Solvation-Driven Actuation of Anion-Exchange Membranes

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1. Introduction

Ion-exchange membranes, conventionally utilized in separation processes of electrolyte solutions, are electroactive polymers that display a unique coupling between electrochemistry and mechanics. Previous experimental studies have demonstrated the possibility of actuating cation-exchange membranes in salt solution through the application of a remote external electric field. The use of anion-exchange membranes as contactless actuators, however, has never been documented and little is known about the physics of their actuation. Here, it is reported for the first time the possibility of contactless actuating anion-exchange membranes in salt solutions; such an actuation is mediated by the selection of anions in the external salt solution and the membrane. Actuation is attributed to the physical phenomenon of solvation, the interaction between ions and solvent in solution. Contrary to previous studies with cation-exchange membranes, the results show that anion-exchange membranes consistently bend toward the anode. The integration of anion-exchange and cation-exchange membranes in composites promises innovative programmable contactless actuators, with applications in underwater robotics and biomedical engineering.

Ion-exchange membranes are ion-conducting polymers that are widely utilized in separation processes of electrolyte solutions, including electrodialysis, desalination, electrolysis, and energy conversion. Following immersion in an aqueous solution, the microstructure of an ion-exchange membrane consists of: i) a polymeric backbone with fixed charges, the coions, and ii) hydrated, dissolved mobile charges of the opposed sign, the counterions. Ion-exchange membranes are semipermeable, that is, they block ions of the same sign as the coions from entering the membrane. Semipermeability is caused by the sharp change in the electrochemical potential of counterions (the so-called Donnan potential) at the membrane-solution interface, due to the presence of the coions. Depending on the sign of the ions that are able to enter the membrane, we classify ion-exchange membranes as anion-exchange (only anions can enter) or cation-exchange (only cations can enter) membranes.

Applications of ion-exchange membranes are not restricted to separation processes. In fact, ion-exchange membranes display bidirectional coupling between mechanics and electrochemistry, which favor their use as “functional materials” for actuation, sensing, and energy harvesting applications. A well-known example of ion-exchange membranes are ionic polymer-metal composites (IPMCs), which typically consist of a cation-exchange membrane chemically plated with a noble metal, such as gold or platinum. Following the application of an electric voltage between the surface electrodes, IPMCs display macroscopic bending deformations. Vice versa, a mechanical load applied to an IPMC results in a measurable voltage across its electrodes. The physical underpinnings of the IPMC electro-chemo-mechanical coupling are the motion of the counterions within the membrane, triggered by external electrochemical or mechanical stimuli.

Widespread use of IPMCs in real-world scenarios is negatively affected by the difficult-to-control plating process. During the plating process, a composite layer of metal particles and membrane material is created between the surface electrodes and the ion-exchange core. This intermediate layer generates electrodes with a much higher surface area than the nominal one. The capacitance increase resulting from the composite layer is critical to IPMC actuation yet hard to control during the plating process.
An alternative actuator configuration that does not require the plating of electrodes was first proposed by Kim et al.\cite{22} In their setup, a cation-exchange membrane was immersed in a salt solution, between two external electrodes. The application of a voltage between the electrodes elicits bending of the membrane. Removing the influence of the intermediate layer increases the consistency of the actuator performance and allows to further explore free-form fabrication of ion-exchange membrane actuators,\cite{8,23} overcoming the challenge of plating them.\cite{24} Surprisingly, the use of external electrodes results in a reversed bending direction of the cation-exchange membrane compared to the conventional IPMC configuration.\cite{22}

The setup utilized in the experiments of Kim et al.\cite{22} shares similarities with previous studies on polyelectrolyte gels,\cite{25–27} see Figure 1a). However, there are remarkable differences between the actuation of ion-exchange membranes and that of polyelectrolyte gels. The different polymeric structure of ion-exchange membranes\cite{5} and polyelectrolyte gels\cite{28} results in widely different water uptakes, affecting the mechanics and electrochemistry of these material systems. While the water uptake of the investigated anion-exchange membrane is 58%\cite{29} in terms of water weight per weight of dry polymer, polyelectrolyte gels can exhibit water uptakes of more than 100\%\cite{30} in addition, experimental studies on polyelectrolyte gels employed relatively high voltages\cite{31} or current densities\cite{32} compared to ion-exchange membranes in Refs. \cite{22,33}, pointing at the involvement of other actuation mechanisms. Further supporting this claim, the time-scale of the actuation of ion-exchange membranes is in the order of seconds,\cite{33,34} compared to minutes for polyelectrolyte gels.\cite{33}

![Figure 1](image1.png)

**Figure 1.** Experimental approach for the study of contactless actuation of anion-exchange membranes. a) Illustration of the experimental setup. The membrane is placed in a salt solution between external electrodes, across which the electrical voltage $\psi_E$ is applied. The distance of the external electrodes is $w_E$. The tip displacement $d$ is measured with a displacement laser sensor. The free length of the membrane is $l_F$ and $H$ is its semi-thickness. The dashed line illustrates the membrane in the reference configuration before the application of the electrical stimulus. b) Typical current $I$ (left) and tip displacement response $d$ (right) after the application of the external voltage at $t = 1$s. The peak current $I_{pk}$ and the normalized peak tip displacement $d_{pk}/H$ are marked with a blue circle and a red triangle, respectively. The time to reach the peak tip displacement $t_{pk}$ is defined as the time difference between the peak current and the peak tip displacement. The values of the tip displacement are nondimensionalized with respect to the semi-thickness $H$ of the membrane. Positive values of the tip displacement are in the opposite direction to the electric field. c) Membrane cross-section with the anion fluxes entering and leaving the membrane at the anode and cathode side. d) Side view of the membrane in the deformed configuration after application of an electric field $E$ for external anions with a small (left) and large (right) hydration number.
Building on the work of Kim et al.,\cite{22} we proposed a series of experimental and theoretical endeavors to elucidate the inner workings of cation-exchange membrane actuation.\cite{33-35} We identified solvation as the key physical mechanism underlying the actuation of cation-exchange membranes in salt solution. Solvation describes the interactions between the solvent and the dissolved solute in a solution, and plays a remarkable role in a variety of chemical and biological processes,\cite{36,37} such as the folding of proteins.\cite{38} When water is the solvent, solvation is commonly referred to as hydration. In an electrolyte solution, complex interactions between the dissolved ions and water molecules take place.\cite{39} As a result, water molecules form hydration shells that surround the ions. Hydration shells are defined by the distance between the water molecules and ions, the number of water molecules, and the angles of the ion-water bonds.\cite{40,41} The first layer of water molecules around the ion represents the first hydration shell. The second layer, usually characteristic of multivalent ions, contains water molecules hydrogen-bonded to the first hydration shell. The average number of water molecules in the first and, if present, second hydration shells defines the hydration number of the ion.\cite{39}

The application of a voltage across the external electrodes causes the ions in the solution to migrate. While anions cannot cross the cation-exchange membrane, cations in the external solution enter the membrane at the anode side. Cations bring along water in their solvation shell, which contributes to swelling of the anode side of the membrane. Similarly, hydrated cations from within the membrane on the cathode side migrate in the external solution, causing contraction at the membrane cathode. Such a differential swelling generates the macroscopic deformation of the membrane.\cite{13}

Contrarily, actuation of anion-exchange membranes remains entirely untapped. In general, the coupling between mechanics and electrochemistry in anion-exchange membranes is still elusive, even for IPMCs, whereby only a few studies have utilized anion-exchange membranes as the IPMC core.\cite{42-45} Asaka and Fujiwara\cite{42} were the first to demonstrate the feasibility of using anion-exchange membranes as the core of an IPMC. By considering different countercations, they found a linear increase of the actuation response with the charge density of the used anions. Building on this evidence, Refs. \cite{43,44} investigated the influence of the countercations and the polymeric structure of the anion-exchange membrane on the actuation response. Overall, there is consensus about bending in the opposite direction of cation-exchange membrane-based IPMCs, with an actuation time and magnitude inferior to commonly employed Nafion-IPMCs. Due to the limited technical literature, there is a dire need for experimental investigations about the actuation of anion-exchange membranes. Not only can these studies help to better understand the physical underpinnings of electrochemical actuation, but also they can enable new, enticing actuator concepts based on a combined use of cation- and anion-exchange membranes.

In this paper, we conduct a series of hypothesis-driven experiments on anion-exchange membranes in salt solution to demonstrate the feasibility of contactless anion-exchange actuators. Towards detailing the role of solvation on actuation, we systematically vary the hydration number of the anions in the external salt solution and in the membrane. Figure 1b) shows typical current and displacement (in terms of tip motion) responses of an anion-exchange membrane upon the application of an electric field. From the time series of these two quantities, we extract the peak current and peak tip displacement, as the maximum values of current and tip displacement, respectively, following the voltage step. Additionally, we evaluate the time to reach the peak tip displacement as the time difference between the occurrence of the peak current and the peak tip displacement. The time to reach the peak tip displacement characterizes the actuation time and may be used in combination with the peak tip displacement as a figure of merit to determine the actuation performance of these membranes.

The peak current is determined by the resistance of the membrane-solution system. Due to the negligible width of the membrane in comparison to the electrode width, we do not expect the membrane to play a major role on charge migration in the salt solution. As a result, the anion-exchange membrane should not contribute additional resistance to the current, and the peak current should be determined by the ionic conductivity of the external solution ions, at least to a first degree of approximation. (Accompanying analyses on the influence of the membrane on the peak current included in the Supporting Information corroborate this claim.) Given that we always utilize the same type of cations in the external solution, we formulate the first experimental hypothesis as follows:

(H1) The peak current is influenced by the external salt solution and increases with the ionic conductivity of the solution anions.

In order to quantify the influence of the hydration number on the tip displacement, we need to consider how it affects the differential swelling at the membrane anode and cathode. In fact, the pile-up and depletion of anions is limited to thin electrical double layers in the membrane, in proximity of the membrane-solution interface.\cite{15} At the membrane cathode, solution anions enter the membrane, pushing counterions initially inside of the membrane into the external solution. At the membrane anode, counterions leave the membrane due to the electric field. Volume changes at the cathode and anode side can be related to local anions’ and water concentration changes. Using the hydration number of the anions, concentration changes of water molecules can be related to concentration changes of anions. These concentration changes create a differential swelling in the membrane, which results in a macroscopic bending motion. Changing the hydration number of either the counterions or the solution anions influences the swelling of the anode and cathode sides and, therefore, the mechanical response of the membrane, as depicted in Figure 1c,d). Thus, our main experimental hypothesis, testing the influence of solvation, is:

(H2) The actuation response of the anion-exchange membrane is determined by the hydration number of both the counterions and the anions in the external salt solution.

To explore the dependence of the tip displacement on the hydration number of counterions and salt anions, we can estimate the magnitude of the occurring concentration changes at the anode and cathode side. The amount of counterions leaving the membrane anode and cathode is limited by the initial concentration of counterions inside of the membrane.
Under the premise that anion-exchange membranes show a similar behavior to cation-exchange membranes, charge pile-up caused by anions that enter at the cathode side should be limited only by steric effects. Even accounting for these effects, this concentration change at the membrane cathode is expected to be much larger than the initial concentration of counterions. Consequently, we anticipate a dominant role of the solution anions, which will elicit a swelling of the membrane cathode and therefore a macroscopic bending toward the anode, against the electric field. Solution anions with a larger hydration number transport more water molecules from the external solution into the membrane, causing a larger volume expansion of the cathode side and an increase of the tip displacement. Therefore, we formulate the following hypothesis regarding the influence of the solution anions:

(H2a) Increasing the hydration number of the anions in the external solution results in an increase of the tip displacement.

Similar to our previous experimental investigation, we differentiate two cases for the effect of membrane counterions, depending on the size of the anions in the external solution. For small anions in the external solution, a large charge pile-up at the cathode side occurs. As a consequence, more anions are pushed out of the cathode side compared to the amount of anions leaving the anode side. Increasing the hydration number of the counterions brings out more water at the cathode side, counteracting the cathode side swelling due to the solution anions and reducing the tip displacement. For large anions in the external solution, the charge pile-up at the cathode side is less pronounced. Thus, the water transport out of the membrane at the anode side may be larger compared to the charge pile-up at the cathode side. In this case, increasing the hydration number of the counterions brings out more water at the anode side. This effect results in a stronger contraction of the membrane anode and an increase of the tip displacement. This allows for the formulation of our last hypothesis:

(H2b) For anions with a small (large) hydration number in the external salt solution, increasing the hydration number of the counterions results in a decrease (increase) of the tip displacement.

2. Results and Discussion
2.1. Preparation of the Anion-Exchange Membrane

Experiments were conducted with a novel type of poly(biphenylene) based anion-exchange membranes with trimethylammonium coions and chloride counterions Cl\(^-\). The mobile counterions results in a decrease (increase) of the tip displacement. For small anions in the external solution, a large charge pile-up at the cathode side occurs. As a consequence, more anions are pushed out of the cathode side compared to the amount of anions leaving the anode side. Increasing the hydration number of the counterions brings out more water at the cathode side, counteracting the cathode side swelling due to the solution anions and reducing the tip displacement. For large anions in the external solution, the charge pile-up at the cathode side is less pronounced. Thus, the water transport out of the membrane at the anode side may be larger compared to the charge pile-up at the cathode side. In this case, increasing the hydration number of the counterions brings out more water at the anode side. This effect results in a stronger contraction of the membrane anode and an increase of the tip displacement. This allows for the formulation of our last hypothesis:

(H2b) For anions with a small (large) hydration number in the external salt solution, increasing the hydration number of the counterions results in a decrease (increase) of the tip displacement.

2.2. Experimental Setup

The experimental setup consisted of a cantilevered anion-exchange membrane immersed in 1 L of a dilute salt solution with a concentration of 0.1M, similar to Refs. [22,33,34], see Figure 1a). The membrane was fixed between acrylic clamps with a free wet length of \(l_c = 70\) mm and positioned in the middle of external electrodes. The external electrodes were mounted in a 3D printed holder and kept at a distance \(w_e = 12\) mm throughout the experiments. During trials, we applied an electrical voltage across the external electrodes and measured the membrane tip displacement utilizing a laser displacement sensor. We also measured the voltage across and the electric current through the external electrodes. To allow for the measurement of the tip displacement of the membrane, which is transparent, we attached reflective tape to the tip.

2.3. Experimental Procedure

We systematically varied the anions in the external salt solution and in the membrane to investigate the influence of their hydration number on the tip displacement of the membrane. Sodium bromide NaBr, sodium chloride NaCl, sodium bicarbonate NaHCO\(_3\), and sodium acetate CH\(_3\)COONa were utilized as the external salt solution, and bromide Br\(^-\), chloride Cl\(^-\), bicarbonate HCO\(_3\)\(^-\), and acetate CH\(_3\)COO\(^-\) ions as the counterions. Thus, we had 16 combinations of anions in the external salt solution and membrane. Each combination was tested twice, for a total of 32 experimental runs. Each experimental run consisted of five experimental trials. In the first and last experimental trials, no membrane was mounted in the solution and only the electrical variables were measured. These two trials were used to probe the electrochemical properties of the solution and monitor the influence of long-term effects on the solution properties. In each of the three remaining trials, one of the three membranes in the set was immersed in the solution and 10 voltage pulses with
Alternating polarity were applied for 60 s, separated by 60 s when the electrodes were shorted. The polarity was changed to prevent asymmetries in the membrane-solution system to affect the results. The voltage signal was controlled by an electrical circuit similar to our previous works.[33,34] A data acquisition system was employed to record the voltage across the external electrode, the current passing through the electrodes, and the membrane tip displacement.

2.4. Hydration Number of Anions

There are several methods to quantify the hydration number of ions.[40,41] As recommend in Ref. [37], we used the hydration number from electrostriction or, if not available, the entropy of hydration. In doing so, we recognize that the microstructure of the anion-exchange membrane affects the hydration of the mobile anions inside the membrane. Therefore, the hydration number of the anions in the bulk water differs from the hydration number after entering the anion-exchange membrane. Interactions between the fixed coions, the mobile counterions, and the water molecules form a complex hydration picture inside of the anion-exchange membrane. For bromide and chloride, hydration numbers of counterions inside of an organic solvent are available from molecular dynamic simulations,[39] and follow a similar trend to electrostriction measures.

To the best of our knowledge, quantification of the electrostriction of bicarbonate and acetate ions inside ion-exchange membranes has not been studied yet. Hence, we opted to use the hydration numbers from entropy of hydration as a proxy. We highlight that, for the entering anions, we utilized the hydration numbers of anions inside the membrane rather than the ones in the external solution. This choice is consistent with Ref. [33] and it is motivated by the time-scale of solvation, which is much faster than the time-scale of the mechanical response. While the exchange of water molecules takes place on the scale of μs to ps,[40] the time to reach the peak displacement is on the order of a few seconds.[33] As a result, we propose that anions entering the membrane from the external solution should immediately assume the hydration number inside the membrane. The used hydration numbers can be found in Table 1.

2.5. Pre-Processing and Statistical Analysis

Before the statistical analysis in R,[51] the peak current and the peak tip displacement were extracted from the time series of the current and tip displacement using MATLAB.[52] In the statistical analysis, the experimental hypotheses were tested against a set of linear-mixed and generalized linear-effect models that use Gamma errors with inverse or log-link functions. The external salt anions, the counterions, and interactions between the solution anions and the counterions were utilized as explanatory variables. In order to avoid pseudoreplications, the membrane identification number was used as a random effect. We used backward elimination to obtain the most parsimonious model that minimizes the corrected Akaike Information Criterion (AICc).[33] For the selected model, the statistically significant explanatory variables were identified using two-way analysis of variance (ANOVA). Then, Tukey’s honest significance difference was used in post-hoc tests to find significant pair-wise differences between experimental conditions.[54] A significance level of 0.05 was used in all statistical tests.

2.6. Results

Before presenting the results of the tested hypotheses, we examined the bending direction of the membranes in the different experimental conditions. In agreement with our expectation, all membranes bent in the opposite direction of the electric field. Figure 3 shows the time response of the membrane with the median peak tip displacement in each experimental condition. Membranes with acetate counterions showed an initial displacement overshoot, followed by a decay towards a steady tip displacement. In contrast, the tip displacement of bromide membranes increased towards the peak tip displacement and slightly oscillated around the corresponding peak tip displacement. For membranes in their chloride and bicarbonate form, the response type depended on anions in the external salt solution. In comparison to other salt solutions, bromide and bicarbonate membranes in the sodium acetate solution showed stronger actuation response with an initial overshoot. In the remaining salt solutions, the response was qualitatively similar to that of bromide membranes.

To emphasize the influence of the external salt solution on the actuation response, Figure 4 shows the tip displacement of the same membranes with different counterions in the same salt solution. With sodium bromide solutions, the tip displacement of membranes remained approximately the same once it reached its peak value. With sodium acetate solutions, for all counterions except bromide, membranes displayed an initial displacement overshoot. Generally, differences in the actuation response between counterions in the same external solution were small. The magnitude of the peak tip displacement increased for larger hydration numbers in the external solution. These observations indicate a key role of the anions in the solution on the tip displacement.

Figure 5 shows box plots of the peak current for different external salt solutions. The peak currents of sodium chloride and sodium bromide solutions were comparable, and they were larger than those of sodium bicarbonate and sodium acetate solutions. The observed variance can be explained by experimental uncertainty related to slight differences in the solution concentration, influence of the electrode clamping, and material differences between the electrode sets.

Table 1. Hydration number of Br\(^{-}\), Cl\(^{-}\), HCO\(_3\)\(^{-}\), and CH\(_3\)COO\(^{-}\). The hydration number of Br\(^{-}\) and Cl\(^{-}\) stem from electrostriction, while the hydration number of HCO\(_3\)\(^{-}\) and CH\(_3\)COO\(^{-}\) are calculated from the entropy of hydration.[37]

| Anion       | Hydration number |
|-------------|------------------|
| Br\(^{-}\)   | 1.2              |
| Cl\(^{-}\)   | 1.7              |
| HCO\(_3\)\(^{-}\) | 4.4              |
| CH\(_3\)COO\(^{-}\) | 5.7              |
In the statistical analysis, we determined the most parsimonious model describing the peak current to be a linear-mixed effect model with the anions in the external solution as the explanatory variable. Additionally, the model used the membrane identification number as a random effect and accounted for differences in the variance between different salt solutions. Through ANOVA, we found the effect of anions in the external solution to be statistically significant ($\chi^2 = 11945, df = 3, p < 0.001$). In post-hoc comparisons, the difference between all combinations of anions in the external solution were significant.

Figure 6 shows the box plots of the peak tip displacement for all investigated combinations. For all counterion forms, the trend of the peak tip displacement displayed a decrease for smaller hydration numbers. Generally, the peak tip displacement showed a large variance within an experimental condition, caused by differences between the membranes in the same membrane set.

Through backward elimination, we determined the most parsimonious model describing the peak tip displacement to be a linear-mixed effect model with the anions in the external solution, the counterion form, and their interactions as explanatory variables. The model also employed the membrane identification number as a random effect and accounted for differences in the variance of the counterions. Through ANOVA, we found all explanatory variables to be statistically significant (counterions in the membrane: $\chi^2 = 154.01, df = 3, p < 0.001$; anions in the external salt solution: $\chi^2 = 797.53, df = 3, p < 0.001$; interactions between the counterions in the membrane and the anions in the external solution $\chi^2 = 297.80, df = 9, p < 0.001$).

A detailed overview of the post-hoc tests is presented in Table 2. In post-hoc comparisons, either the membrane counterion or the external salt solution was held constant, while the other variable was systematically varied. For chloride and acetate membranes, post-hoc comparisons indicated significant differences between all external solution except sodium bicarbonate and sodium chloride solutions. For bromide membranes, the comparisons between sodium bicarbonate and sodium chloride, sodium bicarbonate and sodium bromide, and sodium chloride and sodium bromide were significant in post-hoc comparisons. For bicarbonate membranes, the comparison between sodium acetate and all remaining salt solutions was statistically significant as well from post-hoc comparison. Notably, post-hoc tests did not identify significant differences between different counterions in the same external salt solution.

The time to reach the peak tip displacement is described by a linear-mixed effect model with the anions in the external solution, the counterion form, and their interactions as explanatory variables. The model employed the membrane identification number as a random effect. Only the interactions between the solution anions and counterions were found to be statistically significant.
From Figure 7 it is evident that the time to reach the peak displacement was almost independent from the solution anions and the counterion form and lied in the range of 2 - 4s. Only the comparison of acetate with bicarbonate, chloride, and bromide anions for the bromide membranes indicated a statistically significant difference. This trend is in agreement with the results on cation-exchange membranes,[34] whereby the time-scale of actuation is dominated by the added mass effect from the displacement of the solution surrounding the membrane.[35,36] Such an effect scales with the width and length of the membranes, which are fixed in the current experiments.

2.7. Discussion

We conducted a series of hypothesis-driven experiments to unveil the actuation of anion-exchange membranes in salt solution. Specifically, we investigated the influence of the hydration number of the counterions and solution anions on the tip displacement. Based on the description of solvation-driven actuation,[33] we formulated the following experimental hypotheses:

• (H1) The peak current is influenced by the external salt solution and increases with the ionic conductivity of the solution anions.

• (H2) The actuation response of the anion-exchange membrane is determined by the hydration number of both the counterions and the anions in the external salt solution.

• (H2a) Increasing the hydration number of the anions in the external salt solution results in an increase of the tip displacement.

• (H2b) For anions with a small (large) hydration number in the external salt solution, increasing the hydration number of the counterions results in a decrease (increase) of the tip displacement.

Results about the peak current confirm hypothesis H1. As expected, the peak current is determined by the anions in the external solution only, while the counterions have no influence on the peak current. Varying the anions in the external salt solution altered the resistance of the salt solution and therefore affected the peak current. Thus, the higher peak current of sodium chloride and sodium bromide solutions can be explained by the higher ionic conductivity of sodium and bromide anions compared to bicarbonate and acetate anions.[37]
some of the membranes after immersion in salt solution. Furrness. The pre-stresses caused severe bending or twisting of membranes, whose effect was exacerbated by their small thickness. The manufacturing process may have induced pre-stresses in our compared to the commercial membranes used in Ref. [33]. The hypothesis H2b. In fact, we failed to detect any significant membrane on the peak tip displacement, corresponding to material properties could have occurred.

With respect to the tip displacement, we first examined the bending direction of the membrane. After the application of the external voltage, all membranes bent in the direction opposite to the electric field. Notably, no combination of external salt solution and counterions in the membrane resulted in a negative peak tip displacement. This result supports our theory that actuation is driven by solvation.

Through our statistical analysis, we found a significant influence of the anions in the external salt solution on the peak tip displacement, corroborating our hypothesis H2a. For chloride and acetate membranes, we recorded a significant difference between all external salt solutions except for sodium bicarbonate and sodium chloride. For bromide membranes, all comparisons including sodium acetate solution were not statistical significant. We attribute the lack of significance of these tests to large variability in the peak tip displacement values of membranes. The increase in the variance of the response compared to the previous experiments with cation-exchange membranes[33] is traceable to the in-house manufacturing of the anion-exchange membranes and to the smaller thickness compared to the commercial membranes used in Ref. [33]. The manufacturing process may have induced pre-stresses in the membranes, whose effect was exacerbated by their small thickness. The pre-stresses caused severe bending or twisting of some of the membranes after immersion in salt solution. Further, even though all membranes were cut from the same sheet of anion-exchange material, local differences in thickness and material properties could have occurred.

We argue that the large variation in the response of the membranes masked the influence of the counterions in the membrane on the peak tip displacement. As argued in the theoretical prediction and shown in our previous experiments with Nafion membranes,[33] the influence of the counterions is expected to be less prominent than that of anions in the external solution, such that it could be more easily concealed by experimental variability.

The time to reach the peak tip displacement did not allow to find a distinct influence of the anions in the external solution and the counterions. The actuation time was found to be in the range of 2 – 4s, independent of the counterion and external salt solution. These results are in agreement with our expectations on the dominant role of added mass in determining the timescale of actuation.

Even though individual membranes exhibited absolute peak tip displacements on the same order of Nafion membranes,[33,34] the median of the absolute actuation magnitude was three times smaller. Accounting for differences in the Young’s modulus and the smaller moment of inertia, the strength of the actuation is considerably lower than in cation-exchange membranes (a comparison between actuation in anion- and cation-exchange membranes can be found in the Supporting Information). As the actuation magnitude is determined by the electrochemistry inside the membrane, the weaker actuation response might be explained in terms of a smaller charge pile-up at the membrane boundary layers. In terms of the time to reach the peak tip displacement, both membrane types showed comparable performance, even though the anion-exchange membranes were slightly slower.[33]

Overall, it is safe to propose that the actuation performance of the investigated anion-exchange membrane is inferior to Nafion membranes, in agreement with previous work on anion-exchange membrane-based IPMCs.[42–45]

Ultimately, our results demonstrate, for the first time, the use of anion-exchange membranes as contactless soft actuators, with potential applications in soft robotics and biomimetic applications.[57–59] An advantage that arises from the utilization of ion-exchange membranes as soft actuators is the streamlining of the manufacturing process through the use of freeform fabrication and the omission of additional fabrications steps like plating, as the membrane is directly used as the active material. Simplifying the manufacturing is an important step toward the application of functional materials in real-world scenarios. Furthermore, multiple actuators can be used with one pair of electrodes, thus simplifying the design and wiring that would be challenging with IPMCs. As the actuation response depends on the presence of an external salt solution, these actuators require electrolyte environments to operate.

In our experiments, we observed a bending in the direction opposite to that of the electric field, opposite to cation-exchange membranes. This difference in the bending direction could enable the realization of complex deformation states by combining anion-exchange and cation-exchange membranes in attentively designed composite structures. Moreover, the combination of membranes with different ion-permeabilities allows us to develop programmable actuators. A key shortcoming of the actuators utilized in our study is the large variation in their bending performance, as well as their weaker actuation performance compared to Nafion membranes. A detailed experimental characterization of different membrane materials and material
standardization should be undertaken in future research to establish reliable anion-exchange actuators with desired actuation performance. These characterizations should include the study of the influence of the applied voltage and the concentration of the external salt solution on the actuation.\cite{34} As a critical line of future research, experiments that separately investigate the influence of the entering and leaving anions are required to fully corroborate our hypotheses. These experiments could be afforded by ad-hoc modifications of the membrane microstructure, seeking to affect anions’ motion in one of the two double layer regions without influencing the other. Finally, optimizing the actuation performance of anion-exchange membranes with the aim of matching cation-exchange membranes is an important next step to enable composite actuators of both materials.

3. Experimental Section

**Material:** Sodium bicarbonate (S6014), sodium chloride (S9888), sodium bromide (310506), and sodium acetate (241245) with a purity of 99.0% were all purchased from Sigma Aldrich.

**Manufacturing of the Anion-Exchange Membrane:** Precursor polymer (BPBr-100): A mixture of 7-Bromo-1,1,1-trifluoroheptan-2-one (1.12 g,
After 6 h. Deionized water (1.0 mL) was added to the solution to dissolve the precipitate. A sequence of addition of trimethylamine, stirring with water, and pouring slowly into methanol. White fiber formed was filtered and washed with hot methanol. After drying under vacuum, 1.70 g of white solid was obtained for BPBr-100 (yield: 97%). 1H NMR (CDCl3): δ (ppm) 7.56 (4H, Ha), 7.35 (4H, Hb), 3.21 (2H, H3), 3.02 (9H, N(CH3)3), 2.54 (2H, H5), 1.61 (2H, H6), 1.28 (2H, HA), 1.21 (2H, HB). 19F NMR (DMSO-d6): δ = -64 (s, CF3).

Poly(biphenylene) (BPNI-100): BPBr-100 (0.2 g) was dissolved in THF (2.0 mL). Aqueous solution of trimethylamine (2.0 mL) was added to the solution, which was then stirred at room temperature. The solubility of polymer gradually decreased, and the ionic polymer was precipitated after 6 h. Deionized water (1.0 mL) was added to the solution to dissolve the precipitate. A sequence of addition of trimethylamine, stirring at room temperature for 6 h, and dissolution of the precipitate with addition of water was repeated one more time. Volatile solvent was evaporated using a rotary evaporator and the residue was redissolved with a small amount of MeOH (approximately 2.0 mL). The ammonium polymer was precipitated by adding ether, filtered, and dried under vacuum (0.227 g, yield: 97%). 1H NMR (DMSO-d6): δ (ppm) 7.39 (4H, Ha), 7.39 (4H, Hb), 3.21 (2H, H3), 3.02 (9H, N(CH3)3), 2.54 (2H, H5), 1.61 (2H, H6), 1.28 (2H, HA), 1.21 (2H, HB). 19F NMR (DMSO-d6): δ = -64 (s, CF3).

Preparation of the Salt Solutions: In order to obtain the salt solution for the ion-exchange and the external salt solution, appropriate amounts of the sodium salts were mixed with deionized water. The used mass depended on the desired concentration, the volume of the solution, and the molar mass of the compound. The beaker with sodium salt was then filled up with deionized water to provide the needed solution volume V. We prepared 1 L with a concentration of 0.1 M for the external salt solution and 30 mL with a concentration of 1.0 M for the ion-exchange solution. The external salt solutions were mechanically stirred for at least 1 min at 700 rpm. The ion-exchange solutions were mechanically stirred for at least 1 min at 3000 rpm.

Due to their basic character, bicarbonate and acetate anions reacted with water to form carbonic acid and acetic acid, respectively. Thus, the precipitate. A sequence of addition of trimethylamine, stirring with water, and pouring slowly into methanol. White fiber formed was filtered and washed with hot methanol. After drying under vacuum, 1.70 g of white solid was obtained for BPBr-100 (yield: 97%). 1H NMR (CDCl3): δ (ppm) 7.56 (4H, Ha), 7.35 (4H, Hb), 3.21 (2H, H3), 3.02 (9H, N(CH3)3), 2.54 (2H, H5), 1.61 (2H, H6), 1.28 (2H, HA), 1.21 (2H, HB). 19F NMR (DMSO-d6): δ = -64 (s, CF3).

### Table 2: Results of post-hoc comparisons for the peak tip displacement. In the left half of the table, the type of counterions in the membrane is held constant, while varying the anions in the external solution. In the right half of the table, the external salt solution is held constant, while varying the type of counterions in the membrane. Statistically significant comparisons are marked bold.

| Comparison solutions | Br− counterion | p | NaBr solution | NaHCO3 solution |
|----------------------|----------------|---|---------------|-----------------|
| CH3COONa - NaHCO3   | CH3COO− - HCO3− | 1.000 | CH3COO− - HCO3− | 0.001 |
| CH3COONa - NaCl     | CH3COO− - Cl−   | 0.719 | CH3COO− - Cl−   | 0.747 |
| CH3COONa - NaBr     | CH3COO− - Br−   | 0.348 | CH3COO− - Br−   | 0.001 |
| NaHCO3 - NaCl       | HCO3− - Cl−     | <0.001 | HCO3− - Cl−     | 0.874 |
| NaHCO3 - NaBr       | HCO3− - Br−     | <0.001 | HCO3− - Br−     | 1.000 |
| NaCl - NaBr         | Cl− - Br−       | 0.17 | Cl− - Br−       | 0.901 |

| Comparison solutions | Cl− counterion | p | NaCl solution |
|----------------------|----------------|---|---------------|
| CH3COONa - NaHCO3   | CH3COO− - HCO3− | 1.000 | 1.000 |
| CH3COONa - NaCl     | CH3COO− - Cl−   | 0.277 | 0.438 |
| CH3COONa - NaBr     | CH3COO− - Br−   | 0.096 | 1.000 |
| NaHCO3 - NaCl       | HCO3− - Cl−     | 0.309 | 0.896 |
| NaHCO3 - NaBr       | HCO3− - Br−     | 0.100 | 1.000 |
| NaCl - NaBr         | Cl− - Br−       | 0.629 | 0.286 |

| Comparison solutions | HCO3− counterion | NaHCO3 solution |
|----------------------|------------------|-----------------|
| CH3COONa - NaHCO3   | CH3COO− - HCO3− | 1.000 |
| CH3COONa - NaCl     | CH3COO− - Cl−   | 0.001 |
| CH3COONa - NaBr     | CH3COO− - Br−   | 0.001 |
| NaHCO3 - NaCl       | HCO3− - Cl−     | 1.000 |
| NaHCO3 - NaBr       | HCO3− - Br−     | 1.000 |
| NaCl - NaBr         | Cl− - Br−       | 0.001 | 0.966 |
in the equilibrium state the concentration of acetate and bicarbonate ions was lower than the initial concentration of the sodium salt. The concentration reduction of bicarbonate and acetate anions in the equilibrium state lay within our experimental tolerance. We did not consider the occurring reaction in determining the mass of salt for the solutions. Detailed calculations can be found in the Supporting Information.

Ion-Exchange: To change the mobile counterion of the anion-exchange membrane, the membranes were stored for 48 h in 30 mL of a 1.0 M solution of the desired anion. During the ion-exchange, the membranes were separately stored between stabilizing meshes in rectangular containers. The use of stabilizing meshes prevented bending and twisting of the membranes during ion-exchange, which was particularly critical during the first ion-exchange with the dry membranes. The membranes that were not used in an experimental run or underwent an ion-exchange were stored in deionized water.

Figure 7. Box plot of the time to reach the peak tip displacement of the different counterion forms inside of NaBr, NaCl, NaHCO₃, and CH₃COONa solution. The median is depicted as the line in the middle of the box and the first and third quantiles as the vertical limits of the box. The whiskers show the 1.5 interquantile range and outliers are marked as crosses. Differences between experimental conditions that were found to be statistically significant in post-hoc tests are identified by a brace with an asterisk.

Reusing of the Anion-Exchange Membranes: The twelve membranes were divided into four sets of three membranes each, where each set had the same type of counterions. Therefore, experimental conditions with the same counterions were conducted with the same set of membranes. The division of the membranes into counterion sets helped preventing impurities in the membranes, due to the presence of an anion other than the desired counterion in the membrane. Each experimental condition in which counterions were different from the anions in the external salt solution introduced impurities. To allow for their reuse, the membranes underwent another ion-exchange in a concentrated 1.0 M solution of their counterion salt after the completion of an experimental run.

Procedure of an Experimental Trial: In the first half of the experiments the chloride and bromide membranes were tested in the order of sodium bicarbonate, sodium chloride, sodium bromide, and sodium acetate solution. The bicarbonate and acetate membranes were tested in the reversed order. During the second half of the experiments the order...
of solution was reversed for each membrane set. Experiments in the same external salt solution were conducted with the same set of external electrodes. After the first half of the experiments, the electrode sets were assigned to another external solution. The electrodes that had been used in sodium bromide, sodium chloride, sodium bicarbonate, and sodium acetate in the first half of the experiments were used in sodium acetate, sodium bicarbonate, sodium chloride, and sodium bromide, respectively, during the second half of the experiments.

Before the start of an experimental run, each electrode (100 mm x 100 mm x 4 mm) was mounted inside of an electrode holder, connected to alligator clips, and placed inside of a clear acrylic box (120 mm x 120 mm x 100 mm) filled with 1 L external salt solution. The resistance between the alligator clips and the electrodes was ensured to be below 1.0 kΩ. The two electrode holders were positioned in the solution leaving additional space between them to allow for an easier mounting of the membrane. Due to their small thickness, the membranes were extremely sensitive to dehydrate once exposed to air. Thus, special care had to be taken during the mounting of the membranes. The membrane was clamped between acrylic plates and mounted in the external salt solution leaving a free wet length of l = 70 mm. Due to the varying water uptake of the membranes in different counterion forms,[60] the clamped length of the membranes varied. To allow the membrane to rehydrate after the mounting process, we waited at least five minutes before the start of the measurement. Next, the two parts of the electrode holder were carefully brought together and fixed with clamps. In the closed state the distance between the electrodes was w_e = 12 mm. The filling height of the solution after the mounting of the electrodes and the membrane was 76.4 ± 0.01 mm, which resulted in a submerged electrode area of S_e = 1.148 mm^2.

Due to the low-frequency shift associated with the rehydration of the membrane, the tip displacement could approach the limits of the laser displacement sensor. If the output signal approached the upper or lower bound, the laser was zero-shifted during the time period in which the electrodes were shortened, thus not affecting the results. In case voltage pulses were not recorded during the original measurement, the missing pulses were repeated after the initial measurements and the data sets were merged during the pre-processing.

After the end of an experimental trial, the tested membrane was immediately immersed in deionized water. Once the five experimental trials were completed, the membranes and all parts of the experimental setup in contact with the salt solution (the electrode holder, the electrodes, the membrane clamps, and the acrylic clamps) were thoroughly cleaned with deionized water. Finally, the membranes were immersed in an ion-exchange solution for 48 h to allow for the removal of impurities.[61]

Laser Calibration: The laser displacement sensor utilized in our experiments is calibrated to be used in air. To account for differences in the refraction index of air and the salt solution, we determined the relation between the output voltage of the laser and the measured displacement in millimeter through additional, controlled measurements. During these measurements, the laser was positioned at the same distance from the acrylic box and the 1 L 0.1 M solution was prepared as for the experiments. Distance holders of known thickness were stacked in the back of the acrylic box and the associated output voltage was measured. For each solution, we obtained the conversion coefficient as the slope of the linear regression of the output voltage against the known distance values. The coefficients used for each salt solution can be found in Table 3.

Pre-Processing of the Data: From the current signal, we found the peak current as the maximum absolute value of the time series after the application of the voltage pulse. In the analysis, only the peak current values associated with the charging of the electrodes were considered. Before the extraction of the peak tip displacement, high frequency noise was removed from the displacement time series by using a sixth order Butterworth filter with a cutoff frequency of 50 Hz provided by the built-in MATLAB function butter. Due to slow rehydration process following the mounting of the membrane, the tip displacement displayed a low frequency drift. To remove this effect, we subtracted from the filtered signal a displacement offset, determined as the mean tip displacement in the 5 s before the application of the voltage. The peak tip displacement was found as the absolute maximum of the tip displacement in the 1.4 s following the voltage pulse. This time range was manually tuned to select the first displacement peak. We identified the bending direction from the sign of the peak tip displacement. A positive peak tip displacement corresponded to a bending in the direction opposite to the electric field, while a negative peak tip displacements corresponded to a bending in the direction of the electric field.

The time to reach the peak tip displacement was calculated as the time difference between the peak tip displacement and the applied voltage pulse. The time of the voltage pulse was identified from the associated current peak. Finally, outliers in the data were removed by the MATLAB function rmoutliers and replaced by a random sample from the data in the same experimental condition.

Repetition of Experimental Conditions: After the immersion in sodium acetate solution, chloride and bromide membranes experienced a severe twisting or bending motion. In some cases, the membrane tip twisted up to ninety degrees from its initial orientation, making a measurement with the laser displacement sensor impossible. Even though all membranes were cut from the same anion-exchange membrane sheet, this behavior was limited to certain membranes of the bromide and chloride set. Thus, we suspect local differences of the microstructure and pre-stresses in the manufacturing process to cause this problem. The two affected experimental conditions were repeated with the spare membranes. In accordance with the main experimental investigation, each experimental condition was repeated twice and all of the spare membranes received a unique membrane identification number. In the statistical analysis the data from the repeated measurements was used. In the bromide form, one of the the spare membranes showed the same problematic behavior as the original membranes. In order to provide a complete data set for the bromide-sodium acetate condition, the measurements of two spare membranes were combined with the ones of a membrane of the original membrane set that did not twist.

Table 3. Conversion coefficient between the output voltage of the laser and the membrane tip displacements in of NaBr, NaCl, NaHCO_3, and CH_3COONa solutions.

| Salt solution | Conversion coefficient [mm/V] |
|---------------|-----------------------------|
| NaBr          | 0.1961                      |
| NaCl          | 0.1956                      |
| NaHCO_3       | 0.1879                      |
| CH_3COONa     | 0.1906                      |

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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anion-exchange membranes, electrochemistry, electrolyte, soft actuators, solvation