

# Polyelectrolytes as Building Blocks for Next-Generation Membranes with Advanced Functionalities

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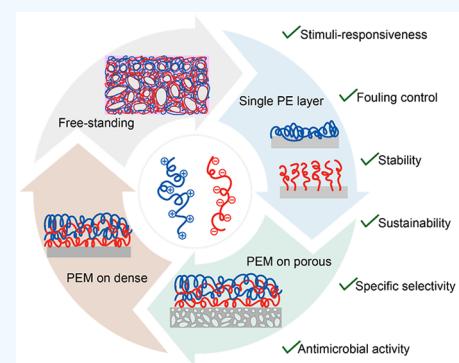
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**ABSTRACT:** The global society is in a transition, where dealing with climate change and water scarcity are important challenges. More efficient separations of chemical species are essential to reduce energy consumption and to provide more reliable access to clean water. Here, membranes with advanced functionalities that go beyond standard separation properties can play a key role. This includes relevant functionalities, such as stimuli-responsiveness, fouling control, stability, specific selectivity, sustainability, and antimicrobial activity. Polyelectrolytes and their complexes are an especially promising system to provide advanced membrane functionalities. Here, we have reviewed recent work where advanced membrane properties stem directly from the material properties provided by polyelectrolytes. This work highlights the versatility of polyelectrolyte-based membrane modifications, where polyelectrolytes are not only applied as single layers, including brushes, but also as more complex polyelectrolyte multilayers on both porous membrane supports and dense membranes. Moreover, free-standing membranes can also be produced completely from aqueous polyelectrolyte solutions allowing much more sustainable approaches to membrane fabrication. The Review demonstrates the promise that polyelectrolytes and their complexes hold for next-generation membranes with advanced properties, while it also provides a clear outlook on the future of this promising field.

**KEYWORDS:** review, polyelectrolytes, polyelectrolyte multilayers, membranes, functionality, polyelectrolyte complexes, advanced functionalities, ion selectivity



## 1. INTRODUCTION

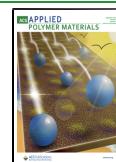
Membranes find their place in countless applications from the production of drinking water to the separation of valuable pharmaceuticals, from gas sweetening to hemodialysis.<sup>1,2</sup> As the demand for reliable and efficient separations increases, the membrane market will continue to grow. The membrane separation and technology market size was estimated as USD 17.5 billion in 2020 and is expected to grow to USD 25.2 billion by 2027.<sup>3</sup> Since the 1960s, when the membrane industry was born, membrane technology has developed rapidly.<sup>1</sup> Polymeric membranes have become the norm in sectors, such as desalination processes, and it has been demonstrated that these membranes can be applied for many challenging separations like the separation of azeotropic mixtures,<sup>4</sup> the removal of micropollutants from wastewater streams,<sup>5</sup> and high-temperature gas separations.<sup>6</sup> With such a large range of well-developed membranes now being commercially available, it becomes important to think about the future of this field, how can we still push it forward? We foresee that the next milestone of this technology will be on the development of membranes with functionalities that go beyond standard separation (i.e., advanced functional mem-

branes). Here, we define advanced functionalities as properties that ease the operation, that enhance the separation performance, or any other feature that makes the membrane preferable over others. In this context, they can also be seen as design parameters that follow naturally from the PE material properties. For example, the antifouling behavior of a membrane enables longer-term operations,<sup>7</sup> stimuli-responsiveness provides great control over separation performance,<sup>8</sup> while more sustainable membrane production is becoming a much more important factor when selecting a membrane for specific applications.<sup>9</sup> Moreover, membranes with a highly specific separation behavior, for example ion selectivity, would allow novel membrane processes to recover valuable components,<sup>10–13</sup> while membranes with improved stability can allow separations under the extreme conditions (pH, T,

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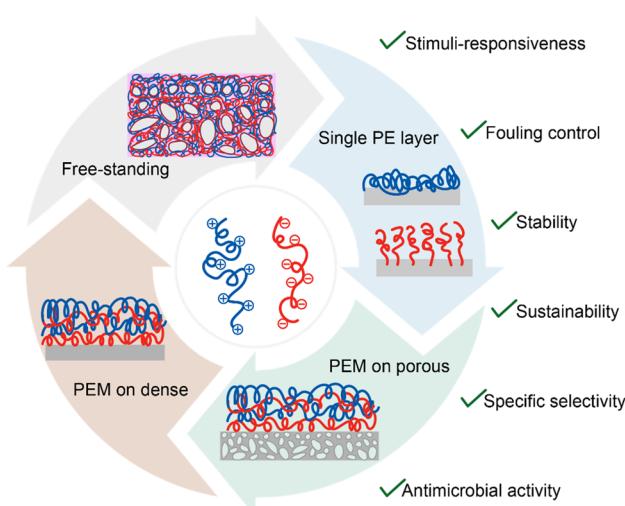
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salinity etc.) sometimes required for industrial separations.<sup>13–17</sup>

One group of membrane materials that are especially promising to allow these advanced properties, are polyelectrolytes (PEs), polymers that have charged repeating units. Because of their charge, they are often soluble in water and when oppositely charged PEs interact, they can form insoluble polyelectrolyte complexes (PECs). Their unique properties make PEs very good candidates for building blocks of advanced functional membranes (Figure 1). For example,

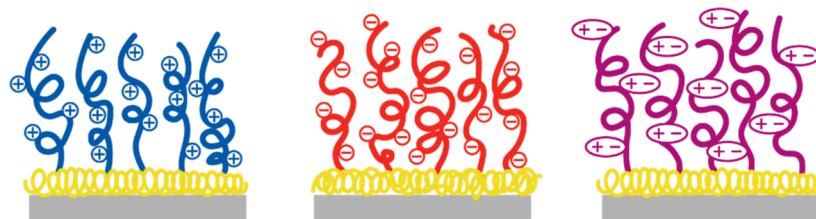


**Figure 1.** PE- and PEC-based membrane systems and their general functionalities.

unlike typical polymers used in membrane production, PEs are hydrophilic due to their charged nature. Hydrophobic membranes suffer from fouling which decreases the production rate and increases the energy cost of the operation. On the other hand, hydrophilic polymers are less prone to foul and easier to clean.<sup>18</sup> Hydrophilicity is also required for applications such as pervaporation<sup>19</sup> (especially for dehydration of organic/aqueous mixtures) or oil–water separations.<sup>20</sup> PEs are highly desired for these kinds of applications, not only because of their hydrophilic nature, but also due to the possibility to tune their features (e.g., swelling and charge density). Especially for weak PEs, where chain conformation can be easily controlled with external stimuli like pH, it is possible to tune the membrane performance by using these features. Moreover, besides other rejection mechanisms, charge exclusion will substantially contribute to the performance of the charged membranes. Indeed, even when the membrane pores are larger than the charged solute, high rejections can be

achieved with the help of electrostatic repulsion.<sup>21,22</sup> Interactions between the solute and the membrane is a major determining factor for separation properties and it is not necessarily be limited to electrostatic interactions. Certain PE-based membranes exhibit specific selectivities for certain compounds.<sup>23,24</sup> For example, PEC multilayers of poly(sodium 4-styrenesulfonate)/(poly(diallyldimethylammonium chloride) (PSS/PDADMAC) are selective for fluoride,<sup>25</sup> sulfate,<sup>26</sup> and phosphate<sup>27</sup> while polyionic liquids (PILs), a subgroup of PEs, show a good selectivity for CO<sub>2</sub> depending on the molecular structure of the PILs.<sup>28,29</sup> In applications including organic solvents, most of the polymeric membranes need a post-treatment to have good chemical resistance to the solvent. Polyelectrolyte complexes, however, are very stable in solvents because of their ionic cross-linking,<sup>30</sup> and as a result, there are already many examples in literature for PEC membranes being used for pervaporation<sup>19</sup> and organic solvent filtration.<sup>31</sup> The chemical stability of PECs is not restricted to organic solvents, with a good selection of PEs it is possible to obtain membranes with remarkable stability against hypochlorite<sup>32</sup> and extreme pH conditions.<sup>11,33,34</sup>

While some Reviews have focused on the production of PE-based membranes<sup>35</sup> or their possible applications like electrolysis, electrodialysis, and fuel cells,<sup>36–38</sup> so far there has been a lack of focus on the advanced functionalities that can be obtained by smart use of these promising materials. Therefore, in this review, we take a detailed look at the advanced functionalities that can be obtained using the large variety of PE- and PEC-based systems that have been developed in recent years. The Review brings together the recent literature on advanced functional PE-based membranes with the focus on the last ten years. In general, advanced functionalities stem from the unique features and material properties of PEs, these can also be considered as design parameters and can be utilized to tune membrane properties. In Figure 1, we show an overview of the systems and functionalities discussed in this work. First, we discuss the simplest use of polyelectrolytes as adsorbed monolayers, but in particular as PE brushes. These coatings are mostly used to change the surface properties (e.g., wettability and surface charge) of the coated membrane, leading to excellent examples of antifouling and responsive membranes. After this section, polyelectrolyte multilayer (PEM) coatings are discussed in two parts: PEM-coated porous substrates, where the PEM coating becomes the effective separation layer, and PEM-coated dense membranes, where the PEM coating helps to improve the separation performance. For the PEM coatings applied to dense membranes a large data set is compiled comparing ion selectivities of ion-exchange membranes in literature with an emphasis on the need for consistency in reported values.



**Figure 2.** Three types of charged brushes are considered: cationic polymers (left), anionic polymers (middle), and zwitterionic polymers (right). The surface anchors (in yellow) to obtain long-term stable polyelectrolyte brushes (PEBs) are often composed of hydrophobic blocks and/or molecular structures that allow for multiple surface bonds. These anchors are not drawn to scale and in reality much thinner than the brush.

Subsequently, free-standing, integrally skinned PE-based membranes will be discussed, demonstrating that membranes can now also be prepared completely from polyelectrolytes. Finally, in the outlook we highlight the logical next steps and the significant opportunities that can be pursued for these systems, given their remarkable properties and chemical diversity. We believe that, by the end of this Review, it will be clear how remarkably useful PEs and their complexes are to create the next-generation of advanced functional membranes.

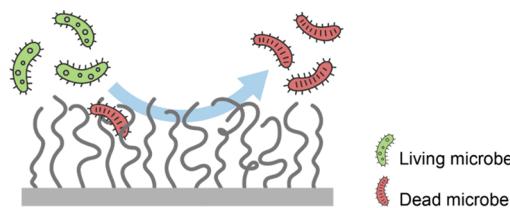
## 2. SINGLE POLYELECTROLYTE LAYERS

Single polyelectrolyte layers can be composed of either positively or negatively charged polymers. Moreover, the polymers in these single layers can bear both positive and negative charges in their side chains (zwitterionic polymers). In the following, we will consider these three types of polymers (Figure 2). These polymers can be applied via different techniques to the substrate to form single PE layers. They can be physisorbed or covalently bonded to the substrate to form PE films, for example, via catechol groups,<sup>39</sup> and they can be prepared by spin coating<sup>40</sup> or vapor deposition.<sup>41</sup>

When the polyelectrolytes or zwitterionic polymers are attached with one chain-end to the substrate at a density that is high enough for the polymers to stretch away from the grafting plane, so-called polyelectrolyte brushes (PEBs)<sup>42–44</sup> are formed. They can be prepared by grafting to<sup>45</sup> or grafting from<sup>46</sup> techniques. The conformation of PEs in brushes is different from neutral polymers in brushes. For neutral brushes, polymers stretch away from the surface due excluded volume interactions,<sup>47,48</sup> while PEBs swell by the high osmotic pressure induced by trapped counterions.<sup>49,50</sup> PEBs have gained a lot of attention because of their lubricious,<sup>51,52</sup> antifouling<sup>53</sup> and stimuli-responsive<sup>54,55</sup> properties. For membrane applications, the latter two properties are of particular interest,<sup>56</sup> so they will be treated in more detail in the next two sections, before discussing ways to increase the layer stability in section 2.3.

**2.1. Fouling Control.** Polymers that prefer to interact with the water molecules, instead of foreign elements are good candidates for antifouling brushes, since they will effectively repel all fouling matter.<sup>57,58</sup> Many PEBs, such as poly(3-sulfopropyl methacrylate) (PSPMA) brushes and zwitterionic brushes, such as poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC) swell strongly in water. Therefore, these brushes are often employed in antifouling coatings.<sup>59,60</sup> Other polymers that are often utilized in antifouling coatings are based on sulfobetaines,<sup>61,62</sup> carboxybetaines,<sup>63</sup> and hydroxyl acrylamides.<sup>64</sup> It has been shown that the latter displays the best antifouling performance against nonspecific adsorption of proteins, cells, and microorganisms.<sup>65</sup> Antifouling brushes have been applied in different membrane systems, such as on forward osmosis<sup>66</sup> and filtration<sup>67</sup> membranes for oil–water separations or filtration membranes for (drinking) water treatment.<sup>68,69</sup> More details on antifouling solutions on membranes will be discussed in sections 3.2, 4.2, and 5.4. It is, however, important to already mention here that while antifouling coatings can be very effective to reduce membrane fouling, reducing flux decline, they do tend to come with their own penalty to membrane permeance.

Recently, it has been realized that coatings with both antifouling and antimicrobial functions (Figure 3) are needed to effectively prevent biofouling<sup>60,70–72</sup> and several strategies have been designed to achieve this. For example, binary

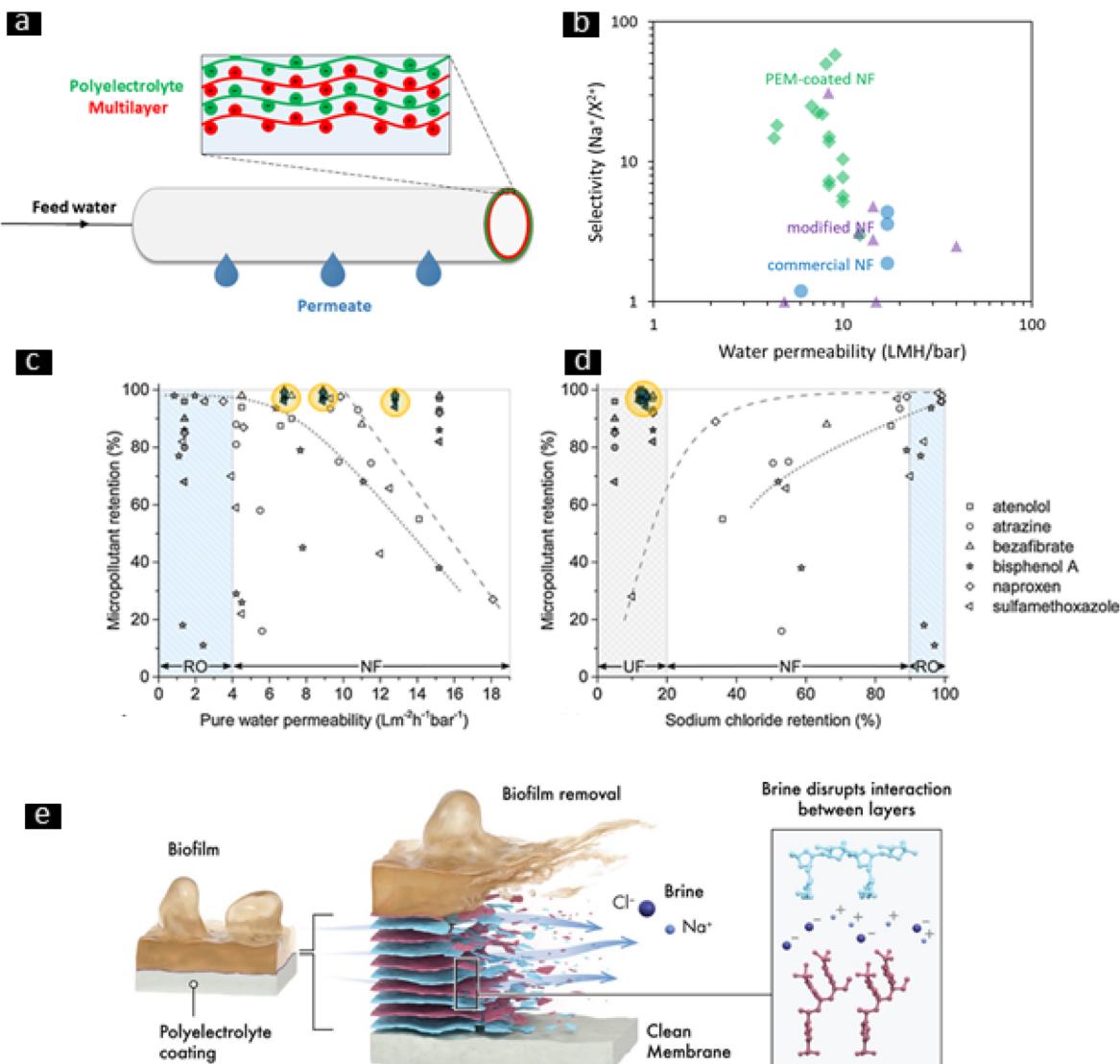


**Figure 3.** Polyelectrolyte brushes with both antifouling and antimicrobial function. Living microbes will be killed after contact with the brush due to the antimicrobial function, while the dead microbes are repelled by the antifouling function of the coating.

brushes can be synthesized that are composed of antifouling polymers, such as PMPC and antimicrobial cationic poly(2-(methacryloyloxy)ethyl trimethylammonium chloride (alkynyl-PMETA) polymers with alkynyl functionalities.<sup>71</sup> Often specific types of coatings need to be designed to prevent fouling by specific types of microbes. For instance, low-fouling brushes can be combined with components that kill bacteria, such as Cu ions<sup>60</sup> or Ag nanoparticles,<sup>73</sup> to prepare antibacterial coatings, while for antiviral coatings a cationic polymer, such as poly(ethylenimine) (PEI), can be utilized directly<sup>74</sup> or functionalized with Cu or Ag particles for a better performance.<sup>75</sup> The latter two examples have been shown to effective kill and repel viruses in microfiltration membranes for application in drink water with only a small decrease in the transport properties. Moreover, antimicrobial antifouling brush coatings have been applied in reverse osmosis membranes with good permeability.<sup>76</sup>

For optimal performance of antifouling PEBs, it is important to consider the design parameters of the brushes. The grafting density has a strong effect on the low-fouling performance of brushes.<sup>77,78</sup> A higher grafting density will give rise to a higher polymer density, which increases the osmotic pressure. This makes it more difficult for foreign bodies to penetrate the brush,<sup>79–81</sup> though exceptions can be expected for penetrants that are charged.<sup>82</sup> In situations where it is difficult to prepare brushes with high grafting densities, branched or comb-polymer brushes can provide an alternative route to obtain high polymer density and, thus, increased effectiveness in preventing fouling.<sup>83</sup> Dispersity of the polymers in the brush will alter the polymer density distribution from approximately parabolic to convex.<sup>84–86</sup> Since this change reduces the polymer density near the brush surface, the antifouling performance against small particles will be reduced as well.<sup>87,88</sup> However, the opposite can occur for large particles, since polydisperse brushes are more difficult to compress.<sup>87</sup>

**2.2. Responsiveness.** The conformation of PEs depends strongly on the environment and can be controlled by parameters, such as the ionic concentration or the pH. For example, poly(acrylic acid) (PAA) changes its conformation depending on the pH.<sup>89</sup> In basic solutions, the pendant acidic groups deprotonate and charges are created in the side chains. Consequently, the water affinity increases and the polymer swells. In contrast, in an acidic solution, PAA chains collapse because of the protonation of the carboxyl groups. In the form of PEBs, strong interchain effects can enhance the responsiveness and strongly changes the swelling of these brushes. Therefore, the brushes can show a dramatic response to stimuli, such as pH and salt concentration. While PEBs of strongly dissociating PEs, such as PSS tend to be rather insensitive to the pH,<sup>42</sup> they respond strongly to the presence of ions.<sup>90</sup> Brushes composed of weak PEs, such as PAA, tend to



**Figure 4.** (a) Illustration of a PEM application on hollow fibers for membrane filtration. (b) Comparison of membrane divalent ion-selectivity ( $\text{Na}^+/\text{X}^{2+}$ ) and water permeability ( $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ ) as a function of different surface modifications from literature. Green diamonds represent single data points for PEM-coated nanofiltration (NF) membranes,<sup>118–121</sup> purple triangles modified NF membranes,<sup>122–129</sup> and blue circles commercial NF membranes.<sup>119,122,123</sup> (c) Permeability vs micropollutant retention and (d) sodium chloride retention vs micropollutant retention for asymmetric and symmetric PEM-coated membranes in comparison with commercial NF and reverse osmosis (RO) membranes. White symbols, commercial membranes; gray symbols, symmetric PEM-coated membranes from Brinke et al.;<sup>130</sup> dark symbols inside yellow circles, asymmetric membranes from Brinke et al.;<sup>130</sup> dashed lines, best single results obtained with commercial membranes; dotted lines, best single results obtained with commercial membranes for bisphenol A. (e) Sacrificial layer concept applied to control biofilm growth. (c and d) Reproduced with permission from ref 130. Copyright 2020 Elsevier. (e) Reproduced with permission from ref 131. Copyright 2020 Elsevier.

respond to both the pH and the ionic strength of the solution.<sup>91</sup> Besides the solvent composition, electric fields can also be utilized to control the conformation of PEBs.<sup>92</sup> Since this stimulus can be applied externally, without the need to change the solution conditions, it provides an easy and effective control. The responsiveness of PEBs has made them popular systems for the design of functional surface coatings, because the swelling state of the brushes controls the surface properties of the coating.<sup>55</sup> Therefore, they can be used in the development of smart adhesives,<sup>93–95</sup> switchable lubricants,<sup>96,97</sup> and for wetting control.<sup>98,99</sup> Moreover, it allows for the controlled release of fouling components,<sup>100</sup> which can be particularly useful in membrane applications. In addition, responsiveness of PEBs to the pH can be employed to tune the oil-adhesiveness of these coatings,<sup>101</sup> which is relevant for oil-

water separations. More examples of the usage of PE responsiveness in specific membrane applications will be given in sections 3.3 and 5.3.

**2.3. Stability.** Because of the strong hydration capability of PEBs, the polymers can be strongly stretched, which introduces enhanced tension near the anchor points.<sup>102</sup> Moreover, water can reach any hydrolysis-sensitive surface bonds.<sup>103,104</sup> This can potentially lead to degrafting of the PEBs, as has been observed for PAA brushes attached to Si wafers kept in 0.1 M ethanolamine buffer (pH 9.0) with 0.5 M NaCl.<sup>105</sup> Similar degrafting has been observed for carboxylated poly(oligo(ethylene glycol) methacrylate-random-2-hydroxyethyl methacrylate) (poly(OEGMA-r-HEMA)) brushes grafted from metal surfaces and kept in phosphate buffered saline solutions<sup>106</sup> and even for PSPMA brushes attached to Si

wafers, exposed to humid air.<sup>107</sup> To prevent such degrafting of PEBs, several strategies for strong anchoring of the brushes have been developed (see Figure 2). They are based on the incorporation hydrophobic structures to prevent water from reaching hydrolysis-sensitive bonds or on increasing the number surface bonds. For example, when grafting block copolymers from surfaces that consist of hydrophobic blocks close to the surfaces and hydrophilic blocks exposed to the aqueous liquid,<sup>108–111</sup> the hydrophobic blocks will collapse and protect the sensitive surface bonds. Alternatively, enhanced stability can be achieved by utilizing hydrophobic macroinitiators,<sup>112,113</sup> tannic acids,<sup>72</sup> or mussel-adhesive inspired catechol-based anchoring layers,<sup>71,114</sup> that allow for multiple surface bonds. In particular, poly(glycidyl methacrylate) (PGMA) based surface anchors have been shown to be promising solutions for membrane applications.<sup>112</sup> PMPC brushes grown from these anchors keep their hydrophilicity even after immersion for 100 000 ppm hours in sodium hypochlorite solution. These strong surface anchors are much thinner (0.5–3 nm) than the PEBs (10–100 nm) and are, therefore, not expected to affect the transport properties of membranes.

### 3. POLYELECTROLYTE MULTILAYERS ON POROUS SUBSTRATES

Self-assembly of polyelectrolytes via electrostatic interactions can be used to build up multilayered materials with unique functionalities. Already in 1997, Decher demonstrated that the alternating exposure of a charged surface to positive and negative polyelectrolyte solutions, allows for layer-by-layer (LbL) deposition of thin films of polyelectrolytes, so-called polyelectrolyte multilayers (PEMs).<sup>115</sup> The versatility of PEM fabrication via LbL technique on flat surfaces, as well for hollow multilayer capsules, allows for a class of stimuli-responsive materials with a wide range of applications, such as microreactors, microsensors, and drug delivery, for medicine, cosmetics, and pharmaceuticals.<sup>116</sup> Such stimuli-responsive multilayers, which exhibit specific response to changes in the environmental conditions, like pH, temperature, ionic strength, magnetic field or light,<sup>116</sup> are still having a huge impact on today's chemistry, physics, biology, and materials science.<sup>117</sup>

Particularly, in the last 10 years, the knowledge on LbL assembly of PEMs on porous supports, as schematically illustrated in Figure 4a for hollow fiber nanofiltration (NF) membranes, has been translated into application<sup>35</sup> and production of commercial membranes with advanced separation properties and functionalities.<sup>36</sup> PEM coatings allow for a nanometer-control over the membrane active layer thickness and chemistry.<sup>132–134</sup> In particular, the availability of different polyelectrolytes as building blocks<sup>115,121</sup> as well as coating conditions (e.g., salinity<sup>135,136</sup> and pH<sup>137,138</sup>) allow the production of thin films with engineered functionality for multiple membrane applications, such as ion selectivity,<sup>139</sup> fouling control,<sup>140</sup> stability against harsh wastewaters,<sup>34,141</sup> removal of contaminants from water,<sup>142,143</sup> and responsiveness.<sup>144</sup>

Despite the good separation properties reached by commercial membranes in the past decade, PEM-coated membranes provide a class of advanced functionalities which would benefit the membrane field. Below, we discuss in detail the most relevant ones, with a focus on unique separations, fouling control, responsiveness, and stability.

**3.1. Specific Selectivity.** A tailored ion selectivity is still believed to be the *holy grail* of membrane filtration processes. Commercial membranes do exhibit high water-salt selectivity, but their ability to discriminate between different types of ions is still limited.<sup>145</sup> Nevertheless, PEM-coated membranes can already tackle challenging separations, including the separation of mono- and divalent ions.<sup>121,139,143,146</sup>

Cheng et al. demonstrated that a (PDADMAC/PSS)<sub>5.5</sub>-coated commercial NF membrane at low salinity (50 mM) can selectively remove several divalent cations ( $X^{2+}$ ), such as  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$ , and  $Ba^{2+}$ , from feedwater with mild salinity, like brackish water.<sup>119</sup> The rejection of divalent cations and therefore the  $Na^+/X^{2+}$  selectivity of the NF membranes allows for highly selective separations of divalent cations and anions,<sup>143,146</sup> which are the main culprits in inorganic scaling.<sup>119</sup>

In Figure 4b, PEM-coated membranes<sup>118–121</sup> are directly compared to commercial NF membranes and to NF membranes prepared by other modification techniques, such as polymer grafting,<sup>122</sup> atomic and molecular layer deposition,<sup>124,125</sup> graphene oxide,<sup>127</sup> and carbon nanotubes incorporation.<sup>126</sup> It can be clearly seen that the  $Na^+/X^{2+}$  selectivities of PEM-based membranes are higher than those of commercial NF membranes, such as the popular DOW N90<sup>122</sup> and NF270,<sup>123</sup> while retaining good water permeabilities. Clearly, PEM assembly is an attractive surface modification, which allows for outstanding mono-/divalent ion selectivity also compared to the competing surface modifications.<sup>122–129</sup>

Specific membrane selectivities are also urgently needed to combat the increasing concentrations of emerging contaminants in the waste and surface waters. Persistent, non-biodegradable, and bioaccumulative contaminants in surface waters, also known as micropollutants (MPs), pose a severe threat to human health.<sup>147</sup> While the densest available reverse osmosis (RO) membranes can remove these contaminants sufficiently, they do so at very low water permeability and by producing a highly saline, difficult to treat, MP waste stream.<sup>148</sup>

Wang et al. recently fabricated and applied PEM-coated NF membranes with tailored selectivity for the effective removal of MPs from saline wastewaters, allowing a relatively high passage of salt, including for scale-forming divalent cations.<sup>143</sup> Brinke et al. succeeded in the preparation of a new class of membranes with unique separation properties, called "Chimera", via asymmetric assembly of PEMs.<sup>130</sup> Coating first an open PSS/poly(allylamine hydrochloride) (PAH)-based multilayer to prevent defects, and second, a thin and dense PAA/PAH-based multilayer for fine-tuned separation properties, makes it possible to design these novel membranes with outstanding retention of micropollutants (98%, Figure 4c) and high water permeability (up to  $\sim 13$   $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$ ), outperforming commercial membranes.<sup>130</sup> An additional advantage of these asymmetric PEM membranes is their low salt retention (Figure 4d) as salt does not accumulate in the MP-rich stream, facilitating the postfiltration treatment.

We can conclude that coating of porous membranes with PEMs allows for the fabrication of nanofiltration membranes with advanced separation properties compared to traditional membranes. In Table 1, we report various polyelectrolyte systems that, coated on ceramic and polymeric supports, allow for challenging separations of ions, pollutant removal, and water purification. Here, we also report the coating and process conditions to help the reader to evaluate the performance of

**Table 1. Overview of Coating Conditions and Performance of Commonly Used Polyelectrolyte Systems Successfully Applied on Various Membrane Supports for the Fabrication of PEM-Based NF Membranes<sup>a</sup>**

PE <sub>s</sub>	coating conditions	support	process conditions	performance	ref
PDADMAC/PSS	(PSS/PDADMAC) <sub>4,5</sub> dip coating with 0.02 M polymer and 0.5 M NaCl	PES UF membrane	crossflow filtration 4.8 bar flow rate: 18 mL/min	13.9 L·m <sup>-2</sup> ·h <sup>-1</sup> ·bar <sup>-1</sup> 95.9% SO <sub>4</sub> <sup>2-</sup> rejection	149
(PDADMAC/PSS) <sub>6,5</sub>	dip coating with 0.1 g/L polymer and 0.5 M NaCl	dense UF HF SPES membrane	crossflow filtration <i>Re</i> ~ 3800	32 chloride/sulfate selectivity 10.3 L·m <sup>-2</sup> ·h <sup>-1</sup> ·bar <sup>-1</sup>	135
(PDADMAC/PSS) <sub>7</sub>	dip coating with 0.1 g/L polymer and 0.05 M NaCl	dense UF HF SPES membrane	crossflow filtration <i>Re</i> ~ 3800	79% CaCl <sub>2</sub> rejection 15.6 L·m <sup>-2</sup> ·h <sup>-1</sup> ·bar <sup>-1</sup>	135
(PDADMAC/PSS) <sub>5,5</sub>	dip coating with 0.1 g/L polymer and 0.2 M NaCl	TFC NF membrane	crossflow filtration, 3.45 bar crossflow velocity 21.4 cm/s	71% NaCl and 96% Na <sub>2</sub> SO <sub>4</sub> rejection 8.48 L·m <sup>-2</sup> ·h <sup>-1</sup> ·bar <sup>-1</sup> 97% Mg <sup>2+</sup> rejection >30 Na <sup>+</sup> /Mg <sup>2+</sup> selectivity	119
(PDADMAC/PSS) <sub>4</sub>	dip coating with 0.1 g/L polymer and 0.2 M NaCl	PSf HF UF membrane	crossflow filtration, 6.9 bar crossflow velocity 21.4 cm/s	16.1 L·m <sup>-2</sup> ·h <sup>-1</sup> ·bar <sup>-1</sup> 90% emerging organic contaminants removal	150
(PDADMAC/PSS) <sub>8</sub>	dip coating with 0.1 g/L polymer, 0.05 M NaCl, and pH 6.0	PES UF membrane	crossflow filtration, 5 bar crossflow velocity 1.1 m/s	<20% scale forming ions passage excellent stability with 10.7 L·m <sup>-2</sup> ·h <sup>-1</sup> ·bar <sup>-1</sup> 95.5% MgSO <sub>4</sub> rejection	34
(PDADMAC/PSS) <sub>8</sub>	dip coating with 0.02 M polymer, 0.5 M NaCl	porous alumina (UF)	crossflow filtration, 4.8 bar pH 8.4 flow rate: 18 mL/min	279 g/mol MWCO after ~1600 h exposure to both 0.1 M HNO <sub>3</sub> and 0.1 M NaOH ~20.8 L·m <sup>-2</sup> ·h <sup>-1</sup> ·bar <sup>-1</sup> 98% phosphate rejection	27
PAH/PSS	cross-linked (PAH/PSS) <sub>s</sub> dynamic LbL coating with 1 g/L polymer, 0.5 M NaCl, pH ~ 7 and coating flux 30 L·m <sup>-2</sup> ·h <sup>-1</sup> ; 1 wt % GA solution filtrated at 2.5 bar for 2 h	tubular ceramic $\alpha$ -Al <sub>2</sub> O <sub>3</sub> MF membrane	crossflow filtration, 4 bar <i>Re</i> ~ 6000	48 chloride/phosphate selectivity MWCO 170 Da >90% NaCl rejection	151
(PSS/PAH) <sub>5</sub>	dip coating with 0.02 M PSS at 0.5 M NaCl and pH 2.3, and 0.02 M PAH at 1 M NaCl and pH 2.3	porous alumina (UF)	crossflow filtration, 4.8 bar flow rate: 18 mL/min	~7 L·m <sup>-2</sup> ·h <sup>-1</sup> ·bar <sup>-1</sup> 95% MgCl <sub>2</sub> rejection 22 Na <sup>+</sup> /Mg <sup>2+</sup> and 50 Na <sup>+</sup> /Ca <sup>2+</sup> selectivity	121
(PSS/PAH) <sub>7</sub>	dip coating with 0.02 M PSS at 0.5 M NaCl and pH 2.1, and 0.02 M PAH at 0.5 M NaCl and pH 2.3	porous alumina (UF)	crossflow filtration, 4.8 bar flow rate: 18 mL/min	~11.3 L·m <sup>-2</sup> ·h <sup>-1</sup> ·bar <sup>-1</sup> 50 glycine/L-glutamine selectivity	152
(PSS/PAH) <sub>4,5</sub>	dip coating with 0.02 M PSS at 0.5 M MnCl <sub>2</sub> and pH 2.1, and 0.02 M PAH at 0.5 M NaBr and pH 2.3	porous alumina (UF)	crossflow filtration, 4.8 bar, flow rate: 18 mL/min	99.4% sucrose and >99.9% reactive dyes rejection with small NaCl rejections (~29%)	153
(PSS/PAH) <sub>10</sub>	dip coating with 0.1 g/L polymer and 0.05 M NaCl; pH 5.5 for PSS and pH 2.0 for PAH	positively charged tight HF UF membrane	crossflow filtration, 6.2 bar crossflow velocity 1 m/s	9 L·m <sup>-2</sup> ·h <sup>-1</sup> ·bar <sup>-1</sup> >95% MgCl <sub>2</sub> rejection	154
(PAH/PSS) <sub>8</sub>	dip coating with 0.1 g/L polymer, 0.05 M NaCl, and pH 6.0	PES HF UF membrane	crossflow filtration, 5 bar crossflow velocity 1.1 m/s	267 g/mol MWCO excellent stability with 9.7 L·m <sup>-2</sup> ·h <sup>-1</sup> ·bar <sup>-1</sup> 97.5% MgSO <sub>4</sub> rejection	34
(PSS/PAH) <sub>8,5</sub>	dip coating with 20 mM polymer, 0.5 M NaCl; pH 6.5 for PSS and pH 3.0 for PAH	modified MF alumina	dead-end filtration other conditions not available	249 g/mol MWCO after ~1600 h exposure to 0.1 M HNO <sub>3</sub> 4.8 L·m <sup>-2</sup> ·h <sup>-1</sup> ·bar <sup>-1</sup> 50.5 1-butyl-3-methylimidazolium chloride/ cellulose selectivity	155
PAH/PAA	(PAH/PAA) <sub>6</sub> dip coating with 0.1 g/L polymer, 0.005 M NaNO <sub>3</sub> , pH 6	dense HF SPES membrane	crossflow filtration, 1.5 bar crossflow velocity 4.5 m/s	48–80% MPs retention with low salt rejection (~17% NaCl)	156
(PAH/PAA) <sub>15</sub>	dip coating with 0.1 g/L polymer, 0.005 M NaNO <sub>3</sub> , pH 6; annealed in 100 mM NaNO <sub>3</sub>	hydrolyzed PAN membrane	dead-end filtration, 2 bar flow rate: 1 mL/min	11.8 L·m <sup>-2</sup> ·h <sup>-1</sup> ·bar <sup>-1</sup> 69.8% HPO <sub>4</sub> <sup>2-</sup> rejection	157
(PAH/PAA) <sub>10,5</sub>	dip coating with 1 g/L polymer, 0.01 M NaCl, pH 6	PES UF membrane	crossflow filtration, 1.8 bar	3.6 L·m <sup>-2</sup> ·h <sup>-1</sup> ·bar <sup>-1</sup>	158

PEs	coating conditions	support	process conditions	performance	ref
PEI/PSS	(PSS/PEI) <sub>10</sub> dip coating with 0.1 g/L polymer and 0.05 M NaCl, and pH 5.5 for PSS and pH 2.0 for PEI	positively charged tight HF UF membrane	pH 2 crossflow filtration, 6.2 bar	44% Cu <sup>2+</sup> rejection	154
	(PSS/PEI) <sub>10</sub> spin-coated at 3000 rpm with 0.2 mL/s of 0.02 M polymer, 0.05 M NaCl, and pH 8.0		crossflow velocity 1 m/s	4 L·m <sup>-2</sup> ·h <sup>-1</sup> ·bar <sup>-1</sup> >95% Na <sub>2</sub> SO <sub>4</sub> rejection	
PAS/PSS	(PSS/PAS) <sub>10</sub> dip coating with 0.1 g/L polymer and 0.05 M NaCl; pH 5.5 for PSS and pH 2.0 for PAH	PSf UF membrane	crossflow filtration, 10 bar	239 g/mol MWCO	159
	(PAH/PVSA) <sub>8</sub> dynamic LbL coating with 1 g/L polymer, 0.5 M NaCl, pH ~7 and coating flux 30 L·m <sup>-2</sup> ·h <sup>-1</sup>	positively charged tight HF UF membrane	crossflow velocity 0.65 m/s	0.9 L·m <sup>-2</sup> ·h <sup>-1</sup> ·bar <sup>-1</sup> 94% MgCl <sub>2</sub> rejection	154
PAH/PVSA	(PAH/PVSA) <sub>8</sub> dynamic LbL coating with 1 g/L polymer, 0.5 M NaCl, pH ~7 and coating flux 30 L·m <sup>-2</sup> ·h <sup>-1</sup>	tubular ceramic $\alpha$ -Al <sub>2</sub> O <sub>3</sub> UF membrane	crossflow filtration, 6.2 bar	22 L·m <sup>-2</sup> ·h <sup>-1</sup> ·bar <sup>-1</sup> >95% Na <sub>2</sub> SO <sub>4</sub> rejection	151
PVA/PVS	(PAH/PVS) <sub>8</sub> dip coating with 0.01 M polymer, 1 M NaCl, pH 1.7	PAN/PET membrane	crossflow filtration, 4 bar	713 g/mol MWCO	160
PEI/PAA	cross-linked (PEI/PAA) <sub>5</sub> dynamic LbL coating with 3 g/L PEI and 0.6 g/L PAA; immersion in 3 wt % GA solution for 20 min	hydrolyzed PAN membrane	flow rate: 40 L/h	MWCO 115 Da Re ~ 6000 dead-end filtration, 5 bar 2.27 L·m <sup>-2</sup> ·h <sup>-1</sup> ·bar <sup>-1</sup> 95% MgCl <sub>2</sub> rejection	161

<sup>a</sup>HF: Hollow fiber. MF: Microfiltration. NF: Nanofiltration. Re: Reynolds number. TFC: Thin-film composite. UF: Ultrafiltration.

such PEM-coated membranes. The examples reported here highlight the large variety of possible applications of PEM-based membranes in the field of nanofiltration and, therefore, their significant potential for commercialization.

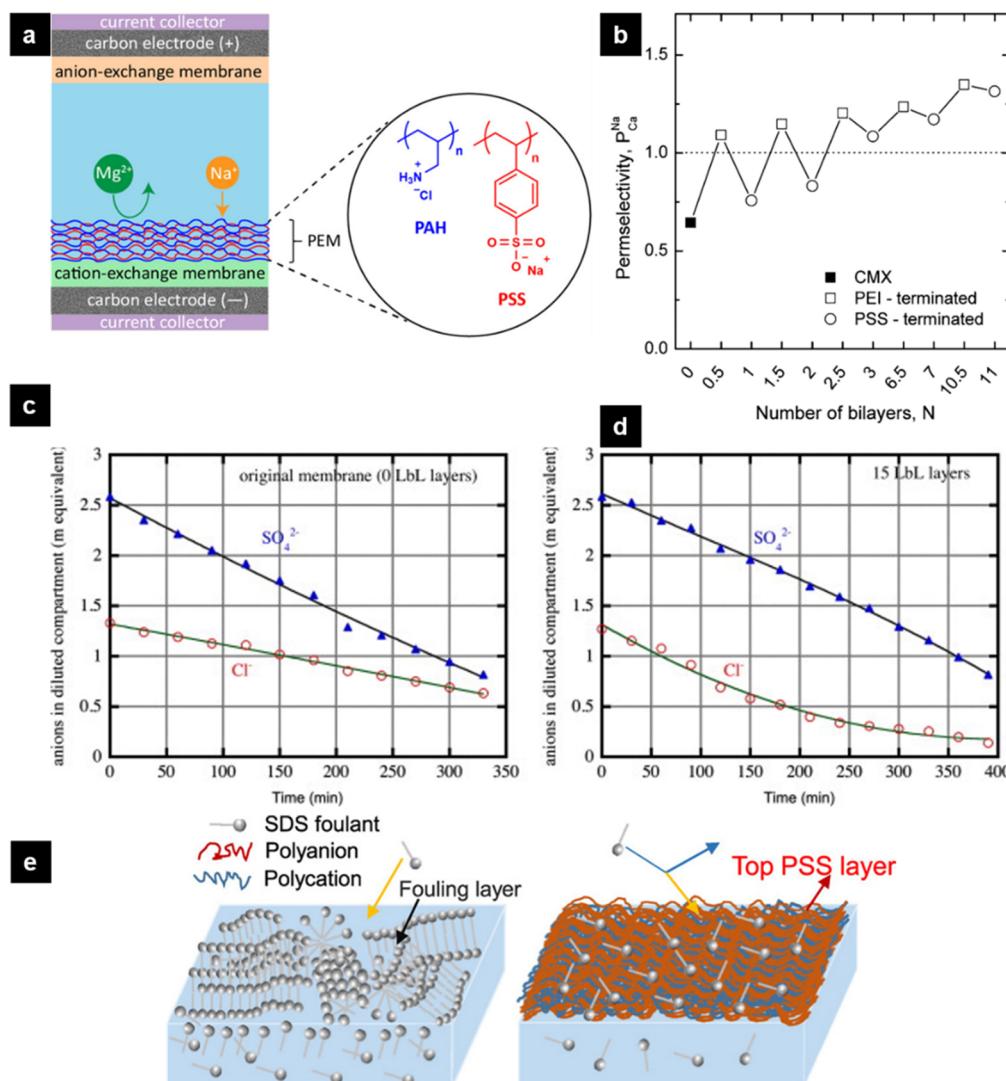
**3.2. Fouling Control.** One of the major challenges of any membrane filtration is the occurrence of membrane fouling. This phenomenon leads to an increase in operating costs<sup>162</sup> and the need for chemical cleaning of the membrane,<sup>163</sup> which in turn compromises the membrane stability and permeate quality over time.<sup>164</sup> As membrane fouling is a phenomenon that occurs at the water-membrane interface, membrane surface chemistry plays a crucial role in fouling.<sup>165</sup>

One of the main advantages of PEM coatings is the great deal of control over the membrane surface chemistry, which in turn helps to alleviate membrane fouling.<sup>166</sup> For example, Fadhillah et al. produced (PDADMAC/PSS)-based NF membranes with relatively high fouling resistance to protein filtration, presenting only a 10% decrease in permeation flux from its initial value (3.32 L·m<sup>-2</sup>·h<sup>-1</sup>·bar<sup>-1</sup>).<sup>167</sup> In addition, Virga et al. recently prepared PEM-based NF membranes with a zwitterionic poly(2-methacryloyloxyethyl phosphorylcholine-*co*-acrylic acid) (PMPC-*co*-AA) top layer to filtrate surface water with different contaminants (e.g., proteins, polysaccharides, colloidal nanoparticles, and humic acids).<sup>168</sup> These membranes with bioinspired zwitterionic phosphorylcholine coatings exhibit excellent fouling resistance (with a flux decline <5% of its original value, that is, 5.45 L·m<sup>-2</sup>·h<sup>-1</sup>·bar<sup>-1</sup>) and stable selectivity during filtration of surface water.

A different approach used to alleviate fouling focuses on the buildup of “sacrificial” multilayers based on PEs that can be removed, together with the fouling layer, to facilitate the membrane cleaning process,<sup>140,169</sup> as illustrated in Figure 4d. The PEM removal is triggered by a quick change in pH,<sup>169</sup> surfactant content,<sup>140</sup> or ionic strength<sup>131</sup> of the feedwater, allowing for organic fouling and biofouling control, both in spiral wound and hollow fiber membrane systems. Finally, the multilayer can be rebuilt on the membrane surface to restore its separation properties.

**3.3. Responsiveness.** Polyelectrolytes are also well-known to be used as building blocks for responsive<sup>116</sup> and self-healing<sup>170</sup> materials. Recently, Jiang et al. prepared pH-responsive (poly(methacrylic acid)/poly(alkyl methacrylate))<sub>n</sub> (PMAA/PAMA) multilayers with tunable interfacial properties,<sup>171</sup> while Xu et al. used block copolymer micelles (BCM) and hyaluronic acid (HA) biopolymers to develop temperature-responsive, hydrogen-bonded multilayers.<sup>172</sup> However, multilayers can also be salinity-responsive. Irigoyen et al. reported that polyelectrolyte multilayers based on (PDADMAC/PSS)<sub>n</sub> assembled at 3 M NaCl can reduce their thickness of 46% at low ionic strength, offering interesting applications such as controlled barrier for saline streams.<sup>173</sup> Lately, incorporating a zwitterionic polymer via LbL technique, de Groot et al. prepared (poly(sulfobetaine methacrylate) (PSBMA)/PDADMAC)<sub>n</sub> electrolyte-responsive membranes.<sup>174</sup> They observed an increase in membrane permeability of even more than 100% at 1.5 M NaCl, mostly due to the increased swelling of the zwitterionic layers at high salinity. Such responsiveness can potentially be used to facilitate the membrane backwash and, therefore, its cleaning.

**3.4. Stability.** Membranes are often used to treat challenging wastewaters, where the stability of traditional membranes can become compromised. PEMs allow the production of very stable membranes, which can go beyond



**Figure 5.** (a) Illustration of a PEM application on a standard cation-exchange membrane to achieve  $Na^+$ / $Mg^{2+}$  selectivity in capacitive deionization. PAH and PSS stand for poly(allylamine hydrochloride) and poly(styrenesulfonate), respectively. Reproduced with permission from ref 183. Copyright 2020 American Chemical Society. (b) Trend in permselectivity ( $P$ ) as a function of the type of the terminating layer. CMX and PEI stand for standard cation-exchange membrane and poly(ethylenimine), respectively. The empty squares represent the PEI-terminated and the empty circles represent the PSS-terminated multilayers. Reproduced with permission from ref 184. Copyright 2014 American Chemical Society. (c) Change in the anion concentration in time in the diluted compartments of the experiments with the bare membrane and (d) the membrane with 15 layers. (c and d) Reproduced with permission from ref 185. Copyright 2013 Elsevier. (e) Comparison of the bare (left) and the PEM-coated (right) membranes for SDS (sodium dodecyl sulfate) fouling. Reproduced with permission from ref 186. Copyright 2018 Elsevier.

that of commercial alternatives. Researchers have investigated different polyelectrolyte chemistries and stabilization strategies, including chemical cross-linking, to prepare stable PEM-coated membranes that can withstand challenging filtration conditions where the presence of organic solvents,<sup>31</sup> extreme pH conditions,<sup>34</sup> and high salinity<sup>175</sup> make difficult the application of commercial membranes.

In particular, Li et al. showed that hydrolyzed polyacrylonitrile supports coated with a sulfonated poly(ether ether ketone) (SPEEK/PDADMAC)<sub>n</sub> multilayer to be very promising and stable for the filtration of challenging aprotic organic solvents, such as THF and DMF.<sup>176</sup> Elshof et al. demonstrated how (PDADMAC/PSS)<sub>n</sub>-based NF poly(ether sulfone) membranes show excellent and stable performances even under long-term exposure to extreme pH conditions, that is, 1 M  $HNO_3$  ( $pH \approx 0$ ) and 1 M  $NaOH$  ( $pH \approx 14$ ).<sup>34</sup> Even after more than two months of exposure, the membrane perform-

ance was still stable, with a pure water permeability of  $10.7 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ , 95.5%  $MgSO_4$  retention and molecular weight cutoff of  $279 \text{ g} \cdot \text{mol}^{-1}$ . Furthermore, as cleaning processes can also affect the stability of the membranes, different researchers have demonstrated that PEMs based on strong polyelectrolytes, such as PDADMAC and PSS, can withstand physical (e.g., backwash)<sup>32,177</sup> and chemical (via hypochlorite)<sup>32</sup> cleaning.

When weak polyelectrolytes are used to build the multilayer<sup>131</sup> or when the wastewater to treat contains small, charged molecules (like surfactants),<sup>178</sup> PEM-based membranes can suffer from stability issues. In these cases, the stability of PEM membranes can be further increased via covalent cross-linking.<sup>151,175,179,180</sup> PAH/PSS-coated poly(ether sulfone) membranes, stabilized via chemical cross-linking, can for example be used to successfully treat

Table 2. Commonly Used Ion Selectivity Definitions in the Literature

symbol	equation	description
$P_j^{184}$ or $S_j^{190}$	$\frac{J_i \cdot c_j}{J_j \cdot c_i}$	$J_i$ and $J_j$ are the flux (in $\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ ) of the target and competing ions, respectively. $c_i$ and $c_j$ (in mol/L) are the concentrations of the target and the competing ion on the dilute side, respectively.
$F_j^{188,a}$	$\frac{J_i}{J_j}$	$J_i$ and $J_j$ are the flux (in $\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ ) of the target and competing ions, respectively, when the source phase contains equal concentrations of the target and the competing ions.
$\rho_j^{i183}$ or $\beta_j^{197}$	$\frac{(c_{i,0} - c_{i,f})}{(c_{j,0} - c_{j,f})}$	$c_{i,0}$ and $c_{i,f}$ are initial and final concentrations of the target ion. $c_{j,0}$ and $c_{j,f}$ are initial and final concentrations of the competing ion.
$R_j^{190}$	$\frac{R_j}{R_i}$	$R_i$ and $R_j$ are the resistance (in $\Omega \cdot \text{cm}^2$ ) of the target and the competing ion, respectively.

<sup>a</sup>In literature, there is no symbol used for this type of selectivity; here, we introduce  $F$  for matters of clarity.

challenging wastewaters containing surfactants, such as produced water.<sup>181</sup>

#### 4. POLYELECTROLYTE MULTILAYERS ON DENSE MEMBRANES

Similar to the formation of PEMs on porous supports, PEMs have also been built on dense membranes such as reverse osmosis membranes (ROMs) and various ion-exchange membranes (IEMs), including cation-exchange (CEM), anion-exchange (AEM), Nafion, and bipolar membranes (BPMs). Although such dense membranes are already designed to be selective for a certain type of ions (IEMs) and/or show size-based exclusion properties,<sup>182</sup> incorporation of PEMs can further tune their selectivity or impart other desired functionalities.<sup>36</sup>

**4.1. Specific Selectivity.** Following the successes of PEM coatings on porous supports, one of the most common applications of PEM-coated dense membranes is tuning the ion selectivity of IEMs in desalination processes. Figure 5a demonstrates the main mechanism to achieve monovalent/divalent cation selectivity via PEM-coated dense membranes. The alternating adsorption of PAH and PSS on a standard cation-exchange membrane can tune the monovalent cation selectivity in desalination. In 2014, Abdu et al. modified a standard-grade CEM (CMX) with an LbL assembly of PEI and PSS and implemented the PEM-coated membrane in an electrodialysis (ED) system.<sup>184</sup> The (PEI/PSS)<sub>n</sub> coating resulted in a higher  $\text{Ca}^{2+}$  rejection compared to the pristine CMX and moderate increase in ohmic resistance (PEM-CMX = 60.06  $\Omega \cdot \text{cm}^2$ , CMX = 45.25  $\Omega \cdot \text{cm}^2$ ) Figure 5b and 5c depict the change the chloride concentration in the diluted compartments for the bare and PEM-coated anion-exchange membranes. In case of PEM-coated AMX, the chloride concentration is lower than the one with bare AMX, meaning an increase in chloride over sulfate selectivity. Therefore, the addition of a PEM is a feasible way of introducing selectivity in ED. Furthermore, the terminating layer makes a small but distinct difference in selectivity: PEI-terminated layers demonstrated higher  $\text{Na}^+/\text{Ca}^{2+}$  selectivity values compared to the PSS-terminated layers (~18% increase). The selectivity was rationalized by the charge exclusion of divalent cations and the higher hydrophobicity of the PEI-terminated CMX. 6.5 bilayers of PEI/PSS were enough to reach a permselectivity value ( $P_{\text{Ca}}^{\text{Na}}$ ) of 1.24, which is comparable with the commercial monovalent cation-selective membrane (CMS)  $P_{\text{Ca}}^{\text{Na}} = 1.23$ . Also, PEM-CMX required ~50 Wh/mol  $\text{Na}^+$  while CMS

required ~80 Wh/mol  $\text{Na}^+$ , meaning that similar selectivity values can be achieved with a lower energy consumption value by using PEM-coated CMX. In another ED study, White et al. implemented (PSS/PAH)<sub>n</sub> layers on a Nafion 115 membrane and obtained  $\text{K}^+/\text{Mg}^{2+}$  selectivity as high as >1000.<sup>187</sup> In 2016, White et al. coated (PAH/PSS)<sub>5,5</sub> on Nafion 117 to achieve  $\text{Li}^+/\text{Co}^{2+}$  and  $\text{K}^+/\text{La}^{3+}$  selectivities in ED.<sup>188</sup> Compared to the mono/divalent cation selectivity of bare Nafion (<2), they reported  $\text{Li}^+/\text{Co}^{2+}$  and  $\text{K}^+/\text{La}^{3+}$  selectivities exceeding 1000. Yang et al. used the same approach in Donnan dialysis with (PAH/PSS)<sub>5,5</sub>-coated Nafion 115 membrane to differentiate within the monovalent cations and reached  $\text{K}^+/\text{Li}^+$  selectivity values between 8 and 60,<sup>78</sup> although later the authors reported lower selectivities due to variations in different batches of the Nafion membranes.<sup>189</sup> The selectivity was attributed to the larger hydrated radius of  $\text{Li}^+$  that resulted in a lower diffusion coefficient through the dense PEM layer. Besides, a pH-induced swelling resulted in a further increase of the  $\text{K}^+/\text{Li}^+$  selectivity, which was believed to be related to an increased accessibility of cation-exchange sites within the PEM at lower pH. In 2019, Rijnaarts et al. further investigated the mechanism of monovalent cation selectivity in ED and explained that after 8 layers of PAH/PSS the multilayer starts to have excess of PAH in the multilayer.<sup>190</sup> The overall positive charge, due to excess PAH, increased with higher number of layers, resulting in increased charge-exclusion toward divalent cations. Sahin et al. reported a similar observation where bare CMX demonstrated selectivity to  $\text{Mg}^{2+}$ , while the addition of a PEM resulted in a  $\text{Na}^+/\text{Mg}^{2+}$  selectivity of ~3 in a capacitive deionization (CDI) system due to the charge-exclusion effect of the PEM toward  $\text{Mg}^{2+}$  ions.<sup>183</sup> The positively charged PEM rejected the  $\text{Mg}^{2+}$  more than  $\text{Na}^+$ , resulting in monovalent cation selectivity.

PEMs were also coated on AEMs to achieve mono-/divalent anion selectivity in multiple studies, including ED,<sup>185,191</sup> reverse ED,<sup>192</sup> dialysis,<sup>193</sup> and CDI.<sup>194</sup> For instance, Mulyati et al. used (PAH/PSS)<sub>7,5</sub> on a standard-grade AEM (Neosepta, AMX) and achieved  $\text{Cl}^-/\text{SO}_4^{2-}$  selectivity in ED<sup>185</sup> (Figure 5c and 5d). Recently,  $\text{Cl}^-/\text{SO}_4^{2-}$  selectivity between 7 and 14 was reported by using PDADMAC/PSS-coated AEM in CDI.<sup>194</sup> The authors reported that  $\text{Cl}^-$  selectivity was preserved even at low concentrations of  $\text{Cl}^-$  in the solution. Additionally, recent studies reported on the use of biodegradable polyelectrolytes (for example, 2-hydroxypropyltrimethylammonium chloride chitosan, HACC<sup>191,195,196</sup> and *N*-O-sulfonic acid benzyl chitosan, NSBC<sup>196</sup>) as alternatives for synthetic polyelectro-

Table 3. Overview of Selectivity Values and Experimental Details of the Reported Studies Towards Mono/Divalent Cations<sup>a</sup>

entry	PEM/membrane	no. layers	method	conditions	flux (nmol·cm <sup>-2</sup> ·s <sup>-1</sup> )	selectivity	ref
1	PEI/PSS on CMX	21	ED	CC, 15 mA/cm <sup>2</sup> , 0.05 M NaCl and 0.05 M CaCl <sub>2</sub>	Ca <sup>2+</sup> : 44.0 Na <sup>+</sup> : 60.1	$P_{\text{Ca}}^{\text{Na}} = 1.35$	184
2	CMX	bare	ED	CC, 15 mA/cm <sup>2</sup> , 0.05 M NaCl and 0.05 M CaCl <sub>2</sub>	Ca <sup>2+</sup> : 64.5 Na <sup>+</sup> : 40.3	$P_{\text{Ca}}^{\text{Na}} = 0.64$	184
3	CSO	bare	ED	CC, 15 mA/cm <sup>2</sup> , 0.05 M NaCl and 0.05 M CaCl <sub>2</sub>	Ca <sup>2+</sup> : 35.2 Na <sup>+</sup> : 60.8	$P_{\text{Ca}}^{\text{Na}} = 1.72$	184
4	CMS	bare	ED	CC, 15 mA/cm <sup>2</sup> , 0.05 M NaCl and 0.05 M CaCl <sub>2</sub>	Ca <sup>2+</sup> : 41.8 Na <sup>+</sup> : 53.1	$P_{\text{Ca}}^{\text{Na}} = 1.23$	184
5	PSS/PAH on Nafion 115	11	ED	CC, 1.27 mA/cm <sup>2</sup> , 0.01 M KNO <sub>3</sub> and 0.01 M Mg (NO <sub>3</sub> ) <sub>2</sub>	K <sup>+</sup> : 6.9 ± 0.2 Mg <sup>2+</sup> : <0.005	$F_{\text{Mg}}^{\text{K}} > 1000$	187
6	PSS/PAH on Nafion 115	11	ED	CC, 2.54 mA/cm <sup>2</sup> , 0.01 M KNO <sub>3</sub> and 0.01 M Mg (NO <sub>3</sub> ) <sub>2</sub>	K <sup>+</sup> : 6.28 ± 0.58 Mg <sup>2+</sup> : 0.318	$F_{\text{Mg}}^{\text{K}} = 22.1 \pm 3.5$	187
7	PSS/PAH on Nafion 115 (1-side)	11	ED	CC, 2.54 mA/cm <sup>2</sup> , 0.01 M KNO <sub>3</sub> and 0.01 M Mg (NO <sub>3</sub> ) <sub>2</sub>	ND	$F_{\text{Mg}}^{\text{K}} = 10.0 \pm 3.8$	187
8	PSS/PAH on Nafion 115	11	ED	CC, 2.54 mA/cm <sup>2</sup> , 0.02 M KNO <sub>3</sub> and 0.02 M Mg (NO <sub>3</sub> ) <sub>2</sub>	K <sup>+</sup> : 13.5 ± 0.6 Mg <sup>2+</sup> : 0.149	$F_{\text{Mg}}^{\text{K}} = 96 \pm 26$	187
9	PSS/PAH on Nafion 115	11	ED	CC, 2.54 mA/cm <sup>2</sup> , 0.1 M KNO <sub>3</sub> and 0.1 M Mg (NO <sub>3</sub> ) <sub>2</sub>	K <sup>+</sup> : 25.2 ± 1.6 Mg <sup>2+</sup> : < 0.001	$F_{\text{Mg}}^{\text{K}} > 20\,000$	187
10	Nafion 115	bare	ED	CC, 1.27 mA/cm <sup>2</sup> , 0.01 M KNO <sub>3</sub> and 0.01 M Mg (NO <sub>3</sub> ) <sub>2</sub>	K <sup>+</sup> : 6.4 ± 0.3 Mg <sup>2+</sup> : 3.6 ± 0.1	$F_{\text{Mg}}^{\text{K}} = 1.8 \pm 0.1$	187
11	PSS/PAH on Nafion 117	11	ED	CC, 0.63 mA/cm <sup>2</sup> , 0.01 M LiNO <sub>3</sub> and 0.01 M Co (NO <sub>3</sub> ) <sub>2</sub>	Li <sup>+</sup> : 2.95 ± 0.2 Co <sup>2+</sup> : 1.29 ± 0.51 (pmol·cm <sup>-2</sup> ·s <sup>-1</sup> )	$F_{\text{Co}}^{\text{Li}} > 1600$	188
12	PSS/PAH on Nafion 117	11	ED	CC, 0.63 mA/cm <sup>2</sup> , 0.02 M LiNO <sub>3</sub> and 0.02 M Co (NO <sub>3</sub> ) <sub>2</sub>	Li <sup>+</sup> : 3.18 ± 0.3 Co <sup>2+</sup> : 2.55 ± 1.71 (pmol·cm <sup>-2</sup> ·s <sup>-1</sup> )	$F_{\text{Co}}^{\text{Li}} > 360$	188
13	PSS/PAH on Nafion 117	11	ED	CC, 0.63 mA/cm <sup>2</sup> , 0.1 M LiNO <sub>3</sub> and 0.1 M Co (NO <sub>3</sub> ) <sub>2</sub>	Li <sup>+</sup> : 6.79 ± 0.18 Co <sup>2+</sup> : < 1 (pmol·cm <sup>-2</sup> ·s <sup>-1</sup> )	$F_{\text{Co}}^{\text{Li}} > 6500$	188
14	PSS/PAH on Nafion 117	4	ED	CC, 0.63 mA/cm <sup>2</sup> , 0.01 M LiNO <sub>3</sub> and 0.01 M Co (NO <sub>3</sub> ) <sub>2</sub>	Li <sup>+</sup> : 2.39 ± 0.10 Co <sup>2+</sup> : 3.85 ± 2.49 (pmol·cm <sup>-2</sup> ·s <sup>-1</sup> )	$F_{\text{Co}}^{\text{Li}} > 430$	188
15	PSS/PAH on Nafion 117	3	ED	CC, 0.63 mA/cm <sup>2</sup> , 0.01 M LiNO <sub>3</sub> and 0.01 M Co (NO <sub>3</sub> ) <sub>2</sub>	Li <sup>+</sup> : 1.62 ± 0.10 Co <sup>2+</sup> : 37.3 ± 25.5 (pmol·cm <sup>-2</sup> ·s <sup>-1</sup> )	$F_{\text{Co}}^{\text{Li}} > 23$	188
16	PSS/PAH on Nafion 117	11	ED	CC, 0.63 mA/cm <sup>2</sup> , 0.01 M K(OAc) and 0.01 M La (OAc) <sub>3</sub>	K <sup>+</sup> : 0.46 ± 0.27 La <sup>3+</sup> : 1.58 ± 1.00 (pmol·cm <sup>-2</sup> ·s <sup>-1</sup> )	$F_{\text{La}}^{\text{K}} > 93$	188
17	PSS/PAH on Nafion 117	11	ED	CC, 0.63 mA/cm <sup>2</sup> , 0.02 M K(OAc) and 0.02 M La (OAc) <sub>3</sub>	K <sup>+</sup> : 4.40 ± 0.02 La <sup>3+</sup> : 1.27 ± 0.46 (pmol·cm <sup>-2</sup> ·s <sup>-1</sup> )	$F_{\text{La}}^{\text{K}} > 2400$	188
18	PSS/PAH on Nafion 117	11	ED	CC, 0.63 mA/cm <sup>2</sup> , 0.1 M K(OAc) and 0.1 M La (OAc) <sub>3</sub>	K <sup>+</sup> : 7.85 ± 0.69 La <sup>3+</sup> : < 1 (pmol·cm <sup>-2</sup> ·s <sup>-1</sup> )	$F_{\text{La}}^{\text{K}} > 7000$	188
19	Nafion 117	bare	ED	CC, 0.63 mA/cm <sup>2</sup> , 0.01 M LiNO <sub>3</sub> and 0.01 M Co (NO <sub>3</sub> ) <sub>2</sub>	Li <sup>+</sup> : 1.9 ± 0.4 Co <sup>2+</sup> : 3.0 ± 0.7	$F_{\text{Co}}^{\text{Li}} = 0.66 \pm 0.08$	188
20	Nafion 117	bare	ED	CC, 0.63 mA/cm <sup>2</sup> , 0.01 M K(OAc) and 0.01 M La (OAc) <sub>3</sub>	ND	$F_{\text{La}}^{\text{K}} = 1.61 \pm 0.26$	188
21	PSS/PAH on Nafion 115	11	DD	0.01 M KNO <sub>3</sub> and 0.01 M LiNO <sub>3</sub> + 0.01 M HNO <sub>3</sub> in RP	K <sup>+</sup> : 2.01 ± 0.21 Li <sup>+</sup> : 0.039 ± 0.013	up to $F_{\text{Li}}^{\text{K}} = 57 \pm 22$	78, 189
22	PSS/PAH on Nafion 115	11	DD	0.02 M KNO <sub>3</sub> and 0.02 M LiNO <sub>3</sub> + 0.01 M HNO <sub>3</sub> in RP	K <sup>+</sup> : 2.83 ± 0.31 Li <sup>+</sup> : 0.035 ± 0.003	$F_{\text{Li}}^{\text{K}} = 80 \pm 9$	78
23	PSS/PAH on Nafion 115	11	DD	0.1 M KNO <sub>3</sub> and 0.1 M LiNO <sub>3</sub> + 0.01 M HNO <sub>3</sub> in RP	K <sup>+</sup> : 5.28 ± 0.69 Li <sup>+</sup> : 0.25 ± 0.05	$F_{\text{Li}}^{\text{K}} = 38 \pm 13$	78
24	PSS/PAH on Nafion 115	11	DD	0.01 M KNO <sub>3</sub> and 0.01 M LiNO <sub>3</sub> + 0.02 M HNO <sub>3</sub> in RP	K <sup>+</sup> : 0.35 ± 0.06 Li <sup>+</sup> : 0.047 ± 0.010	$F_{\text{Li}}^{\text{K}} = 8.3 \pm 1.8$	78
25	Nafion 115	bare	DD	0.01 M KNO <sub>3</sub> and 0.01 M LiNO <sub>3</sub> + 0.02 M HNO <sub>3</sub> in RP	K <sup>+</sup> : 4.97 ± 0.44 Li <sup>+</sup> : 3.03 ± 0.36	$F_{\text{Li}}^{\text{K}} = 1.7 \pm 0.3$	78
26	PSS/PAH on Nafion 115	11	ED	CC, 0.64 mA/cm <sup>2</sup> , 0.01 M KNO <sub>3</sub> and 0.01 M LiNO <sub>3</sub> + 0.01 M HNO <sub>3</sub> in RP	K <sup>+</sup> : 2.99 ± 0.13 Li <sup>+</sup> : 1.33 ± 0.03	$F_{\text{Li}}^{\text{K}} = 2.3 \pm 0.1$	78
27	Nafion 115	bare	ED	CC, 0.64 mA/cm <sup>2</sup> , 0.01 M KNO <sub>3</sub> and 0.01 M LiNO <sub>3</sub> + 0.01 M HNO <sub>3</sub> in RP	K <sup>+</sup> : 5.56 ± 0.81 Li <sup>+</sup> : 4.19 ± 0.38	$F_{\text{Li}}^{\text{K}} = 1.3 \pm 0.1$	78

Table 3. continued

entry	PEM/membrane	no. layers	method	conditions	flux (nmol·cm <sup>-2</sup> ·s <sup>-1</sup> )	selectivity	ref
28	PAH/PSS on CMX (recipe 1)	11	RM	0.5 M NaCl, 0.5 M MgCl <sub>2</sub>	ND	$R_{\text{Mg}}^{\text{Na}} = 5.7$	190
29	PAH/PSS on CMX (recipe 1)	21	RM	0.5 M NaCl, 0.5 M MgCl <sub>2</sub>	ND	$R_{\text{Mg}}^{\text{Na}} = 5.8$	190
30	PAH/PSS on CMX (recipe 2)	11	RM	0.5 M NaCl, 0.5 M MgCl <sub>2</sub>	ND	$R_{\text{Mg}}^{\text{Na}} = 7.8$	190
31	CSO	bare	RM	0.5 M NaCl, 0.5 M MgCl <sub>2</sub>	ND	$R_{\text{Mg}}^{\text{Na}} = 6.9$	190
32	CMX	bare	RM	0.5 M NaCl, 0.5 M MgCl <sub>2</sub>	ND	$R_{\text{Mg}}^{\text{Na}} = 3.5$	190
33	PAH/PSS on CMX (recipe 2)	11	ED	CV, 3.5 V, 25 mM NaCl and 10 mM MgCl <sub>2</sub>	$\text{Na}^+ \approx 3.5 \times 10^4$ $\text{Mg}^{2+} \approx 0.5 \times 10^{4b}$	$P_{\text{Mg}}^{\text{Na}} = 1.7$	190
34	CMX	bare	ED	CV, 3.5 V, 25 mM NaCl and 10 mM MgCl <sub>2</sub>	$\text{Na}^+ \approx 2 \times 10^4$ $\text{Mg}^{2+} \approx 1.5 \times 10^{4b}$	$P_{\text{Mg}}^{\text{Na}} = 0.5$	190
35	PAH/PSS on CMX	11	MCDI	CV, 0–1 V, 4 mM NaCl, 4 mM MgCl <sub>2</sub>	ND	$\beta_{\text{Mg}}^{\text{Na}} = 2.8 \pm 0.2$	183
36	CMX	bare	MCDI	CV, 0–1 V, 4 mM NaCl, 4 mM MgCl <sub>2</sub>	ND	$\beta_{\text{Mg}}^{\text{Na}} = 0.5 \pm 0.04$	183
37	CMS	bare	MCDI	CV, 0–1 V, 4 mM NaCl, 4 mM MgCl <sub>2</sub>	ND	$\beta_{\text{Mg}}^{\text{Na}} = 0.4 \pm 0.1$	183

<sup>a</sup>ED: Electrodialysis. DD: Diffusion dialysis. RM: Resistance measurement. MCDI: Membrane capacitive deionization. RP: Receiving phase. CC and CV represent a desalination process with constant current or constant voltage, respectively. <sup>b</sup>Estimated from the graphs reported in the cited references.

lytes. Upon the addition of the resulting PEMs, the Cl<sup>−</sup>/SO<sub>4</sub><sup>2−</sup> selectivity increased.

So far, multiple ion selectivity definitions have been used by various research groups, which often limits the possibility to directly compare reported selectivity values. The most common selectivity definitions are listed in Table 2.

There are several factors that may affect the ion selectivity of a PEM-modified membrane during desalination operations. Therefore, we summarized cation and anion selectivity studies in Tables 3 and 4, respectively, to understand the effects of these factors on selectivity. For each selectivity value of a modified or bare membrane, the number of layers in the PEM, the desalination method and the operational conditions, as well as the flux values (if applicable) are listed. Standard-grade AEMs and CEMs (i.e., Fujifilm type 1 AEM and CEM, Neosepta CSE and ASE, and CJMA-2 standard CEM from Hefei Chemjoy Polymer Material) were abbreviated as CMX and AMX in Tables 3 and 4, respectively. Special-grade cation-exchange membranes (CSO (Selemion) and CMS (Neosepta)), as well as anion-exchange membranes (ASV (Selemion) and ACS (Neosepta)), were added in the tables for comparison, as they are commercially available monovalent ion selective membranes.

As stated above, building PEMs on dense membranes improves their mono-/divalent ion selectivities. The terminating layer has a major effect on monovalent ion selectivity since the main mechanism of selectivity is the charge exclusion of divalent ions. As can be seen in multiple entries of Table 3 (i.e., 1, 5–9, 11–13), the terminating layer needs to be the polycation in order to achieve monovalent cation selectivity. Similarly, the terminating layer should be the polyanion to achieve monovalent anion selectivity as shown in multiple entries (i.e., 1, 3, 5–7, 9–12, 14) in Table 4. In entry 10 of Table 3, bare Nafion 115 shows  $F_{\text{Mg}}^{\text{K}} \approx 2$  selectivity and by using the same conditions,  $F_{\text{Mg}}^{\text{K}} > 1000$  was achieved with PEM-coated Nafion 115. In an anion selectivity study (entries 1 and 2 of Table 4), a similar switch can be observed. Since the bare CMX and AMX have fixed negative and positive charges, respectively, divalent cations interact more with CMX, while AMX shows affinity toward divalent anions. Another important parameter for tuning ion selectivity is the number of layers in the PEM, as the increased charge density and thickness of the

PEM can further increase the rejection of divalent ions. For instance, by increasing the number of PE layers from 3 to 11,  $F_{\text{Co}}^{\text{Li}}$  increased from >23 to >6500 (in entries 13–15 of Table 3). The effect of the number of layers on anion selectivity can be seen, for example, in entries 39–42 of Table 4, where the rejection of SO<sub>4</sub><sup>2−</sup> with 5 layers was reduced by a factor of ~2 with 15 layers of PEs. However, increasing the number of layers to 23 did not improve the Cl<sup>−</sup> selectivity further. As explained in detail<sup>36,198</sup> and demonstrated in numerous studies,<sup>183,185,190,194</sup> the overcompensation of charge by the polycation can result in an excess of positive charges in the PEM. While, in case of monovalent cation selectivity, this is a desired effect, an overall positive charge can reduce the rejection of divalent anions and therefore result in a lower mono/divalent anion selectivity. The examples show that the type and the amount of charge of the PEM and the valence of ions can determine the affinity of the PEM toward ions. Next to the effect of charge (type and valency), also the hydration energy of ions is a key factor in selectivity. For instance, K<sup>+</sup>/Li<sup>+</sup> (entry 21, Table 3), NO<sub>3</sub><sup>−</sup>/Cl<sup>−</sup> and H<sub>2</sub>PO<sub>4</sub><sup>−</sup> (entries 46 and 47, Table 4) selectivities can be explained by the differences in the hydration energy values. To be specific, ions with a smaller hydration energy will pass through the PEM-coated membranes more easily.

Moreover, the coating procedure of the PEMs can have a significant effect on the selectivity value. For instance, in entries 28 and 30 of Table 3, the only difference in between the experiments was the recipe for preparing the coating. In recipe 1 (entry 28) has a 15 min rinsing step with 0.5 M NaCl, while in recipe 2 (entry 30), the rinsing step (1 min) is with demineralized water. Faster rinsing steps with demineralized water causes a higher intrinsic charge compensation between the PEs, resulting in a denser and less hydrated PEM. Therefore, with recipe 2, a less hydrated PEM can be established and a higher selectivity value ( $R_{\text{Mg}}^{\text{Na}} = 7.8$ ) was achieved compared to the PEM prepared with recipe 1 ( $R_{\text{Mg}}^{\text{Na}} = 5.7$ ). The degree of hydration in PEMs can also be tuned by cross-linking as shown in an anion separation study, which can be explained by two factors. First, cross-linking causes more compact PEMs that increases the rejection larger ions. Second, the sulfonate groups of the cross-linking agent increase the amount of negative charge within the PEM, resulting in a

Table 4. Overview of Selectivity Values and Experimental Details of the Reported Studies Towards Mono-/Divalent Anions<sup>a</sup>

entry	PEM/membrane	no. layers	method	conditions	flux (nmol·cm <sup>-2</sup> ·s <sup>-1</sup> )	selectivity	ref
1	PSS/PAH on AMX	15	ED	CC, 2 mA/cm <sup>2</sup> , 0.01 M NaCl, 0.01 M Na <sub>2</sub> SO <sub>4</sub>	ND	$P_{SO_4}^{Cl} \approx 2.5^b$	185
2	AMX	bare	ED	CC, 2 mA/cm <sup>2</sup> , 0.01 M NaCl, 0.01 M Na <sub>2</sub> SO <sub>4</sub>	ND	$P_{SO_4}^{Cl} \approx 0.8^b$	185
3	PSS-MA and HACC (cross-linked)	15	ED	CC 15 mA/cm <sup>2</sup> , 50 mM NaCl and 50 mM Na <sub>2</sub> SO <sub>4</sub>	ND	$P_{SO_4}^{Cl} = 4.81$	191
4	AMX	bare	ED	CC 15 mA/cm <sup>2</sup> , 50 mM NaCl and 50 mM Na <sub>2</sub> SO <sub>4</sub>	ND	$P_{SO_4}^{Cl} = 0.81$	191
5	PSS/HACC on AMX	18	ED	CC, 5 mA/cm <sup>2</sup> , 0.02 M NaCl and 0.02 M Na <sub>2</sub> SO <sub>4</sub>	ND	$P_{SO_4}^{Cl} = 2.9$	200
6	PSS/HACC on AMX	14	ED	CC, 5 mA/cm <sup>2</sup> , 0.02 M NaCl and 0.02 M Na <sub>2</sub> SO <sub>4</sub>	ND	$P_{SO_4}^{Cl} \approx 2^b$	200
7	PSS/HACC on AMX	6	ED	CC, 5 mA/cm <sup>2</sup> , 0.02 M NaCl and 0.02 M Na <sub>2</sub> SO <sub>4</sub>	ND	$P_{SO_4}^{Cl} \approx 1.5^b$	200
8	AMX	bare	ED	CC, 5 mA/cm <sup>2</sup> , 0.02 M NaCl and 0.02 M Na <sub>2</sub> SO <sub>4</sub>	ND	$P_{SO_4}^{Cl} = 0.66$	200
9	PSS/HACC on AMX + cross-linked	17	ED	CC, 5 mA/cm <sup>2</sup> , 0.05 M NaCl and 0.05 M Na <sub>2</sub> SO <sub>4</sub>	ND	$P_{SO_4}^{Cl} \approx 3.8^b$	195
10	PSS/HACC on AMX + cross-linked	11	ED	CC, 5 mA/cm <sup>2</sup> , 0.05 M NaCl and 0.05 M Na <sub>2</sub> SO <sub>4</sub>	ND	$P_{SO_4}^{Cl} = 4.36 \pm 0.13$	195
11	PSS/HACC on AMX + cross-linked	5	ED	CC, 5 mA/cm <sup>2</sup> , 0.05 M NaCl and 0.05 M Na <sub>2</sub> SO <sub>4</sub>	ND	$P_{SO_4}^{Cl} \approx 1.5^b$	195
12	PSS/HACC on AMX	11	ED	CC, 5 mA/cm <sup>2</sup> , 0.05 M NaCl and 0.05 M Na <sub>2</sub> SO <sub>4</sub>	ND	$P_{SO_4}^{Cl} \approx 2.1^b$	195
13	AMX	bare	ED	CC, 5 mA/cm <sup>2</sup> , 0.05 M NaCl and 0.05 M Na <sub>2</sub> SO <sub>4</sub>	ND	$P_{SO_4}^{Cl} = 0.39 \pm 0.06$	195
14	NSBC/HACC on AMX	15	ED	CC, 10 mA/cm <sup>2</sup> , 0.05 M NaCl and 0.05 M Na <sub>2</sub> SO <sub>4</sub>	ND	$P_{SO_4}^{Cl} = 47.04$	196
15	AMX	bare	ED	CC, 10 mA/cm <sup>2</sup> , 0.05 M NaCl and 0.05 M Na <sub>2</sub> SO <sub>4</sub>	ND	$P_{SO_4}^{Cl} = 0.81$	196
16	ACS	bare	ED	CC, 10 mA/cm <sup>2</sup> , 0.05 M NaCl and 0.05 M Na <sub>2</sub> SO <sub>4</sub>	ND	$P_{SO_4}^{Cl} = 13.6$	196
17	ASV	bare	ED	CC, 10 mA/cm <sup>2</sup> , 0.05 M NaCl and 0.05 M Na <sub>2</sub> SO <sub>4</sub>	ND	$P_{SO_4}^{Cl} = 22.3$	196
18	PSS/PEI on CMX	11	RED	CC, 4.0 mA/cm <sup>2</sup> , 0.05 M NaCl and 0.05 M Na <sub>2</sub> SO <sub>4</sub>	Cl <sup>-</sup> : 106.5 SO <sub>4</sub> <sup>2-</sup> : 50.1	$P_{SO_4}^{Cl} = 1.67$	192
19	PSS/PEI on CMX	15	RED	CC, 4.0 mA/cm <sup>2</sup> , 0.05 M NaCl and 0.05 M Na <sub>2</sub> SO <sub>4</sub>	Cl <sup>-</sup> : 106.0 SO <sub>4</sub> <sup>2-</sup> : 43.3	$P_{SO_4}^{Cl} = 2.44$	192
20	PSS/PEI on CMX	21	RED	CC, 4.0 mA/cm <sup>2</sup> , 0.05 M NaCl and 0.05 M Na <sub>2</sub> SO <sub>4</sub>	Cl <sup>-</sup> : 85.5 SO <sub>4</sub> <sup>2-</sup> : 42.1	$P_{SO_4}^{Cl} = 1.89$	192
21	CMX	bare	RED	CC, 4.0 mA/cm <sup>2</sup> , 0.05 M NaCl and 0.05 M Na <sub>2</sub> SO <sub>4</sub>	Cl <sup>-</sup> : 103.2 SO <sub>4</sub> <sup>2-</sup> : 95.3	$P_{SO_4}^{Cl} = 1.1$	192
22	ACS	bare	RED	CC, 4.0 mA/cm <sup>2</sup> , 0.05 M NaCl and 0.05 M Na <sub>2</sub> SO <sub>4</sub>	Cl <sup>-</sup> : 105.3 SO <sub>4</sub> <sup>2-</sup> : 35.1	$P_{SO_4}^{Cl} = 2.7$	192
23	PSS/PAH on AMX	11	DD	0.01 M NaCl and 0.01 M Na <sub>2</sub> SO <sub>4</sub>	Cl <sup>-</sup> : 1.47 ± 0.20 SO <sub>4</sub> <sup>2-</sup> : 0.31 ± 0.16	$F_{SO_4}^{Cl} = 5.3 \pm 1.7$	193
24	PSS/PAH on AMX	11	DD	0.1 M NaCl and 0.1 M Na <sub>2</sub> SO <sub>4</sub>	Cl <sup>-</sup> : 8.14 ± 0.39 SO <sub>4</sub> <sup>2-</sup> : 0.06 ± 0.01	$F_{SO_4}^{Cl} = 137 \pm 31$	193
25	PSS/PAH on AMX	11	DD	0.01 M NaCl and 0.1 M Na <sub>2</sub> SO <sub>4</sub>	Cl <sup>-</sup> : 1.55 ± 0.06 SO <sub>4</sub> <sup>2-</sup> : 0.57 ± 0.09	$F_{SO_4}^{Cl} = 27.9 \pm 5.0$	193
26	PSS/PAH on AMX	11	DD	0.1 M NaCl and 0.01 M Na <sub>2</sub> SO <sub>4</sub>	Cl <sup>-</sup> : 7.40 ± 0.53 SO <sub>4</sub> <sup>2-</sup> : not detected	$F_{SO_4}^{Cl} > 200$	193
27	AMX	bare	DD	0.01 M NaCl and 0.01 M Na <sub>2</sub> SO <sub>4</sub>	Cl <sup>-</sup> : 6.12 ± 0.12 SO <sub>4</sub> <sup>2-</sup> : 3.70 ± 0.22	$F_{SO_4}^{Cl} = 1.66 \pm 0.08$	193
28	AMX	bare	DD	0.1 M NaCl and 0.1 M Na <sub>2</sub> SO <sub>4</sub>	Cl <sup>-</sup> : 30.0 ± 1.9 SO <sub>4</sub> <sup>2-</sup> : 2.30 ± 0.19	$F_{SO_4}^{Cl} = 13.0 \pm 0.4$	193
29	AMX	bare	DD	0.01 M NaCl and 0.1 M Na <sub>2</sub> SO <sub>4</sub>	Cl <sup>-</sup> : 2.85 ± 0.07 SO <sub>4</sub> <sup>2-</sup> : 6.61 ± 0.12	$F_{SO_4}^{Cl} = 4.3 \pm 0.1$	193
30	AMX	bare	DD	0.1 M NaCl and 0.01 M Na <sub>2</sub> SO <sub>4</sub>	Cl <sup>-</sup> : 35.16 ± 3.17 SO <sub>4</sub> <sup>2-</sup> : 0.361 ± 0.064	$F_{SO_4}^{Cl} = 9.9 \pm 1.0$	193
31	PSS/PAH on AMX	11	ED	CC, 1.13 mA/cm <sup>2</sup> , 0.01 M NaCl and 0.01 M Na <sub>2</sub> SO <sub>4</sub>	Cl <sup>-</sup> : 6.72 ± 0.13 SO <sub>4</sub> <sup>2-</sup> : 0.91 ± 0.09	$F_{SO_4}^{Cl} = 7.4 \pm 0.6$	193
32	PSS/PAH on AMX	11	ED	CC, 1.13 mA/cm <sup>2</sup> , 0.1 M NaCl and 0.1 M Na <sub>2</sub> SO <sub>4</sub>	Cl <sup>-</sup> : 19.37 ± 0.37 SO <sub>4</sub> <sup>2-</sup> : 0.28 ± 0.02	$F_{SO_4}^{Cl} = 69.3 \pm 5.2$	193

Table 4. continued

entry	PEM/membrane	no. layers	method	conditions	flux (nmol·cm <sup>-2</sup> ·s <sup>-1</sup> )	selectivity	ref
33	PSS/PAH on AMX	11	ED	CC, 1.13 mA/cm <sup>2</sup> , 0.01 M NaCl and 0.1 M Na <sub>2</sub> SO <sub>4</sub>	Cl <sup>-</sup> : 4.54 ± 0.21 SO <sub>4</sub> <sup>2-</sup> : 2.65 ± 0.28	$F_{SO_4}^{Cl} = 17.3 \pm 2.4$	193
34	PSS/PAH on AMX	11	ED	CC, 1.13 mA/cm <sup>2</sup> , 0.1 M NaCl and 0.01 M Na <sub>2</sub> SO <sub>4</sub>	Cl <sup>-</sup> : 18.38 ± 0.77 SO <sub>4</sub> <sup>2-</sup> : 0.018 ± 0.008	$F_{SO_4}^{Cl} > 81$	193
35	AMX	bare	ED	CC, 1.13 mA/cm <sup>2</sup> , 0.01 M NaCl and 0.01 M Na <sub>2</sub> SO <sub>4</sub>	Cl <sup>-</sup> : 7.38 ± 0.31 SO <sub>4</sub> <sup>2-</sup> : 5.57 ± 0.26	$F_{SO_4}^{Cl} = 1.32 \pm 0.01$	193
36	AMX	bare	ED	CC, 1.13 mA/cm <sup>2</sup> , 0.1 M NaCl and 0.1 M Na <sub>2</sub> SO <sub>4</sub>	Cl <sup>-</sup> : 34.11 ± 1.63 SO <sub>4</sub> <sup>2-</sup> : 3.13 ± 0.12	$F_{SO_4}^{Cl} = 10.9 \pm 0.2$	193
37	AMX	bare	ED	CC, 1.13 mA/cm <sup>2</sup> , 0.01 M NaCl and 0.1 M Na <sub>2</sub> SO <sub>4</sub>	Cl <sup>-</sup> : 3.62 ± 0.29 SO <sub>4</sub> <sup>2-</sup> : 11.34 ± 0.57	$F_{SO_4}^{Cl} = 3.2 \pm 0.1$	193
38	AMX	bare	ED	CC, 1.13 mA/cm <sup>2</sup> , 0.1 M NaCl and 0.01 M Na <sub>2</sub> SO <sub>4</sub>	Cl <sup>-</sup> : 57.76 ± 5.04 SO <sub>4</sub> <sup>2-</sup> : 0.695 ± 0.11	$F_{SO_4}^{Cl} = 8.4 \pm 1.1$	193
39	PSS/PDADMAC	15	CDI	CV, (±)1 V, 10 mM NaCl, 10 mM Na <sub>2</sub> SO <sub>4</sub>	ND	$7 < \beta_{SO_4}^{Cl} < 14$	194
40	PSS/PDADMAC	14	CDI	CV, (±)1 V, 10 mM NaCl, 10 mM Na <sub>2</sub> SO <sub>4</sub>	ND	$\beta_{SO_4}^{Cl} \approx 2$	194
41	PSS/PDADMAC	5	CDI	CV, (±)1 V, 10 mM NaCl, 10 mM Na <sub>2</sub> SO <sub>4</sub>	ND	$3 < \beta_{SO_4}^{Cl} < 6$	194
42	PSS/PDADMAC	23	CDI	CV, (±)1 V, 10 mM NaCl, 10 mM Na <sub>2</sub> SO <sub>4</sub>	ND	$\beta_{SO_4}^{Cl} \approx 1^b$	194
43	PSS/PDADMAC	14	CDI	CV, (±)1 V, 10 mM NaCl, 10 mM Na <sub>2</sub> SO <sub>4</sub>	ND	$\beta_{SO_4}^{Cl} \approx 1.5^b$	194
44	AMX	bare	CDI	CV, (±)1 V, 10 mM NaCl, 10 mM Na <sub>2</sub> SO <sub>4</sub>	ND	$\beta_{SO_4}^{Cl} \approx 2$	194
45	ACS	bare	CDI	CV, (±)1 V, 10 mM NaCl, 10 mM Na <sub>2</sub> SO <sub>4</sub>	ND	$\beta_{SO_4}^{Cl} \approx 7$	194
46	PSS/PDADMAC	15	CDI	CV, (±)1 V, 10 mM NaCl, 10 mM Na <sub>2</sub> HPO <sub>4</sub>	ND	$1.5 < \beta_{H_2PO_4}^{Cl} < 5.5^b$	194
47	PSS/PDADMAC	15	CDI	CV, (±)1 V, 10 mM NaCl, 10 mM NaNO <sub>3</sub>	ND	$\beta_{Cl}^{NO_3} \approx 1.5^b$	194

<sup>a</sup>ED: Electrodialysis. RED: Reverse electrodialysis. DD: Diffusion dialysis. CDI: Capacitive deionization. CC and CV represent a desalination process with constant current or constant voltage, respectively. PSS-MA stands for poly(styrenesulfonic acid-co-maleic acid) sodium salt.

<sup>b</sup>Estimated from the graphs reported in the cited references.



**Figure 6.** Schematic representation of the main parameters that affect the mono/divalent cation selectivity in PEM-coated dense membranes. The values are taken from the citations that are listed in Tables 3 and 4 and, as such, do not represent optimized values. AC and UV stand for alternating current electrical field and ultraviolet approaches to establish cross-linking between PEs with agents like 1,4-bis(2',3'-epoxypropyl) perfluoro-1-butane and (4,4-diazot-tilbene-2,2-disulfonic acid disodium salt, respectively.

higher rejection of divalent anions. In Table 4, the cross-linked PEM (entry 10, Table 4) shows a ~2 times higher  $F_{SO_4}^{Cl}$  value compared to the PEM without cross-linking (entry 12, Table 4).

Not only the characteristics of the PEM and ions, but also the experimental conditions of desalination process are crucial while optimizing the ion selectivity. We first highlight an example that includes an ED process performed at different salt concentrations. With a source phase concentration of 0.01 M for both KNO<sub>3</sub> and Mg(NO<sub>3</sub>)<sub>2</sub>,  $F_{Mg}^K$  was found to be 22.1 ± 3.5 (Table 3, entry 6). For the same system, when the concentration of both salts was increased to 0.02 M,  $F_{Mg}^K$  increased to 96 ± 26 (entry 8, Table 3). Similarly, when the salt concentrations were 0.1 M,  $F_{Mg}^K$  was reported to >20 000, further indicating the importance of the salt concentration for the system. It was hypothesized that the relatively lower source-phase concentrations caused more water splitting and

therefore a higher Mg<sup>2+</sup> flux. In entries 11 and 12 of Table 3, the same effect can be observed, where the higher concentration resulted in increased  $F_{Co}^{Li}$  (>360 vs >1600). Also, in another ED study, a 10 times higher source-phase concentration resulted in ~10 times higher  $F_{SO_4}^{Cl}$  (entries 31 and 32, Table 4). Although the higher  $F_{SO_4}^{Cl}$  could be sourced from the charge screening or ion adsorption in the PEM, a ~10 times increase in  $F_{SO_4}^{Cl}$  even with the bare AMX (entries 35 and 36, Table 4) showed that this increase is not due to the PEM. Instead, the increase in Cl<sup>-</sup> flux in a higher source concentration is the main reason for the improved selectivity. Moreover, in both ED and diffusion dialysis (DD) studies,  $F_{SO_4}^{Cl}$  are higher when the source-phase contains an excess of Cl<sup>-</sup> compared to SO<sub>4</sub><sup>2-</sup> (entries 26 and 34, Table 4). Therefore, both total salt concentration and the ion ratio affect the ion selectivity.

Another experimental condition is that the amount of driving force during the desalination process. In a constant current (CC) operation, when the current density increases, less rejections of divalent ions are observed. For instance, increasing the current density from 1.27 to 2.54 mA/cm<sup>2</sup>,  $F_{\text{Mg}}^{\text{K}}$  decreased from >1000 to 22.1 (entries 5 and 6, respectively, in Table 3). Therefore, while comparing two  $F_{\text{Mg}}^{\text{K}}$  values from two different studies, the amount of current/voltage as well as the type of method should be considered to achieve a fair comparison. One indication is the flux values of the ions to compare the selectivity values. For instance, in an ED study,  $F_{\text{Mg}}^{\text{Na}}$  is 1.7 when the flux of Na<sup>+</sup> is  $\sim 3.5 \times 10^4$  nmol·cm<sup>-2</sup>·s<sup>-1</sup> (entry 33, Table 3). However, in another ED study,  $F_{\text{Mg}}^{\text{K}} > 1000$  can be achieved since the driving force, and therefore the flux of the monovalent cation (K<sup>+</sup>, in this case) is much ( $\times 10^4$ ) smaller (entry 5, Table 3).

In conclusion, for an optimized system, the coating conditions of the PEM build-up (i.e., rinsing step, number of layers, degree of cross-linking), operational parameters (i.e., the composition of the salt solution), as well as the current density/voltage values should be considered carefully. To sum up, the combination of higher number of layers, therefore the charge density of the PEM, higher inlet concentration, and the smaller driving force (current/voltage) lead to higher X<sup>+</sup>/Y<sup>2+</sup> selectivity values (Figure 6). Also, the stability of the PEM depends on the duration of the process, as well as the operating conditions. For instance, overlimiting current values (depending on the operation) can cause water splitting and even electromigration of the PEs.<sup>188</sup> As a result, reduction in current efficiency, fouling of membrane with insoluble metal hydroxides, and even lack of stability in long-term operations can occur. Also, film stability in ED can be affected by the chlorine generation during the operation.<sup>199</sup>

**4.2. Fouling Control.** PEM-coated AEMs were also used in antifouling studies in ED<sup>185,186</sup> and reverse ED.<sup>192</sup> When the terminating layer is PSS, the negatively charged hydrophilic outermost layer improved the antifouling properties of the AEM against various foulants including sodium dodecylbenzenesulfonate,<sup>185</sup> sodium dodecyl sulfate (SDS),<sup>186</sup> and humic acid.<sup>192</sup> For example, Zhao et al. demonstrated that deposition of (PSS/PDADMAC)<sub>5.5</sub> on AEM prevented the SDS formation on the membrane, and therefore, the electrical resistance reduced and ion transport through the membrane was unaffected in the presence of SDS (Figure 5e).<sup>186</sup> Moreover, a PEM coating can simultaneously enhance the energy conversion efficiency by 3-fold compared to the pristine AEM, while still perform as an antifouling layer.<sup>192</sup> Likewise, ROMs have been combined with PEMs to reduce membrane fouling.<sup>201–203</sup> For instance, Ishigami et al. coated ROMs with (PAH/PSS)<sub>3</sub> and (PAH/PSS)<sub>6</sub> and concluded that the surface roughness decreased, and hydrophilicity increased with higher number of layers.<sup>201</sup> In filtration experiments, the modified membranes were tested against hydrophobic foulants, humic acid and dodecyl trimethylammonium bromide (DTAB). The polyanion-terminated PEM coating reduced the amount of fouling in all cases, even for a cationic surfactant (DTAB). Moreover, a real-time surface technique called quartz crystal microbalance with dissipation (QCM-D) was used to determine bovine serum albumin (BSA) fouling. The QCM-D fouling study showed that the PEM coating resulted in  $\sim 2$  times less protein fouling. The surface mass densities of adsorbed BSA were calculated as 3.0 and 1.5 mg·m<sup>-2</sup> for pristine gold sensors and gold sensors coated with (PAH/

PSS)<sub>3</sub>, respectively, further proving the antifouling character of the PEM. More recently, PEMs were used as sacrificial coatings for fouling control for ROMs.<sup>131,204</sup> When the membrane was fouled with organic foulants, both the biofilm and the PEM were flushed with concentrated brine solution and a fresh PEM was coated *in situ* (Figure 5e).<sup>204</sup>

**4.3. Catalytic Effect in Dissociation Water.** Another application of PEM-coated IEMs is to improve the water splitting capability of the membrane.<sup>184,205</sup> In 2013, Abdu et al. deposited a PEM in between the anion-exchange and cation-exchange layers of a BPM.<sup>205</sup> The PEM enhanced the rate of water dissociation because of the fixed charge groups of the PEM that behave as catalysts. In 2014, the same research group reported this also for a PEM-coated CEM.<sup>184</sup> In that work, water dissociation occurred with PEI-terminated multilayers, while PSS-terminated multilayers showed no significant catalytic effect, allowing switchable water splitting at the membrane–PEM interface.

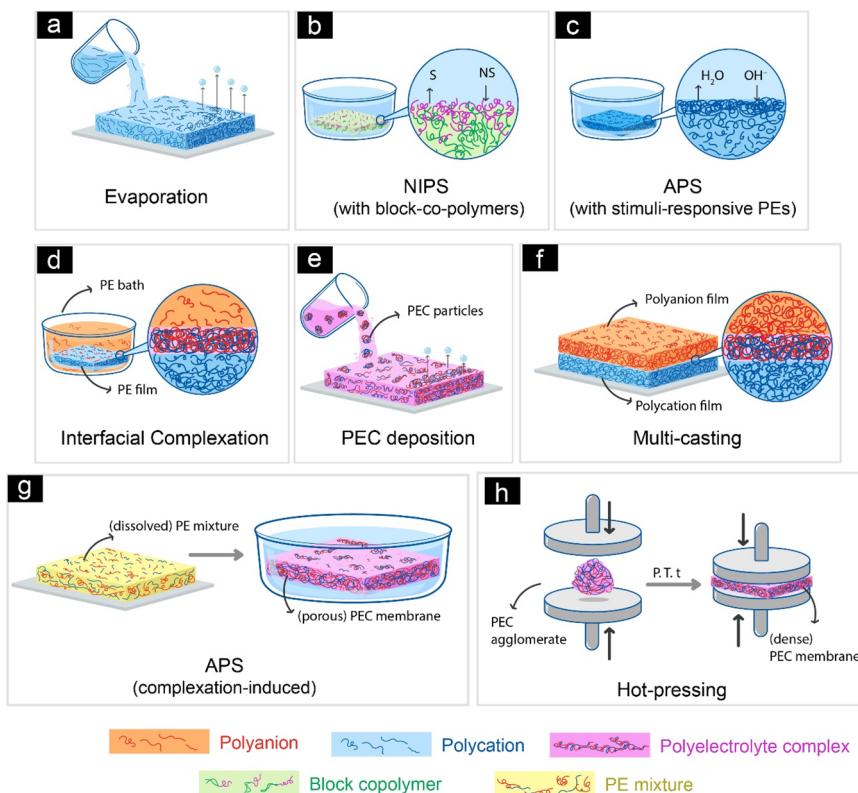
**4.4. Solvent Transport and Separation.** Furthermore, PEMs can improve the performance of direct methanol fuel cells when applied on Nafion membranes.<sup>206,207</sup> Jiang and Tang showed that (PDADMAC/PAA)<sub>n</sub> multilayers reduced the methanol transport of Nafion membranes significantly as well as lowered the proton conductivity of the membrane.<sup>206</sup> LbL assembly of different polyelectrolyte combinations have also been employed in RO for the separation of isopropanol–water mixtures yielding promising separation factors up to 1075.<sup>208</sup>

**4.5. Stability.** Besides their various applications, PEMs also have been proven to be highly stable coatings on dense membranes. They can be built at different pH values ranging from 2.3 to 9.3,<sup>78</sup> remain intact in salt solutions up to 0.5 M,<sup>190</sup> and under electric fields.<sup>183,194</sup> To improve the chemical and physical stability of PEMs further, covalent bonds within the loose multilayers can be formed via UV irradiation.<sup>195,209</sup>

## 5. POLYELECTROLYTES AND POLYELECTROLYTE COMPLEXES AS FREE-STANDING MEMBRANES

So far, PE or PEM coatings on membranes have been discussed, and we gave numerous reasons and examples why PEs are advantageous for many membrane applications by their nature. In this part, we will discuss membranes that are entirely composed of PEs either in homopolymer form or in copolymer form. To distinguish from the membranes with PE or PEM coatings, in this section, membranes will be referred to as “free-standing membranes”. Most of the membranes discussed, here, are indeed free-standing; however, the ones on macroporous substrates (for mechanical support during filtration) are also included. Blends or cases where PEs are incorporated to the membrane after the membrane formation are out of the scope of this part. First, material properties of PEs and PECs for membrane applications will be discussed. Next an oversight is given of free-standing membrane preparation, and finally, the advanced functions of these kinds of membranes will be discussed in detail.

**5.1. General Properties and Functionalities.** As explained earlier, PEs are water-soluble because of the charges along their polymer chains. However, when oppositely charged PEs form a complex via electrostatic interactions, strong ionic cross-linking makes the material resistant to many solvents.<sup>30</sup> While such stability can be considered as a real advantage, it also means that it is not possible to process PECs in a conventional manner. Until the end of the 2000s, the lack of



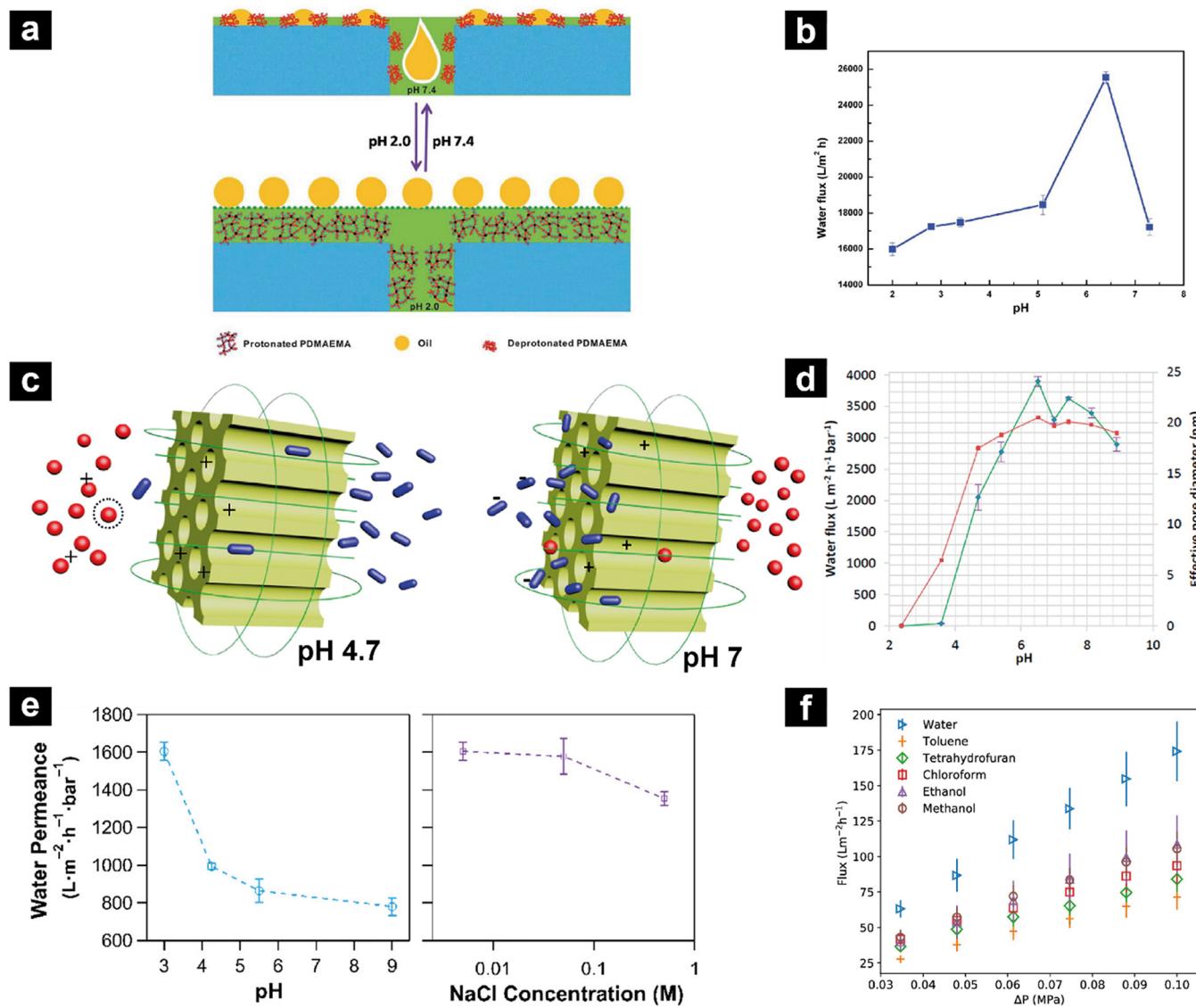
**Figure 7.** Schematic drawings of PE and PEC free-standing membrane preparation methods. (a) Solvent evaporation method (solvents including water), (b) membrane preparation from block copolymers via NIPS technique, (c) membrane preparation with stimuli-responsive PEs via APS, (d) interfacial complexation technique, while the type of PE is not important, here, the viscous film is the polycation which is immersed in polyanion bath, (e) PEC deposition membranes prepared through removing water from PEC dispersion, (f) multicasting technique, each layer can be with any type of PE solution, as well as with PEC solutions, (g) membrane preparation via complexation induced APS, (h) dense membrane preparation by hot-pressing.

processability of PECs was still an issue. Some dense films from PECs could be obtained and were studied mostly for pervaporation applications.<sup>210</sup> However, obtaining a porous film with good control over structure was not possible. In 2009, Schlenoff and co-workers showed that these materials are plasticized by salt and introduced the term “saloplastic”.<sup>211</sup> Using salt as a plasticizer allowed the PECs to be formed in different shapes and sizes, proving that PECs are actually processable just like thermoplastics.<sup>3,212–214</sup> This accelerated the research on saloplastics materials, and many papers have been published on advanced functional saloplastics with self-healing,<sup>215–217</sup> shape recovery,<sup>218</sup> patternability,<sup>219</sup> antifouling,<sup>18</sup> gas barrier,<sup>220</sup> and chemical stability<sup>212</sup> features. Additionally, incorporation of PECs with other kinds of materials, such as nanoparticles, is also demonstrated indicating it is possible to have materials with even more advanced functions.<sup>221–224</sup> Moreover, PECs are plasticized and then processed after being exposed to saline aqueous solutions without using toxic organic solvents suggesting saloplastics materials can be prepared in a sustainable manner. The introduction of saloplastics to the literature signaled that PEC films can be obtained in many ways and these films can have numerous functions, which will be particularly useful for membrane applications.

**5.2. Free-Standing Membrane Formation.** Investigations on PEC film<sup>225</sup> and membrane<sup>30,226</sup> formation already started decades ago. However, it hit the significant obstacle of lack of processability of PECs as discussed above. When dry, PECs are infusible, brittle, and resistive to most of the

solvents.<sup>30,227</sup> Therefore, shaping PECs in desired forms, including membrane formation, was not possible with conventional methods like phase separation. On the other hand, PE bulk films were soft, sticky, highly swollen in the presence of water, and very sensitive to humidity. Although these are desired features for some applications, they are not ideal for filtration-based separations, and a complex formation or a kind of cross-linking is needed for most of the cases to suppress these effects.<sup>228</sup>

Preparation of the free-standing membranes from only one PE was possible with conventional methods, such as solvent evaporation<sup>229</sup> (Figure 7a) or nonsolvent induced phase separation (NIPS)<sup>230</sup> (Figure 7b). On the other hand, to prepare free-standing PEC membranes, researchers had to develop new methods. Therefore, most of the research is focused on preparing and evaluating the performance of the membranes rather than developing them further to have advanced functions. Interfacial complexation, multicasting, and PEC deposition are among these methods which are illustrated in Figure 7. In interfacial complexation (Figure 7d), a PE film is immersed in a bath containing oppositely charged PEs.<sup>19,231</sup> In multicasting methods (Figure 7f), either PEC dispersion is cast, dried, and cast again on top of the previous one,<sup>22</sup> or a PE solution is cast followed by casting of oppositely charged PE solution on top of it.<sup>226,232</sup> In the PEC deposition method (Figure 7e), dilute solutions of oppositely charged PEs mixed to obtain a dispersion. Then, this PEC dispersion is cast followed by evaporation of the solvent (usually water) to form the film<sup>228,233–236</sup> or the dispersion is filtered where the



**Figure 8.** (a) Sketch showing the pH-responsive oil/water separation of PVDF-*co*-PDMAEMA membranes and (b) pH-responsive pure water flux of PVDF-*co*-PDMAEMA membranes. (a and b) Reproduced with permission from ref 20. Copyright 2015 The Royal Society of Chemistry. (c) A sketch showing the separation of similarly sized proteins with positively charged polystyrene-*b*-poly-4-vinylpyridine block copolymer (PS-*co*-P4VP) membranes, which protein to be retained is depending on the net charge of the protein which depends on the pH of the medium and (d) pure water flux (green line) vs pH plot for PS-*co*-P4VP membranes. (c and d) Reproduced with permission from ref 21. Copyright 2012 American Chemical Society. (e) pH- and ionic strength-dependent behavior of the flux of membranes completely composed of P4VP homopolymer. Reproduced with permission from ref 251. Copyright 2019 American Chemical Society. (f) Flux over transmembrane pressure plot showing the linear relationship for PSS-poly(N-ethyl-4-vinylpyridinium) (QVPC2) PEC membranes. Reproduced with permission from ref 254. Copyright 2019 American Chemical Society.

membrane is obtained on that filter.<sup>237,238</sup> Mostly for these methods, membrane formation occurs completely in aqueous media, which is a very desired feature, especially in terms of sustainability and clean production. However, these methods suffer from several problems including nonuniform ionic cross-linking, very long evaporation times, lack of scalability, and low control over membrane structure (i.e., mostly dense films are obtained). Recently, Krishna B et al. demonstrated a new method for the formation of dense PEC membranes, which is obtained by pressing a PEC agglomerate at a certain temperature<sup>33</sup> (Figure 7h), and many of the drawbacks mentioned before are not seen for hot-pressed membranes. It is also possible to have free-standing membranes with conventional phase separation methods. For this, either

poly(ionic liquids) (PILs)<sup>28,239–242</sup> or copolymers of regular membrane polymers with PEs<sup>20,243–248</sup> are used. Although the organic solvent used in the phase separation methods becomes a big issue,<sup>9</sup> membrane preparation is very well established with great control over the structure.

If it is possible to process PECs just like regular thermoplastics, it means that it is also possible to prepare free-standing PEC membranes with a phase separation approach just like NIPS membranes. Indeed, de Vos introduced the aqueous phase separation (APS) approach for the preparation of membranes made of PEs and PECs in totally water-based processes.<sup>249</sup> To make membranes from a single polymer, weak PEs are used. Casting solutions are prepared at a pH where the weak PE is charged, and soluble in

water, and after casting, the film is immersed in a bath at a pH that the PE is insoluble in water<sup>250,251</sup> (Figure 7c). On the other hand, PEC membranes are obtained either via the pH- or salinity-switch method (Figure 7g). In the former, a homogeneous mixture of oppositely charged PEs is obtained by keeping the pH at a point where weak PE is uncharged and not interacting with the other one. Casting is followed by immersion of the mixture in a bath where both of the PEs are charged, interacting with each other, and forming the PEC membrane.<sup>252</sup> In the salinity-switch method, a casting solution is prepared at high salinity to screen the charges of the PEs and, therefore, preventing the complex formation. When this solution is in the coagulation bath of low salinity, then the charge screening disappears, and PEs form the complex.<sup>253</sup> The last method is also investigated by others with the emphasis of how sustainable and scalable the method is.<sup>254,255</sup> It is clear that with the APS approach, it is possible to combine the know-how and versatility of the NIPS method with the desired features of PE membranes.

**5.3. Responsiveness.** Most of the recent research on advanced functional, free-standing PE-based membranes is on stimuli-responsive behavior. PEs change the chain conformation depending on several factors, including ionic strength, solvent type, temperature, and pH. Therefore, membranes made from a PE that responds to these external stimuli would be expected to be stimuli-responsive as well. There are many papers on pH-responsive membranes made with both homopolymers<sup>251,256–258</sup> and copolymers.<sup>20,21,238,243,245–247,259–264</sup> The responsive behavior is observed as either a change in surface properties, a gating mechanism where pore size changes with the external stimuli, or swelling of the whole material. Weak polyelectrolytes such as poly(2-dimethylamino ethyl methacrylate) (PDMAEMA), poly(4-vinylpyridine) (P4VP), and PAA are frequently used. Mostly, at a pH where the PE is charged, the polymer chains get an extended conformation due to repulsion of the monomers leading to swelling of the polymer. Xiang et al. showed that it is possible to control hydrophilic properties of the membranes composed of PDMAEMA and poly(vinylidene fluoride) (PVDF) copolymer.<sup>20</sup> At pH ~7, PDMAEMA chains are collapsed and PVDF is more exposed; therefore, the membrane is more hydrophobic letting oil permeate. On the other hand, at low pH (~2), PDMAEMA chains are extended and cover the PVDF, resulting in more hydrophilic membranes where oil/water separations are possible (Figure 8a). Figure 8c shows the pH-dependent flux of PS-*b*-P4VP membranes, where a small pH change enables one to alter the water flux by orders of magnitude.<sup>21</sup> Here, the flux is higher when P4VP chains are collapsed (i.e., when the gates are open). On the other hand, Figure 8e also shows the pH-dependent flux behavior of a membrane composed completely of P4VP homopolymer.<sup>251</sup> Unlike the previous ones, this membrane has a lower resistance for water permeation at low pH where P4VP is charged and extended since the swelling of the whole material leads to more open structures.

Since the transition between a coiled and extended form of the PE chains is not sharp, membrane permeability can easily be fine-tuned with pH. Moreover, especially for the membranes from copolymers, permeability also depends on the surface properties. When the hydrophilic PE is in a coiled form, the hydrophobic part of the copolymer is more in contact with the filtration medium, a decrease in membrane flux can be observed with the increase of the hydrophobicity

(Figure 8b, d).<sup>20,21</sup> Finally, the pH affects the charge density of the weak PEs and consequently the charge exclusion mechanism of the separation, which is a key factor for the separation of charged compounds like proteins, dyes, salts, and micropollutants. For example, Qiu et al. studied the separation of similarly sized proteins where the membrane charge is one of the factors to control this separation as sketched in Figure 8d.<sup>21</sup>

Most of the papers on stimuli-responsive membranes investigated the effect on flux. However, only a few investigated the membranes with a rejection test of a compound,<sup>245,246,248,251,265,266</sup> and to our knowledge, there are very few investigating the separation of similar species.<sup>21,258</sup> The reported rejection tests are very frequently done with BSA to examine the fouling behavior of the membranes, which will be discussed later.

Other than pH, also ionic strength,<sup>230,251,263,266</sup> temperature,<sup>243,247,259,267</sup> and redox-responsive<sup>268</sup> behavior of PE bulk membranes is studied. The mechanism is again completely dominated by the conformation of the PE. The gate mechanism studied for drug-release and dialysis membranes as well that are excluded from this Review.

**5.4. Fouling Control.** As stated earlier, fouling is a major problem for membrane applications. Hydrophobic membranes tend to foul easily, but as membranes get more hydrophilic, there will be more water molecules between the membrane and the foulant and therefore it will be less favorable for the foulant to be adsorbed on the surface.<sup>246,248</sup> Therefore, many membrane studies have been dedicated to increasing the hydrophilicity of the membranes using PEs. PEs due to their charged nature are hydrophilic, a feature that can even be tuned by their charge density. Many studies on stimuli-responsive behavior of the membranes also investigated the fouling behavior of the PE free-standing membranes.<sup>245,246,248,251,265,266</sup> It is reported that as the membranes get hydrophilic, it becomes more difficult to foul the membrane.<sup>20,246,269</sup> Moreover, when fouled it is easier to clean the membrane by adjusting the pH where the PE is charged. Willott et al. showed that cross-linking P4VP free-standing membranes introduces fixed charges and by controlling the cross-linking degree, it is possible to control the self-cleaning degree of the membranes.<sup>251</sup> Very frequently, the flux recovery data (pure water flux after cleaning with respect to the one before fouling) of PE-based free-standing membranes is over 90%. This means that although it is not possible to do the filtrations at a pH where the membrane shows high resistance to fouling, it can be easily cleaned, and cleaned membranes can perform as well as new membranes. The literature on this is predominantly on copolymer membranes which are prepared with NIPS. There are a few studies on antifouling saloplastic material,<sup>18</sup> and to our knowledge, the work of Willott et al. is the only study that investigates stimuli-responsive and self-cleaning functions of homopolymer free-standing membranes<sup>251</sup> prepared with APS.

**5.5. Stability.** PECs and many PEs are known with being chemically resistive toward organic solvents. As in other polymers, the chemical stability of PEs and PECs is highly dependent on solvent–polymer interactions. Moreover, the chemical stability of a membrane is determined by the stability of the polymer, the extent of cross-linking, and the extent of the entanglements. For PECs, electrostatic interactions between oppositely charged PEs, which are also called ionic cross-links, contribute to the stability of the membrane. Free-

standing pervaporation membranes and PEMs used for organic solvent nanofiltration (OSN) already indicate the great compatibility of PE-based membranes. For free-standing PEC membranes, Sadman et al. reported stable fluxes over varying transmembrane pressure for several organic solvents *Figure 8f*<sup>254</sup> and Fares showed swelling behavior of PSS–PDADMAC-based saloplastics,<sup>270</sup> pointing out that PEC membranes will be particularly useful for filtrations with organic solvents. Other than stability against organic solvents, pH stability of these membranes is also important. Here, the extent of ionic cross-linking is more important which is mostly dependent on PE type. For example, Baig et al. reported the pH stability of PSS–PEI free-standing membranes is only up to pH 10;<sup>271</sup> this is because of the pH-dependent behavior of the weak polycation PEI. It is speculated that, at conditions higher than pH 10, the membrane starts to decomplex because of PEI becomes less charged because of the excessive deprotonation. On the other hand, it is reported that PSS–PDADMAC membranes are stable at pH 0–14.<sup>33,253</sup> Pham et al. showed that anion exchange membranes from ionenes, a class of PEs, are stable in alkaline solutions and organic solvents like dimethyl sulfoxide, *N*-methyl-2-pyrrolidone and dimethylacetamide.<sup>272</sup> Krishna B et al. exposed the hot-pressed PSS–PDADMAC membranes to 1 M HCl and 1 M NaOH solutions for 60 days and the membranes exhibit great stability against this extreme pH without sacrificing from the permselectivities.<sup>33</sup> The difference in the stability of these PEC membranes does not only result from different types of PEs, as also the polyanion to polycation ratio in the complex, the strength of ion–ion interactions, and the extent of cross-linking and entanglements are affecting factors. This implies that it is possible to tune the stability of these membranes further with an informed selection of PEs and membrane preparation conditions.

## 6. CONCLUSION AND OUTLOOK

In the past decade, the use of polyelectrolytes to modify or produce membranes has received much attention and has led to many examples of highly promising functionalities. Attaching just a single layer of polyelectrolyte, either as a brush or a physiosorbed layer, is already enough to produce membranes with excellent antifouling properties, responsive membranes through a gating mechanism and even antiviral and/or antibacterial properties. Moreover, when applying polyelectrolytes in a complex form, through the formation of polyelectrolyte multilayers, more advanced functionalities become possible. Next to antifouling and pH- and salt-responsive coatings, it has now also become possible to create membranes with sacrificial coatings, for easy cleaning, and membranes with very specific selectivities. Polyelectrolyte multilayers, both on porous and dense membranes can allow very high selectivities between multivalent and monovalent ions, going beyond what is possible with more traditional membrane coatings and materials. Other specific selectivities, including selectivity between monovalent ions and membranes with a high retention to small organics molecules and a low salt retention also become possible. In the past decade, it has also become clear that porous free-standing membranes can be completely made out from polyelectrolyte complexes. Some approaches are especially promising as they allow the formation of membranes without use of organic solvents, providing a platform to make membrane production much more sustainable. The produced free-standing membranes can

be as diverse as membranes produced with organic solvents, besides they can have the same advanced functionalities, ranging from stimuli-responsive properties to separation behavior. Some of the PEM- and PEC-based free-standing membranes also demonstrate very high stabilities under problematic conditions, for example in organic solvents or when exposed to extreme pH conditions.

Overall, it can thus certainly be concluded that polyelectrolytes are highly promising materials to allow the formation of next-generation membranes with advanced functionalities. However, in many ways the field is still developing, and much more exciting work on these versatile materials are expected in the near future. For example, by focusing not on just one single functionality but rather using polyelectrolytes in smart ways to achieve multifunctional membranes, where for example, low fouling, easy to clean, and specific selectivities are combined.<sup>169</sup>

A natural advantage of polyelectrolytes is their solubility in water, allowing the fabrication of polyelectrolyte coatings and even complete membranes without the need for organic solvents. While a clear advantage from a sustainability point of view, this can certainly be pushed further. One idea is to use biobased PEs in membrane separations. Although, there are few recent studies that have focused on the monovalent anion selectivity and pervaporation with biodegradable PEs (mostly chitosan derivatives),<sup>192,196,197,228</sup> there is much room to explore the use of PEs such as pectin, alginic acid, and cellulose derivatives in the context of membrane-based separations.

Moreover, it has been well established that polyelectrolyte complexes have self-healing properties, allowing them to heal from small and larger damage in sufficiently salt water. For PEM coatings and for the free-standing membranes such self-healing properties would be a huge advantage, one that has the potential to lengthen the product lifetime, further improving sustainability. Still, up until now the self-healing properties of PEC membranes and PEM membrane coatings has received no real attention. In addition, polyelectrolyte complexes tend to lose their stability under extremely saline conditions, or in the presence of surfactants. For those conditions good cross-linking approaches will become necessary. For example, microfiltration membranes made from PILs by Dani et al. are stable against high ionic strength solutions since the films are covalently cross-linked by UV-light.<sup>273</sup> On the other hand, this feature can be useful for membrane reuse. Wu et al. showed it is possible to reprocess PIL–PAA membranes in high concentration salt solutions.<sup>274</sup>

One other great advantage of PE- and PEC-based materials is that additives can easily be incorporated/intercalated to allow additional functionalities and further improvement of membrane properties. Indeed, based on the successes of the early examples of PEMs including ion-selective receptors,<sup>275–278</sup> the recovery and harvest of specific ions from aqueous solutions via PEM-coated dense membranes can be further tuned in the future. The incorporation of tailored ion-selective groups<sup>184</sup> may allow selectivity between monovalent ions for PEM-based membranes. Recently, the intercalation of SDS bilayers in a (PDADMAC/PSS)<sub>n</sub> multilayer allowed for thinner multilayers, with increased pore size, and a higher hydrophilicity, which resulted in a 100% increase in water permeability without compromising the SO<sub>4</sub><sup>2-</sup> rejection.<sup>279</sup> These results highlight how small molecular additives may become a novel approach to enhance and fine-tune the performance of PEM-coated membranes. Additionally, nano-

particles<sup>280–282</sup> and metallo-polyelectrolytes<sup>283</sup> can be incorporated into the multilayer to increase PEM-based membrane performance (e.g., permeability, selectivity, strength, and hydrophilicity).<sup>280,284</sup> Here, future research is expected to focus on membranes with incorporated ion-selective nanoparticles for selective adsorption and recovery (via pH regeneration) of specific resources from wastewater, thereby combining filtration and adsorption in a single step process. Finally, polyelectrolyte multilayers could be combined with functional biological moieties, such as enzymes. Current PEM-based membranes can stop already stop MPs with a high efficiency. However, recent work on PEM-based biocatalytic membranes, with incorporated, show that MP rejection and degradation could be combined in a single process.<sup>285–287</sup>

We do stress that, in future research on improved membrane selectivities, it is very important to work with standardized process conditions, and standardized selectivity definitions and rejection/permeation performances that allow direct comparison of different studies. Moreover, these separation performance values should be reported as an average of multiple (minimum 3) experiments and standard deviations should be reported to facilitate a better understanding of the reproducibility of the production process of modified and new membranes.

Finally, the natural stability of polyelectrolytes and their complex in organic solvents, coupled to their high cross-link densities make PE- and PEC-based membranes relevant for many applications that go beyond water treatment. It has already been shown that PEM-based membranes can be very relevant for solvent filtration,<sup>36</sup> while PEC-based membranes have also been shown to dramatically reduce the permeability of oxygen in packaging materials.<sup>220,288</sup> Such oxygen barrier properties, also point to the relevance of these materials for the fabrication of advanced gas separation membranes, which are relevant for, for example, CO separation and storage.<sup>289</sup> We, thus, foresee a very bright future for polyelectrolyte-based advanced functional membranes, for applications in water treatment, but also in industrial processes that require the separation of organic solvents and gases.

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### Notes

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## ABBREVIATIONS

AEM	anion-exchange membrane
AMX	standard-grade anion exchange membrane
APS	aqueous phase separation
BCM	block copolymer micelles
BPM	bipolar membrane
BSA	bovine serum albumin
CC	constant current
CDI	capacitive deionization
CEM	cation-exchange membrane
CMX	standard-grade cation exchange membrane
CV	constant voltage
DD	diffusion dialysis
DMF	dimethylformamide
DTAB	dodecyl trimethylammonium bromide
ED	electrodialysis
HA	hyaluronic acid
HF	hollow fiber
IEM	ion-exchange membrane
LbL	layer-by-layer
MF	microfiltration
MP	micropollutant
NF	nanofiltration
NIPS	nonsolvent induced phase separation
OSN	organic solvent nanofiltration
PE	polyelectrolyte
PEB	polyelectrolyte brush
PEC	polyelectrolyte complex
PEM	polyelectrolyte multilayer
PIL	poly(ionic liquid)
QCM-D	quartz crystal microbalance with dissipation
RED	reverse electrodialysis
RM	resistance measurement
RO	reverse osmosis

ROM	reverse osmosis membrane
RP	receiving phase
SDS	sodium dodecyl sulfate
TFC	thin-film composite
THF	tetrahydrofuran
UF	ultrafiltration

## Polymers

alkynyl-PMETA	poly(2-(methacryloyloxy)ethyl trimethylammonium chloride)
HACC	2-hydroxypropyltrimethylammonium chloride chitosan
NSBC	N-O-sulfonic acid benzyl chitosan
P4VP	poly(4-vinylpyridine)
PAA	poly(acrylic acid)
PAH	poly(allylamine hydrochloride)
PAMA	poly(alkyl methacrylate)
PAN	poly(acrylonitrile)
PAS	poly(phenylene sulfone)
PDADMAC	poly(diallyldimethylammonium chloride)
PDMAEMA	poly(2-dimethylamino ethyl methacrylate)
PEI	poly(ethylenimine)
PES	poly(ethersulfone)
PET	poly(ethylene terephthalate)
PMAA	poly(methacrylic acid)
PMPC	poly(2-methacryloyloxyethyl phosphorylcholine)
PMPC- <i>co</i> -AA	poly(2-methacryloyloxyethyl phosphorylcholine- <i>co</i> -acrylic acid)
poly(OEGMA- <i>r</i> -HEMA)	poly(oligo(ethylene glycol) methacrylate-random-2-hydroxyethyl methacrylate)
PSf	poly(sulfone)
PSBMA	poly(sulfobetaine methacrylate)
PS- <i>co</i> -P4VP	polystyrene- <i>b</i> -poly-4-vinylpyridine block copolymer
PSPMA	poly(3-sulfopropyl methacrylate)
PSS	poly(sodium 4-styrenesulfonate)
PSS-MA	poly(styrenesulfonic acid- <i>co</i> -maleic acid) sodium salt
PVA	poly(vinyl alcohol)
PVDF	poly(vinylidene fluoride)
PVS	poly(vinyl sulfonate)
PVSA	poly(vinylsulfonic acid) sodium salt
QVPC2	poly( <i>N</i> -ethyl-4-vinylpyridinium)
SPEEK	sulfonated poly(ether ether ketone)
SPES	sulfonated poly(ether sulfone)

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