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Synthesis of Catalytic Nanoporous Metallic Thin Films on Polymer Membranes

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Abstract

Composite membranes were produced with a metallic thin film forming the upper layer of the composite on a porous polymer support. Commercially available membranes were used as supports with both micron and nanometer scale pores. Alloy films of ~110 nm thickness were deposited via magnetron sputtering to produce the top layer of the composite. Dealloying the film with sulfuric acid allowed the creation of a nanoporous film structure with a ligament size of 7.7 ± 2.5 nm. Resulting composite membranes were permeable to water at all stages of production, and a UF PSf membrane with 90 nm of nanoporous Fe/Pd on top showed a flux of 183 LHM/bar. The films were evaluated for dechlorination of toxic polychlorinated biphenyls from water. At a loading of 6.6 mg/L of Pd attached to 13.2 cm² support in a 2.5 ppm PCB-1 solution with 1.5 ppm dissolved H₂, over 90% of PCB-1 was removed from solution in 30 minutes, which produced the expected product biphenyl from the dechlorination reaction.

Graphical Abstract

Keywords

composite membranes; dechlorination; nanoporous metals; dealloying

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Author Contributions

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Introduction

Thin film composite membranes made from multiple polymer layers are popular in broad separation applications as nanofiltration and reverse osmosis membranes.¹ These types of composite membranes consist of different layers of material bonded together, for instance a thin polyamide layer forming a comparatively dense top layer supported by a thicker, more porous layer such as polysulfone (PSf) ultrafiltration membrane. The dense polyamide layer serves as the primary separations layer, while the polysulfone layer provides mechanical support. As with all composites, the properties of both materials are utilized to more effectively serve the purpose neither material may fulfill alone.

This research focuses on an alternative type of composite membrane, in which the top layer of the composite is a thin, nanoporous metallic film produced on a porous polymer membrane layer. Metals have many properties that are advantageous for membrane applications. Generally speaking, metal films are resistant to degradation from temperature or organic solvents. Additionally, transition metals are important catalysts in many widely used processes such as the use of Raney nickel for hydrogenation of organics^{2–3} or noble metals for CO oxidation in catalytic converters. Inorganic membranes are found in certain industries, such as gas separations, but have struggled to find application in many important liquid-based separations due to challenges in fabricating inorganic membranes with both small pore size and high overall porosity.

Metallic Layers in TFC Membranes

Composite membranes consisting of thin layers of metals produced on top of more traditional polymer membrane supports hold promise to marry the positive attributes of both inorganic and polymeric membranes in a single structure. Magnetron sputtering is a physical vapor deposition method that allows fine control over the deposited film's structure and composition. Furthermore, through the use of magnetron sputtering, metal films of thicknesses from tens of nanometers to micron scale thickness may be produced on top of pre-existing membranes and various other substrates. The resulting metallic thin film composite membranes (MTFCs) should possess many of the desirable characteristics of the metal active layer (solvent resistance, catalytic activity) while retaining the attributes that make polymer based membranes broadly successful in liquid separations applications (flexibility, high porosity).

For certain separations applications these films are desirable as active layers, but for many other purposes a higher porosity layer is much more desirable. To this end the deposited films were produced to function as precursors for producing nanoporous metal films through a process called dealloying or selective dissolution.^{4–5} Dealloying involves submerging an alloy material in an etchant solution to selectively leach one component of the alloy. Atoms of the other, more noble element surface diffuse during etching to form ligaments. These ligaments are made up of the remnant noble material and are the "beams" that connect at nodes to make up the nanoporous metal structure. An example ligament is highlighted in Fig. 5. This process continues through the thickness of the film to produce a high surface area pore/ligament structure whose characteristic size is dependent upon system conditions.⁶ This two-step process creates a membrane with a top layer of high surface area nanoporous

metal anchored to a porous polymer substrate, in this paper abbreviated as an npMTFC membrane, or nanoporous metallic thin film composite membrane.

Applications of Nanoporous Metals

The structure of nanoporous metals is desirable for separations-based membrane applications because the materials possess a high porosity structure of interconnected pores and ligaments. The pore size of the nanoporous metal may be controlled by varying dealloying conditions such as etchant temperature, concentration, or dealloying time.^{6–8} In addition to these considerations, kinetics of dealloying have been investigated with brass foils in a cross-flow dealloying setup to consider the influence of the corroded metal ions in solution on the dealloying process.⁹ In addition to separations, the structure of nanoporous metals make them interesting for a variety of catalysis applications.^{10–14} Studies have shown that nanoporous gold is active towards catalyzing low temperature CO oxidation, performing comparably to gold nanoparticles of much smaller characteristic size.^{15–16} This phenomenon is generally attributed to the highly curved structure of the nanoporous gold and the prevalence of step and kink sites on the surface of the material¹⁷, though for certain reactions the picture may be more complex.¹³

Beyond nanoporous gold, many other metals have been produced as nanoporous structures and investigated as catalysts. Nanoporous silver has been used as a cathode material in carbon dioxide reduction.^{18–19} Platinum plated nanoporous gold has been hot pressed onto a Nafion membrane in order to produce composite structures as catalysts for use in proton exchange membrane fuel cells.²⁰ Finally, unsupported nanoporous palladium has been used to dechlorinate chlorinated organic compounds (COCs) through electrocatalysis.²¹ In this process, hydrogen was evolved on the Pd surface through the application of an electric potential and then worked with Pd as a catalyst to dechlorinate the chlorinated organic compounds.

Dechlorination of Chlorinated Organic Compounds

The last study mentioned is of special relevance to this research, as nanoporous Fe/Pd is the material we chose to investigate and to incorporate into our composite membranes. Pd was chosen because of its ability to degrade COCs in the presence of hydrogen gas and its passivity in most aqueous conditions. Iron is used due to its low cost and because it has been studied in proximity to Pd in many dechlorination settings as is discussed below. The catalytic application we will investigate as part of this research is the dechlorination of COCs using nanoporous Fe/Pd films incorporated into composite membranes. COCs are listed as priority contaminants by the EPA and have penetrated water reservoirs through industrial and commercial channels driving a need for new remediation techniques for polluted water sources.

Degradation of COCs such as trichloroethylene (TCE) and polychlorinated biphenyls (PCBs) with a Pd catalyst has been investigated using a variety of methods. Due to the high cost of palladium, nanostructured catalysts are preferred to maximize the catalyst's effect for a given amount. Nanoparticles have been extensively studied for this purpose and, as previously mentioned, nanoporous Pd has also been used. Pd functions as a catalyst for

dechlorination of COCs by dissociating hydrogen in order to form hydrogen radicals which function as strong reductants. These radicals in turn dechlorinate the COCs and form less toxic compounds.^{22–24}

In order to drive dechlorination, palladium requires that hydrogen be near its surface. This may be accomplished in a variety of ways. Bimetallic structures are often used, such as Fe/Pd alloys. Often in core/shell nanoparticle form these structures generate H₂ through iron corrosion which is then used for dechlorination when dissociated by the Pd.^{22–24} A bias may also be applied which can generate H₂ on the Pd surface itself, a process known as electrocatalysis.^{21, 25} Hydrogen gas may also be applied directly to the solution as is the case in our study. This technique has been studied previously in the degradation of aromatics and TCE by nanoparticles and alumina particles decorated with Pd.^{26–27}

Fe/Pd nanoparticles have shown potential for treating COC contaminated water because they may be directly injected into contaminated groundwater plumes²⁸ for treatment. The primary drawback to this method is that the nanoparticles will agglomerate over time²⁹ reducing their surface area and losing effectiveness. Some researchers have investigated methods of immobilizing nanoparticles in existing structures as an alternative treatment method^{30–33} to mitigate the issues found with use of disperse nanoparticles. Supported nanoporous films present an alternative, novel method to fabricate a nanostructure that has been shown in other catalytic reactions^{14–15, 17} to be similarly reactive to nanoparticles. The nanoporous films show a high surface density of active sites, but avoid the concerns of dispersion and agglomeration that may accompany nanoparticle systems.

This paper will focus on MTFC membranes which have an unleached metallic top layer and npMTFC membranes with a nanoporous metallic layer on top, both produced with iron palladium alloy films. The objectives of this study are the production of novel composite structures through sputtering and subsequent dealloying, characterization of those structures through electron microscopy techniques and FIB cross-sectioning, testing of the transport properties of the composites through permeation testing, and exploring the catalytic capabilities of the structures by testing them for dechlorination of chlorinated organic compounds (COCs).

Experimental

Composite Membrane Fabrication

MTFC membranes were produced by magnetron sputtering alloy films on top of porous polymer substrates. Two types of membranes were used as substrates for depositions. Nanostone polysulfone ultrafiltration (UF) membranes (pore size 21 ± 6 nm by SEM) of the type commonly used for reverse osmosis membrane supports were used to produce composites with a tight top layer of the sort that may be useful for separations. Millipore Durapore 0.1 μ m microfiltration (MF) PVDF membranes were also used, these membranes have larger pores allowing better kinetics for catalysis applications. The MF membranes have also been treated to present a hydrophobic surface and have no backing reducing problems of adsorption that may occur during catalysis experiments. <100> oriented single

crystal silicon wafers (Virginia Semiconductor) were also used as substrates for method development and imaging.

An AJA Int. Orion magnetron sputtering system was used to deposit the alloy films. Targets of iron (99.98% pure) and palladium (99.95% pure) were co-sputtered to generate alloys of the desired composition. A thin layer (10 nm) of tantalum (99.99% pure) was used as an interlayer material to aid adhesion of the film to the polymer. The substrates were cleaned for 1.5 minutes by an argon plasma before any material was deposited in order to increase surface energy of the substrate and promote adhesion. Deposition parameters were optimized to mitigate film cracking on the flexible substrate. This included adjusting argon pressure during deposition and adding a 5W RF bias to the substrate material during deposition.

Precursor films were deposited with compositions of 80 at.% Fe / 20 at.% Pd as determined by EDS and at a thickness of approximately 110 nm determined via FIB cross-section and imaging. These precursor alloy films were dealloyed in 25% Sulfuric Acid (Fischer Scientific) for 60–120 minutes to generate optimal porosity and final composition under agitation on a shaker table. The final compositions of the films were 20 at.% Fe / 80 at.% Pd. Films were removed from acid and rinsed and stored in ethanol to remove residual acid and preserve a pristine surface. This complete fabrication process is summarized in Fig. 1.

Materials Characterization Studies

The composition of the films was characterized at various stages through EDS using a Zeiss EVO MA 10 SEM. The membranes and films were imaged using an FEI Helios Nanolab 660 Dual Beam which has both an electron beam for imaging and a gallium focused ion beam (FIB) that may be used for sample imaging and also milling/cutting of the sample on the nanoscale. Some supplementary images were also taken using a Hitachi S-4300 SEM. TEM imaging was done with a JEOL 2010F TEM. Some TEM images were taken using the high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) mode of the TEM. This imaging method uses electrons scattered at high angles from the specimen and shows a large contrast according to atomic number of the material. The polymer substrates and metallic films are easily differentiated using this imaging technique. Pure water permeabilities of the resulting composite membranes were characterized using GE Osmonics Sepa ST flow cells at various transmembrane pressures. The flow cell uses pressurized gas to push water through the membrane being tested and the flow of water through the membrane is measured as mass of water passed over a given time. Flux is calculated from this flow rate after accounting for membrane area. A schematic of the testing setup used is shown in Fig. 2.

Organic Degradation Studies

The high surface area catalyst npMTFC membranes were tested for their ability to initiate dechlorination of 2-chlorobiphenyl (PCB-1). Batch experiments were done in a dead end flow cell with an aluminum disc at the end to block flow through the cell. 4 mL samples were taken from an initial volume of 50 mL at specified time points. PCB-1 solutions were made from an ethanol solution produced using PCB-1 powder (ULTRA Scientific LOT #

NTO54177). PCB-1 degradation experiments were performed under a pressurized hydrogen gas environment in a solution of water set to pH 5. The increased hydrogen pressure resulted in an increased concentration of dissolved hydrogen in solution. This ensured the palladium had enough hydrogen gas to catalyze the reaction effectively and minimized the impact of the iron component of the system.

Samples were taken of the PCB-1 solution at various time points and extracted into hexanes with biphenyl-D10 used as an internal standard. This extract was run on a Varian CP-3800 GC with Varian Saturn 2200 MS and an Agilent DB-5ms column. The PCB-1 and biphenyl concentrations were quantified against a standard curve with a lower limit of detection of 0.1 ppm. The same procedure was used in PCB-1 dechlorination testing with palladium decorated alumina particles with 1 wt.% loading (Aldrich Lot# MKBX4178V) of the same type used in commercial processes and other dechlorination studies^{34–36}.

Results and Discussion

Both the MTFC and npMTFC membranes were characterized at various stages of production. First the structure of the membranes was characterized through SEM and TEM with some FIB preparation. This gave confirmation that the as-deposited or nanoporous metallic films remained anchored to the membrane through production and that the expected structures were generated. The flow characteristics of the membranes were also inspected through the use of the dead end cell discussed earlier and were found to be water permeable in both MTFC and npMTFC forms. Finally, the films were tested as catalysts for the dechlorination of PCB-1 in water with the presence of hydrogen gas and found to perform comparably to commercially available catalysts in this setting.

Metallic thin film composite (MTFC) membrane structure

Polymeric membranes were used as substrates for the sputter deposition of films 110 nm thick of iron palladium alloy. Different pore size membrane structures were used as substrates, including 0.1 μ m PVDF microfiltration (MF) membranes and PSf ultrafiltration (UF) membranes with pore diameter of 21 ± 6 nm as determined by SEM. The resulting optimized structures are shown in Fig. 3A and 3B. Optimization parameters included tantalum interlayer thickness, RF bias applied during sputtering, and argon pressure during deposition. Tantalum was chosen as an interlayer material because of its reactivity with surfaces and its ductility. Adjustment of these deposition parameters caused variations in film morphology, and more importantly in the intrinsic film stress. Film stress needed to be minimized in order to improve film adhesion to the substrate during and after dealloying. An RF bias of 5 W was applied to the substrate during deposition to reduce the tensile stress in the film.

The different structures of the two substrates were propagated through the films deposited on top of them. Substrates with large pore sizes, such as the 0.1 μ m MF PVDF, had a templating effect on the film. This caused the as-deposited films to exhibit a porosity of the same size scale as the substrate even before dealloying. Rather than producing a continuous top layer, the membrane structure was essentially retained and simply coated with Fe/Pd. The membrane substrates with small pore sizes relative to the film thickness such as the UF PSf

membrane resulted in a continuous film in the as-deposited state. The membrane pores were largely filled in or bridged by the metal film during the deposition process. Some pores remain in the film even on the UF PSf substrate as is demonstrated by later water permeation experiments.

Substrate morphology had additional effects on the deposited film in addition to porosity. With the rougher substrates shadowing during deposition became an important consideration. Sputtering is a line of sight deposition process, this means that areas of the substrate exposed to the target directly will accumulate material and build up a deposited film. When a relatively flat substrate is used (such as silicon wafer or the UF polysulfone) this influence is minimal, but when a substrate has significant roughness (such as the MF PVDF membrane) the shadowing effects become obvious. The deposited film structure of the various MTFC membranes was investigated through cross-sectional imaging. The cross-sections shown in Fig. 4 were prepared through FIB milling with a gallium ion beam. Before milling a protective platinum layer was deposited onto the substrate. Cross-sections were taken of both the UF polysulfone (Figs. 4A and B) and MF PVDF substrates (Fig. 4C). In both cases it is clear that the as-deposited film conforms well to the roughness of the different surfaces.

For the case of the MF PVDF substrate the roughness is so large that some parts of the membrane are shadowed as was previously discussed. Fig. 4B shows the variation in thickness clearly. On the top of the rounded area the film is nearly its full thickness. As the substrate curves, changing the angle between the substrate and the incident metal atoms, the film thickness is reduced until the polymer finally is completely uncoated. This effect has interesting repercussions for the structure of the films deposited onto rough or textured substrates. First, depending on the size of the pores and the angle of the sputtering guns to the substrate the metal atoms will penetrate different depths into the pore mouth. This geometry problem, when considered with the deposited film thickness should to govern whether or not the pore mouth is spanned (as in the UF polysulfone membrane) or if the pore is propagated through the deposited film by the substrate (as in the MF PVDF membrane). In the case of large pores metal may be deposited deep inside the porous structure. Through cross-sectioning as in Fig. 4 it was found that Fe/Pd had been deposited 1.2 μm deep into the structure, though at much reduced film thickness.

Nanoporous MTFC (npMTFC) membrane morphology

The structures generated through sputtering shown in Figs. 3 and 4 were then dealloyed in 25% sulfuric acid as described in the experimental section. This transformed the MTFC membranes shown above into the npMTFC membranes which possess a top layer of nanoporous metal as shown in Figs. 5 and 6. In order for the dealloying process to produce the desired structure many of the dealloying conditions had to be tuned. The dealloying acid chosen and the acid's concentration will both affect the nanoporous film structure. Correct precursor film composition is also essential to produce a film with sufficient porosity, but without many cracks and defects. These procedures must be developed for each new system used in dealloying.

During the dealloying process employed here the Fe/Pd film and its substrate are exposed to an acidic environment for an extended period of time from 60–120 minutes depending on the substrate. This process generates the porosity shown in the metallic film layers of the composite by removing the iron component in the film. The Pd in the precursor and some remnant iron form a high surface area ligament structure as in Figs. 5 and 6. Precursor composition averaged approximately 80 at.% Fe / 20 at.% Pd. The dealloyed films were Pd heavy, with compositions clustered around 20 at.% Fe / 80 at.% Pd. The resulting dealloyed films are thinner than the as-deposited precursors by 20 nm. During dealloying, films may contract during the corrosion and surface diffusion process while the void space is being created. That effect is exhibited in these films as well.

The npMTFC membrane produced on top of the UF polysulfone membrane (Fig. 5) shows a well-defined pore ligament structure has been produced on top of the membrane substrate. Forty representative ligaments were measured from TEM images to give an average ligament size of 7.7 ± 2.5 nm for the nanoporous film produced on the UF polysulfone substrate. HAADF-STEM imaging also Fig. 5c shows how well the metallic film contours to the rough surface of the membrane. Even after dealloying in acid the film remains well adhered. It is difficult to determine with cross-sectional TEM if the pores in the substrate are propagated through the unleached metallic films. Water permeation experiments were used below to investigate this phenomenon.

The npMTFC membranes produced on top of the MF PVDF substrate are similar in many respects to the MTFC structures they are generated from. The large membrane pores are still propagated through the film, effectively producing a supported catalyst structure more so than a porous selective layer. Perhaps most obviously, some amount of cracking and delamination can be seen in the MF PVDF based composite structure (Fig. 6), while very little occurs in the UF polysulfone based composite (Fig. 5). This is likely due to the much higher curvature of the PVDF substrate material. During dealloying the film enters a tensile stress state, this makes it more likely to crack when supported by a convex curved substrate material.³⁷ It is also possible that due to the higher porosity of the MF PVDF membrane that the dealloying process proceeds more quickly, because of higher diffusion rates of the Fe ions away from the surface. This higher rate of corrosion could lead to increased cracking.

Water Permeability Behavior

The membrane properties of the different membranes produced have also been investigated. This was done through permeation testing in a dead end flow cell arrangement, a schematic of which is shown as Fig. 1. Flow properties of the membrane were characterized at the three stages of production. That is, the base polysulfone membrane used as a substrate, the MTFC membrane which possesses a comparatively dense metallic film layer, and the npMTFC membrane which is covered in the nanoporous film. The polysulfone membrane was used as a substrate for these studies as its smaller pore size allowed a continuous metal film to be produced as a selective layer on top of the polymer support, analogous to polymer TFC membranes. A fourth type of membrane was also studied, the base polysulfone membrane exposed to the acid bath used in dealloying. This was done to check if the polysulfone membrane is damaged by the sulfuric acid bath. Fig. 7 shows a plot of flux

versus pressure for the base polysulfone membrane and an accompanying fit for membrane permeability. This relationship should be linear and is expressed by Eq 1 when there is no osmotic pressure difference across the membrane and a constant thickness.

$$J_{H_2O} = A\Delta p \quad (1)$$

J_{H_2O} is the pure water flux of the membrane (given here as LMH or liters/meter²/hour), p is the pressure applied to the flow cell (here given in bar), and A is the permeability coefficient of the membrane (LMH/bar).

The measured pure water fluxes may be used to determine effective pore sizes for these membranes using a modified Hagen-Poiseuille equation³⁸, Eq 2.

$$\frac{J}{J_0} = \left(\frac{d}{d_0}\right)^4 \quad (2)$$

Where J is the pure water flux through the modified membrane and d is its effective pore diameter. J_0 is the pure water flux of the unmodified membrane and d_0 is the effective pore diameter of the same. This equation assumes constant membrane thickness, constant pore density, and cylindrical pore geometry. Constant membrane thickness is a reasonable assumption if we consider the Fe/Pd film thickness small compared to the overall membrane thickness. Two of the three stages of membrane production tested (Base UF PSF and npMTFC) as well as the acid wash UF PSf sample were analyzed with this equation. Pore size for the MTFC membranes was not estimated in this way, since the primary resistance layer is no longer the PSf membrane and many of the assumptions applied are no longer valid in that case. The relation may still be applied to the npMTFC case with the assumption that the PSf layer, not the nanoporous metallic layer, is the primary impediment to water flow. The bare UF polysulfone was used as a basis and its pore diameter was estimated to be 21 ± 6 nm based on 100 measurements from SEM imaging. The other effective pore sizes were calculated using the Hagen-Poiseuille equation described above and are listed in Table 1.

It can be seen that the permeability of the MTFC membrane is low compared to that of the base membrane. This result is to be expected since earlier microscopy shows pores are largely covered or blocked by the deposited Fe/Pd film. The water flow seen through this film likely occurs either through gaps between the grains of the sputtered film or possibly through small defects in the film. These MTFC membranes are similar in some respects to other thin film composite membranes produced entirely from polymers, such as polyamide TFC nanofiltration membranes used in nanofiltration applications.

The permeability of the npMTFC membrane, that is of the UF polysulfone membrane after thin film deposition and subsequent dealloying, was found to be higher than that of the base membrane alone. In the absence of other effects, adding an additional layer to a membrane

will reduce permeability due to an increased membrane thickness. The increase in flux from base polysulfone to npMTFC despite an additional layer indicates more is changing in the membrane than just an increase in thickness. This result can be explained by a deformation of the underlying polymer in the acid bath needed to etch the precursor film during the dealloying process. Tests were run with a bare polysulfone membrane bathed in acid under the same conditions as were used during dealloying. This membrane showed a permeability of roughly five to ten times that of the base membrane. Additionally, there is significant variability in resistance of the UF PSf to the acid bath is shown by the high difference between the permeabilities of the two replicates in Table 1. This is not seen in the npMTFC membranes, likely because the attached metallic film layer protects the polymer on one side from full exposure to the acid. Without the metallic film layer, and to a lesser degree with the film, the polysulfone membrane is “loosened” by acid, or the effective pore size is increased as the polysulfone is deformed by acid exposure. Due to this “loosening” via acid, even though the membrane thickness is marginally increased, the overall flux increases due to an increase in effective pore size.

Dechlorination Behavior

The npMTFC membranes may have a variety of uses, such as separations in harsh environments or at elevated temperature, but the primary application studied here is their use in catalytic processes for water detoxification. Hydrogen gas was supplied directly into the PCB-1 solution by H₂ pressurization of the headspace of the testing cell to study the catalytic aspects of the Pd. While some iron is present in the nanoporous structure, it is a small amount (20 at.%) relative to the palladium content. Henry’s law (Eq 3) may be used to estimate dissolved H₂ in the water given a certain pressure.³⁹ Where H^{cp} is the Henry solubility, c_a is the concentration of the species (here hydrogen) in the aqueous phase and p is the applied pressure. For the batch PCB-1 degradation testing a pressure of 1 bar H₂ was used unless otherwise stated. This corresponds to a concentration of 1.5 ppm dissolved H₂ at 25 °C.

$$H^{cp}p = c_a \quad (3)$$

Before the npMTFC membranes were tested for their dechlorination capability, a known control catalyst was used in the experimental setup. Alumina particles decorated with Pd (1 wt. %) were used in a PCB-1 solution of 2.5 ppm. The dechlorination results are shown in Fig. 8. It may be seen that PCB-1 is rapidly degraded, and is almost completely removed within 15 minutes. Biphenyl, the product of PCB-1 dechlorination, is detected and its concentration increases as PCB-1 degrades. This fits well with expected behavior. After increasing through 15 minutes as PCB-1 degrades the biphenyl concentration in solution plateaus afterwards. The total amount of biphenyl never reaches a molar balance with the PCB-1 degraded, however. To account for this a control experiment was run (PCB-1 control in Fig 8), with a hydrogen pressurized headspace and no catalyst loading. A sample was taken in the same way as before after 30 minutes and both biphenyl and PCB-1

concentration dropped by about 20%. This indicates that a portion of the compounds is escaping the solution phase during the course of the experiment.

After the initial proof of concept was tested with the commercially available Pd-alumina catalyst testing moved on to the Fe/Pd npMTFC membranes produced in this study. The larger pore size membrane substrates, the PVDF MF membranes from Millipore were used for all PCB-1 degradation studies. This is because they were not supported by a backing material and were hydrophilized. These two considerations considerably reduce the amount of PCB-1 and biphenyl that adsorbed onto the membranes allowing more accurate study of the reactions. The membranes used were all cut to pieces and added to the PCB-1 solution for testing. A concentration of 2.5 ppm PCB-1 was used again as was the 1 bar H₂ pressurization. Solution phase concentrations of PCB-1 and biphenyl for three different membranes are summarized in Fig. 9.

A steady decline of PCB-1 concentration in solution is seen with 90% removal in 30 minutes at 6.6 mg/L Pd loading. Biphenyl production was also detected verifying that the dechlorination reaction was indeed taking place. The possibility of adsorption of the two compounds to the membrane surface was accounted for by extracting the membrane in 20 mL of hexanes at the end of the experimental run. On average for batch dechlorination with npMTFC samples 9% of the initial PCB-1 is found to have adsorbed to the surface of the membrane and remained attached for the duration of the experiment. 12% of the PCB-1 molar content is found to have been converted to biphenyl and adsorbed to the membrane surface. In total, about 20% of the PCB-1 in the initial solution adsorbs to the membrane surface. Of that total 20%, 12% was converted to biphenyl before adsorption. The 9% of PCB-1 that adsorbs to the membrane surface without converting is too small to account for the overall loss of PCB-1 from solution that has been measured here. As seen in the commercial control catalyst study, biphenyl leaves the solution phase such that a molar balance cannot be made.

Despite the influence of biphenyl loss in this study, these experiments clearly demonstrate that the membranes are active towards catalyzing dechlorination of PCB-1. Over 90% of PCB-1 was removed from solution and biphenyl was produced. A thin film of nanoporous Fe/Pd on top of the PVDF membrane functioned as an effective catalyst with the dissolved hydrogen and performed in a comparable way to the commercial Pd decorated alumina catalyst we obtained. While their catalytic performance in these batch tests is comparable, the benefit the reactive membrane holds over a powdered catalyst such as the commercial alumina is a finer level of control over the reaction kinetics during processing. Water flow through membranes is well understood and by simply varying pressure and therefore flow through the membrane, contact time of the reactant with the catalyst surface may be reliably optimized. The anchoring of a catalyst to a membrane surface also opens the possibility of combining multiple process steps, such as separations and reactions.

Conclusions

Magnetron sputtering technique demonstrated the direct synthesis of thin metallic films on porous polymer membrane substrates. These films were then used to generate nanoporous

palladium with remnant iron, through the dealloying of an Fe/Pd precursor in sulfuric acid bath. Additionally, these nanoporous films have been produced on top of porous polymer substrates to fabricate composite membrane structures. It has been found that the porosity of the substrate material can be used to template the resulting film structure. The composite membranes produced in this way (MTFCs) show permeability and smaller effective pore sizes comparable to other composite membranes used for nanofiltration applications. The npMTFC membranes created through dealloying were found to be effective catalysts for PCB-1 degradation when hydrogen gas was supplied. Permeation testing additionally shows that the composite npMTFC membranes have permeabilities comparable to those of the pre-existing substrates. This shows that the nanoporous films have low resistance to water flow and may be used in reactive membranes without significant loss of flux.

These composite membranes hold promise for demanding membrane applications. MTFC type membranes are likely most relevant for separations applications as they are most similar to other TFC membranes made with polymers. The metallic top layer is more resistant to organic solvents and high temperatures than typical polymers, allowing application of the membranes in otherwise difficult application environments. As mentioned in the introduction, a wide variety of metals can be made nanoporous through chemical dealloying methods, allowing npMTFC membranes to be used in various catalysis applications with further development.

In future research, alternative dealloying processes will be investigated that will allow better control of final film structure. The use of a less noble sacrificial element in precursor films such as magnesium or aluminum would allow use of a milder etchant such as water so that the use of strong or concentrated acids could be avoided. This would make production less costly and more environmentally friendly, as well as reduce possible damage to polymer substrates.

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ABBREVIATIONS

PSf	polysulfone
PVDF	polyvinylidene fluoride
PCB-1	2-chlorobiphenyl
TFC membrane	thin film composite membrane
MTFC	metallic thin film composite

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Figure 1. Schematic of the three stages of fabrication. A.) is the first stage, a bare membrane substrate. B.) shows the MTFC stage, when a metallic film has been deposited onto the membrane substrate by sputtering. C.) is the npMTFC stage. Here, after dealloying, the film is nanoporous and anchored to the membrane.

Figure 2.
Schematic of dead-end permeation cell used for flux measurements in determination of permeability of membranes.

Figure 3. SEM images of Fe/Pd films sputtered on various substrates: (A) PVDF MF membrane (B) Polysulfone UF membrane.

Figure 4.

Cross-sectional SEM micrographs of as-deposited Fe/Pd film on membrane substrate. (A) Low magnification view of the MF PVDF composite structure, with (B) showing a higher magnification image of the red outlined section of (A). (C) Is a micrograph showing a cross-section of the polysulfone UF based composite after FIB milling. The darker regions correspond to the polymer membrane; the membrane is coated with a Fe/Pd layer approximately 110 nm thick; the top coating of protective platinum (added for FIB work) is visible near the top of the image.

Figure 5.

Cross-sectional images of composite membrane consisting of the nanoporous Fe/Pd layer on UF polysulfone substrate. (A) HAADF-STEM image of a FIB milled lamella of npMTFC sample shows a strong Z contrast. This region is a magnified image of the area noted in red box of (B). Red arrows point out a single ligament of the nanoporous structure. (B) A low magnification STEM image of the lamella produced via FIB milling. The brighter regions of (B) and (C) correspond to the high atomic number Fe/Pd alloy and the Pt layer, and the darker region corresponds to polymer membrane region. (C) SEM of a sample cross-sectioned using FIB. Designations: Above the blue line is a protective Pt layer deposited using the FIB; the nanoporous Fe/Pd layer is between the blue and green lines; polymer membrane is below the green line. Image taken at an angle of 54° for FIB milling. This tilt results in a shortening effect of the film thickness in images that does not correspond to true film thickness. This effect explains the seeming different thickness of the film when viewed in the SEM mode in the Helios FIB (at an angle of 54°) and the HAADF-STEM images where the sample is not tilted.

Figure 6.

SEM images of npMTFC microfiltration membrane (PVDF substrate). (A) Shows a large view cross-section of the npMTFC membrane after FIB milling. (B) Depicts a surface view of the membrane at an angle of 60°, showing the roughness of the membrane and the porosity of the metallic layer. (C) Shows a magnified view of the cross-section as in (A). The film at this depth is thinner because of shadowing effects as discussed in the text. As a result, only a single layer of ligaments is formed on the polymer here. The darker regions correspond to the polymer substrate (PVDF), whereas the brighter, porous layer is the nanoporous Fe/Pd layer; this is covered with a thick protective platinum layer for FIB milling.

Figure 7.

Variation of pure water flux with applied pressure for base polymer membrane, sulfuric acid treated PSf membrane, and unleached and leached metal-polymer membranes. Linear fit corresponds to Eq 1 and the slope provides water permeability for the first set of membrane replicates. Inset shows magnified plot of MTFC flux.

Figure 8. Dechlorination of PCB-1 by commercial Pd alumina particles. 6.6 mg/L Pd loading in solution. 1 bar H₂ pressure was used. The solid points show the result of a control experiment without catalyst of a solution containing initial amounts of PCB-1 and biphenyl.

Figure 9. Dechlorination of PCB-1 by nanoporous Fe/Pd in the presence of hydrogen gas of 1 bar for three different membrane batches. Pd loading is determined to be 6.6 mg/L.

Table 1.

Water flux behavior of composite membranes at different stages of synthesis and estimated pore size. Measurements for two separate batches of each membrane type are shown here with their associated permeabilities.

Membrane	Permeability (LMH/bar) Replicate 1	Permeability (LMH/bar) Replicate 2	Effective Pore Diameter (nm) Replicate 1
Base UF PSf	118 ± 9	148 ± 20	21 ± 6
PSf + Fe/Pd film (MTFC)	3 ± 1	3 ± 1	-
PSf with np Fe/Pd film (npMTFC)	184 ± 15	181 ± 7	24 ± 7
PSf after 1 hour 25% H ₂ SO ₄ bath	543 ± 56	1262 ± 74	31 ± 10