

Synthesis of Amorphous Lepidocrocite Thin Films via Spin-Spray Ferrite Plating

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Spin-spray ferrite plating (aka spin-spraying) has proven to be a valuable method for the synthesis of oxide films on a variety of substrates.¹ The method relies upon the surface adsorption of metal hydroxides followed by their oxidation to the target oxide. For the case of iron, by varying the processing parameters (for example, precursor chemistry, oxidizing agents, and molar concentration and pH of these solutions), it is possible to stabilize the γ - or α -forms of Fe_2O_3 or Fe_3O_4 . Other processing parameters, such as substrate temperature and sample rotation, have been found to affect the resulting films' morphology.² In this communication we describe the growth of iron oxyhydroxide thin films on polymer substrates using this technique. This paper presents for the first time the synthesis of uniform amorphous lepidocrocite films via spin-spray ferrite plating.

Iron oxyhydroxide, especially in its so-called "amorphous" form, is an ideal film for the study of metal oxide respiration by metal-reducing bacteria such as *Shewanella oneidensis*.³ Iron oxyhydroxide films have been synthesized using aqueous techniques; however, it is difficult to obtain uniform films on polymer substrates. The spin-spray process is capable of utilizing similar aqueous techniques to grow thin films on polymer substrates, such as Kapton.

In the spin-spray process, represented in Figure 1a, substrates are mounted on a rotating table and reactants are sprayed onto the spinning substrates whereupon an adsorption/oxidation cycle allows the growth of a film. In our case, thin sections of Kapton sheets were cleaned thoroughly and soaked in acetic acid, leaving a hydrophilic surface for iron adsorption. The substrates were rotated at 50 rpm while maintaining a temperature of 25 °C. A 0.01 M solution of FeCl_2 and an oxidizing solution of 0.001 M NaNO_2 , buffered to pH 8.3 using sodium acetate, were simultaneously pumped through a nebulizer onto the spinning substrates.

In the early stages of film growth, see Figure 1b, the Fe^{2+} is adsorbed onto the surface of the hydrophilic-terminated substrate. As the substrates are exposed to

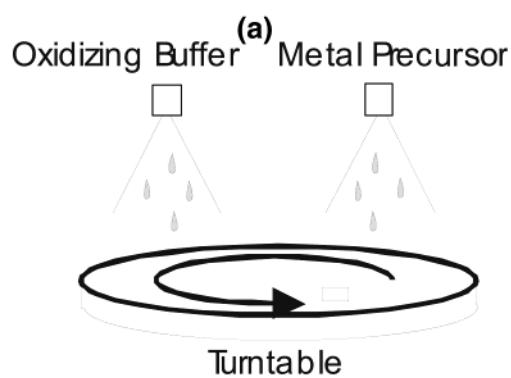


Figure 1. (a) Schematic representation of the spin-spray process. (b) Principle of spin-spraying using aqueous $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ as presented by Abe.¹

the oxidizing solution, the Fe^{2+} is oxidized to Fe^{3+} in the form of $\text{Fe}(\text{OH})_3$. Since the surface is terminated with hydroxides, the process repeats as the film encounters the metal-chloride spray. In this manner the film grows in a layer-by-layer fashion until the desired thickness is reached. To help ensure oxidation to the desired γ - FeOOH structure, the reaction chamber is continuously purged with 5 psi of air. The resulting films were allowed to dry in air before they were characterized by SEM, AFM, and EXAFS.

Film smoothness was measured using a Digital Instruments 3000 atomic force microscope (AFM) operating in contact mode. Scanning electron micrographs were obtained using a LEO 1550 field emission SEM operating at 15 kV. Samples for SEM analysis were prepared by freezing the thin film in liquid nitrogen for 10 min and then fracturing. The fractured sample was then sputtered with a 250-Å coating of platinum to limit surface charging. A representative micrograph displaying a dense, granular morphology is presented in Figure 2. The thickness of the film was determined from SEM to be ~150-nm thick. There was evidence of stress fracturing during sample preparation along the edges, but not in the bulk of the film. The root-mean-square of the surface roughness was measured 13.5 nm across a 10- μm section.

Since the films were amorphous as measured by X-ray powder diffraction, the local structure of the film was measured using Fe K-edge X-ray absorption fine struc-

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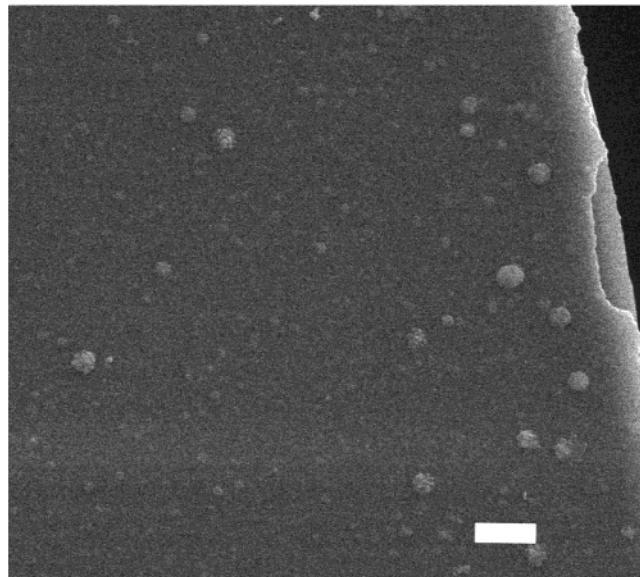


Figure 2. Scanning electron microscope image of the γ -FeOOH film sample. The image was collected using 10-keV electrons. The white bar represents 2 μm .

ture (EXAFS) spectroscopy. Measurements⁴ were made on the iron oxide film deposited on Kapton at the MRCAT insertion device beamline at the Advanced Photon Source.⁵ The incident X-ray energy was selected by using Si(111) crystal reflections. Tapering the undulator by approximately 1.25 keV resulted in less than 26% deviation in incident X-ray intensity over the energy range of the XAFS scan.

Higher order harmonics were rejected with an Rh mirror. Incident X-ray intensity was monitored with a nitrogen gas ion chamber, and the fluorescent X-ray intensity was monitored using an argon gas ion chamber of the Stern–Heald geometry.⁶ A Mn filter of three absorption lengths was used to reduce elastically scattered radiation. Linearity tests⁷ of the experimental setup indicated less than 0.5% nonlinearity for 50% attenuation of the incident X-ray intensity. The Fe XAFS data from the iron oxide film and the lepidocrocite standards were analyzed with the MacXAFS (ver. 4.0) analysis software.⁸

The basic structural unit of common iron oxides is the $\text{Fe}(\text{O})_6$ or $\text{FeO}_3(\text{OH})_3$ octahedron, or the $\text{Fe}(\text{O})_4$ tetra-

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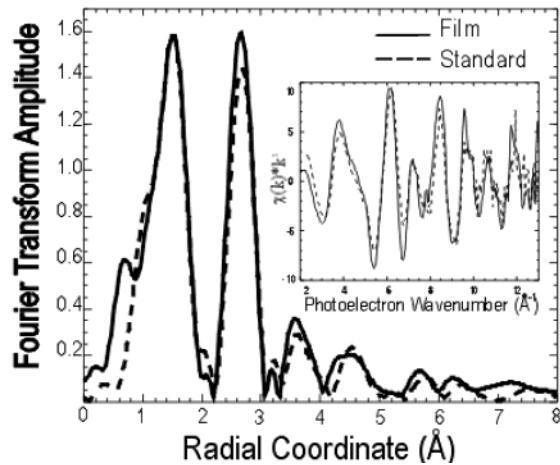


Figure 3. Fourier transforms ($\Delta k = 2.0$ – 12.3 \AA^{-1} , $dk = 1 \text{ \AA}^{-1}$) of the $\chi(k)*k^2$ data and normalized $\chi(k)*k^3$ data (inset) from the iron oxide film deposited on Kapton (solid line) and the lepidocrocite standard (dashed line). The first peak in the Fourier transform corresponds to the oxygen shell surrounding the Fe atoms. The second peak corresponds to the cation, where the third peak corresponds to the cation and next nearest-neighbor oxygen.

hedron. These entities may be linked by corners, edges, or faces to form different structural lattices.^{9,10} The Fe–Fe coordination number and radial distances, measured using the EXAFS technique, have been shown to be useful for visualizing the different structures and identifying the major iron oxide phases present.⁹ The Fourier transforms of these oxide film data are shown in Figure 3 together with the data from the lepidocrocite standard. The inset plot similarly shows the comparison in photoelectron wave vector as $\chi(k)*k^3$. This comparison shows that the local structure of the iron oxide film matches closely that of the lepidocrocite environment, indicating that the major fraction, that is, 90%, of the iron oxide film is indeed lepidocrocite (γ -FeOOH). These films are very uniform both in composition and roughness.

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