

Molecular Sieving in a Nanoporous *b*-Oriented Pure-Silica-Zeolite MFI Monocrystal Film

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Chemical sensor and zeolite-modified electrode (ZME) applications have been one of the major driving forces for the development of zeolite thin films and layers.^{1,2} When integrated with an appropriate sensor platform, a zeolite film can improve the selectivity and sensitivity of the sensor due to its ability to selectively adsorb a component out of a mixture. To achieve selective adsorption and quick response, the zeolite film is required to be continuous² (i.e., free of nonzeolitic pores) and thin, and have proper orientation. For facile mass transport, a monocrystal-thick film is also preferred because there are no grain boundaries in the mass transport direction, which have proved to decrease diffusion in zeolite by orders of magnitude.³ Strong adhesion between the zeolite film and the sensor surface is also critical for the durability of the sensor.² There have been a large number of publications in the area of ZME, and a comprehensive review on this topic is available.² However, previous work on zeolite film/layer-based sensors or ZMEs used either loose randomly oriented zeolite crystals buried in an inorganic/polymer matrix, linked to the electrodes by covalent bonds,^{2,4–11} or an oriented zeolite film¹² grown by secondary growth method.¹³ These zeolite films are either noncontinuous or have multiple zeolite crystal layers that are not desirable for sensor applications.

We have synthesized a continuous *b*-oriented thin (0.4 μm thick) pure-silica-zeolite (PSZ) MFI monocrystal-thick film by a simple direct in situ crystallization method.^{14,15} Due to the preferred *b*-orientation and the monocrystal nature of the film, the straight channels in MFI are perpendicular to the substrate surface, and through the whole film thickness. The main goal of this study is to demonstrate for the first time the molecular sieving capability of this *b*-oriented PSZ MFI film using a ZME configuration. We followed published electrochemistry protocols and selection of redox couples of different sizes.¹⁶

The *b*-oriented PSZ MFI film was prepared following previously reported methods.^{14,15} A continuous MFI film of ~0.4 μm thick was formed by in-situ crystallization (Figure 1a and 1b). The crystals protruding out are mostly due to twin-growth, and these crystals can be readily removed by slight polishing to obtain a smooth and featureless surface. No cracking and peeling-off of the film was observed during polishing, indicating that the film has excellent mechanical strength and adhesion. This is consistent with our previous findings.¹⁷ After calcinations to remove the template to free-up the zeolite pores for permeation, no obvious changes of film morphology were observed. The *b*-orientation was confirmed by XRD (Supporting Information, Figure 1).

Figure 1c is a schematic showing how the zeolite film can achieve size-selectivity or molecular sieving. Briefly, the *b*-oriented MFI thin film was directly grown on the surface of an electrode (stainless steel) and then exposed to an aqueous solution of a mixture of redox probe species. In this particular study, we have focused on two redox couples with different diameters: Ru(NH₃)₆³⁺ (diameter ~5.5 Å) and Co(phen)₃²⁺ (diameter ~13.0 Å).¹⁶ If the

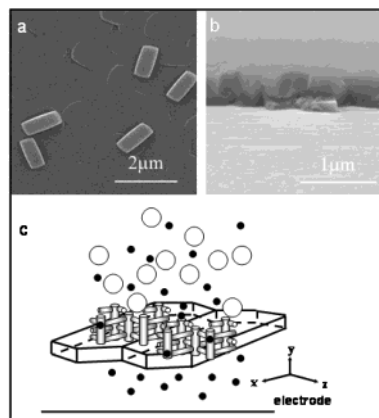


Figure 1. (a) SEM top view of *b*-oriented pure-silica-zeolite (PSZ) MFI monocrystal-thick film; (b) cross-sectional view of sample in (a) after slight polishing; (c) schematic illustration of molecular sieving in *b*-oriented PSZ MFI monocrystal-thick film. A distance was intentionally kept between the MFI film and the electrode so that the sieving behavior can be illustrated more clearly.

oriented film is continuous and defect-free, then the only passage for these probes is through the zeolite channels. Ru(NH₃)₆³⁺ has a molecular size close to the film pore size (5.5 Å) and may be able to traverse the film to yield a redox response at the underlying electrode, while Co(phen)₃²⁺ may be excluded from reaching the electrode due to its large size.

A solution of Ru(NH₃)₆³⁺ generates well-defined redox peaks on the bare electrode (Figure 2a), and the peaks become deformed on the *b*-oriented MFI coated electrode (Figure 2a) due to diffusion limitation. A solution of Co(phen)₃²⁺ also gives well-defined redox peaks but at a higher potential (vs Ru(NH₃)₆³⁺). These peaks disappear completely for the electrode coated with *b*-oriented MFI film (Figure 2b), indicating the molecular sieving capability of the MFI film. For the mixture of Ru(NH₃)₆³⁺ and Co(phen)₃²⁺, the CV response (Figure 2c) is almost identical to that of Ru(NH₃)₆³⁺ solution (Figure 2a), confirming again that the larger Co species was excluded from reaching the electrode. A control experiment was carried out on a spin-on PSZ MFI coated electrode (Figure 2d). The spin-on film is about 0.4 μm thick, and its top-view and cross-sectional view SEM images are shown in Supporting Information, Figure 2. Our previous study showed that the spin-on film has a bimodal pore size distribution with zeolitic micropores (0.55 nm) and the interparticle mesopores (2.7–3.3 nm).¹⁸ The electrode coated with spin-on film shows peaks similar to those of the bare electrode, and this indicates that both Ru and Co species are small enough to penetrate this film to reach the underlying electrode. No significant effects on peak currents were observed.

This sharp size cutoff of the *b*-oriented MFI film indicates that the Ru species reaches the electrode mainly through the zeolite pore system and not through defects and/or grain boundaries that are in general larger than 1 nm. The good continuity of the film is

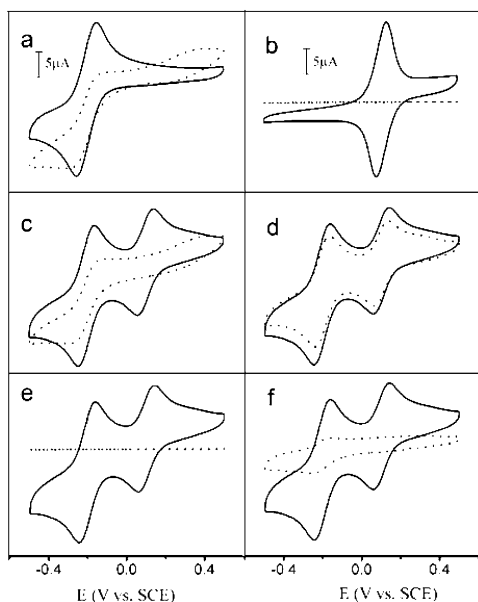


Figure 2. Cyclic voltammograms of $\text{Ru}(\text{NH}_3)_6^{3+}$ and/or $\text{Co}(\text{Phen})_3^{2+}$ in aqueous solutions. Solid line, bare electrode; dotted line, coated electrode. (a) $\text{Ru}(\text{NH}_3)_6^{3+}$ on MFI film; (b) $\text{Co}(\text{Phen})_3^{2+}$ on MFI film; (c) $\text{Ru}(\text{NH}_3)_6^{3+} + \text{Co}(\text{Phen})_3^{2+}$ on MFI film; (d) $\text{Ru}(\text{NH}_3)_6^{3+} + \text{Co}(\text{Phen})_3^{2+}$ on spin-on MFI film; (e) $\text{Ru}(\text{NH}_3)_6^{3+} + \text{Co}(\text{Phen})_3^{2+}$ on as-synthesized MFI film; (f) $\text{Ru}(\text{NH}_3)_6^{3+} + \text{Co}(\text{Phen})_3^{2+}$ on silylated MFI film. Supporting electrolyte: 0.5 M KCl. Scan rate: 0.1 mV/s. Reference electrode: sodium saturated calomel electrode (SCE). Note that MFI film means *b*-oriented MFI for brevity.

also evident from the CV response of the noncalcined film coated electrode (Figure 2e), where no peaks were observed due to the plugging of the zeolite channels by the organic template molecules.

PSZ MFI with a neutral framework is known for its hydrophobicity.¹⁹ However, the ion species in the aqueous solution were found to be able to diffuse through the PSZ MFI film. This suggests that there are some surface hydroxyl groups on the zeolite crystals, making the film hydrophilic to a certain extent and thus compatible with aqueous solution. This is consistent with our results on moisture sensitivity of PSZ zeolite films.¹⁷ To examine the effect of hydrophobicity of the film on the diffusion of the redox species, the oriented MFI film was treated with trimethylchlorosilane to cap off the hydroxyl groups using a procedure we developed.¹⁷ The treated electrode (Figure 2f) yields a weaker CV response as compared to the nonsilylated film (Figure 2c).

We have also carried out experiments on negatively charged ion species Γ^- (diameter ~ 2.5 Å) and neutral species $\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4-\text{CH}_2-\text{OH})$ (diameter ~ 4.5 Å). However, poorly defined CV peaks were observed, showing that stainless steel was not a suitable electrode for these redox species.

To quantify the ion diffusion coefficient inside the zeolite films, chronocoulometry for $\text{Ru}(\text{NH}_3)_6^{3+}$ species on a bare electrode, spin-on MFI film, and *b*-oriented MFI film coated electrode was determined (Figure 3). The data collected follow the Cottrell equation ($Q = nFA(D/\pi)^{1/2}Ct^{-1/2}$). The diffusion coefficients of the $\text{Ru}(\text{NH}_3)_6^{3+}$ can be determined from the slopes of the curves. The diffusion coefficient of $\text{Ru}(\text{NH}_3)_6^{3+}$ on bare electrode is 5.38×10^{-6} cm²/s, whereas through the spin-on film and the *b*-oriented film the diffusion coefficients are 3.49×10^{-6} and 1.46×10^{-7} cm²/s, respectively. The diffusion coefficient of spin-on MFI film is only slightly lower than that of the uncoated electrode. The diffusion coefficient of the *b*-oriented MFI film is much lower, and this is consistent with the assumption that $\text{Ru}(\text{NH}_3)_6^{3+}$ reaches the electrode through the zeolitic pores instead of the large nonzeolitic

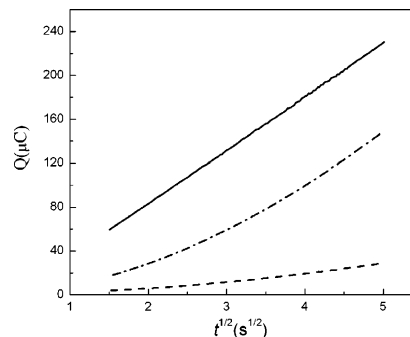


Figure 3. Chronocoulometry for $\text{Ru}(\text{NH}_3)_6^{3+}$ on bare stainless steel electrode (—), spin-on film (- · - ·), and *b*-oriented film (- - -) coated stainless steel electrode. Supporting electrolyte: 0.5 M KCl. Potential step: -0.22 V.

defects. All of these results prove that the *b*-oriented MFI film possesses molecular sieving properties toward mixtures of ion species with different diameters and the film is absent of nonzeolitic defects. Thus, the *b*-oriented MFI film prepared in this study is a very promising candidate as a coating for sensors and ZME applications to achieve higher selectivity, sensitivity, stability, and durability. Another advantage of the PSZ MFI film is that it is highly resistant to strong acid and bases, making it a more versatile film than aluminosilicate zeolite films such as FAU and LTA.²⁰ It is recognized that the stainless steel electrode used here is not ideal for a number of ion pairs, and we are currently working on preparation of the *b*-oriented MFI films on other electrode materials. Our previous work showed that we cannot generate the *b*-oriented MFI film on gold (Au),²¹ and this may be generally true for other precious metals such as Pt. However, this oriented MFI film will likely work for oxide-based electrode materials. Because both the in-situ *b*-oriented and the spin-on MFI films show nanoporosity in an electrochemical environment, these films can also potentially be used as templates for electrodeposition of nanostructures.

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Supporting Information Available: Experimental procedure and Figures S1 and S2 (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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