Materials Science

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Highly Proton-Conducting Self-Humidifying Microchannels Generated by Copolymer Brushes on a Scaffold**

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Proton-exchange membranes (PEMs) play a pivotal role in many technological devices, including fuel-cell vehicles, mobile devices, and even power stations for home use.[1–3] The membranes are typically constituted of perfluorinated polyelectrolytes, such as nafion.[4,5] However, these perfluorinated polymers display several deficiencies as they are costly to produce, lack mechanical strength and dimensional stability, and their proton-conducting characteristics are highly dependent on the humidity.[6–14] In a low-humidity environment, dehydration of the nafion occurs and the collapse of the physical architecture of the membrane leads to a significant loss of conductivity.[15] As a consequence, the performance of PEM-based devices is critically dependent on the humidity of the membrane.[16]

We and others have demonstrated that the use of composite membranes synthesized by pore-filling surface polymerization results in a valuable alternative for proton-conducting membranes which combines the mechanical stability of the hydrophobic matrix with the functionality of the polyelectrolyte domains.[17–19] A remaining challenge in the materials science of composite membranes lies in the molecular design of proton-conducting channels with optimized properties similar to the well-known perfluorinated polyelectrolytes. Herein, we report promising results on the facile molecular design of materials that display high proton conductivity over a wide range of humidity. Our approach is centered on the surface-initiated polymerization of polyelectrolyte brushes by using photo-electrochemically etched silicon membranes as scaffolds to build-up structurally and chemically well-defined hydrophilic channels. The experimental results show that the polyelectrolyte-brush-based pore-filling approach, in which sulfonated monomers are used as proton carriers and polyethylene glycol based monomers are used as humidifying agents, provides a unique and powerful tool to fabricate proton-conducting membranes with conductivity values above $10^{-2}\,\mathrm{S\,cm^{-1}}$, irrespective of the humidity level.

The synthesis of the polyelectrolyte brushes used in this study involved the use of surface-initiated atom transfer radical polymerization (ATRP[20]; Figure 1). ATRP has been demonstrated to be a very powerful strategy to grow a wide variety of macromolecular architectures[21] and, consequently, has evolved as a versatile tool for the molecular design of polymeric materials. Firstly, we modified a macroporous silicon scaffold (Figure 2 a), which was prepared by a photo-electrochemical etching process,[22] with self-assembled monolayers of 2-bromo-2-methyl-*N*-(3-triethoxysilylpropyl)propionamide (Figure 1).

We then proceeded with the surface-initiated polymerization of the polymer brushes.[23] Polyelectrolytes (PELs) bearing sulfonate groups (SO_3^-) have been used extensively to create hydrophilic channels and to transport protons in phase-separated polymer membranes[11,12] and, more recently, in hybrid membranes.[17,18] However, as mentioned above, dehydration at low relative humidity promotes a pronounced decrease in the proton conductivity.

To overcome this problem we could simply introduce comonomers into the molecular design of the proton channel to improve the hydration of the polyelectrolyte bearing sulfonate groups. Poly(ethylene glycol) (PEG) derivatives are known to have excellent hydroscopic properties, namely, they attract and retain moisture from the atmosphere, and are commonly used as moisturizers and additives in the cosmetics industry.[24] In the presence of PEGylated macromolecular architectures, water molecules are able to hydrogen bond with the ethylene oxide units of the polymer chains, thereby leading to the formation of large clusters and dynamic hydrogen-bonded networks.[25,26] These properties make PEG-like species ideal building blocks for manipulating the affinity of different materials to water.[27,28] Interestingly, recent results by Rodrigues et al.[29] demonstrated that a blend film containing PEG and poly(3-hydroxybutyrate) (PHB) in a 0.05:0.95 ratio displayed a 200% increase in water permeability compared to pure PHB films. These results show that, even in very small amounts, the PEGylated constituents play a key role in governing the water affinity of the polymer film.

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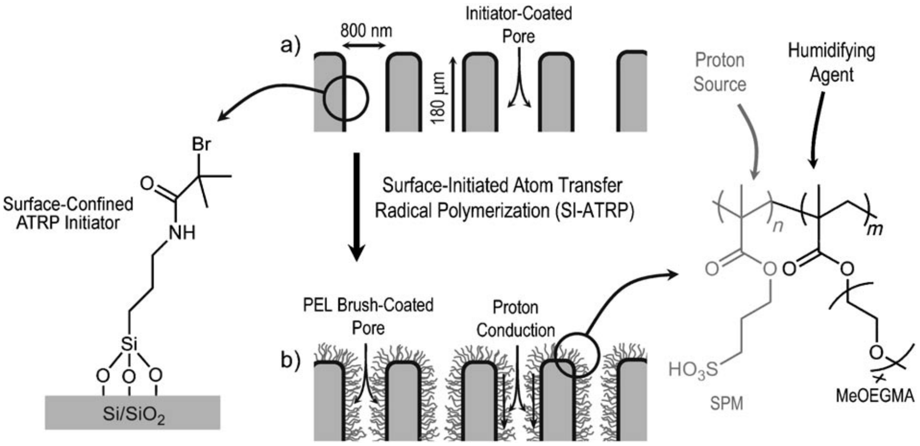

Figure 1. Simplified illustration of the pore-filling surface polymerization used to create the proton-conducting channels. The macroporous silicon scaffold was modified with initiator-terminated self-assembled monolayers (a) and then immersed in the ATRP solution where the surface-initiated copolymerization of SPM and MeOEGMA was carried out (b). Also depicted are the chemical structures of the copolymer brush ($n=0.87$, $m=0.13$, $x=5$) and the surface-confined ATRP initiator.

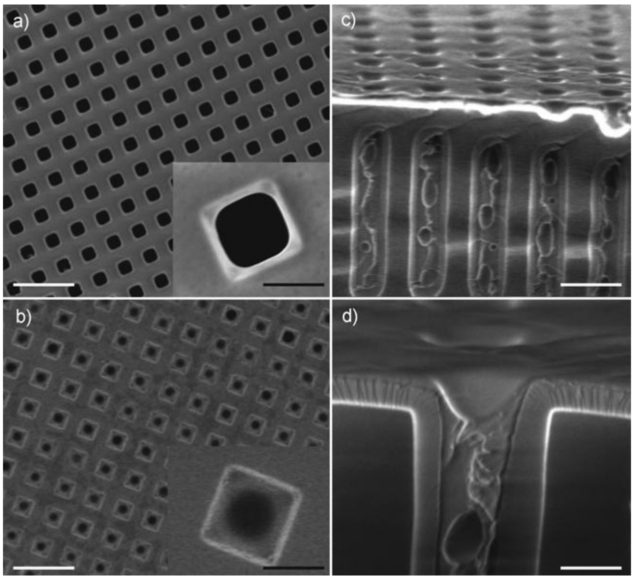

Figure 2. Scanning electron micrographs corresponding to: a) Top view of the macroporous silicon scaffold (scale bar: 4 µm). The inset shows the pore geometry in detail (scale bar: 800 nm). b) Top view of the silicon membrane modified with polySPM-*co*-MeOEGMA brushes (scale bar: 4 µm). The inset shows the brush-modified pore in detail (scale bar: 800 nm). c) Longitudinal cross-sectional imaging of the brush-modified membrane (scale bar: 1.5 µm). d) Cross-sectional view showing in detail the filling of the pore as a result of the surface-initiated polymerization (scale bar: 800 nm).

In our case, the role of the PEG-like co-monomer would be to act as a "humidifying agent" and keep the brush hydrated while the polyelectrolyte acts as the proton source. To verify this hypothesis we modified the macroporous membranes with polymer brushes by simply copolymerizing sulfopropyl methacrylate (SPM) and monomethoxy oligo(ethylene glycol) methacrylate (MeOEGMA) in a 10:1 monomer ratio (Figure 1). After a preset polymerization time the membrane channels were completely filled with polySPM-*co*-MeOEGMA brushes, thus indicating that the surface-initiated copolymerization proceeded smoothly in the confined environment of the membrane channels (Figure 2b–d). Chemical analysis indicated that the polymer growth resulted in a copolymer with a SPM/MeOEGMA monomer ratio of 0.87:0.13. The ion-exchange capacity was 0.12 meq g^{-1}, which is slightly lower (ca. 14%) than the homopolymeric SPM-based analogue (0.14 meq g^{-1}).[18] As expected, this finding indicates that the replacement of SPM by MeOEGMA monomers in the brush quantitatively affects the ion-exchange capacity of the membrane. Characterization by impedance spectroscopy (at 100% relative humidity) revealed that the proton conductivity of the membrane modified with copolymer brushes was very good and the values were comparable to those observed with nafion (ca. 10^{-2} S cm^{-1}; Figure 3).[15]

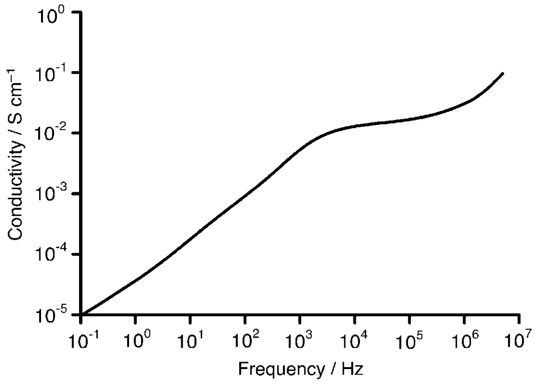

Figure 3. Bode plot showing the conducting characteristics of the silicon membrane modified with polySPM-*co*-MeOEGMA brushes at 100% relative humidity and 25 °C. A specific conductivity of 1.4×10^{-2} S cm^{-1} was calculated from the plateau of the Bode plot.

Our next, and ultimate, goal was to study how the proton conductivity was affected by variations in the humidity. These experiments were performed in a temperature-controlled climate chamber, with the conductivity monitored by impedance spectroscopy. Surprisingly, we observed that the high conductivity values (ca. 10^{-2} S cm^{-1}) measured at high humidity (90% relative humidity) remained almost constant over the large range of 30–90% relative humidity (Figure 4a). The membrane modified with polySPM-*co*-MeOEGMA brushes displayed a proton-conductivity value of 4×10^{-2} S cm^{-1} at 30% relative humidity. This represents an unprecedented result in the molecular design of new proton-conducting

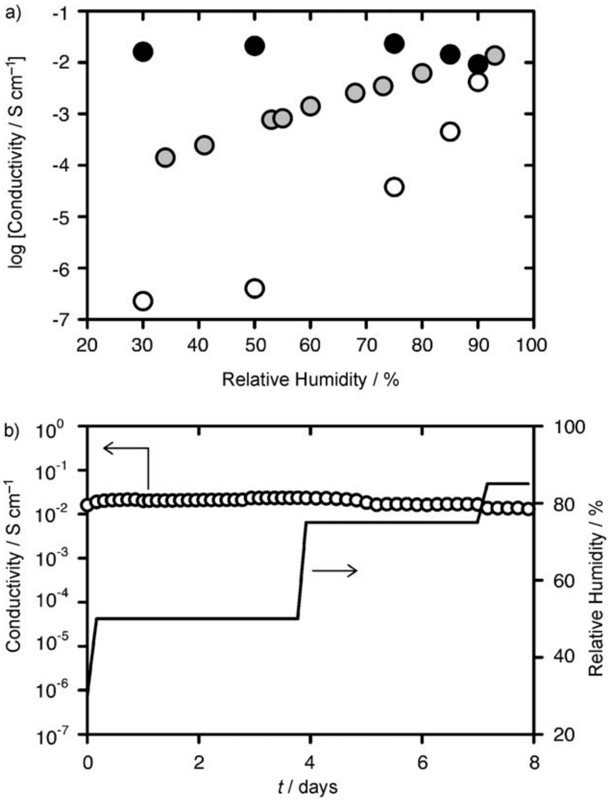

Figure 4. a) Conductivity versus relative humidity plots corresponding to: the silicon membrane polySPM-*co*-MeOEGMA modified with brushes (●), the silicon membrane modified with polySPM brushes (○) (data taken from Ref. [18]), the nafion 117 membrane (●) (data taken from Ref. [15]). b) Variation of the proton conductivity of the membrane based on polySPM-*co*-MeOEGMA brushes upon changes in the relative humidity. The proton conductivity remains fairly constant over several days regardless of the relative humidity.

platforms with optimized properties. For clarity and to better illustrate the relevance of these results we also show in Figure 4a the conductivity values obtained at different relative humidities for a hybrid membrane modified with SPM brushes[18] and a nafion 117 film.[15] The results show that, at low relative humidities, the incorporation of a minor amount of oligo(ethylene glycol) into the brush architecture promotes drastic changes in the proton conductivity of membranes modified with SPM brushes. In fact, replacement of about 13% of the SPM monomer units by MeOEGMA resulted in a five orders of magnitude increase in the proton conductivity at 30% relative humidity. This finding shows the critical role of the molecular design of the proton-conducting channels and the versatility of SI-ATRP to achieve this goal. A comparison with the results of the nafion membrane also revealed striking differences. The proton conductivity in nafion drastically decreases when the relative humidity is varied from about 90 to 30% (Figure 4a), with values of approximately 10^{-4} S cm^{-1} being reached at low humidity. It is worthwhile mentioning that this conductivity is two orders of magnitude lower than that measured at similar humidity in the membrane modified with polySPM-*co*-MeOEGMA brushes. This fact highlights the remarkable and outstanding performance of the polySPM-*co*-MeOEGMA brush platform compared to that of polymeric materials currently used in PEM-based devices. Their proton conductivities are comparable only at high relative humidities. Furthermore, in contrast to nafion, the conductivity values of the membrane based on polySPM-*co*-MeOEGMA brushes are not affected by significant changes in the relative humidity. This particular feature is extremely relevant for achieving highly stable and reliable PEMs.

To further explore the reliability of the polySPM-*co*-MeOEGMA brush platform we monitored the proton-conductivity values at different relative humidities over a period of eight days. Figure 4b clearly shows that the proton conductivity is nearly constant (with values of about 10^{-2} S cm^{-1}) over the monitoring period, during which the relative humidity was varied from 30 to 90%. These results further corroborate the robustness and reliability of the hybrid membrane modified with polySPM-*co*-MeOEGMA brushes. Finally, we studied the proton conductivity over the 20–100 °C range at high humidity. The experimental evidence revealed that the proton conductivity displays a remarkably stable behavior, with values above 10^{-2} S cm^{-1} (Figure 5) even at close to 100 °C—the temperature at which water evaporation dramatically affects the hydration of currently used PEMs.

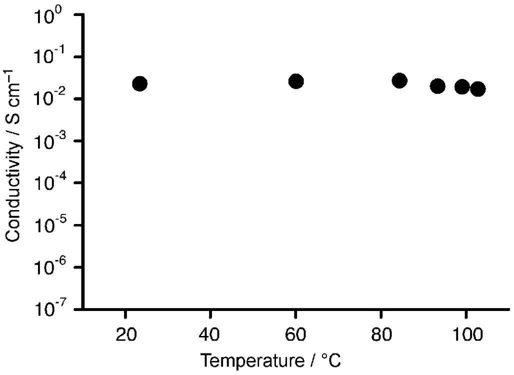

Figure 5. Conductivity versus temperature plot corresponding to the silicon membrane modified with polySPM-*co*-MeOEGMA brushes. Relative humidity: ca. 90%.

In summary, our results demonstrate that the synthesis of hybrid membranes by pore-filling surface polymerization is a new approach to create proton-conducting channels with tailor-made, finely tuned physicochemical characteristics. Macroporous silicon membranes were modified with sulfonated polymer brushes to create proton-conducting membranes with outstanding properties. We observed that incorporating a small fraction of MeOEGMA monomer units in the polyelectrolyte brush architecture promotes a five orders of magnitude increase in the proton conductivity measured at low relative humidities. More importantly, these platforms displayed high conductivity values (ca. 10^{-2} S cm^{-1}) regardless of the humidity, thus surpassing the performance of nafion. On the basis of these results we envision that this simple and straightforward strategy that enables the facile generation of tailor-made proton-conducting channels by ATRP-based pore-filling surface polymerization will constitute a benchmark for the molecular design of PEMs with highly optimized physical and chemical characteristics. Creating new monomer units compatible with the harsh conditions of fuel-cell operation will play a key role in further expanding the technological applications of pore-filled hybrid membranes. As such, we consider that this approach could lead, in the not too distant future, to new methods for the production of PEMs that meet the demanding industrial requirements.

Experimental Section

Materials and methods: (3-Aminopropyl)triethoxysilane (99 %), 2-bromopropionyl bromide (97 %), 2,2′-bipyridine (99 %), copper(II) chloride ($\geq$ 98 %, Fluka), and 3-sulfopropyl methacrylate potassium salt (98 %) were used as received from Sigma–Aldrich (Schnelldorf, Germany). 2-Bromo-2-methyl-*N*-(3-triethoxysilylpropyl)propionamide was synthesized following procedures reported in the literature.[18] Copper(I) chloride ($\geq$ 97 %, Fluka) was purified by washing five times with glacial acetic acid.[1] Monomethoxy oligo(ethylene glycol) methacrylate (MeOEGMA, average $M_n \approx 300$, Sigma–Aldrich), was passed through a short plug of basic alumina to remove the stabilizer. The proton conductivity was measured by dielectric spectroscopy using either an Alpha high-resolution dielectric analyzer equipped with a Novocontrol active sample cell to expand the frequency range to approximately 10 MHz or an SI 1260 impedance/gain-phase analyzer. The ion-exchange capacity was determined by procedures reported elsewhere.[18] X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Physical Electronics 5600 A instrument. The $Mg_{K\alpha}$ (1253.6 eV) X-ray source was operated at 300 W. A pass energy of 117.40 eV was used for the survey spectra. The spectra were recorded at a 45° take-off angle relative to the surface normal. The XPS scans were analyzed using the MultiPak 5.0 software.

SI-ATRP of polySPM-*co*-MeOEGMA brushes: 3-Sulfopropylmethacrylate (5.3 g, 20 mmol) and MeOEGMA (0.6 g, 580 μL, 2 mmol) were dissolved by stirring in methanol/water mixture (2:1, 8.7 mL) at room temperature. 2,2′-Bipyridine (191.5 mgg) and $CuCl_2$ (3.5 mg) were added to this solution. The mixture was stirred and degassed by bubbling N_2 over one hour prior to adding CuCl (48.5 mg). The mixture was degassed with bubbling N_2 for another 15 min. Initiator-coated macroporous silica samples were sealed in a schlenk tube and degassed by four high-vacuum pump/N_2(g) refill cycles. The reaction mixture was added by syringe into the schlenk tube, with enough solution added to cover the sample completely, and the mixture was left under N_2. The polymerization was allowed to proceed for 4–5 days before termination. The samples were then removed and rinsed thoroughly with deionized water. The samples were then kept overnight in 0.01N aq HCl to exchange the K^+ ions (which originally coordinated to the monomer) with H^+ ions.

Estimation of the MeOEGMA content in the copolymer by ^{1}H NMR spectroscopy: In addition to the SI-ATRP experiments, copolymerizations of SPM and MeOEGMA were also carried out in the solution under similar conditions by using ethyl 2-bromopropanoate as an initiator (monomer/initiator ratio 260:1). The polymerization was terminated by exposing the polymerization solution to air. The polymers were purified by dialysis (molecular-weight cut-off (MWCO) = 3500) against water and the obtained solutions were lyophilized to give pure polymers as white powders. The percentage of MeOEGMA in the copolymer was estimated by comparing the integration corresponding to the two protons (at $\delta = 4.09$ ppm) which are adjacent to the ester linkage in SPM monomer with the protons of the -CH_2-O- (at $\delta = 3.67$ ppm) linkage in MeOEGMA. The MeOEGMA content in polySPM-co-MeOEGMA was found to be 13 mol %.

Proton-conductivity measurements: The proton conductivity was measured by dielectric spectroscopy with a two-electrode geometry. The combination of a high conductivity and a thin sample can lead to distortions of the impedance plots above 1 MHz. We initially used an Alpha high-resolution dielectric analyzer and a Novocontrol active sample cell to expand the frequency range to ca. 10 MHz. After proving that the resonance was below 1 MHz, the spectra were recorded using an SI 1260 impedance/gain-phase analyzer and a Novocontrol broadband dielectric converter. An atmosphere of saturated humidity was generated by using a closed sample cell with a water reservoir on the bottom that was not in contact with the sample. The saturation was controlled by a Sensirion SHT75 humidity sensor and determined to be 100 % (within the error of the sensor (2 %). Humidities between 18 and 95 % were created with a temperature-controlled climate chamber (Binder KBF 240). The resistance of the composite membrane was estimated from Cole–Cole and Bode plots. The specific conductivity of the composite membrane was then calculated from the apparent thickness and electrode area.

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