VIP Zeolite Coatings

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Ionothermal Synthesis of Oriented Zeolite AEL Films and Their Application as Corrosion-Resistant Coatings**

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Over the last 15 years there has been considerable and increasing interest in the synthesis of zeolite films for separation-membrane and membrane-reactor applications.[1] Preparation of zeolite films on nonporous substrates for chemical sensor applications has also been reported.[2] These efforts were mostly motivated by the desire to take advantage of zeolites' inherent molecular-sieve characteristics. But recently, other interesting applications, which do not rely on the molecular-sieve effect, have been demonstrated,[3] such as corrosion-resistant coatings,[4] films with low dielectric constants,[5] hydrophilic and antimicrobial coatings,[6] and heat pumps.[7] These new applications promise to offer even more exciting opportunities.

High-silica zeolite (HSZ) MFI coatings for aluminum alloys, stainless steels, and carbon steels show excellent corrosion resistance, strong adhesion to the substrates, and extraordinary thermal and mechanical properties.[4] All these properties, plus the fact that zeolites are nontoxic, suggest that zeolite coatings have the potential to become an environmentally friendly alternative for the most commonly used, toxic, carcinogenic, and strictly regulated chromate conversion coating. However, zeolite coatings are normally synthesized on the substrates in water (hydrothermal synthesis) or other traditional organic solvents (solvothermal synthesis) in sealed reactors. The current hydrothermal deposition process for HSZ-MFI coatings is considered inconvenient by the surface-finishing industry, because it involves the autogenous pressure (about 9 atm at 175 °C for HSZ-MFI coating synthesis), while the chromate conversion coating can be deposited at ambient pressure.

Recently, a new ionothermal method was introduced to the synthesis of zeolite powders under ambient pressure in open vessels,[8–10] in which ionic liquids were used instead of water or organic solvents. An ionic liquid is a substance that consists only of ions and has a melting temperature below 100 °C. Ionic liquids have been recognized as environmentally benign solvents and "designer solvents", because they have negligible vapor pressure, high chemical and thermal stability, high ionic conductivity, wide electrochemical potential windows, can act as catalysts, are nonflammable, and have tunable physicochemical properties by suitable choice of cations and anions.[11,12] These remarkable properties enable ionic liquids to be widely used in organic, inorganic, polymer, and biocatalytic synthesis.[12]

AEL powder is the first example of a zeolite successfully synthesized ionothermally.[8] It was prepared under ambient pressure in a convection oven in 68 h at 150 °C using 1-methyl-3-ethylimidazolium bromide ([emim]Br) as both solvent and template. This method is also successful with microwave heating, in which case only one hour was needed for the crystallization owing to the rapid microwave absorption of ionic liquids.[9]

Herein, we present the first ionothermal synthesis of zeolite films by in situ crystallization on AA 2024-T3 under ambient pressure. AA 2024-T3 was chosen because it is the most widely used aluminum alloy in aerospace and defense applications but has serious corrosion problems owing to its high copper content. Coatings of both AlPO-11 and SAPO-11 were prepared at 150 °C. These alumino- and silicoaluminophosphate zeolites have an AEL-type framework. Microwave heating was used to allow rapid, ambient-pressure preparation of zeolite coatings. Metal panels were not a concern during microwave heating once they were immersed inside the synthesis solution. For SAPO-11 coatings, tetraethyl orthosilicate (TEOS) was added as the silicon source to the synthesis mixture, and the procedure was repeated (two-stage synthesis) to produce continuous coatings. The anticorrosion performance of different AEL coatings was investigated by direct current (DC) polarization.

The presence and identity of the AEL coatings, both AlPO-11 and SAPO-11, on AA 2024-T3 were confirmed by X-ray diffraction (XRD, Figure 1). No byproducts were found. A preferred orientation is evident for the SAPO-11 coatings. AEL consists of a ten-membered-ring channel (0.40×0.65 nm) parallel to the c axis of the crystal. The strong (002) reflection peak in the SAPO-11 XRD pattern indicates that the one-dimensional channels are perpendicular to the Al alloy surface. However, the XRD pattern of the AlPO-11 coating suggests random orientation.

Scanning electron microscopy (SEM) images (Figure 2) show that both AlPO-11 and SAPO-11 crystals have a typical hexagonal, rod-like morphology. For AlPO-11, crystal bundles are deposited on the substrate randomly with poor crystal intergrowth. In contrast, SAPO-11 crystals with an average hexagon diameter of 1.5 μm are packed densely, with their

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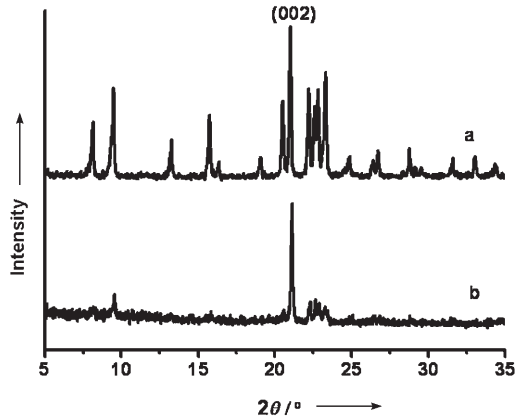

Figure 1. XRD patterns of AEL coatings on AA 2024-T3. a) AlPO-11; b) SAPO-11.

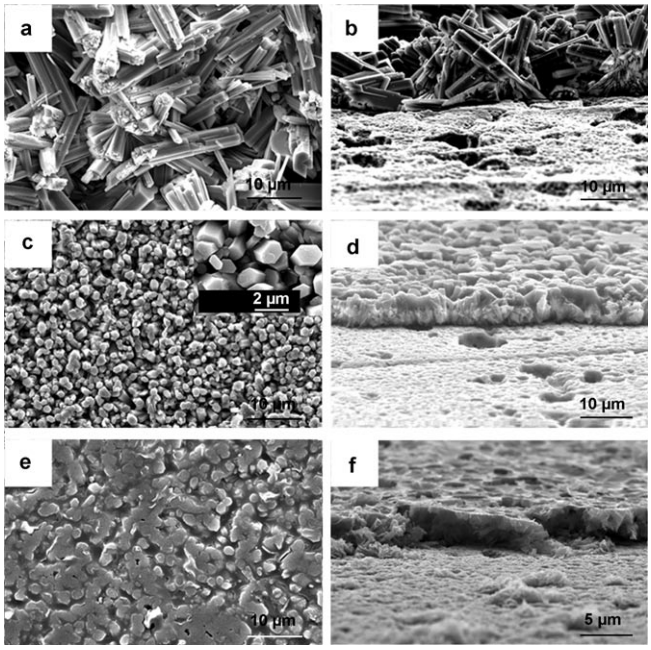

Figure 2. SEM images of different as-synthesized AEL coatings on AA 2024-T3. a) AlPO-11 (surface); b) AlPO-11 (cross section); c) SAPO-11 (surface, inset is higher magnification); d) SAPO-11 (cross section, mildly polished surface); e) SAPO-11 with spin-on BTSM-MEL (surface); f) SAPO-11 with spin-on BTSM-MEL (cross section).

c axes perpendicular to the substrate surface, which is consistent with the XRD result. Moreover, from the cross-sectional SEM picture (Figure 2d), the intergrowth between the oriented crystals is well-developed near the surface of the substrate, which demonstrates that the SAPO-11 film forms a compact and continuous coating.

Crystallization from solution generally occurs through nucleation and growth of the nuclei to larger crystals by incorporation of material from the solution.[13] During the film synthesis, the nuclei deposited on the substrate serve as the growth centers for zeolite crystallization.[14] According to the competitive growth model,[15] anisotropic crystals preferentially grow along their fastest growing axis, which is the *c* axis in our case, because the AEL crystals show a hexagonal, rod-like morphology. Xu et al. found that AlPO-11 had a fast crystallization rate under microwave heating, but the introduction of Si into the synthesis mixtures hindered the crystallization of the AEL structure,[9] which can explain the different orientation of AlPO-11 and SAPO-11 films that we detect. Owing to the fast crystallization rate of AlPO-11, it is difficult to have a dense nuclei layer on the surface before crystallization. This means that the nutrient concentration surrounding the growth centers can be regarded as isotropic, and the growing crystals should not exhibit any preferred orientation.[14] Both off-plane and in-plane crystals are observed in the SEM images (Figure 2a,b). The SAPO-11 film was obtained by a two-stage synthesis. The first stage, because of its slow crystallization rate, is a seeding process rather than a crystallization. During the second synthesis stage, the space between growth centers (formed in the first stage) is limited, so that in-plane growth is suppressed. As a result, the fastest out-of-plane, *c*-oriented growth dominates the crystallization process and makes it possible to form a highly oriented film.

Although oriented zeolite coatings are of particular interest for size-selective chemical sensors, separation membranes, and optical systems,[16] our motivation is to find a new route to synthesize corrosion-resistant coatings under ambient pressure. Thus, we investigated the anticorrosion performance of ionothermally synthesized AEL-type zeolite coatings by DC polarization tests in 0.1 M aqueous NaCl solution, in which chloride ions are known as an aggressive pitting corrosion species.

Figure 3 shows that bare AA 2024-T3 pits at its open circuit potential (OCP, ca. −0.5 V vs. standard calomel electrode (SCE)). That is, the pitting corrosion occurs once the metal is immersed in the corrosive media. This OCP corrosion is related to the intermetallic interaction of Cu in the Al matrix and to the presence of Cl^- in the electrolyte.[17] The OCPs of samples coated with both SAPO-11 (ca. −0.65 V vs. SCE) and AlPO-11(ca. −0.6 V vs. SCE) are more negative

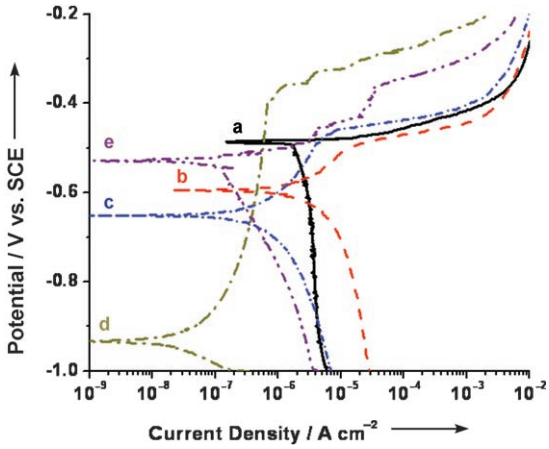

Figure 3. DC polarization curves for bare and coated AA 2024-T3 in 0.1 M NaCl at room temperature. a) Bare AA 2024-T3; b) AA 2024-T3 coated with AlPO-11; c) AA 2024-T3 coated with SAPO-11; d) AA 2024-T3 coated with SAPO-11 with spin-on BTSM-MEL; e) AA 2024-T3 with spin-on BTSM-MEL.

than bare AA 2024-T3, which means the AEL coatings inhibit the OCP corrosion of the samples. The corrosion current density of samples coated with SAPO-11 and A1PO-11 is about two and one orders of magnitude, respectively, smaller than that of the bare Al alloy. The poor crystal intergrowth of the AlPO-11 coating makes it a porous structure, through which electrolyte can easily penetrate to the Al alloy surface. The natural passive oxide layer of the Al alloy may also be damaged during the ionothermal synthesis. These negative effects cause the higher cathodic kinetics and even lower pitting potential of the sample coated with AlPO-11 than of the bare substrate. Thus, AlPO-11 coating does not have the desired corrosion resistance. For SAPO-11 coating, the pitting potential is slightly higher than the OCP of AA 2024-T3, which means the favored sites for pit initiation (mostly copper) are at least partially covered by the SAPO-11 coatings. The cross-sectional SEM image of the SAPO-11 coating (Figure 2d) shows that the film consists of two major components: the dense barrier layer adjoining the metal and a porous layer extending from the barrier layer to the outer surface of the film, which is similar to the anodized film of Al alloys.[18] This kind of structure has the advantage of being able to be dyed. To obtain maximum corrosion resistance, the porous coating must be sealed. A silane with added zeolite nanoparticles was used as the sealing agent. Several aspects were considered in choosing it: 1) The silane has very good adhesion properties,[19] which can act as a binder layer between the zeolite coating and the polymer topcoat. 2) The silane film itself has good corrosion resistance for Al alloys.[20] 3) Silane films with added nanoparticles offer better mechanical properties,[21] and those with added MEL nanocrystals also improve the corrosion resistance (Figure 3). 4) The silane film can improve the surface hydrophobicity, which benefits the corrosion resistance. In this study, a dilute 1,2-bis(triethoxysilyl)methane (BTSM) solution mixed with 20 ppm MEL nanocrystals was spun on the mildly polished SAPO-11 coating. The SEM images show the polished SAPO-11 coating before (Figure 2d) and after the sealing process (Figure 2e,f). The surface of the modified coating is much more even than before modification, and the pores were sealed by BTSM-MEL. The water contact angle increases from approximately 0–20° to about 70–90° after sealing. No cracking or peeling of the as-synthesized SAPO-11 film was observed during polishing, thus indicating that the film has excellent mechanical strength and adhesion. The DC polarization results (Figure 3) show that the SAPO-11 coating modified with BTSM-MEL has very good corrosion resistance. The OCP is more negative than −0.9 V, and the corrosion current is less than 10^{-8} A cm^{-2}. The pitting potential also increases to −0.4 V, which is even higher than that of pure Al under similar conditions.[22] The DC polarization behavior of a sample with BTSM-MEL spin-on coated directly on bare AA 2024-T3 was also tested (Figure 3). The resulting sample shows good corrosion resistance, but the combination of SAPO-11 coating and BTSM-MEL sealing shows the best anticorrosion performance in this study.

In summary, a highly oriented SAPO-11 film has been ionothermally synthesized under ambient pressure and with microwave heating. This method is a novel, simple, fast, environmentally benign, and safe way to prepare oriented zeolite films. The SAPO-11 coating sealed with BTSM-MEL showed very good anticorrosion properties. This method produces the first reported oriented SAPO-11 film, which can be explored for other applications, such as size-selective chemical sensors, separation membranes, optical systems, and as a nanostructure host for advanced material synthesis.

Experimental Section

Coating solution formulation: A mixture of the molar composition [emim]Br/Al(OC_3H_7)$_3$/H_3PO_4/HF = 32:1:3:0.8 was stirred for 4 h at 100 °C. For SAPO-11, tetraethyl orthosilicate (TEOS) was introduced to the synthesis mixture with the molar ratio Si/Al = 0.25:1. AA 2024-T3 substrates were pretreated by an alconox detergent solution. The substrate was then fixed vertically inside the synthesis mixture in a teflon vessel designed for the MARS5 (CEM Co.) microwave reaction system. The unsealed vessel (with holes in the cover) was then quickly heated to 150 °C and held at that temperature for 2 h under microwave irradiation. After the synthesis, the coated sample was thoroughly washed with deionized (DI) water and acetone and dried with compressed air. For SAPO-11 samples, the synthesis procedure was repeated (two-stage synthesis) with fresh synthesis solution.

BTSM-MEL coatings: A BTSM solution was prepared by adding silane to a mixture of DI water and ethanol. The volume ratio BTSM/water/ethanol = 1:1:20 was used. Acetic acid was added to adjust the pH value of the solution to pH 4.5–5. The solution was then stirred at room temperature for at least 24 h before an MEL gel was added. MEL concentration in the solution was about 20 ppm. The sample coated with SAPO-11 was polished on a Buehler Ecomet 3 grinder–polisher using 0.05-μm silica slurry and thoroughly cleaned with DI water and acetone under sonication. The nanoparticle suspension was then spun onto the sample at room temperature on a Laurell spin coater. Afterward, the sample was heated at 80 °C overnight and then at 200 °C for 30 min.

Characterization: The XRD patterns were obtained on a Siemens D-500 diffractometer using $Cu_{K\alpha}$ radiation. SEM images were obtained on a Philips XL30-FEG scanning electron microscope. Samples were etched for cross-sectional SEM imaging by dipping the samples in 0.5 wt% HF for several seconds. A VCA-Optima XE was used for contact-angle measurement.

DC polarization testing was carried out with a Solartron potentiostat SI 1287 in a three-electrode flat cell (Princeton Applied Research Model K0235) with a Pt counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The corrosive medium was 0.1 M aqueous NaCl. The samples were immersed in the corrosive medium for 30 min prior to the DC polarization test with a sweep rate of 1 mV s^{-1}.

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