Molecular-Sieve Films

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In Situ Electrochemical Synthesis of Oriented and Defect-Free AEL Molecular-Sieve Films Using Ionic Liquids

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Abstract: *Simply preparing oriented and defect-free molecular-sieve films have been a long-standing challenge both in academia and industry. Most of the early works focus on the careful and multiple controls of the seeds layer or synthesis conditions. Herein, we report a one-step in situ electrochemical ionothermal method that combines a controllable electric field with ionic liquids. We demonstrate that an in-plane oriented and defect-free AEL (one molecular-sieve framework type) molecular-sieve film was obtained using an Al electrode as the Al source. The excellent corrosion-resistant performance of the film makes this technology promising in multiple applications, such as anti-corrosion coatings.*

Molecular sieves are crystalline materials with uniform channels and/or cages that find extensive industrial use as catalysts, adsorbents, and ion exchanges.[1] Molecular-sieve films have been widely explored as separation membranes and membrane reactors for 20 years.[2] Recently, they have also been recognized and demonstrated in a wide range of emerging applications,[3] such as sensors,[4] corrosion-resistant coatings,[5] low dielectric constant insulators,[6] hydrophilic and microbiocidal coatings,[7] and wear-resistant coatings.[8] These diverse applications of molecular-sieve films primarily require to features, such as preferred orientations and being free of defects.[3,9] Thus, innovative technologies to prepare such molecular-sieve films may have enormous potential to revolutionize existing industries, even create new markets.[10]

How to simply prepare oriented and defect-free films remains a great challenge for the implementation and industrialization of molecular-sieve films technologies.[11] Although a simple in situ crystallization method is favored for large-scale growth of molecular-sieve films, the random orientation and defects significantly limit performance of the films produced.[3,11a] Oriented and defect-free films could be obtained by secondary (seeded) growth,[12] whereby a seed layer of molecular-sieve crystals was deposited prior to film growth. To form an oriented seed monolayer, multi-steps are required to carefully manipulate the deposition of the seeds onto the substrate. During the subsequent film growth, defects can be minimized by the optimization of microstructures,[13] or with sealing materials in post-synthesis repair technologies.[9c,14] Nonetheless, defects cannot be completely eliminated because the sealing materials could not be deposited in nanometer-sized defects.[15] To solve this problem, rapid thermal processing[11c] and molecular layer deposition[16] have been reported to fabricate defect-free molecular-sieve membranes. However, the complexity of those methods limits their widespread application in industry.

An external electric field can be applied to align molecular sieve crystals on substrates to form an oriented layer of molecular-sieve crystals[17] or seed layer[18] for the secondary growth of polycrystalline molecular sieve films. However, this process must be followed by a hydrothermal step to obtain a fully dense molecular-sieve film. Although electrodeposition techniques have been widely used in both industry and academia for preparing advanced ceramic films,[19] the in situ electrodeposition of molecular-sieve films under hydrothermal conditions is technically impractical because of the high autogenous pressure in a sealed vessel at high temperature and the narrow electrochemical window of water.

The ionothermal method for the synthesis of molecular sieves[20] and molecular-sieve films[5a,21] under ambient pressure in open vessels, uses ionic liquids as the solvent instead of water in the hydrothermal synthesis. Ionic liquids have negligible vapor pressure, high ionic conductivity, and wide electrochemical windows.[22] These features readily overcome the disadvantages encountered when an electric field is applied to a hydrothermal system. Herein we demonstrate a one-step in situ electrochemical synthesis of molecular-sieve films using ionic liquids, obtaining an in-plane oriented and defect-free AEL film with excellent corrosion protection for aluminum.

We found that hexagonal rod-like $AlPO_4$-11 (AEL framework topology) crystals easily precipitated on the Al substrate in the ionothermal synthesis solution in the presence of an Al source. Simultaneously, many crystals deposited as embryonic seed crystals on the Al substrate as a result of homogeneous nucleation.[23] This deposition resulted in a random oriented film (see Figure 2a, and Figure S1 in the Supporting Information) with a poor reproducibility and a significant amount of $AlPO_4$-11 powders in the solution. To obtain an oriented $AlPO_4$-11 film, the homogeneous nucleation has to be hindered. To this end, we excluded the Al source (isopropoxide aluminum in this work) from the ionothermal synthesis solution and used the Al substrate itself as an Al source. The synthesis solution consisted of only ionic liquid 1-ethyl-3-

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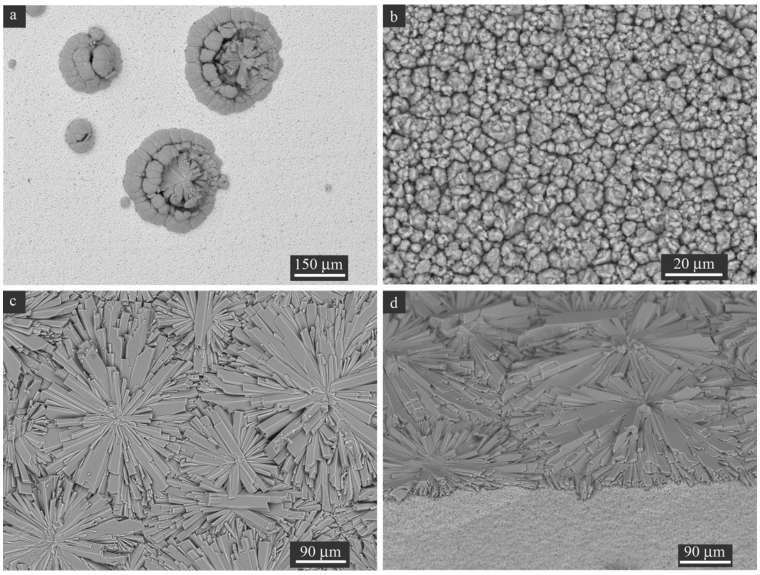


Figure 1. SEM images of non-electrochemically synthesized sample (a) and electrochemically synthesized samples (b–d). All electrochemical synthesis was carried out in the absence of aluminum isopropoxide. a) Scattered aggregates on the Al substrate; b) Dense-phase $AlPO_4$ on the Al anode after 4 h synthesis; c) Surface and d) cross section of in-plane oriented $AlPO_4$-11 on the Al cathode after 4 h synthesis.

methylimidazolium bromide ($[emim]^+Br^-$), phosphorus source H_3PO_4, and the mineralizing agent HF. In the initial tests, only a few scattered cauliflower-like aggregates were found on the Al substrate after four-hour ionothermal synthesis in an open vessel at 190 °C, and the $AlPO_4$-11 crystals were found inside these aggregates (Figure 1 a). These results indicated that the amount of Al dissolved by acid at ambient pressure was not sufficient to form a continuous $AlPO_4$-11 film without an additional Al source in the synthesis solution. In accordance with our observation, Tian and co-workers[21] also reported that aluminophosphate molecular-sieve membranes can only be ionothermally synthesized on δ-Al_2O_3 through substrate surface conversion in a sealed vessel. Electrochemical oxidation can effectively generate a suitable amount of Al ions precisely at the surface of the Al substrate without adding an Al source directly to the synthesis solution. To implement this method, we used a three-electrode electrochemical cell with one Al panel as a working electrode, another Al panel as a counter electrode, and a Pt wire pseudo-reference electrode.

We had expected, by applying a current, that molecular sieve would be deposited on the anode on which the Al surface was electrochemically oxidized. However, only dense-phase $AlPO_4$ was found on the surface (Figure 1 b). Surprisingly, an in-plane orientated intergrown sea-urchin-like $AlPO_4$-11 film was successfully synthesized on the cathode after 4 h synthesis (Figure 1 c). These sea-urchin-like $AlPO_4$-11 crystals were densely packed and composed of typical hexagonal rods with their *c* axes parallel to the substrate surface. The X-ray diffraction (XRD) result confirmed the in-plane orientated growth since almost all *c*-direction reflection peaks in the $AlPO_4$-11 XRD pattern disappeared (Figure 2 b and insert). Moreover, the cross-sectional scanning electron microscope (SEM) image (Figure 1 d) showed a well-developed intergrowth between the crystals, which demonstrated that the $AlPO_4$-11 film formed a compact and continuous coating with an average thickness of approximately 50 µm on the Al cathode substrate.

These intriguing observations promoted us to ask why the $AlPO_4$-11 film formed only at the Al cathode by applying an electric field in the absence of aluminum isopropoxide. The Al substrate was stable in the ionothermal synthesis solution without an electric field, generating very small amount of hydrogen bubbles even at 190 °C. Once an electric field was applied, a large amount of bubbles appeared on both the anode and cathode. Gas evolution on the anode could only be caused through a chemical reaction whereby the reacting Al was exposed after electro-oxidation, whereas gas on the cathode could be attributed to that chemical reaction and the electrochemical reduction of protons (Scheme 1). Thereby the electric field was essential to activate both Al electrodes, accelerate the interface reactions, and provide an Al source. However, these chemical and electrochemical reactions still could not explain why an $AlPO_4$-11 film was only generated on the cathode. Because the ionic liquid is a highly concentrated electrolytic solution, the surface of the electrode is overscreened by counterions or even covered by a condensed layer of counterions in the presence of electric field.[24] At the negatively charged cathode, the $[emim]^+$ cations are electrostatically adsorbed and act as the structure-directing agents (SDA)[20] for $AlPO_4$-11 formation. Under the effect of the SDA, the cathode reacts with protons and converts the electrode surface to $AlPO_4$-11 with PO_4^{3-} (Scheme 1). At anode, the $[emim]^+$ cations are repelled. Although a large amount of Al can be supplied by

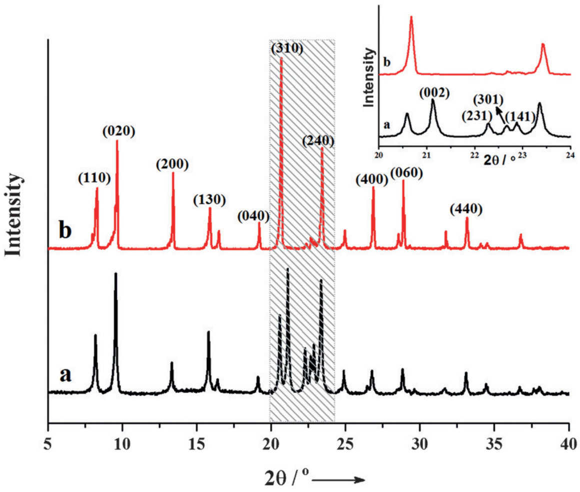
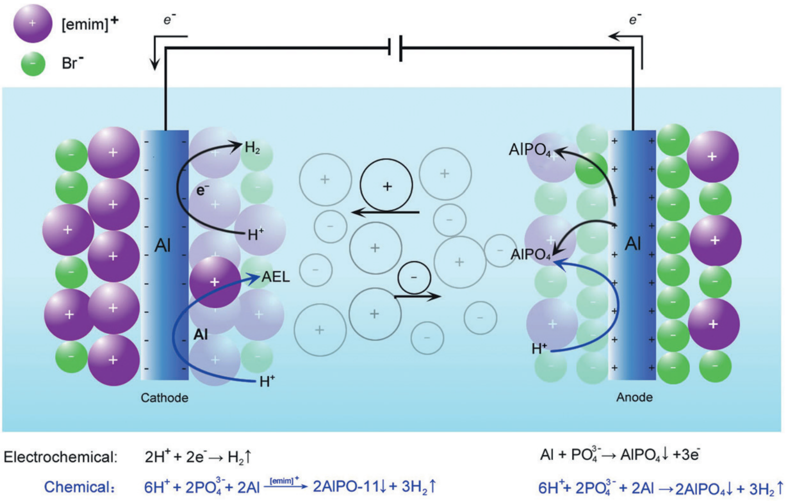


Figure 2. XRD patterns of $AlPO_4$-11 a) random oriented film (black); b) electrochemically synthesized in-plane oriented film on cathode (red). Inset: expansion of the hatched region.



Scheme 1. Illustration of the in situ electrochemical synthesis of the $AlPO_4$-11 film on Al electrodes.

either electrochemical reaction or chemical reaction, only a dense-phase $AlPO_4$ rather than an $AlPO_4$-11 film was formed on the anode due to the lack of the SDA.

We then asked why is the $AlPO_4$-11 film formed with an in-plane orientation? It was noted that there was no solid precipitate in the solution after synthesis, suggesting that the amount of dissolved Al^{3+} in ionic liquid was minimal. Therefore, very little Al could be provided from the solution, a situation that effectively hinders the out-of-plane growth of AEL film. When the Al cathode was replaced by Cu cathode, no $AlPO_4$-11 crystals formed on the cathode (Figure S2), suggesting that the Al anode is a negligible Al source. Thus the only source of Al is produced through the chemical reaction at the cathode–solution interface, rather than from the anode. In addition, many crystals were observed on the surface of the Al cathode (Figure S3) when the synthesis time was only 30 min, suggesting a rapid crystallization rate of $AlPO_4$-11 at 190 °C. It is anticipated that the rapidly grown crystals would shield the cathode surface, reduce the surface coverage of nuclei. As a result, a dense nuclei layer cannot be formed before crystallization, inhibiting the out-of-plane oriented growth.

It is noted that the entire cathode surface could be completely converted to $AlPO_4$-11 because positively charged protons and $[emim]^+$ cations could readily reach any bare place on the Al cathode's surface under electric field and enable $AlPO_4$-11 formation. As a result, the Al cathode surface was converted into a defect-free molecular-sieve film that was associated with a near-zero current, indicating that it was no longer affected by the electric field as a result of insulation by the $AlPO_4$-11 film. To further verify the important role of the electrochemical method in controlling the formation of defect-free film, we carried out a synthetic process, in which the Al panel was under the electrochemical conditions for only 2 h (instead of 4 h) with the ending current of approximately −1 mA, and subsequently was treated for another 2 h at the same condition but without adding any electric field. As expected, a nearly in-plane oriented $AlPO_4$-11 film (Figure S4 and insert) with visible defects (Figure S5) was obtained, further confirming the advantage of electrochemical process for defect-free films.

DC polarization is a common technique to test the anticorrosion performance of films.[5a,c,d,25] Moreover, the performance is also related to the film defects which degrade the performance by providing penetrable pathways for corrosive media. A lower corrosion current density (obtained from the intercept of the two linear segments of the Tafel slope) should correspond to a better corrosion resistance, and fewer film defects. Samples coated with $AlPO_4$-11 films were immersed in 0.1 mol L^{-1} aqueous NaCl solution, which is an aggressive corrosive media to Al metal. Both random oriented and nearly in-plane oriented $AlPO_4$-11 film showed poor protection (Figure 3 b,c), indicating the corrosive medium could easily penetrate through the film defects to the Al surface. In contrast, the in situ electrochemically synthesized in-plane oriented AEL sample exhibited an excellent corrosion resistance (Figure 3 d). The corrosion current density was about 3×10^{-8} A cm^{-2}, approximately 2 orders of magnitude smaller than that of the bare Al (Figure 3 a) and of the sample coated with nearly in-plane oriented $AlPO_4$-11 film. This result indicates the in situ electrochemically synthesized in-plane oriented $AlPO_4$-11 film is a defect-free coating with excellent corrosion resistance.

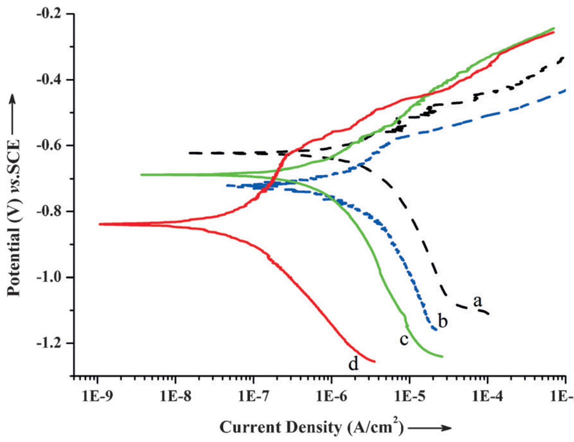


Figure 3. DC polarization curves for bare and coated Al in 0.1 M NaCl at room temperature. a) bare Al; b) Al coated with random oriented $AlPO_4$-11 film; c) Al coated with nearly in-plane oriented $AlPO_4$-11 film; d) Al coated with in-plane oriented $AlPO_4$-11 film.

In summary, we have invented an in situ electrochemical ionothermal method using an Al electrode as the Al source to synthesize oriented and defect-free $AlPO_4$-11 molecular-sieve films that confer a superior protection to the Al substrate against corrosion. To our knowledge, it is the first reported in situ electrochemical synthesis of molecular-sieve films. The simple synthesis, under ambient pressure, and with controllable electrochemical parameters may have a great potential for a scale-up to industrial application, and also offer an unprecedented opportunity to explore the growth mechanism of molecular-sieve films.

Experimental Section

Preparation of molecular-sieve film: Film synthesis-solution formulation: A mixture of the molar composition [emim]Br/H_3PO_4/HF = 32:3:0.8 was stirred for 1 h at 90°C. Before the synthetic experiment was started, the ionic liquids were held under high vacuum and elevated temperature (90°C) for about 15 h to remove any residual water. Al substrates were pretreated by an Alconox detergent solution. Two identical Al substrates were then fixed vertically inside the synthesis solution in an electrochemical cell as cathode and anode. A Pt pseudo-reference electrode was constructed in the form of a separate probe to minimize the effect of the bulk concentration change (especially H^+) during synthesis. The three-electrode cell was then heated at 190°C for 4 h while applying a potential of −1.1 V (vs. Pt reference electrode) on the working Al electrode (cathode in this case), using an EG&G 263A potentiostat. For nearly in-plane oriented $AlPO_4$-11 films, the three-electrode cell was also heated at 190°C for 2 h while applying a potential of −1.1 V (vs. Pt reference electrode) on the working Al electrode with the ending current of ca. −1 mA, and subsequently was ionothermally treated for another 2 h at the same condition but without any electric field. For random oriented $AlPO_4$-11 film, aluminum isopropoxide was introduced to the synthesis mixture with a molar composition [emim]Br/Al-$(OC_3H_7)_3$/H_3PO_4/HF = 64:1:6:1.6. No electric field was applied. After the synthesis, the coated sample was thoroughly washed with deionized (DI) water and acetone and dried with compressed air. Samples were etched for cross-sectional SEM imaging by dipping the samples in 1 wt% HF for several seconds.

Characterization: The XRD patterns were obtained on a Rigaku D/MAX 2500/PC diffractometer using CuK_α radiation. SEM images were obtained on a Hitachi TM 3000 scanning electron microscope.

DC polarization testing: It was carried out with an EG&G 263A or Solartron SI 1287 potentiostat in a three-electrode flat cell with a Pt counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The corrosive medium was 0.1 molL^{-1} aqueous NaCl. The samples were immersed in the corrosive medium for 30 min prior to the test with a sweep rate of 1 mVs^{-1}.

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