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Role of the electric field in selective ion filtration in nanostructures†

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Nafion has received great attention as a proton conductor that can block negative ions. Here, we report the effect of a Nafion coating on an anodic aluminium oxide (AAO) nanoporous membrane on its function of ion rejection and filtering depending on the electric field. In our experiments, Nafion, once coated, was used to repel the negative ions (anions) from the coated surface, and then selectively allowed positive ions (cations) to pass through the nanopores in the presence of an electric field. To demonstrate the proof-of-concept validation, we coated Nafion solution onto the surface of AAO membranes with 20 nm nanopores average diameter at different solution concentration levels. Vacuum filtration methods for Nafion coating were vertically applied to the plane of an AAO membrane. An electric field was then applied to the upper surface of the Nafion-coated AAO membrane to investigate if ion rejection and filtering was affected by the presence of the electric field. Both anions and cations could pass through the AAO nanopores without an electric field applied. However, only cations could well pass through the AAO nanopores under an electric field, thus effectively blocking anions from passing through the nanopores. This result shows that ion filtration of electrons has been selectively performed while the system also works as a vital catalyst in reactivating Nafion via electrolysis. A saturated viscosity ratio of Nafion solution for the coating was also determined. We believe that this approach is potentially beneficial for better understanding the fundamentals of selective ion filtration in nanostructures and for promoting the use of nanostructures in potential applications such as ion-based water purification and desalination system at the nanoscale in a massively electrically integrated format.

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1. Introduction

Nanoscale structures and their properties have been widely used to enable the advancement and development of several key technologies in solving many problems, such as the lack of energy and water resources. Among chemical processing and industrial technologies, in particular, the importance of ion rejection technology is acknowledged, just due to its wide range of utilization but also for its high utility value.¹ Such a separation process could be roughly categorized into two types: physical and chemical technologies.² The processing includes some well-known technologies for separating nanoscale matter, such as ions, consistent with membrane separation technologies,³ such as reverse osmosis (RO)⁴ and electrodialysis,⁵ the activated carbon⁶ filtration process, ion

exchange resin⁷ management processing and Nafion coating⁸ and selective conductivity membrane⁹ technologies. The most widely known example could be RO, which utilizes a semi-permeable membrane to separate ionic compounds, similar to a fine sieve; this is commonly employed in seawater desalination processes, which are used to obtain fresh water from seawater by removing ionic compounds.^{10,11} In addition, other methods for separating particles from liquids by the size of the targeting materials within the liquids include the ultra-filtration membrane (UF membrane), which separates macromolecules, and the microfiltration membrane, which separates larger microorganisms. Also, there is the moderate-quality nanofiltration membrane (NF membrane), which separates micromolecules such as salts and organic acids, and that has a superior function than the UF membrane when separating ionic compounds, as well as being easy to manipulate at relatively lower pressure than the RO membrane (approximately 1 MPa). Such technologies are currently in practical use and have been applied to numerous other fields as well.

On the other hand, beside filtration technologies that depend upon the physical size of the pore, there are also filtration technologies that utilize electrical characteristics; some

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of the prominent examples include the electrodialysis method,⁵ the active carbon absorption method¹² and the ion exchange resin method.¹³ Electrodialysis (ED) refers to the process of separating ionic compounds by using a membrane that selectively permeates the separated cation or anion from electric field applied electrodes, inserted into an electrolyte solution. ED is similar to RO in that both of them use a separation membrane, but they are quite different in that the driving force for RO is pressure, whereas in ED, the driving force is an electric field. A further distinctive difference is that the RO process removes every substance in the solution, whereas ED removes electrically charged substances only. Moreover, ED installation is relatively simple, and so it is easier to maintain and repair. ED, in terms of phase-transition induced by an electric field, is performed by generating an electric field to the membrane, which then has selective permeability to the separated ion. Active carbon could selectively absorb various kinds of organic materials and hence can effectively remove organic materials at low concentration.¹⁴ Due to such characteristics, active carbon is regarded as an important process in environmental science, and is used repeatedly for its easiness in reproduction. It is known to be one of the most cost-effective methods among other techniques for the efficient removal of polar or particle contaminants that are insoluble to water, due to its remarkable absorption characteristics and wide surface area. However, it is known to be relatively less efficient in absorbing water-soluble inorganic ions. Ion exchange resin – a coupling of a 3D-structured fine macromolecular substrate and an ion exchanger – is a functional macromolecule that exchanges (and purifies) ions and ionic compounds dissolved in either polar, or nonpolar solutions. In other words, it is a resin that has a functionality of substituting ions in solution from movable ions that belong to the resin.

In general, such technologies conduct separation by utilizing ionic characteristics rather than utilizing their electric charge.¹⁵ Therefore, in the case of an ion exchange resin, it is less practical by the fact that the ion exchange membrane is changed by the targeting ions.¹⁶ Recently, an ion rejection method that utilizes the electric charge has been actively discussed, with one of the widely known examples being the utilization of Nafion, which can be employed as a proton delivering material, or for attaching metals to the nanopore's template.¹⁷

In the case of an ion-separation process by the ionic concentration polarization method, 99% of the salts could be removed, as well as preventing membrane blockage, and this is even effective in removing small-sized ionic salts, to large particles species with electric charge, such as cells, viruses, microorganisms.¹⁸ Such methods are advantageous in separating multiple ions using a single membrane device by utilizing the electrical characteristics of charged ions, regardless of their ionic characteristics, and thus these methods have been studied further for wider application.^{19,20} By using the ion-separation techniques mentioned above, the application to various fields is possible; not only for the desalination of sea-

water, but in developing fuel cells that could be used in both a liquid and solid state,²¹ as well as for manufacturing a proton membrane. One example could be the ion exchange macromolecule used in the hydrogen ion exchange membrane fuel cell and electrolyzer.²² This macromolecule electrolyte is an electron isolation membrane as well as a hydrogen ion conductor. The macromolecule electrolyte membrane fuel cell utilizes the hydrogen ion conductive macromolecule membrane as an electrolyte, which enables it to be operated in low temperature, and so it is relatively high in electricity generation efficiency, current density and output density, compared to other kinds of fuel cells. Also, its simplicity in stack design, durability to high-pressure difference and longevity lead to its focal position for research into mobile electric power and for use in the home.²³ Nafion, on the other hand, is used as a hydrogen ion exchange membrane for fuel cells, due to its high ionic conductivity, chemical resistance and ion selectivity. Its superior selective permeability allows Nafion to have a high current density and make it suitable for application with carbon nanotubes and graphene nanosheets, such as for use as a detection enhancing agent for adenosine and caffeine.^{24–28}

However, Nafion has a high viscosity, which makes it difficult to be coated. Because of this, extensive studies on nanopore-based filtering research have not yet been conducted, and most of the studies so far are limited to the research on theoretical ion transport velocity. Inspired by research conducted on selective filtration through multi-layered anodic aluminium oxide (AAO), we selected porous AAO as a material for Nafion coating among other materials for two reasons: (1) the pores of the AAO membrane allow the flow-through catalytic reaction, (2) the pore diameter, length and density of the AAO can be easily manipulated through the anodizing condition.^{29–31} In order to coat Nafion onto the AAO surface on a massive scale, the nanopore-based template was coated with conductive Nafion, diluted with ethanol in order to solve the viscosity problem with the coating. With this breakthrough method, ion rejection was conducted by designing and manufacturing on a massive scale nanopore-based conductive ion filters.

2. Experimental

2.1. Preparation of Nafion-coated and uncoated AAO nanofilters

The main objective in this study was to design, manufacture and optimize the functionality of a conductive nanopore ion filter by utilizing the nanopore structure and Nafion to develop a high-end ion filter. Conventionally, ion filtering has a number of problems, such as troublesome absorption methods, and even the method itself has often been limited by utilizing only the natural characteristics of ionized particles. Moreover, there has been a structural issue in using multiple kinds of membrane filtering. To resolve such problems, a singular membrane that utilizes the electrical characteristics

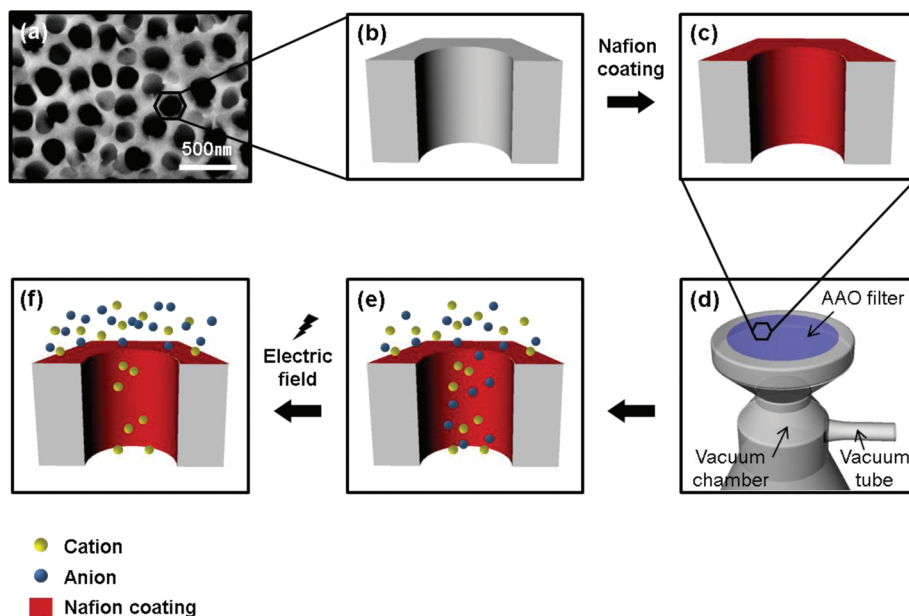


Fig. 1 Schematic for the functional development of a conductive nanopore ion filter coated with Nafion. (a) SEM image of the AAO membrane (frontal view). Note that each pore is funnel-shaped, with a 20 nm diameter at the bottom surface. (b) An enlarged view of a single nanopore (cross-sectional view). (c) An enlarged view of a single nanopore, coated with 30% Nafion solution (ethanol was used as a buffer). (d) An illustration of the nano-filtering experimentation device. The Nafion-coated AAO membrane is mounted on a vacuum filtering device. (e) Ion rejection as the ions flow through the nanopore. Note that a few anions escaped by the coated Nafion as the ions flow through the nanopore. (f) Ion rejection when the electric field was applied. Herein, the anions were captured at a higher rate than in (e).

of charged electrons from the ions is desired for the use of ion rejection.

To conduct the experiments, Nafion-coated AAO was used as a nanopore structure and was placed on a vacuum filtering device, as shown in Fig. 1. The AAO used in the experiments was the WHATMAN® Anodisc inorganic membrane, which was 43 mm in diameter, 60 μm in thickness, with a pore diameter of 20 nm, as shown in Fig. 1(a). There was a size difference between the front and the rear sections of the nanopores, as depicted in Fig. S1†. Also, to ensure the reliability of the experiments, a glass fibre filter was introduced as a pre-processing filter, in order to filter out any macro-sized floating matter. To ensure that the filtration process was solely based on nanopores, the WHATMAN® Vacuum filter set was used, as shown Fig. 1(d). Throughout all the experiments, an average pressure difference of 0.03 MPa was maintained *via* using an electric aspirator (JEIO TECH, Korea) in order to uniformly deliver equal negative pressure in each trial.

Selecting the targeted ionized solution was also necessary to ensure the conductive nano-filter was functioning properly. NaCl solution was nominated among other solutions because salt is abundant in nature. Besides, it is an ideal candidate for evaluating the potential for seawater desalination. To reconstitute the seawater to its maximum extent for the purpose of this study, the electrical conductivity of NaCl solution was adjusted to 50 mS cm^{-1} . Fig. S2† shows the details regarding the salinity of the NaCl solution and the conductivity. To produce NaCl solution with 50 mS cm^{-1} , the concentration

level was adjusted to 1 mol L^{-1} . Then, it was poured onto a vacuum filtering device to conduct the experiments, as shown in Fig. 1(e). As shown in Fig. 1(c), coating Nafion at the inner surface of the nanopore was essential for this study. In this study, ethanol was selected as the solvent for the purpose of the study, because ethanol can be evaporated so that no ethanol residue is created, and, furthermore, it is not reactive to Nafion. The experiments were designed in such a manner that the optimum ratio could be derived by arbitrarily setting up the ratio, followed by repeated experiments, to derive the results for analysis, as in a typical trial-and-error approach. For the purpose of analysis and comparison, the Nafion-coated AAO filter was regarded as the test group, and those filters without Nafion coating were regarded as the control group.

2.2. Filtration set-up combining an electric field generator with a vacuum device

Conductive filtering experiments were designed by connecting the cathodes and anodes with copper tape on the vacuum filtering device. To ensure that the lengths between the electrodes were uniformly aligned, the cathodes and anodes were spaced at 3 cm distance. An electric field was to be applied to the AAO with the optimum ratio, in order to clarify the two points. First, it was performed to confirm whether the ion rejection mechanism was solely based on Nafion's electrical characteristics. Second, it was performed to find the appropriate electric field strength for ion rejection. To aim these objec-

tives, a series of experiments was designed to obtain quantitative results, as in a trial-and-error approach.

2.3. Measurement of conductivity

Quantitative measures of ion rejection were performed by measuring the electric conductivity before and after filtration of the ionized solution. The filtration of the ionized solution was processed as shown in Fig. S3.† The electric conductivity was measured by an electrical conductivity meter (Korea Tech's COND 6+) with revision of the pH value and temperature.

3. Results and discussion

3.1. Finding a certain solvent ratio of dilution for Nafion coating

NaCl solution was poured onto Nafion-coated AAO with different dilution ratios of 10%, 20% and 30% to examine the optimum ratio for ion rejection. As in Fig. 2, the ion rejection rates were 25%, 34% and 55%. Also, the flow rates were 24%, 15% and 11%, in respect of the ascending ratio of Nafion dilution. The results from the repetitive experiments of finding the optimized ratio of Nafion and the ethanol solvent indicated that the Nafion and flow ratios were in an inverse relationship. It was suspected that Nafion, by its nature, had a high viscosity, such that the AAO nanopore diameters were narrowed with the increase in Nafion concentration, which resulted in a flow rate decrease. Through additional experiments, a sharp decline in the flow rate was observed beyond

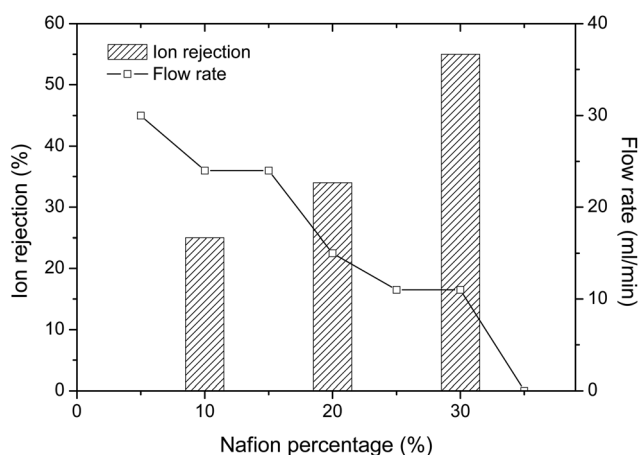


Fig. 2 Changes in the flow rate in respect to the ion rejection percentage and Nafion concentration percentage. Note the inverse correlation between Nafion percentage (as well as ion rejection percentage) and flow rate. With the increase in Nafion percentage, a corresponding increase in the ion rejection percentage occurred. However, the flow rate decreased with the increase in Nafion percentage and ion rejection percentage. This is due to the high viscosity nature of Nafion; when a high concentration of Nafion coating was applied, Nafion narrowed the size of the nanopore, and eventually at higher concentration, suppressed the flow.

30%, such that the flow rate was extremely diminished thereafter. Thus, it was concluded that the optimum ratio for ion-separation functionality with integrity was 30%. Since this study was intended to investigate a Nafion-coated AAO filter for its potential for a feasible substitution of conventional multi-layered membrane filtration, there are some unresolved issues that may require further research, namely Nafion coating on the AAO membrane was performed manually, but this resulted in a high deviation in values in the data, therefore, establishing an accurate preparation protocol may be required for overall quality assurance. Here the optimum ratio of ionic separation efficiency was further clarified by observing the SEM cross-sectional images of the modified AAO membrane by Nafion (data not shown here).

3.2. The presence of an electric field helps to reduce conductivity during filtration

As previously discussed in section 2.2, an electric field was applied to Nafion-coated AAO filter with the optimum ratio to examine the effectiveness of the filter, as well as to derive the ideal electric field strength. Through a repetitive filtering of NaCl solution for the control group (*i.e.* with the absence of an electric field), a drastic decrease in electric conductivity was observed until the second round, and then flattened out beyond the second round of filtration, as shown in Fig. 3(a). As shown in Fig. 3(a), more than two rounds of repetitive filtering seemed to have a marginal influence on the electrical conductivity. However, a significant decrease in electrical conductivity was even observed in the first round. Therefore, the following experiment with the presence of an electric field was conducted on the first round basis. According to the results, the difference in the electrical conductivity with the absence of an electric field was from 53 mS cm^{-1} to approximately 41 mS cm^{-1} , while the difference in the electrical conductivity in the presence of an electric field was from 53 mS cm^{-1} to 20 mS cm^{-1} at 7 V cm^{-1} . In other words, Nafion was able to execute ion separation to some extent without the aid of an electric field, but it was relatively ineffective. The ion separation results for the experiments in the presence of an electric field were examined, as shown in Fig. 3(b). A drastic decrease in conductivity was observed with an increase in the electric field strength up to 4 V cm^{-1} . Such a decreasing trend continued up to 7 V cm^{-1} , and then showed to show a small increase at 10 V cm^{-1} . However, no significant change in conductivity was observed beyond 10 V cm^{-1} . The repetitive experiments were conducted on Nafion-coated AAO at 10 V cm^{-1} , as shown in Fig. 4. The initial conductivity at 55 mS cm^{-1} dropped to 13 mS cm^{-1} at the maximum. The difference in ion-separation functionality by the electric field strength was also confirmed from the results in Fig. 3(b). The electric field strength was applied in an increasing order, and a significant difference in the electric field was observed up to 10 V cm^{-1} . To confirm if any significant change in electrical conductivity may occur at higher intensity, the strength was increased up to 20 V cm^{-1} , but the variability in the electrical conductivity difference was only 5%. Similar trends at 10 V cm^{-1} were identified with

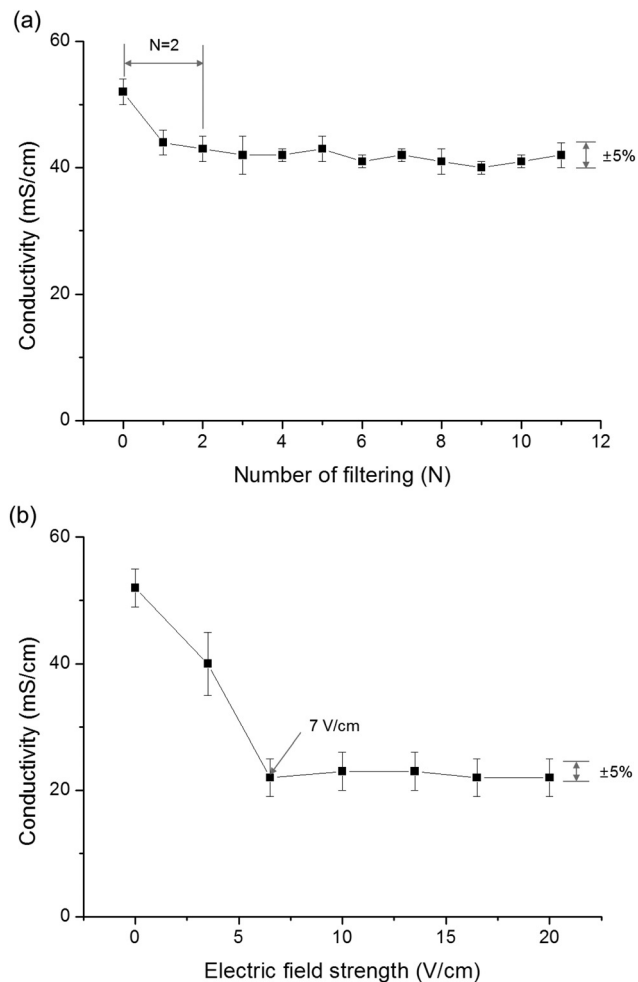


Fig. 3 (a) Relative conductivity versus the number of filtering, using Nafion-coated AAO. The average conductivity after the second round was 41% ± 5% approx. (b) Relative conductivity versus the electric field strength, using Nafion-coated AAO. A drastic decrease in conductivity continued up to 7 V, but such a decrease flattened out at a value greater than 7 V.

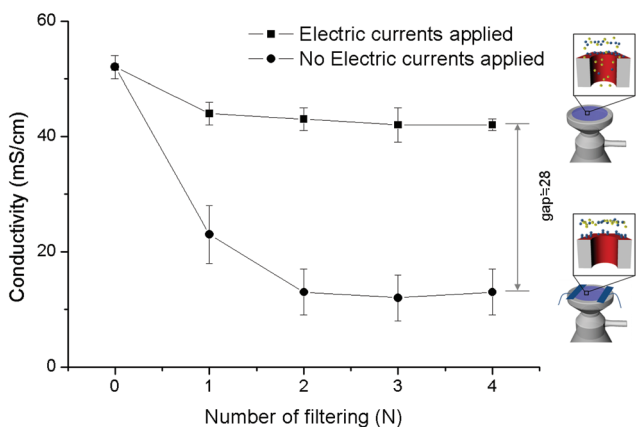
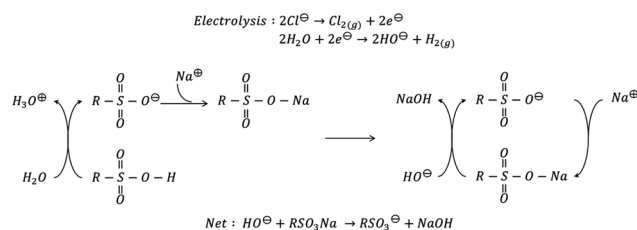


Fig. 4 Relative conductivity versus the number of filtering, using Nafion-coated AAO. The average difference in conductivity was 28 mS cm⁻¹, depending on the existence of the electric field.

various experiments, confirming previous findings with 20 nm nanopores. Fig. S4† shows the details regarding the follow-up experiments. Therefore, it was concluded that 10 V cm⁻¹ was the maximum strength for electric field in order to influence the decrease in electrical conductivity.

As shown in Fig. 4, a repetitive filtering experiment was performed to test for any possible effect on the ion-separation functionality for the Nafion-coated AAO filter with an electric field. The test results were regarded as a test group, and compared to those without an electric field. As shown in Fig. 4, a noticeable difference was observed in comparison. A steady decrease in electrical conductivity was observed up to the second round of the filtering process in the test group, unlike in the control group, where a significant decrease was observed in the first round. One reasonable explanation for this could be the amplification of ion-separation functionality with the aid of the electric field. Based on our hypothesis, in the presence of an electric field, anions will be filtered and an ionic depletion layer will be generated, which can then prevent cations from entering the Nafion-coated nanopores. The mechanism for this reaction is discussed in Scheme 1, and is illustrated in Fig. 5 as well. With the significant increase in separation functionality by the above-mentioned mechanism, a massive amount of anions accumulated on the top layers of the nanopores, thus generating a high degree of repulsive force and thereby creating an electric field on the top layer. This electric field gated the flow of charged particles, and eventually created an ion depletion layer.¹⁸ It might also be possible that a variation in the electric field strength may have an effect on the formation of the ion depletion layer. An investigation of this possibility may be potentially beneficial for enhancing ion-separation functionality. Overall, a massive amount of anions accumulated on the electromediated AAO filter by repetitive filtering, in a manner similar to nanoparticle polarization in electroporation.³² Furthermore, it has been recently found by our group that high possibilities of a time-varying applied bias, due to space charge motion, exist when an external current is applied between the two electrodes.³³ As indicated in Fig. 4, at least two rounds of filtering were required to generate the ion depletion layer, estimated from the fact that no significant decrease in electrical conductivity was observed beyond the second round of filtering. The difference made by the ion depletion layer was estimated to be 28 mS cm⁻¹.



Scheme 1 Hypothesized mechanism of the filtration process by coated Nafion in the presence of an electric field.

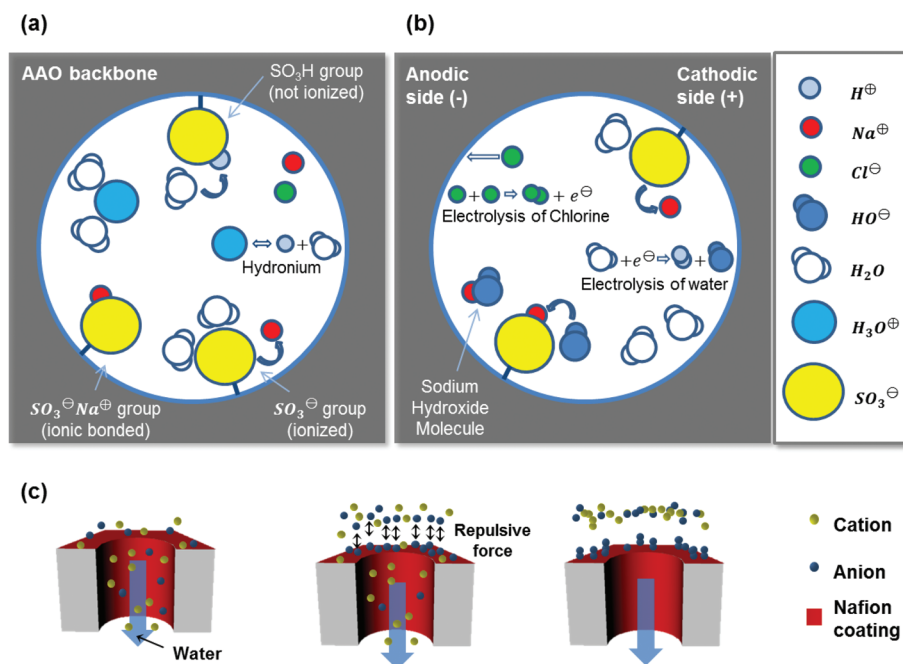


Fig. 5 Hypothesized mechanism of Nafion functionality on the AAO nanopore structure. (a) Illustration for hypothesized mechanism in the absence of an electric field at the pore surface. Negatively charged oxygen atoms in the Nafion compounds attract cations in the solution, such that cations enter at a faster rate than anions into the nanopores. (b) Illustration of the hypothesized mechanism in the presence of an electric field at the pore surface. When the currents are disseminated from the copper tape, water molecules in the solution are electrolyzed to hydrogen gas and hydroxide ions. The ionized hydroxides attract cations bonded to the oxygen atoms in the Nafion compounds. Thus, sodium hydroxide is formed then washed away with the solution, thereby reactivating oxygen atoms in Nafion to create ionic bonds with other cations. Overall, the reaction is catalyzed with the aid of hydroxides, thereby promoting greater functionality in ion separation. By the reactions occurring inside the nanopore, massively accumulated anions on the top layer generate an electric field by the anionic repulsion at high intensity. The electric field then creates an ion deficient layer, which amplifies the ion separation functionality. (c) Illustration of the hypothesized mechanism, both in the absence and/or in the presence of an electric field in the cross-sectional view of the pore.

4. Conclusions

In this study, Nafion-coated AAO nanopore structures were designed and investigated to examine whether this approach could be a feasible candidate for altering conventional multi-layered membrane filtration, which has several limitations as previously mentioned. A number of experiments were performed to confirm the feasibility, as well as to utilize the AAO filter to its maximum potential by applying an electric field. In summary, we discovered the following characterizations of Nafion-coated AAO filter in our experimental set-up: first, the optimum dilution ratio of viscous Nafion and ethanol solvent required to coat the nanopores was found. By conducting repetitive experiments, it was confirmed that the Nafion percentage and flow rates are in an inverse relationship. From this result, it was concluded that the ideal Nafion percentage was about 30% for maximizing the ion-separation functionality without suppressing the flow. Second, a noticeable enhancement in ion separation was discovered when an electric field was applied to the AAO filter with repetitive filtering. Through repetitive experiments, it was estimated that two rounds of repetitive filtering in the presence of an electric field maximizes the ion-separation effect. In comparison, the

difference between the test group and the control group was 28 mS cm⁻¹ at a maximum. We furthermore believe that this approach may not only be potentially beneficial for studying an alternative filtering method, but also for its use in several applications, such as in biological filtering and with environmental studies in the nanoscale.

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