Regular Article

Hot-pressed polyelectrolyte complexes as novel alkaline stable monovalent-ion selective anion exchange membranes

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Highlights

- Dense PSS and PDADMA saloplastics are prepared via a simple hot-press approach.
- These saloplastics function as anion-exchange membranes.
- Water uptake, resistance ion exchange capacity comparable to commercial membranes.
- Long term stability (up to 60 days) observed in extreme alkaline and acidic conditions.
- The membranes show relevant monovalent selectivity for chloride over sulphate ions.

Graphical Abstract

Abstract

Polymeric ion-exchange membranes have come a long way since their invention, benefiting a wide range of processes, ranging from desalination to fuel cells. However, challenges such as alkaline stability, monovalent ion selectivity, cost-effectivity, and process sustainability largely persist. This work showcases alkaline stable anion-exchange membranes made by hot-pressing of a polyelectrolyte complex of poly(styrenesulfonate) (PSS) and poly(diallyldimethylammonium) (PDADMA). This completely aqueous production approach leads to especially dense (non-porous) saloplastic films with an excess of cationic groups, demonstrating good stability even at high salinities (up to 2 M NaCl). On key performance indicators for anion exchange membranes, such as water uptake (~40%), permselectivity (up to 97%), ion exchange capacity (1.01 mmol g⁻¹), and resistance (2.3 O cm²), the membranes show comparable values to commercial membranes. A drop in permselectivity at high salinities, however, indicates that the charge density of the membranes could be further improved. Still, what really sets these membranes apart is their natural long term (up to 60 days) stability at extreme acidic (pH 0) and alkaline conditions.

Abbreviations: IEM, ion exchange membrane; PEC, polyelectrolyte complex; AEM, anion exchange membrane; CEM, cation exchange membrane; Na-PSS, sodium salt of polystyrene sulfonate; PDADMAC, chloride salt of poly(diallyldimethylammonium); APS, aqueous Phase Separation; PEMU, polyelectrolyte multilayer; IEC, ion exchange capacity; WU, water uptake.

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1. Introduction

Although the context of NASA’s Mars mission strategy - “Follow the water” - is a world away, both literally and metaphorically, it precisely describes the very story of human settlements throughout history [1]. Civilizations flourished around rivers and other water bodies since time immemorial because potable water is a human necessity [2]. However, a shortage of clean water has been a cause of growing concern in the last century amidst the global emergency of climate change [3]. Naturally, many technologies [4] have been developed to make potable water [5] and/or harness renewable energy [6]. One such technology assisting man in both these spheres is electrodialysis, being used for seawater desalination [7–9] as well as for sustainable salinity gradient power [10,11], among other applications [12]. Ion exchange membranes, which are mostly polymeric, make electrodialysis possible by selectively allowing certain ions to pass through them depending on their nature. While many commercial ion-exchange membranes have been developed, there is still a pressing need for more sustainable, pH stable [13,14], and economically viable membranes. Such membranes could also play a key role in energy storage, for example, in alkaline fuel cells.

Especially regarding positively charged anion exchange membranes (AEMs), their stability in high pH solutions has been a challenge [15–17]. For example, AEMs based on quaternary ammonium are the most common ones but are known to degrade in alkaline media by Hoffmann elimination [17], nucleophilic substitution [18], and/or ylide formation [19]. Hence, developing AEMs with high alkaline stability is important. Several attempts have been made in this regard but at the cost of sustainable production methods or a loss in other properties of the membrane [16].

Polymeric structures can be (a) covalently bonded network systems, (b) secondary valence bonded linear macromolecular systems, or (c) held together by ionic linkages [20]. The last three decades have garnered interest in ionically bound organic polymeric structures due to advancements in polyelectrolyte research [21]. Nevertheless, (a) and (b), called thermoplastics [22] and cross-linked plastics [23,24] respectively, have been the primary focus of polymer science and technology for very long, including membrane production. Commonly used polymers for making ion exchange membranes include Nafion, polysulfones, polyfluoroethylene, poly divinylbenzenes, and polyphenylene oxide [25]. Copolymers, blends, and composites have also been profusely explored [26–28].

Thermoplastics such as polyethylene, acrylic nitrite butadiene styrene (ABS), and polycarbonate are made by methods such as injection molding, extrusion molding, thermoforming, spin casting, and compression molding (hot pressing). Among these, hot pressing is a favorable one for making dense sheets due to its ability to produce desired shapes and thicknesses, defect-free and tailored compaction, without compromising on homogeneity [29].

Polyelectrolytes, which are polymers bearing chargeable groups, have been in the limelight for more than a decade now. Focussed research has shown their properties to be increasingly interesting and important to several fields of study [20,30–32]. In one interesting scenario, aqueous solutions of oppositely charged polyelectrolytes combine to form a polyelectrolyte complex (PEC) due to enthalpy of coulombic interactions, facilitated by entropy gained by releasing counterners [33]. Several factors like polymer and salt concentrations, molecular weights, and mixing ratio are known to influence the quality and properties of the complex thus formed [34–36]. Yano and Wada observed that water, a known plasticizer of PECs, also plays a dominant role in the attributes of PECs which display specific water uptake values, enough to facilitate ion pair hydration [37].

In the meanwhile, the fundamental understanding of membrane separation mechanisms has synchronously increased, leading to the continuous revision of other facets of membrane fabrication [38–40], assemblage, and characterization over the years [41,42]. Similarly in the field of membrane production, polyelectrolytes and polyelectrolyte complex based materials have led to substantial innovation. Polyelectrolyte multilayers have shown promising separation performances in the fields of nanofiltration [43], reverse osmosis, forward osmosis, and also as highly selective coatings for ion-exchange membranes [44]. More recently, sustainable microfiltration and nanofiltration membranes were made by Aqueous Phase Separation (APS), wherein one study used a pH-responsive polymer, poly (4-vinylpyridine) (P4VP) [45], and the other used a copolymer, polystyrene-alt-maleic acid (PSaMA) [46]. Moreover, polyelectrolyte complexation was shown to allow the fabrication of whole microfiltration, nanofiltration, and ultrafiltration membranes via sustainable Aqueous Phase Separation [47–49].

On the other hand, dense membranes for ion exchange applications such as electrodialysis are typically made using hydrophobic substrates and immobilized charged functional groups [50]. They are called cation exchange membranes (CEMs) or anion exchange membranes (AEMs) depending on whether they contain fixed negative or positive ionic moieties respectively. Anionic moieties include carboxylic, sulfonic, and phosphoric acid groups, while examples of cationic ones are imidazole or quaternary ammonium cations. Ideally, CEMs only allow the passage of cations, while AEMs, anions. Since the 1920s, when Michaelis and Fujita worked on weak acid colloid membranes, several types of ion exchange membranes (IEMs) have been developed [51–53]. These include amphoteric IEMs, inorganic-organic hybrid IEMs, bipolar IEMs, and mosaic IEMs [50]. The most common fabrication method uses polar aprotic solvents to dissolve polymeric materials, casting these solutions, and further evaporating the solvents. Other methods that have been developed over the years include polymer blending, pore filling, electrospinning, and in-situ polymerization [54–56]. The latest ones include polyelectrolyte multilayer (PEMU) membranes wherein oppositely charged polyelectrolytes are adsorbed on a substrate in an alternating fashion [57–59]. The interest in such membranes has increased exponentially as they have displayed outstanding selectivities in myriad applications [60,61], most significantly, ion exchange [62,63].

Both the earlier mentioned sustainable methods, APS and PEMUs, use polyelectrolytes. Polyelectrolyte complexes were thought to be unprocessable until Schlenoff and coworkers successfully compacted saltwater plasticized PECs into dense materials by ultraconcentration and extrusion [64]. They aptly coined the term ‘Saloplastic’ for such materials, accentuating the indispensable role salt plays as a softener, analogous to what temperature

11–20
and pressure do to thermoplastics and baroplastics respectively [65,66]. Although PECs were evidently porous, the Saloplastics they made were relatively dense with pores below 10 μm, and the lowest pore sizes being 100 nm [67].

Among several combinations of polyelectrolytes, the properties of Polystyrene sulfonate (PSS) and Polydiallyldimethylammonium (PDADMA) complexes have been studied relatively well in literature, and are known to have selective properties in the case of polyelectrolyte multilayer membranes [44]. Further, as strong polyelectrolytes, they are known to form stable complexes [64]. Hence, they were chosen for this study.

Both polyelectrolyte multilayers and porous polyelectrolyte complexes have been shown to have highly relevant properties to allow their use as sustainable membrane materials for pressure-driven processes. In this work, we propose that dense polyelectrolyte complexes (saloplastics) could be very relevant as a new generation of sustainable ion exchange membranes, relevant for electrically driven processes. The required density of the saloplastics is achieved by a simple, sustainable, and scalable hot-pressing approach. These dense films are analyzed for their water content, ion-exchange capacity, resistance, and permselectivity, with a direct comparison being made to commercial membranes.

Not only do the saloplastics show very promising properties as cation-exchange membranes, but they also showcase additional benefits such as stability under extreme acid and alkaline conditions and a monovalent selectivity.

2. Materials and methods

2.1. Preparation of polyelectrolyte complexes

Poly(sodium 4-styrene sulfonate) (Na-PSS, Mw = 1000 kg·mol⁻¹, 25 wt% in H₂O), chloride salt of Poly(diallyldimethylammonium) (PDADMAC), Mw = 400–500 kg·mol⁻¹, 25 wt% in H₂O), KCl (>99%), and KBr (>99%) were purchased from Sigma Aldrich and used as received. Milli-Q water from a Millipore Synergy® Water Purification System was used to make polyelectrolyte solutions.

Na-PSS and PDADMAC solutions of 125 mM each were prepared with respect to their monomer repeat unit, with 250 mM KBr in each [67,68]. For example, to make a 100 mL Na-PSS solution, 2.98 g of KBr was first added to about 50 mL Milli-Q water and dissolved. Next, 10.30 g of 25% Na-PSS was added to the salt solution after which the solution was made up to 100 mL by adding sufficient water and mixed under magnetic stirring for 30 min. The PDADMAC solution was made similarly by adding 10.10 g of 20% PDADMAC. The two solutions were poured into a 250 mL beaker under stirring. This precipitate was washed and stored in 250 mM KBr.

Non-stoichiometric ratios of polyelectrolytes were studied, which eventually led to the same final composition of the polyelectrolyte complex. The complex seemed to have a natural preference for a ratio in which the polyelectrolytes combined, and this parameter was not further investigated.

2.2. Preparation of hot-press moulds

Moulds were designed using Delrin for the endplates. PTFE Coated Fiberglass sheets with adhesive on one side (Lubriglas®-CHAP-1540) of thicknesses 0.122 mm and 0.225 mm were purchased from Reichelt Chemietechnik GmbH+Co (Heidelberg, Germany), and were cut in strips to be glued on edges as spacers (Fig. 1).

Thin outlets were made to allow any excess water and polyelectrolyte complex to escape. Two endplates and a spacer constitute a casting mould.

2.3. Hot-pressing

An FV20R Rolling Driptech Rosin Press, FlashVape, Canada was used for hot pressing of the polyelectrolyte complexes. 2 g of wet PEC was placed in the mould. This sandwich was inserted between the aluminum slabs of the hot press. The slabs of the hot press were closed such that they were just together and no pressure was applied. The temperature was set to 80 °C leading to a gradual increase from room temperature to the set temperature in 20 min. Subsequently, a pressure of 200 bar was applied and the PEC remained under these conditions for 5 min. Then, the temperature was set to 25 °C. When 25 °C was reached in ~ 30 min, the plastic PEC sheet was removed from the hot-press.

In order to compare hot pressed membranes with commonly used commercial membranes, Neosepta AMX and Neosepta ACS (purchased from Astom Corporation, Japan) were used.

2.4. Swelling ratio and water uptake

Water Uptake (WU) of the PEC films was determined by measuring the fraction of weight change between a film in its wet and dry states. An as-prepared film was cut into a rectangular strip of 2 cm × 1 cm and dried in an oven at 30 °C for 24 h. The weight, as well as the length, width, and thickness of the sample, were recorded. Further, the sample was immersed in MilliQ water or saltwater for 24 h, after which the weight and dimensions were recorded again. The ratio of the difference in wet and dry weights of a membrane to the dry weight of the membrane gives the fraction of water uptake as shown in the following equation.

\[
\text{Water uptake (WU)} = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}}
\]

where \(m_{\text{wet}}\) and \(m_{\text{dry}}\) are the wet and dry masses respectively.

2.5. Ion exchange capacity

Potentiometric titration was used to determine the ion exchange capacity (IEC) of the film [69]. The anion exchange capacity was measured by the following procedure: The sample was first brought to the Cl⁻ form, then Cl⁻ was replaced by SO₄²⁻, and the released amount of chloride ions was determined by titration with AgNO₃. To achieve this, 0.5 g of the dry membrane was soaked in 150 mL of 1.0 M NaCl for 15 h. Further, it was rinsed and soaked in MilliQ water for 90 min while the water was replaced several times to remove sorbed NaCl. Next, the film was soaked in 50 mL of 1.5 M Na₂SO₄, and the solution was replaced twice to ensure a complete exchange of Cl⁻ with SO₄²⁻. These combined solutions were used to determine the Cl⁻ content by titration with 0.1 M AgNO₃ and a K₂CrO₄ indicator. The IEC was calculated by the following equation:
Anion Exchange Capacity \[ \frac{\text{mmol}}{g} = \frac{V_{\text{AgNO}_3}}{W_{\text{dry}}} \cdot C_{\text{AgNO}_3} \]

where \( V_{\text{AgNO}_3} \) and \( C_{\text{AgNO}_3} \) are the volume and concentration of \( \text{AgNO}_3 \) respectively.

The cation exchange capacity was measured as follows: The sample was first brought to the \( H^+ \) form, then \( H^+ \) was replaced by \( \text{Na}^+ \), and the released amount of \( H^+ \) ions was determined by titration with \( \text{NaOH} \). To achieve this, 0.5 g of the dry membrane was soaked in 150 mL of 1.0 M \( \text{HCl} \) (ACS reagent 37%, Sigma Aldrich) for 15 h. Further, it was rinsed and soaked in MilliQ water for 90 min while the water was replaced several times to remove sorbed \( \text{HCl} \). Next, the film was soaked in 50 mL of 1 M \( \text{NaCl} \), and the solution was replaced twice to ensure a complete exchange of \( H^+ \) with \( \text{Na}^+ \). These combined solutions were used to determine the \( H^+ \) content by titration with 0.1 M \( \text{NaOH} \) and a \( \text{pH} \) electrode (Metrohm pH 491). The IEC was calculated by the following equation:

Cation Exchange Capacity \[ \frac{\text{mmol}}{g} = \frac{V_{\text{NaOH}}}{W_{\text{dry}}} \cdot C_{\text{NaOH}} \]

where \( V_{\text{NaOH}} \) and \( C_{\text{NaOH}} \) are the volume and concentration of \( \text{NaOH} \) respectively.

2.6. Electrical resistance

A plexiglass cell with six compartments [70] was used to measure the electrical resistance to the mobility of ions offered by a membrane. Both direct current (DC) as well as alternating current (AC) measurements were done at a constant temperature of 25 ± 0.2 °C, controlled by a thermostatic bath. Platinum coated titanium electrodes were placed in compartments on either end to apply a specific current, while Haber-Luggin capillaries (HLC in Fig. SI 1) connected to calomel reference electrodes inserted into the central compartments measured the potential drop across the test membrane. These compartments circulated 0.5 M \( \text{K}_2\text{SO}_4 \) solution using a peristaltic pump. The test solution \( \text{KCl} \) was circulated in the two central compartments and a similar solution in the remaining two adjacent compartments. The test membrane was placed in between the central compartments while an auxiliary commercial CEM, Neosepta CMX (purchased from Astom Corporation, Japan), was placed between every other pair of chambers.

The test membranes were each equilibrated for 24 h before testing. DC resistance was the slope of the IV curve generated when currents of 0–200 mA were supplied via the electrodes and corresponding voltage drops measured by the capillaries. All resistances are reported as area resistances after subtracting the solution resistance, as well as multiplying by 0.785 cm², the effective area of the membrane. AC resistance was measured by supplying an AC signal with a fixed amplitude of 5 mA and varying frequency from 1 to 100 MHz, and recording the response using a potentiosstat PGSTAT302N (Metrohm Autolab, The Netherlands). Within the 100–1000 Hz frequency range, the impedance measured with the minimum phase shift value is the AC resistance. The resistance of the diffusion boundary layer is obtained by subtracting the AC resistance from the DC resistance.

2.7. Monovalent ion selectivity

In addition to the electrical resistance of \( \text{KCl} \), that of \( \text{K}_2\text{SO}_4 \) was determined in solutions of the same normality, i.e., 0.25 M \( \text{K}_2\text{SO}_4 \). The monovalent ion selectivity of the ion exchange membrane is given by the following equation:

\[ \text{Selectivity}^{\text{CT}}_{\text{SO}_4^2} = \frac{R_{\text{SO}_4^2}}{R_{\text{CT}}} \]

where \( R_{\text{SO}_4^2} \) is the resistance measured in 0.5 N (0.25 M) \( \text{K}_2\text{SO}_4 \) solution and \( R_{\text{CT}} \) is that measured in 0.5 N (0.5 M) KCl. Such a resistance-based selectivity is known to correspond well to resistances achieved using large scale electrodialysis experiments [71].

2.8. Permselectivity

An ion-exchange membrane, unlike a porous membrane, is dense. A gradient is needed to drive ions to diffuse through it when it is placed between two chambers with salt solutions (Fig. SI 2). Ideally, an AEM allows anions (counterions) to pass and retains cations (co-ions), and vice versa. This property is called permselectivity. A calomel reference electrode (VWR, The Netherlands) was positioned in each of the two test chambers to measure the voltage drop due to the concentration gradient when salt solutions of different concentrations are circulated on either side of the membrane.

Numerically, permselectivity is calculated as the ratio of the experimental voltage measured by electrodes to the theoretical Nernst potential for an ideally permselective membrane.

\[ \text{Permselectivity(\%)} = \frac{V_{\text{Experimental}}}{V_{\text{Nernst}}} \times 100 \]

where,

\[ V_{\text{Nernst}} = \frac{RT}{zF} \ln \frac{C_2 \gamma_2}{C_1 \gamma_1} \]

\( C_1 \) and \( C_2 \) are the concentrations of the salt solutions, \( z \) is the mols of electrons transferred, and \( \gamma_1 \) and \( \gamma_2 \) are the activity coefficients. In addition to permselectivity, these measurements reveal the nature of charges on the membrane. Depending on whether the voltages are positive or negative corresponding to the arrangement of the electrode system, it can be concluded whether a membrane is an anion exchange membrane (AEM) or cation exchange membrane (CEM).

2.9. pH stability

Hot-pressed PECs whose permselectivities were measured were stored in 1 M (pH 0) \( \text{HCl} \) (ACS reagent 37%, Sigma Aldrich) and 1 M (pH 14) \( \text{NaOH} \) (pellets, Sigma Aldrich) for 60 days. The permselectivities were tested again after rinsing with MilliQ water and equilibrating in the KCl test solution for 24 h.

3. Results and discussion

The versatility of polyelectrolyte complexes has been demonstrated in several applications [72], and membrane science is no exception. The objective of this study was to determine if a polyelectrolyte complex based plastic prepared by hot (80 °C) pressin (200 bar) a polyelectrolyte complex of PSS and PDADMA can be used as an anion exchange membrane in electrodialysis. There are several parameters such as pressure, temperature, time, and amount of water that determine the exact properties of the plastic. Here these parameters were optimized to obtain defect-free and completely transparent films. In the present work, the basic morphology of the plastic was first examined, followed by electrochemical characterization, and finally, acid and alkaline stability were studied over time.

As shown in Fig. 2, the high pressure applied to the polyelectrolyte complex in the presence of heat resulted in a dense transparent film. Such hot-pressed plastics are completely transparent, sturdy, and flexible. Under such conditions, defect-free membranes are obtained, also without any presence of bubbles. Transparency is an indication that the material is dense and non-porous.
In electrodialysis we deal with salt solutions of varying ionic strengths, therefore the water content of the hot-pressed membranes was evaluated as a function of ionic strength. The results of these experiments can be found in Fig. 6. Each point represents two samples with duplicate measurements, averaging four values. With an increase in salt concentration, the membranes are expected to swell due to doping, leading to the breaking of the ionic links between the polyelectrolyte pair. This leads to greater hydration, and in turn, swelling [75].

In Fig. 4 it can be seen that water uptake is constant up to 2 M NaCl. Beginning from 2 M salt, the film became visibly weaker and at 3 M, also became sticky and difficult to handle. Above this ionic strength, it also became difficult to accurately determine the hydration of the film, explaining the larger error bar for water uptake at 3 M salt. Fig. S1 4 demonstrates a similar study at 4 different temperatures, demonstrating only a weak effect of temperature on the film hydration. Similar systems such as polyelectrolyte multilayers (PEMUs) of PSS/PDADMA and extruded PSS/PDADMA saloplastics have displayed high water uptake values and increased swelling as the salt concentration was increased. Salt is also known to play a role in the swelling of most commercial ion-exchange membranes such as Nafion membranes, whose water uptake depends on the salt concentration [76]. Our PEC based films are stable even at higher salinities (2 M), which would allow their use for most electrodialysis type applications.

It has been found that the polyelectrolyte complex made by stoichiometric mixing of individual polyelectrolyte solutions contains excess cationic groups [77]. Hence, the presence of a slight positive charge is expected. The ion exchange capacity (IEC) of a membrane indicates the extent of ionic groups in the polymer matrix available for ion exchange. As our membrane is expected to contain both anionic and cationic charges, it was important to measure both capacities. The anion exchange capacity was measured to be 1.37 ± 0.16 mmol g⁻¹, while the cation exchange capacity was 0.36 ± 0.03 mmol g⁻¹. That leaves us with a net ion exchange capacity of 1.01 ± 0.19 mmol g⁻¹. The commonly used commercial membranes, Neosepta AMX, Neosepta ACS (Tokuyama Soda, Japan), and Selenium AMV (Asahi glass, Japan) have IECs of 1.6 ± 0.2 mmol g⁻¹ [79], 1.7 ± 0.3 mmol g⁻¹ [80], and 2.2 ± 0.3 mmol g⁻¹ respectively. This indicates that the charge density is lower than that of these commercial membranes, but is of comparable magnitude.

An ion-exchange membrane with high water uptake tends to have lower selectivity [81], as swelling lowers the charge density in the membrane. This was investigated by measuring permselectivity, i.e., the ability to selectively allow either cations or anions to pass through. This property was evaluated by placing the hot-pressed membrane between two chambers containing solutions with the same salt at different concentrations. As shown in Fig. 5, 0.01/0.05 M salt solutions allowed anions to selectively permeate up to 97%, also indicating that the membranes are positively charged. The values decreased to 88% for the 0.03/0.15 M

Fig. 2. A saloplastic film prepared by hot-pressing a polyelectrolyte complex of poly(styrenesulfonate) and poly(diallyldimethylammonium).

Fig. 3. Field Emission Scanning Electron Microscopy (FESEM) images of a plastic made by hot pressing a polyelectrolyte complex of PSS and PDADMAC at different magnifications.
combination and the values slumped to an average of 60% when the concentrations were increased to 0.05/0.25 M. These measurements indicate that the PSS/PDADMAC based plastics can function as anion exchange membranes with high selectivities. The fact that the permselectivity drops at higher salinity indicates a lower charge density in such a membrane and hence, it can only be used efficiently at lower salt concentrations, or with lower permselectivities at higher salt concentrations. This finding is also supported by literature, which shows that permselectivity decreases as the ionic conductivity (permeability) increases. This can be attributed to the fact that when the salt concentration increases, the sorption of co-ions increases, leading to a decrease in permselectivity [82].

Membrane thickness is known to play an important role in the performance of an ion-exchange membrane [83]. To investigate the effect of thickness on permselectivity, three different membrane thicknesses comparable to the thickness of commercial membranes, 100 ± 2 μm, 150 ± 3 μm, and 200 ± 3 μm, were chosen. The results can be found in Fig. 7 from which it was deduced that permselectivity remains unchanged when the membrane thickness was increased from 100 ± 2 μm to 150 ± 3 μm. However, this value decreased slightly when the thickness was increased to 200 ± 3 μm, although the decrease was limited to less than 10% in each case. Fig. SI 7 shows that the permselectivity is maintained even in very thin membranes (30–80 μm).

The permselectivities of membranes are known to remain relatively constant with changes in membrane thickness. Studies with Nafton membranes, PES blended SPEEK membranes, and other laboratory-made membranes reported in literature have shown small or insignificant changes in permselectivity with respect to thickness [76,83,84].

The resistance that a membrane material offers to the passage of ionic current through it is another important property of ion-exchange membranes that is required to be investigated. This resistance, unlike permselectivity, is known to be dependent on thickness. For an ohmic conductor, the resistance is expected to increase as the thickness of the material increases [85]. In this regard, membranes with thicknesses 30 ± 2 μm, 50 ± 3 μm, 80 ± 2 μm, 100 ± 2 μm, 150 ± 3 μm, and 200 ± 3 μm were used to determine the area resistance, obtained by measuring the potential difference across the membrane after supplying DC. Fig. 6 contains the results, wherein each point is an average of four values, obtained by measuring the area resistance of two membranes twice. The resistance was observed to increase linearly with membrane thickness which is in line with literature. Studies with extruded sulfonated polyimide membranes, Nafion, and other commercial membranes have clearly shown this trend [83,85–87]. The homogeneity of the membrane structure along its thickness can also be inferred from this. As the thickness of a conductive film decreases, ions travel faster through it. Thus, thinner membranes reduce the resistance to ions and are beneficial for electrodialysis. This is clearly shown for membranes thinner than 100 μm wherein the resistances are extremely small, and are almost negligible for 30 μm membranes. This translates to monovalent selectivity, which is shown to be inversely proportional to the membrane thickness (Figs. SI 5 and SI 6), with a 50 μm membrane displaying...
an excellent selectivity of 6.3. Although difficult to handle, a 30 μm membrane further shows an even higher selectivity for Cl⁻ over SO₄²⁻ ions, especially as result of the nearly negligible resistance to Cl⁻. Such a low resistance could indicate the occurrence of defects and needs to be studied in much greater detail. Thinner membranes also reduce the material needed, in turn reducing the fabrication cost.

The increase in selectivity as the membrane becomes thinner, indicates that the selectivity stems from a surface effect rather than a bulk effect. It is thus likely that the monovalent ions are able to more easily approach and enter the membrane compared to the divalent ions. For thinner membranes, such a surface selectivity becomes more dominant.

Table 1 summarises the properties of the PSS/PDADMA membrane and common commercial membranes. The values of ion exchange capacity, area resistance, and permselectivity of hot-pressed membranes indicate that our membranes are comparable to their commercial counterparts.

While reasonable selectivities and low resistance to the transport of ions are the fundamental requirements for membranes to possess ion-exchange characteristics, it is also important for them to be stable in highly acidic or alkaline conditions. This necessity has posed a serious challenge to membrane scientists.

To investigate this, eight membranes were cut in two. Permselectivity was determined for one half of each membrane. Four of the other halves were stored in 1 M NaOH solution at pH 14 and the remaining four were stored in 1 M HCl solution at pH 0 for 60 days. In each case, permselectivity was determined after washing them with Millili Q water, KCl, and equilibrating in it for 24 h. The stability of these membranes in alkaline and acid media was understood by comparing the permselectivity values before and after the pH 14 test. Fig. 7 shows that the values, each point representing 2 membranes with duplicate measurements, have not changed significantly, clearly indicating the good stability of these membranes in alkaline media. This is further supported by water uptake values measured before and after the pH 14 treatment, which were identical. This stability is attributed to the nature of the polyelectrolytes, PSS and PDADAMA, which are both strong and hence remain charged in the entire pH regime. Moreover, both polyelectrolytes have a very high chemical stability, and will not degrade even under extreme pH conditions.

It has been demonstrated by Elshof et al. that PSS/PDADMA based polyelectrolyte multilayer nanofiltration membranes have excellent long-term chemical stability in terms of pure water permeance, molecular weight cut-off, and salt retention [88]. Several studies have made efforts to improve the alkaline stability of anion exchange membranes. Some of these have been successful in making materials with good stability, but possess other drawbacks. For instance, Hibbs used a polyphenylene backbone and trimethylammonium cations and made the material alkaline stable by introducing a hexamethylene spacer between the two [89]. Similarly Tomoi et al., have tethered a polystyrene backbone to an alkyl trimethyl ammonium cation using a variety of ethers [90]. However, the synthesis of such materials is challenging as it requires cations with long tethers which are difficult to obtain, while the membrane itself can degrade via Hofmann elimination [15]. Several cationic functional groups have been explored too as an alternative to benzyltrimethylammonium cations appertaining to their low alkaline stability [96–93]. One such study by Noonan et al. evaluated a tetrakis(dialkylamino)phosphonium cation and obtained impressive stabilities [94]. However, the inclusion of such cations introduces increased complexities as well as higher costs, in addition to low conductivities. In the case of Ruthenium and Cobaltcnenium cations, there is also a risk of interfering with electrode reactions [15]. In comparison, our membranes combine a sustainable approach to production, with very decent ion exchange properties and high alkaline stability.

4. Conclusions

Academia and industry are working on transitioning to more sustainable methods of membrane fabrication, with polyelectrolyte complexation being one attractive route. Here we demonstrate that dense saloplastics made by simple hot-pressing of polyelectrolyte complexed are promising materials to act as anion exchange membranes.

Electrochemical characterization demonstrates that these completely dense saloplastic membranes can selectively allow counterions to pass through them while blocking co-ions with permselectivities up to 97%. Ionic resistance measurements show that these PEC materials offer resistances comparable to commercial anion exchange membranes. They are also selective to chloride ions over sulfate ions, with an excellent selectivity of up to 6.3 for 50 μm films, while their high stability in extreme acidic and alkaline media sets them apart from commercial IEMs.

Table 1
A summary of the properties of a 50 μm thick hot-pressed PSS/PDADMA membrane compared to those of commonly used commercial membranes Neosepta AMX and ACS [78,79]. Permselectivity and area resistance were measured at 25 ± 0.1 °C.

| Membrane          | Membrane wet thickness (μm) | Area resistance (Ohm cm²) | Permeselectivity(0.03/0.15 M KCl) (µm) | Ion exchange capacity (mmol g⁻¹) | Water content (g H₂O/g dry membrane) |
|-------------------|-----------------------------|---------------------------|---------------------------------------|----------------------------------|--------------------------------------|
| Neosepta ACS      | 127 ± 3                     | 3.91 ± 0.03               | 94                                    | 1.7 ± 0.3                        | 0.31 ± 0.03                           |
| Neosepta AMX      | 141 ± 6                     | 2.77 ± 0.07               | 96                                    | 1.6 ± 0.2                        | 0.19 ± 0.02                           |
| Hot pressed       | 52 ± 3                      | 0.67 ± 0.12               | 89                                    | 1.0 ± 0.2                        | 0.41 ± 0.05                           |

Fig. 7. Permselectivity measurements before and after storage in 1 M NaOH (pH 14) and 1 M HCl (pH 0) for 60 days. Each point represents an average of four values (two membranes measured twice each). The error bars indicate the standard deviation. If no error bar is visible, then the error is smaller than the used marker.
It is especially promising that these low-cost saloplastic membranes are simple to make with easily synthesizable and procurable starting materials. They have the potential to be further improved and tailored to specific applications using other polyelectrolyte couples, additives, and crosslinking. Initially, the focus would be on improving the charge density, to guarantee high permselectivities also at higher ionic strengths, and on tuning the internal charge balance to also prepare cation exchange membranes based on this material. With that in place, saloplastic ion exchange membranes hold a real promise to make ion-exchange based processes cheaper, more sustainable, and more selective.

CRediT authorship contribution statement

Ameya Krishna B: Investigation, Validation, Writing - original draft. Saskia Lindhoud: Conceptualization, Supervision. Wiebe M. Vos: Conceptualization, Funding acquisition, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Author Contributions

The manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcts.2021.02.077.

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