Ferrocene-Containing Porous Poly(Ionic Liquid) Membranes: Synthesis and Application as Sacrificial Template for Porous Iron Oxide Films

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Herein, the fabrication of iron-containing porous polyelectrolyte membranes (PPMs) via ionic complexation between an imidazolium-based poly(ionic liquid) (PIL) and 1,1-ferrocenedicarboxylic acid is reported. The key parameters to control the microstructure of porous hybrid membranes are investigated in detail. Further aerobic pyrolysis of such porous hybrid membranes at 900 °C can transfer the ferrocene-containing PPMs into freestanding porous iron oxide films. This process points out a sacrificial template function of porous poly(ionic liquid) membranes in the fabrication of porous metal oxide films.

1. Introduction

Porous polyelectrolyte membranes (PPMs) as an important subclass of porous polymer membranes have attained noticeable interests recently in both academia and industry. In addition to their promising features, e.g., their ionic characteristics and higher mechanical and chemical stability than their neutral counterparts, can provide a versatile range of applications in the area of sensors, separators, actuators, energy devices, bioengineering, controlled release and catalyst. Layer-by-layer deposition and phase separation are currently the most common methods to produce pores of different sizes and size distributions in polyelectrolyte membranes, and more new methods are on the way to be developed.

Poly(ionic liquid)s (PILs) as a subset of polyelectrolytes, are built up by polymerization of monomers that are ionic liquids themselves or by polymer modification to engineer ionic liquid species covalently into polymer chains. The tremendous combination possibilities of anions and cations in ionic liquids, together with the macro-molecular structure design of polymers by mature polymerization techniques, either conventional free-radical polymerization or controlled “living” radical polymerization techniques, e.g., reversible addition-fragmentation chain transfer polymerization and atom transfer radical polymerization, broadens the property window of conventional polyelectrolytes and is revolutionizing the research image of polyelectrolytes. One of the current researches focus of PILs is their potential as innovative membrane materials to enable new membrane technologies, including the ionic liquid/PIL blend membrane for gas separation, PIL/inorganic hybrid membranes for (nano)filtration or detection, and (nano)porous PIL membranes for solvent-responsive filtration. The attractive role of PILs as membrane materials lies in their multifaceted properties and functions enabled by a giant library of their chemical structures that allows for task-specific design. For example, their counterion-adaptive solubility will assist the processing of PILs in almost all common solvents of low to high polarity (e.g., dichloromethane and tetrahydrofuran); their relatively higher thermal and chemical stability than their neutral counterparts allow for separation and concentration of substances at harsher environment; the rich choices of ion pairs in ionic liquid chemistry can offer PILs of precisely tailored gas–PIL interaction for targeted gas separation.

Previously, our group discovered an approach to fabricate freestanding (nano)porous PIL-based membranes by means of an in situ interpolyelectrolyte complexation process in a physical blend film, which consists of a hydrophobic PIL and an organic weak acid such as commercial poly(acrylic acid) (PAA). In such method, a phase separation process and an ionic crosslinking process that are initiated by the parallel diffusion of water and ammonia molecules, respectively, into the PIL/PAA blend film sticking onto a substrate, produced a 3D ionically crosslinked porous membrane; these membranes sometimes bear a clearly identified gradient distribution of property elements (e.g., crosslinking density, chemical composition, and pore size) along the membrane cross-section due to the diffusion track of water and ammonia.

Meanwhile, iron oxides as an important class of vast materials existing in nature and historically used long time in human society, have some common forms at room temperature, e.g., magnetite (Fe₃O₄), maghemite (γ-Fe₂O₃), hematite (α-Fe₂O₃), and their hydroxides. Iron oxides have a broad range of properties,
such as magnetic, catalytic, and semiconducting behaviors. Many research activities have attempted to prepare technologically relevant porous or dense iron oxide films by various techniques from high vacuum methods (e.g., chemical and physical vapor deposition) to nonvacuum methods (e.g., sol–gel, forced hydrolysis, and pyrolysis). Porous iron oxide films can be used in diverse fields such as biomedicine, gas-sensors, catalysis, photoelectrochemical devices, supercapacitors, and batteries. As such, there have been persistent efforts to develop strategies to fabricate porous iron oxide films.

In this contribution, we fabricated ferrocene-containing porous PIL membranes via ionic crosslinking of an imidazolium-based PIL with an iron-containing diacid named 1,1′-ferrocenedicarboxylic acid (fc(COOH)2). The as-synthesized porous PIL membranes could possess a variable content of ferrocenyl units, depending on its amount added, where the membrane of a sufficiently high ferrocenyl content was transformed successfully into a freestanding porous iron oxide film upon aerobic pyrolytic treatment. We foresee that the postsynthesis treatments of PPMs by pyrolysis would expand their application spectrum beyond normal separation barriers, and open up new avenues to fabricate inorganic porous films.

2. Results and Discussion

The fabrication procedure of the iron-containing PPMs via PIL is illustrated in Figure 1, following a modified procedure reported by us previously. Briefly, poly(1-cyanomethyl-3-vinylimidazolium X) (termed PCMVImX, where X denotes the counteranion) as a cationic PIL and 1,1′-ferrocenedicarboxylic acid (fc(COOH)2) as a weak diacid were mixed in dimethyl sulfoxide (DMSO) and formed a clear solution without optically visible aggregates. As the carboxylic acid as a weak acid group in fc(COOH)2, it is protonated in DMSO to reach a homogeneous solution with PCMVImX. The anion X used here is bis(trifluromethane sulfonyl)imide (TFSI−), hexafluorophosphate (PF6−), and tetrafluoroborate (BF4−), and a more hydrophilic anion, bromide (Br−), was used as well as a reference. The synthetic procedure and detailed characterizations of PCMVImX polymers are shown in Figure S1 of the Supporting Information.

Experimentally, we first took the deposition pair of PCMVImTFSI and fc(COOH)2 as a case study to explore the effect of the amount of fc(COOH)2 as a weak acid on the formation of PPMs. A model experiment required 0.200 g of PCMVImTFSI and 0.067 g of fc(COOH)2 to reach a 1:1 stoichiometric molar ratio of the imidazolium and COOH units. As in DMSO, a polar aprotic solvent, fc(COOH)2 stayed in a protonated thus neutral form, the mixture of PCMVImTFSI and fc(COOH)2 formed a fully mixed transparent solution. The homogeneous mixture solution was poured into a thin film state on a glass plate, which next was dried at 80 °C for 2 h to remove most of DMSO. Note that the concentration of PIL/fc(COOH)2 and the size of the glass plate together define the thickness...
of the dried blend film and eventually the thickness of the final PPMs. After 2 h of drying to form a sticky thin film of the physical blend of PCVImTFSI/fc(COOH)$_2$, the glass plate with the film on its top was immersed into a 0.2 wt% aqueous NH$_3$ solution. During this soaking step, a phase separation process occurred to the hydrophobic PCVImTFSI upon the diffusion of water molecules into the blend film; in parallel, a concurrent ionic crosslinking reaction took place between the hydrophobic cationic PCVImTFSI and the dianion fc(COO)$_2^-$, which was derived from the NH$_3$-neutralized fc(COOH)$_2$. Once the diffusion of water and NH$_3$ from the top to the bottom of the blend film was completed, the phase separation and the ionic crosslinking ran across the entire film. As such, a 3D porous network was formed. The thickness of this fabricated membrane is specified by scanning electron microscopy (SEM) characterization to be $157 \pm 6 \ \mu$m (Figure S2, Supporting Information). As mentioned previously, the membrane thickness depends on the PIL/fc(COOH)$_2$ amount and the glass plate size. When the size of the glass plate is fixed, a quasi-linear relationship of the membrane thickness against the mixture mass is observed (Figure S2, Supporting Information). The formed membrane was termed PPM$_{X/r+/−}$, where X and $r_{+−}$ define the type of counteranion and the molar ratio of imidazolium/carboxylate, respectively. After this step, the polymer membrane was ready and pyrolyzed first in vacuum at 600 °C then in air at 900 °C for 30 min to obtain the target iron oxide film.

In order to have an in-depth view of the impact of the relative amount of fc(COOH)$_2$ to the hybrid membrane on the size and shape of pores, a range of imidazolium/carboxylate molar ratios ($r_{+−}$) were examined (Figure 2). A general trend observed is that the average pore size decreases with decreasing $r_{+−}$. A membrane prepared at $r_{+−} = 1/1$, i.e., the imidazolium and carboxylate at an equal molar ratio, has an average pore size of $454 \pm 150 \ \text{nm}$ (Figure 2B). By adding more diacid, i.e., decreasing the $r_{+−}$ value, the average pore size decreased smoothly, reaching a lowest of $162 \pm 56 \ \text{nm}$ at $r_{+−} = 1/6$; thereafter further reduction of the $r_{+−}$ value only affects slightly the average pore size, for example, an average pore size of $208 \pm 68 \ \text{nm}$ at $r_{+−} = 1/20$ (Figure 2D). By contrast, an excessive amount of the imidazolium cation, i.e., the PIL content, can dramatically enlarge the pore size, for instance, a pore size of $4.5 \pm 1.3 \ \mu$m at $r_{+−} = 4/1$ (Figure 2C). An even further surplus of the imidazolium cation
at \( r_{+/-} \geq 6 \) has adverse effects on the ionic crosslinking process in the polymer blend and eventually produced in fact nonporous membranes (Figure S3A, Supporting Information). This experimental observation is caused by the fact that the fc(COOH)₂ serves as crosslinker to PIL; increasing the PIL content will dilute the crosslinker density, and a lower crosslinking density can only mechanically stabilize larger pores. If the crosslinker density is too low, pores can no longer be mechanically stabilized and thus be collapsed.

Next, the role of counteranions on the pore size and morphology of PPMs was examined (Figure 3). It is well-known that the anion exchange can easily modify the physical and chemical properties of PILs without complicated change of the polymer backbone. Here, PILs with different anions were prepared via anion exchange reactions and used for the membrane fabrication. At a fixed \( r_{+/-} = 1/1 \), the average pore size gradually increased from 454 ± 150 nm for PPM\(_{\text{TFSI},1/1}\) to 610 ± 154 nm for PPM\(_{\text{PF6},1/1}\), as shown in Figure 2B and Figure 3B, respectively. The average pore size was expanded further to a micrometer scale of 1.92 ± 0.68 and 2.18 ± 0.65 µm for PPM\(_{\text{BF4},1/1}\) and PPM\(_{\text{Br},1/1}\), respectively. Considering the hydrophobicity sequence of PCMVImX in the order of TFSI > PF₆ > BF₄ > Br, it is reasonable to conclude that the more hydrophobic the PIL is, the smaller the pore size is. By reducing the hydrophobicity in the polycation, the diffusion rate of water molecules into the PIL/fc(COOH)₂ blend film is accelerated, so the water-induced phase separation process (related to the pore formation and expansion step) becomes more fast thus dominant than the ionic complexation process (related to the pore size-locking step) that is driven by ammonia diffusion. Thus, a later coming and less pronounced ionic crosslinking step will give more chance for pores to grow bigger.

The conversion of the porous PIL membrane into the porous iron oxide film was conducted by vacuum carbonization at 600 °C for 1 h followed by aerobic pyrolysis at 900 °C for another 30 min. Figure 4A shows a digital photograph of the iron oxide film obtained from aerobic pyrolysis of the PPM\(_{\text{TFSI},10}\) membrane, where an imidazolium/COOH molar ratio of 1:10 is used. The high content of fc(COOH)₂ in the blend is logically needed to minimize the weight loss during pyrolysis so to produce an intact porous iron oxide film. To note, further increase in the amount of fc(COOH)₂ in our experiments resulted in small broken pieces rather than a film, thus is not further pursued. Based on the powder X-ray diffraction (PXRD) pattern in Figure 4B...
Figure 4. Characterization of the freestanding porous iron oxide film obtained from PPM$_{TFSI-1/10}$. A) A photograph of the iron oxide film. B) Its PXRD pattern indicative of an $\alpha\text{-Fe}_2\text{O}_3$ phase, C) its cross-sectional SEM image, and D) the TGA curve of PPM$_{TFSI-1/10}$ under air from room temperature to 1000 °C.

and its comparison with the standard reference, the diffraction peaks are reasonably assigned to the phase of hematite, $\alpha\text{-Fe}_2\text{O}_3$ (JCPDS No. 33–0664), which is expected for aerobically treated iron species at 900 °C. Besides, the major peaks appeared in the Raman spectra of the same iron oxide sample proves only the presence of $\alpha\text{-Fe}_2\text{O}_3$ (Figure S5, Supporting Information).\cite{57,58} Its SEM image (Figure 4C) visualizes its porous morphology which is a random aggregation and stacking of primary iron oxide particles of 50–150 nm in size, which forms pores of averagely 180 ± 56 nm in size. These pores are interconnected and will benefit their potential applications in catalysis or sorption. Large, interconnected macropores with a high porosity can permit straightforward transport of guest molecules and particles through open channels and even partially open ones during the reaction. Besides, the optimum sized pores around 150–200 nm could demonstrate good performance due to the easier diffusion through the pores and rapid absorption.\cite{59,60} To verify the presence of mesopores and micropores that are not visible in SEM imaging, $\text{N}_2$ sorption measurements were conducted to the iron oxide samples obtained from PPM$_{TFSI-1/6}$, PPM$_{TFSI-1/10}^*$, and PPM$_{TFSI-1/20}$. The $\text{N}_2$ adsorption–desorption isotherms are shown in Figure S6 of the Supporting Information. The specific surface areas ($S_{\text{BET}}$) were calculated from the Brunauer–Emmet–Teller (BET) theory to be <10 m$^2$ g$^{-1}$ for all and the micro-/mesopore volume only <0.02 cm$^3$ g$^{-1}$, which means that the primary iron oxide particles are neither micro- nor mesoporous, but macroporous. In Figure 4D, the thermogravimetric analysis (TGA) of the PPM$_{TFSI-1/10}$ membrane in air shows a 5 wt% mass loss at 270 °C, and then a rapid decomposition up to 500 °C, followed by a slow mass loss till a final residue of 25% at 1000 °C. The PPM$_{TFSI-1/10}$ and its iron oxide products due to their iron content could be reversibly reduced and oxidized electrochemically both
showing one oxidation peak and two reduction peaks (Figure S7, Supporting Information).

3. Conclusions
In summary, 1,1’-ferrocenedicarboxylic acid can ionically crosslink poly(ionic liquid) into porous polyelectrolyte membranes via an in situ aqueous ammonia-trigger phase-separation and crosslinking process. The morphology and the pore structures of such porous polyelectrolyte membranes can be tuned readily by varying the counteranion type and the molar ratio of imidazolium/carboxylate units. The transformation of porous polyelectrolyte membranes into freestanding macroporous iron oxide films was succeeded using a PPM with a suitable ferrocenyl content. This new finding will diversify the future application of porous polyelectrolyte membranes in materials science and processing.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

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