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Driving Electrochemical Membrane Processes with Coupled Ionic Diodes

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Abstract

Ionic diodes have emerged repeatedly in the literature for gel interfaces, for nanopores and channels, for nano-/micro-fluidic systems, and for asymmetrically ionomer-covered microholes. Concentration polarisation is likely to be the key to understanding the diode function and the diode time constant τ_{diode}, *i.e.* the time for approaching steady state following a potential/polarity switch. For frequencies higher than $\omega_{diode} = 2\pi f = (\tau_{diode})^{-1}$, the polarization mechanism is too slow for ion current rectification. Below the frequency associated with the diode time constant, irreversibility in ion flow is induced and the diode switches between two resistive states at opposite potentials ("open" and "closed"). The irreversible flow of ions allows energy conversion from electrical to electrochemical. For energy conversion, two coupled ionic diodes are necessary driven by alternating current (AC) electricity to minimise driver electrode electrolysis and energy losses. Opportunities for AC-desalination and for electroosmotic water harvesting with coupled ionic diodes are discussed.
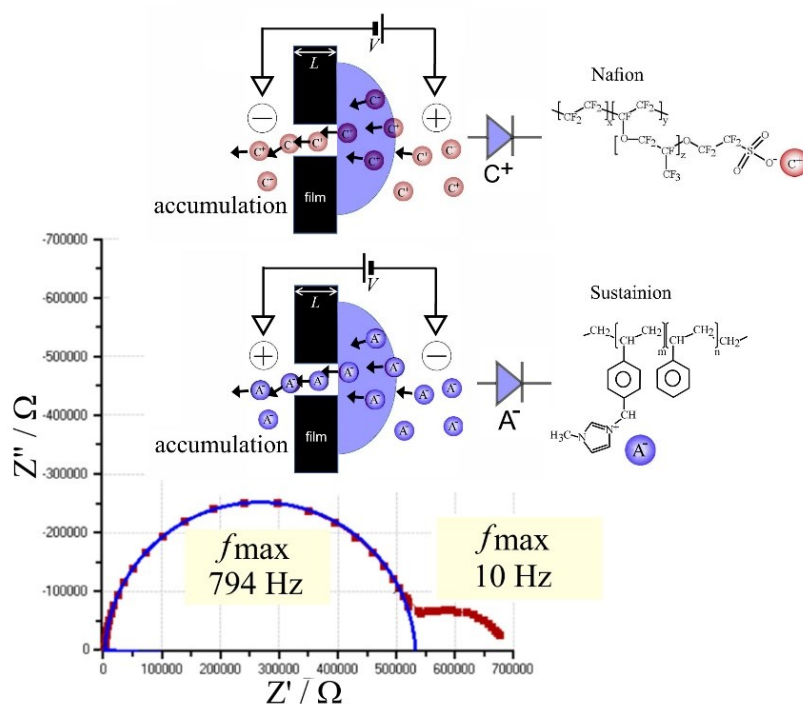
Graphical Abstract

1. Introduction to ionic diodes electrochemistry

Rectification refers to an alternating current (AC) input being rectified into a direct current (DC) output [1,2]. This output signal/current can be in the form of electron flow, ion flow, coupled transport of neutral molecules, or in the form of chemical reactions. Ionic diodes have been suggested initially by Bockris and coworkers at poly-electrolyte junctions [3], and then developed in a range of devices in ionic circuits [4,5] and in hybrid devices coupling electronic and ionic charge flow [6] or in salinity gradient energy harvesting [7]. Photo-switchable [8] and pH-switchable [9] ionic diodes have been reported. This review assesses new opportunities for membrane processes arising from coupled ionic diodes.

Ion transfer through ion-selective membranes can be associated with irreversibility and therefore with energy conversion, *i.e.* any energy conversion process requires some degree of irreversibility. An external potential applied to the membrane leads to (i) ion conduction, (ii) electroosmotic transport, and (iii) concentration polarisation [10]. When membranes are integrated in *asymmetric* devices, concentration polarisation can be exploited to create irreversibility or diode effects when using an AC excitation without any additional external energy conversion phenomena (*e.g.* without unwanted energy losses due to electrolysis at driver electrodes [11]). The literature on ionic diodes is dominated by devices that rectify [12] but without a clear vision of how to exploit the benefits of rectification with AC excitation. Often the driver electrode process is hidden for example in the device reference electrode.

A diode will allow uni-directional transport as shown schematically in Figure 1A. By coupling diodes (Figure 1B) the efficiency of the process can be improved. In the case of ionically conducting membrane processes, similarly single diode processes and coupled diode processes are possible. Ionic diodes based on concentration polarisation in a microhole [2,13] are illustrated in Figure 1C and 1D. An inert substrate (for example a thin Teflon film) with a microhole coated with a cation-conducting ionomer such as Nafion [14] and immersed in aqueous electrolyte will be either in an "open" or "closed" state (corresponding to "conductive" and "resistive", respectively) depending on external applied potential (cationic diode). In such microhole devices, an ion-selective membrane is asymmetrically placed on one side of a hole

(of approximately 5 μm to 40 μm diameter). Ion current rectification is based on accumulation or depletion of ions in the microhole depending on the direction of the applied electrical potential. The microhole serves a bottleneck for ion transport, thus its conductivity determines the overall diode state. Similar to cationic devices, a membrane device with *anion* conducting ionomer such as Sustainion [15] will undergo a transition from "open" to "closed" with the opposite external polarisation (anionic diode). With ionic diodes available for specific types of ions, new possibilities for coupled ionic diode processes arise (*vide infra*).
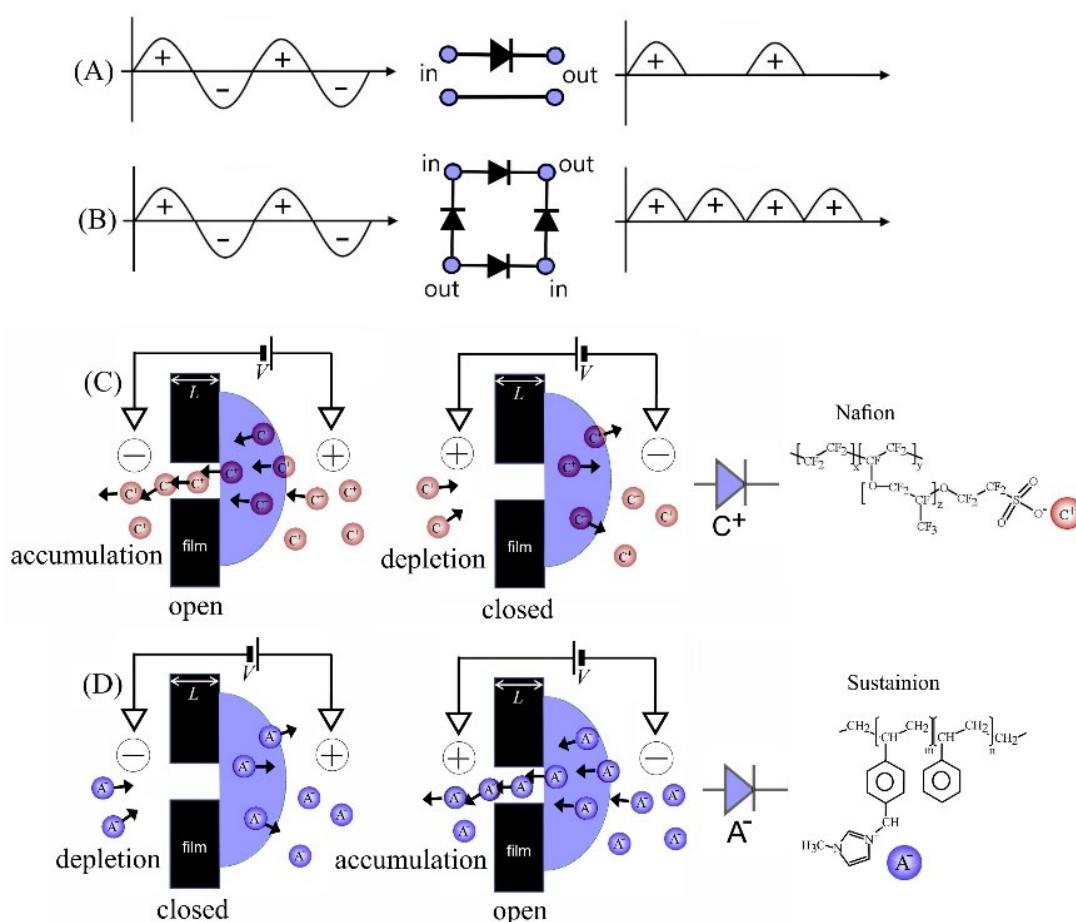
Figure 1. Schematic to illustrate (A) a single diode rectifier, (B) a coupled diode rectifier, (C) a cationic diode based on Nafion, and (D) an anionic diode based on Sustainion (reproduced with permission [15]).

Fundamentally, concentration polarisation in a microhole diode or in a nanohole diode [2] is only one of many options for ionic diode phenomena to occur. Other types of applied potential driven structural (and resistivity) changes can be implemented. The microhole design

introduces a time constant constraint on the performance linked to diffusion-migration of electrolyte. Figure 2A shows a typical data set for cyclic voltammetry data obtained with a 10 μm diameter microhole coated with Sustainion (see inset for experimental configuration). The data (with a scan rate of 0.2 V s^{-1}) are obtained essentially under quasi-steady state conditions (*i.e.* diffusion-migration into the microhole is fast when compared to the time scale of the experiment). The switch from open to closed state due to anion-semipermeable ionomer deposit is observed linked to anionic diode behaviour. An approximate equation describing steady state current *versus* voltage characteristics for ionic diodes has been suggested [16], but also the presence of further resistive/migrational modes has been pointed out by Aoki *et al*. [17].

When increasing the electrolyte concentration (on both sides), both open state current and closed state currents increase. The rectification ratio (here expressed in terms of the current at +2 V divided by the current at -2 V) is lowered with higher electrolyte concentrations indicative of a loss of performance. The diode effects rely on the ionomer being more ion conductive when compared to the aqueous electrolyte, and therefore a higher aqueous electrolyte concentration is detrimental to the rectification ratio. A similar data set for cyclic voltammetry with Nafion ionomer giving a cationic diode is shown in Figure 2B. The effects of higher electrolyte concentration on the diode are due to (i) loss of semi-permeability, (ii) a higher flux of electrolyte into the microhole in closed state limiting the increase in local resistivity, and (iii) an increase in bulk electrolyte conductivity relative to the ionomer ionic conductivity causing smaller concentration polarisation. A future challenge will be to improve both the rectification ratio and the diode time constant, both by better theoretical/computational study and by selection of improved ionomer materials.
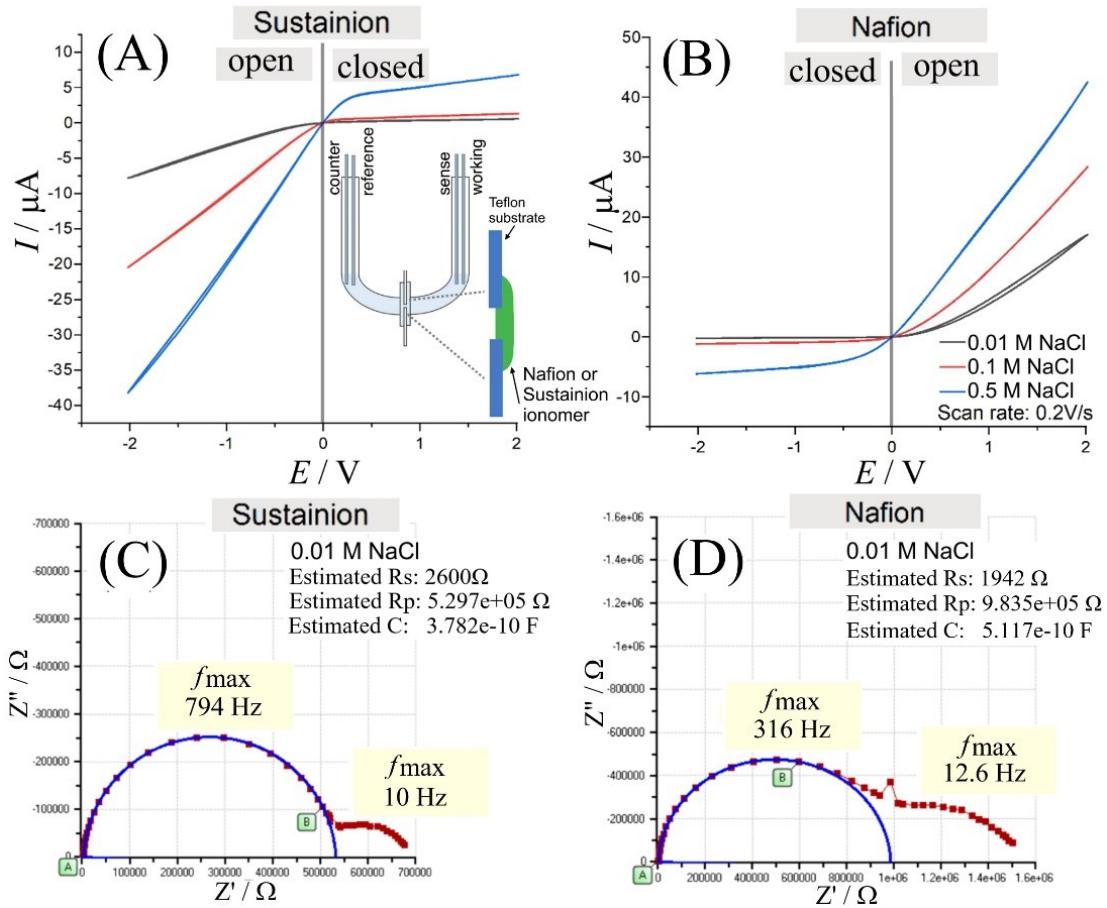
Figure 2. Data for ionic diode voltammetry at steady state (A) for Sustainion, (B) for Nafion, and for impedance spectroscopy (C) for Sustainion, and (D) for Nafion in aqueous 0.01 M NaCl. Ionic diodes are typically 5 μm thick ionomer asymmetrically deposited onto 5 μm thickness Teflon film with 10 μm diameter microhole (reproduced with permission [15]).

Steady state voltammetry can reveal the switching of open to closed state, but transient experiments based on higher scan rate voltammetry, chronoamperometry, or electrochemical impedance spectroscopy can reveal the switching process and the ionic diode time constant $\tau_{\text{diode}} = (2\pi f)^{-1} = (\omega_{\text{max}})^{-1}$. In fact, there are two time constants. The first RC time constant (associated with the high frequency semicircle) is due to the charging of the Teflon film (C_{Teflon}) and current flow via the microhole (R_p). The second time constant (associated with the apparently depressed semicircle at lower frequency (the depression originates from the diffusion-migration process into the microhole linked to the degree of polymer microhole filling) is linked to electrolyte diffusion-migration in the microhole region (typically 10 Hz or $\tau_{\text{diode}} = (2\pi f)^{-1} = 16$ ms) and can be interpreted here as the diode switching time [14]. This diode time constant scales with microhole diameter in a similar way when compared to microelectrode time-to-steady-state behaviour [18], *i.e.* smaller diameter ionic diodes switch

faster. An approximate diode time constant can be estimated based on the time to steady state for an inlaid disk microelectrode based on the Shoup-Szabo expression [19] for the case of reaching twice the current of the final steady state current. This leads to an ionic diode time constant $\tau_{diode} = 4\ r^2\ D^{-1}$. For a 10 µm diameter microhole (assuming no migration effects and $D \approx 10^{-9}$ m²s⁻¹), the approximate time constant is $\tau_{diode} = 100$ ms. For a nanopore of 10 nm diameter the expected time constant would be 0.1 µs (which can be observed only if membrane charging is extremely fast).
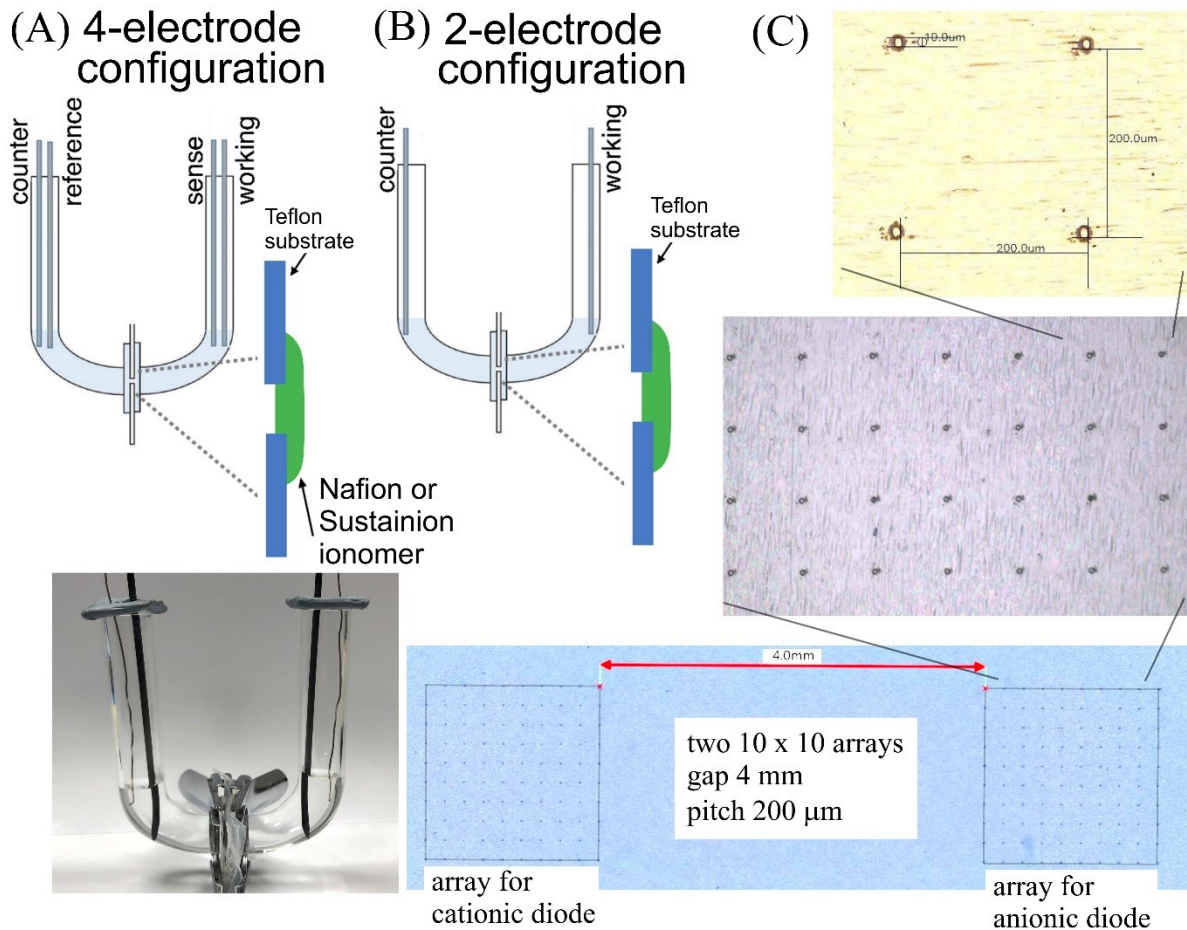
2. Applications of ionic diodes and coupled ionic diodes in desalination

Individual ionic diodes can be employed in sensing and in analytical devices [20,21,22]. This is based on both current magnitude and rectification ratio changing, for example, as a function of pH or specifically bound analyte molecules. In an analytical device, resistivity responses as analytical read-out are global (*e.g.* resistivity effect may arise from interfaces or structural ionomer changes or from adsorption). In contrast, the rectification parameter reports on a localised effect directly within the diode. By dividing the "open current" by the "closed current" signal fluctuations for example due to temperature can be suppressed.

More generally, ionic diodes have to be seen as "ion pumps" [23] with the ability to irreversibly move for example Na⁺ cations from one container into another. On its own, this would not be very useful, but in conjunction with a second ionic diode (moving Cl⁻), this can be developed into a desalination system. Figure 3A shows the classic 4-electrode configuration for applying a well-defined potential across the diodes. This allows diode currents to be measured. However, the 4-electrode configuration does not report the true applied voltage on counter/working driver electrodes. In contrast, the simpler 2-electrode configuration allows the true performance to be measured including energy consumption/losses [15]. An array of ionic diodes (shown in Figure 3C) can be employed to couple cationic (Nafion) and anionic (Sustainion) diodes into a complete desalination system without moving parts. This has been shown to work well for 10 mM NaCl resulting in desalination in one compartment whilst accumulating salt (salination) in the second department. For comparison, electrodialytic desalination has been proposed with a molecular redox shuttle linking anode and cathode (based on pumping liquid between anode and cathode) without the need for ionic diodes [24]. Unfortunately, for higher NaCl

concentrations, the ionic diode process becomes inefficient and further improvements in the diode design/materials are necessary. Selectivity in ion pumping could be an interesting avenue to pursue, but the diffusion-migration mechanism for the ionic diode would need to be improved/changed if only trace ions are pumped/separated from a majority electrolyte. New ionic diode mechanisms based on alternative approaches need to be developed.


Figure 3. Schematics of (A) the 4-electrode and (B) the 2-electrode cell configuration. (C) Micrographs showing arrays of microholes for applications in desalination (reproduced with permission [15]).

3. Future applications of coupled ionic diodes in AC-electroosmosis and beyond

Coupled ionic diodes with an AC-driver voltage can be employed to transport cation and anions to give net desalination/salination effects. However, each cation or anion will carry associated solvent/water molecules (electroosmotic drag [25,26]) to give secondary transport effects. Electroosmotic drag coefficients describe the number of water molecules transported per ion

and this number can vary substantially. For classic Nafion membranes the electroosmotic drag coefficient is usually below 10 [27]. For Sustainion materials the electroosmotic drag coefficient can reach 100 [28]. However, for polymers of intrinsic microporosity (PIMs [29]) the value can be even higher from several hundred up to 5000 depending on solution pH. In a recent report the polymer PIM-EA-TB [30] was investigated as an anionic diode (Figure 4). Tertiary amine sites are protonated with $pK_A = 4$ in aqueous media (and with approx. $pK_A = 3.5$ in ethanolic media [31]) to give a cationomer, and this results in anion transport. The molecular structure of this material is highly rigid at molecular level and therefore allows water molecules to be pushed through channels of typically 1 nm diameter. Figure 4A shows water flux without applied potential and in Figure 4B the effects of applying -1 V bias are shown. Crucial here is the effect of pH and Figure 4D summarises the change in electroosmotic drag coefficient with pH. Unfortunately, the lower degree of protonation not only increases electroosmotic drag coefficient, but also lowers the performance of the anionic diode. Ideally, the ionic diode performance should be maintained when coupled to electroosmotic flow.
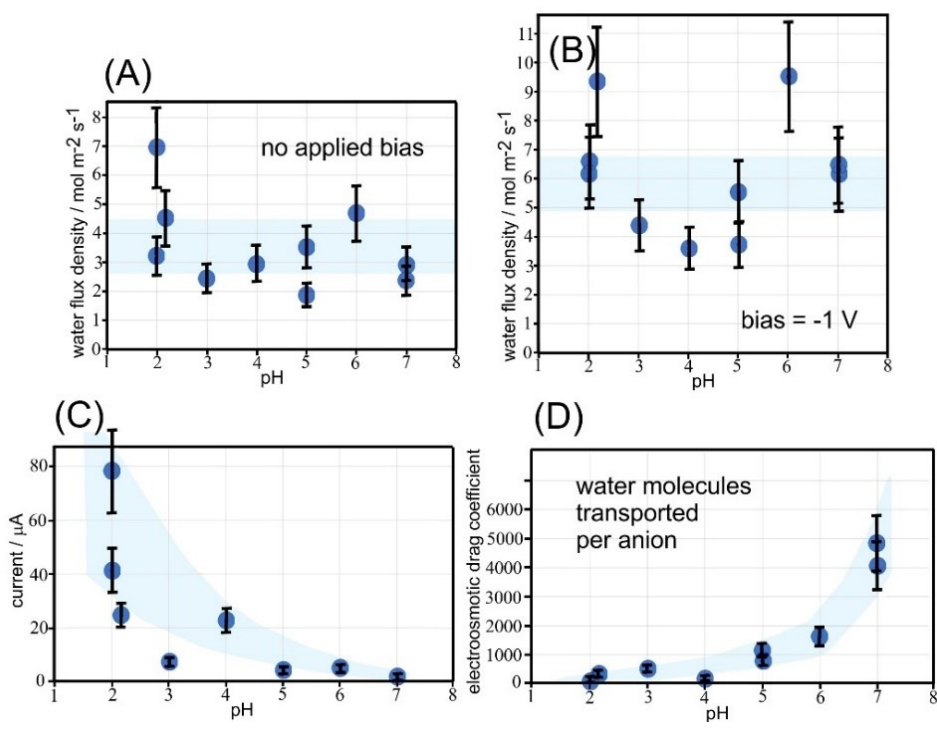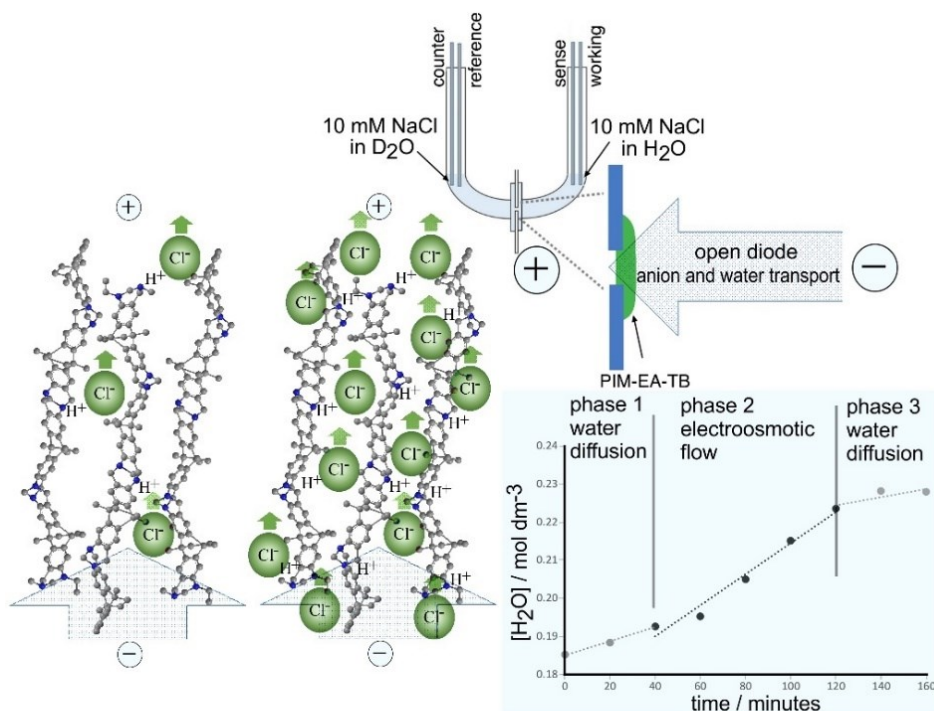
Figure 4. Schematic showing the measurement cell for H_2O transport into D_2O. Without applied current transport is dominated by diffusion across the membrane, which is not pH dependent (A). With applied bias at -1 V a minimum is observed at pH 4 (B). Replotting the data in terms of current (C) and in terms of the electroosmotic drag coefficient (D) shows how the ratio of water to chloride is increased with less protonation, *i.e.* the electroosmotic drag coefficient is defined by the Cl^- to H_2O ratio in the microporous solid (reproduced with permission [30]).

When coupling an anionic diode with high electroosmotic drag coefficient with another anionic diode with low electroosmotic drag coefficient, in principle a net zero anion transport should be observed associated with unidirectional water transport (mimicking biological water pumps [32]). Electroosmotic transport of other small molecules such as caffeic acid has been observed and therefore a coupled ionic diode device could deliver small molecules via AC-electroosmosis [33] (in contrast to devices based on DC electrolysis driving electroosmosis [34]) whilst functioning differently than AC eletroosmotic pumps. In some types of membrane materials heterolytic water splitting occurs (into H^+ and OH^-) due to high fields or added catalysts [35]. Coupled diodes of this nature would result in permanent pH gradients with zero net current flow. Some more coupled diode systems with associated chemical phenomena can be envisioned and summarised as follows:

- Cationic diode coupled to anionic diode: Transport of cations and anions in same direction resulting in net desalination and salination [15]. A combination of cationic diode and ionic resistors can be employed with additional compartments [36].
- Cationic diodes coupled to cationic diode (or anionic diode coupled to anionic diode); different ionomer materials: Transport of cations or anions in opposite direction (zero net ion transport) resulting in net electroosmotic flow of solvent (*e.g.* water transport [30]).
- Cationic diodes coupled to cationic diode (or anionic diode coupled to anionic diode); different ionomer materials: Transport of different cations (or different anions) resulting in electrolyte exchange or ion exchange.
- Cationic diodes coupled to cationic diode (or anionic diode coupled to anionic diode); different ionomer materials: Coupled formation of pH gradients [16] (zero net ion transport) leading to gradients in pH across the membrane.
- Cationic diodes coupled to cationic diode (or anionic diode coupled to anionic diode); different ionomer materials: Coupled formation of redox products (zero net ion transport) leading to gradients in concentration (*e.g.* iodine formation from iodide [37]) across the membrane.

4. Conclusions and future perspectives

Integrating ion-selective membranes into asymmetric device to form ionic diodes allows switching between closed and open states and in this way introduces irreversibility. This irreversibility can be exploited:

- An AC-current driven membrane process based on two coupled ionic diodes allows unidirectional transport of salts, solvents, or small molecules but also produce pH gradients or redox chemical products.
- The AC-driven process avoids driver electrode losses and electrolysis, and in this way removes requirements for external switches or pumps.
- The ionic diode performance especially in media of high ionic strength is currently too low to deliver, for example, effective seawater desalination devices.

Future work on ionic diode materials and on ionic diode mechanisms (developing both experiments and theory) will help overcoming current limitations. Both the rectification ratio and the time constant for diode switching can be improved. Smaller diameter ionic diodes are linked to faster switching time constants and therefore nanopore devices and arrays of nanopores are potentially beneficial. Importantly, there are many more mechanisms to be discovered/exploited for ionic diodes for example based on molecular scale design of membrane | electrolyte interfaces where an applied potential triggers structural/resistivity changes.

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