

SCANNING ELECTROCHEMICAL MICROSCOPY EXAMINATION OF THE O₂ REDUCTION ON CAST IRON

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Cast iron is part of a large family of ferrous alloys that contain a high percentage of carbon. They possess a wide range of microstructures and physical properties that directly affect service performance. The cast structure includes carbon in various sizes and shapes, in a ferrite matrix (Fig. 1).

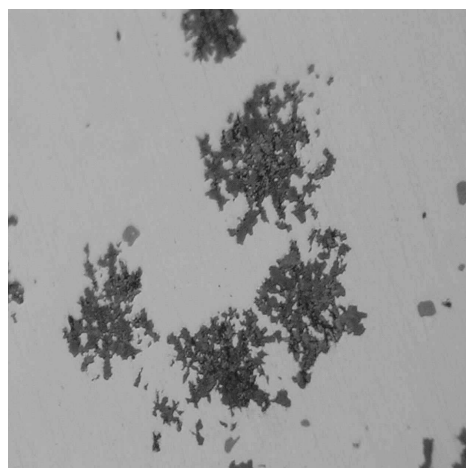
The biphasic nature of the cast iron matrix provides an interesting substrate for investigation by the scanning electrochemical microscopy (SECM). In particular the role of the graphitic inclusions in the corrosion process is investigated.

We demonstrate that the feedback mode of the SECM is useful in studying the variation of the rate of oxidation of ferrocenemethanol on graphite nodules and ferrite matrix thus reflecting the variation in the reactivity on the cast iron surface (Fig. 2). In the feedback mode, the substrate potential is negative and graphite does not corrode significantly, so it allowed us to study the cast iron surface reactivity without interference from corrosion products. Figure 2 shows that a higher feedback tip current is detected on the surface of a graphite nodule indicating a larger rate constant of electron transfer between the mediator and graphite compared to the iron matrix.

O₂ reduction is often the cathodic reaction in the corrosion processes of metals. We used the SECM to show that the O₂ reduction occurs preferentially at the graphite sites (Fig. 3). We show the effect of substrate potential on the rate of O₂ reduction at several negative potential values down to the open circuit potential (OCP). Of interest is the observation of O₂ reduction at the OCP.

Iridium oxide (IrOx)-pH sensitive ultramicroelectrodes (UMEs) were used to image local pH changes on other electrodes. In this work, pH images using IrOx-pH UMEs show expected pH changes on the cast iron surface due to O₂ reduction.

These SECM studies were conducted using poly(oxyphenylene)-coated carbon fiber tips, with diameter < 5 μm, prepared using a simple, inexpensive, and reproducible procedure. A summing of the fabrication and characterization of these tips will also be presented.



10 μm

Figure 1. An optical micrograph of a cast iron sample showing the graphite nodules (darker) in a ferrite matrix.

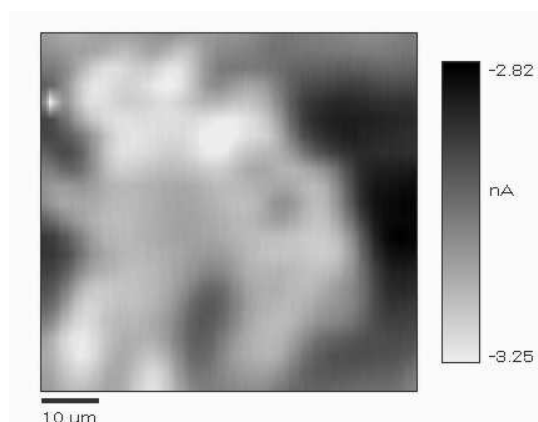


Figure 2. Gray-scale image of a graphite nodule in the cast iron matrix in 2 mM ferrocenemethanol and 0.05 M borax. The tip was a 4-μm-diameter cone-shaped poly(oxyphenylene)-coated C-tip held at +0.550 V, substrate was at OCP. Potential is vs. a Ag/AgCl reference electrode. Scan rate was 10 μm/s.

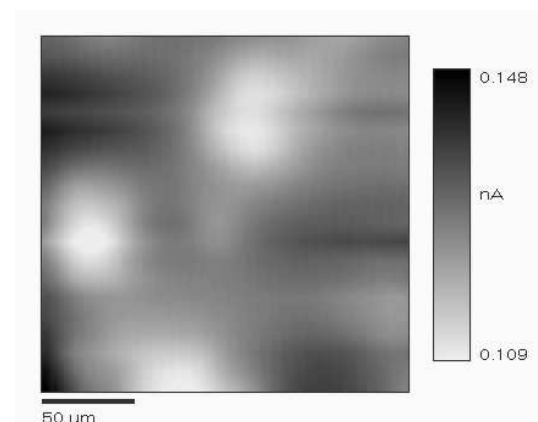


Figure 3. Gray-scale image for the O₂ reduction at the surface of a cast iron sample in 0.05 M Na₃PO₄. The tip potential was -0.700 V and the substrate potential was -0.550 V. Other experimental conditions were as in Fig. 2. Brighter regions indicate regions of depleted O₂ located above the carbon inclusions.