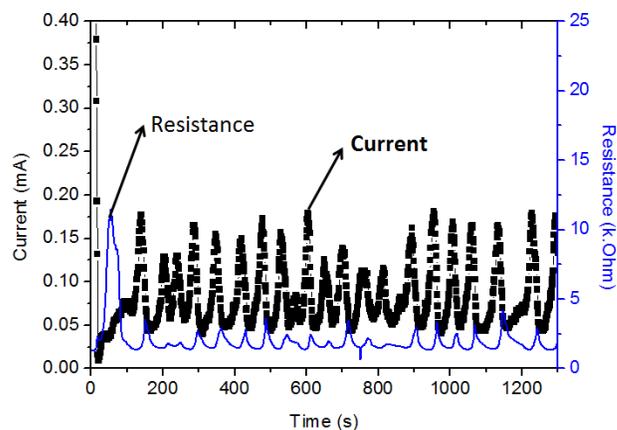


Figure 2 – Current and resistance 1D pit of 304 stainless steel in 1 M NaCl/ 75 mM NaNO₃ at 0.5 V(Ag/AgCl)

Diffraction patterns taken of the salt film in nitrate-free solution and nitrate-rich solutions show the same salt species, even during current oscillations (Figure 3). These patterns approximately match FeCl₂·4H₂O[5], with some minor peaks missing. However, closer examination of the diffraction patterns (not shown) suggests that the presence of nitrate affects the crystallite size and morphology, and preliminary observations suggest that the oscillations may be associated with local breakdown events.

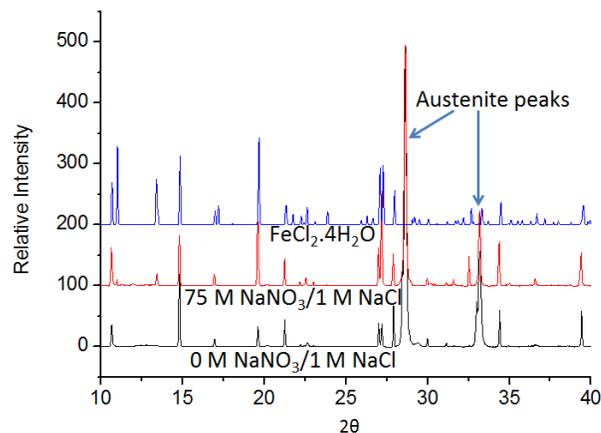


Figure 3 – Diffraction patterns of salt films collect in nitrate-free and nitrate rich solutions, compared to FeCl₂·4H₂O

Acknowledgements

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