



Short communication

Spatially resolved mapping of the relative concentration of dissolved hydrogen using the scanning electrochemical microscope

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ABSTRACT

The scanning electrochemical microscope (SECM) was utilized to detect pre-dissolved hydrogen across an ultra-high strength stainless steel surface. A high strength Fe–11Ni–12Cr–1Mo–0.005C–0.02Mn (wt.%) steel with a high diffusible hydrogen capacity was first cathodically pre-charged to known concentrations of diffusible hydrogen. The steel was subsequently analyzed by the SECM in redox competition mode to detect the location of diffusible hydrogen by examining the effect of the hydrogen in pre-charged and uncharged areas on the oxygen reduction reaction at a platinum micro-electrode tip. The tip current significantly decreased in regions containing hydrogen. The presence of dissolved hydrogen results in enhanced consumption of O₂ (by the oxygen reduction reaction) at the steel surface. Dissolved hydrogen can be detected and resolved at a sub-millimeter length scale.

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1. Introduction

Local hydrogen concentrations are important for understanding hydrogen embrittlement (HE) in steels [1]. Knowledge of localized hydrogen concentrations at crack tips, occluded sites, microstructural features, or other local sources for hydrogen production and absorption, would enhance the understanding of HE. Hydrogen concentrations and diffusion properties have been well quantified in ultra-high strength steels (UHSS) and other pertinent engineering materials, through global measurements over the meso-length scale [2–5]. However, methods for spatial resolution of hydrogen concentrations at the local, <1 mm, scale are lacking. Local hydrogen measurements have been reported using Scanning Kelvin Probe (SKP) and Scanning Kelvin Probe Force Microscopy combined with secondary ion mass spectrometry [6–11]. Nuclear reaction analysis and tritium auto-radiography have also been used [12–17]. While these are valuable tools for hydrogen detection, this study explores the novel application of the SECM for spatial hydrogen measurements.

The SECM enables detection of corrosion processes with spatial resolution [18–20]. When SECM is used in tip generation/substrate collection or substrate generation/tip collection modes, the differences in the current measured at the tip can be related to the local substrate conductivity and/or reactivity [21,22]. The SECM has previously been utilized to measure the effect of hydrogen on corrosion [23,24] and subsequent pitting susceptibility [25]. Also, the exit side of a permeation surface was characterized by an SECM to study the effect of hydrogen on the exit surface oxide [26]. While these methods explored the effect

of hydrogen on anodic reactivity, no prior attempt has been made with the SECM to detect and map spatially pre-dissolved hydrogen concentration across zones of high or low concentrations.

2. Material and methods

UNS S46500 martensitic stainless steel (SS) was utilized in the H900 temper (Table 1). This ultra-high strength temper has a high capacity for diffusible hydrogen, $C_{H,diff}$, of 0–17 wppm for a hydrogen overpotential (η_H) between 0 and –1 V (as measured by electrochemical extraction) [3], and is highly susceptible to hydrogen embrittlement [27]. This, combined with its slow hydrogen effective diffusivity (6.2×10^{-9} cm²/s determined by thermal desorption spectroscopy) made it a suitable candidate for local measurements of hydrogen pre-charged disks in the SECM since the diffusion of hydrogen to reach 10% of the surface concentration is only 120 μ m laterally in 1800 s, the time to perform initial SECM measurements [28].

Steel disks, 1.9 cm in diameter and 500 μ m thick, were flush mounted in epoxy, ground to 1200 grit (SiC), polished to a 3 μ m diamond paste finish, rinsed with DI water, dried with compressed air, and cleaned with ethanol. The diameter of the hydrogen charged area was 1.13 cm. For hydrogen pre-charging, steel disks were polarized cathodically for 24 h at η_H of –800 mV in naturally aerated, room temperature, 0.6 M NaCl + NaOH, pH 10 solution in an electrochemical flat cell with a 1 cm² opening. The resulting diffusible hydrogen concentration of 15 wppm was measured by electrochemical extraction [3]. After 24 h of charging, 1/100 of the surface hydrogen concentration was achieved both at a maximum depth perpendicular to the charged surface of 840 μ m and lateral spread of 840 μ m radially beyond the disk diameter. The steel was removed from the electrochemical flat

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Table 1
Composition (wt.%) of UNS S46500 [34].

	Fe	C	Mn	Si	P	S	Cr	Ni	Mo	N	Ti	Co
UNS S46500	Bal.	0.005	0.02	0.02	0.002	0.002	11.50	11.04	0.94	0.002	1.54	–

cell, rinsed with DI water, cleaned with ethanol, and dried with compressed air. Scans were performed using a Biologic® SECM370, initiated within 30 min of removal from the pre-charging cell.

A 10 μm Pt micro-electrode (ME) tip, flush-mounted, was cleaned prior to testing by cyclic voltammetry (CV) in both 0.01 ferrocenemethanol + 0.005 M NaCl solution and later in 0.005 M NaCl + NaOH, pH 10 solution. The ME performance was verified by standard voltammetric procedures. Approach curves were acquired in the redox mediator solution to determine the optimal ME to surface height. The ME was held at +0.6 V(vs. Ag/AgCl) where the oxidation of ferrocenemethanol was the dominant reaction at the tip in the diffusion limiting regime. After completion of the approach curves and determination of disk to ME tip height, the redox mediator was removed, the cell was rinsed, and the solution was replaced with the 0.005 M NaCl + NaOH, pH 10 without disturbing the ME to steel surface distance. The ME was then held at -0.7 V with the oxygen reduction reaction (ORR) as the dominant electrochemical reaction at the tip. This potential is in the diffusion limiting regime for the ORR occurring at the ME tip, while the steel floated at open circuit potential, thus

operating in redox competition mode with respect to ORR [29]. ORR is the principal cathodic reaction on both the ME and the steel surface under these conditions, and is limited by the diffusion of oxygen. The hemispherical O_2 concentration field of both the ME and working electrode must overlap (Fig. 1). The ME senses O_2 depletion by ORR taking place on the metal if positioned within the diffusional boundary layer (50–1000 μm) [30]. The limiting current density (i_{lim}) at the ME was -2.79 nA at -0.7 V without redox competition (when positioned well above the polymer).

Line scans across the pre-charged and uncharged regions of the steel, and over the epoxy, were taken in the 0.005 M NaCl + NaOH, pH 10 solution with ambient aeration and quiescent stirring in order to study the effects of hydrogen on the ORR occurring at the ME tip. Line scans were utilized instead of area scans due to the short length of time required – less than 15 min per scan. The ME was scanned at a rate of 50 $\mu\text{m}/\text{s}$. The steel and ME shared a Pt counter electrode and Ag/AgCl reference electrode. The ME was held 100 μm above the steel, well within its oxygen concentration field. This optimum distance of ~ 100 μm was determined for operation and signal quality as the

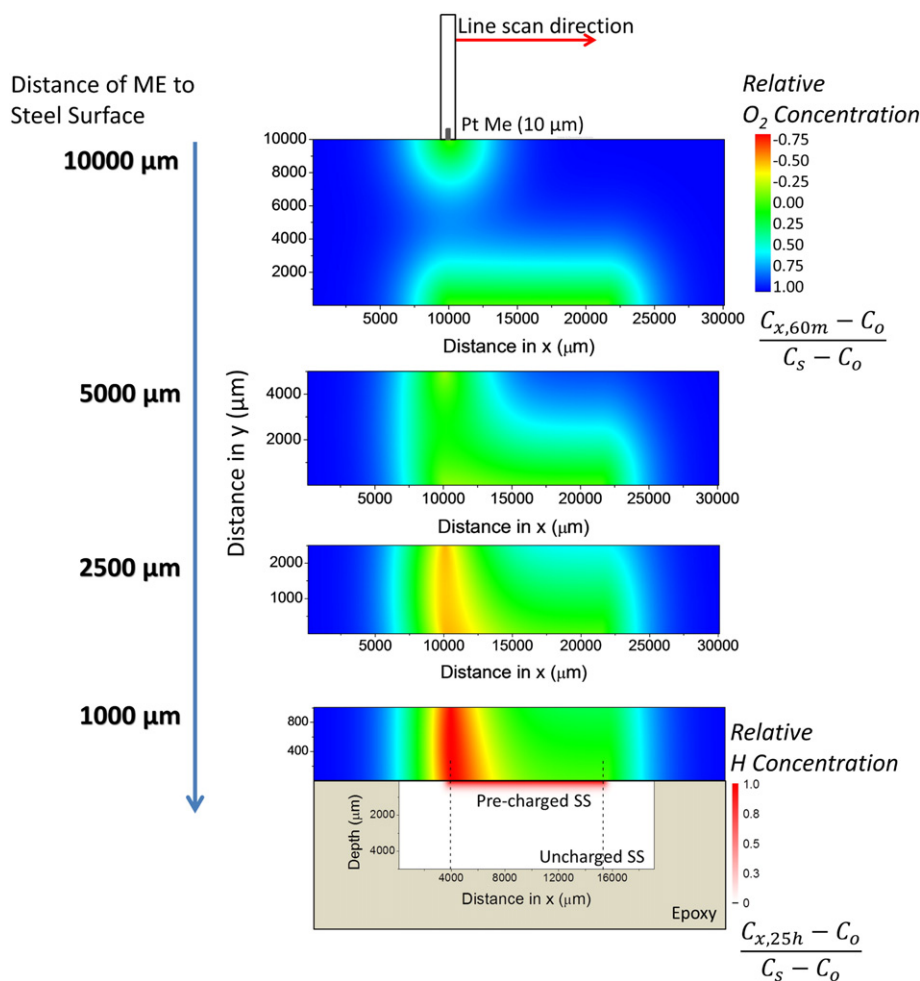


Fig. 1. Analytical concentration profile of O_2 depletion as the SECM ME tip approaches the steel surface (with dissolved H). The oxygen concentration fields arising from the two surfaces overlap at 1000 μm approach distance. These concentration profiles were generated using analytical expressions for estimating diffusion in an infinite plane, with known diffusion coefficients for H in UNS S46500 ($D_{\text{H}} = 6.2 \times 10^{-9}$ cm^2/s) and O_2 in solution ($D_{\text{O}_2} = 1.46 \times 10^{-5}$ cm^2/s). The source concentrations were assumed as fixed and the reactions were considered to be under diffusion control. The working distance used for the line scan experiments is 100 μm .

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