

Ionic Diodes and Ionic Rectifiers in Water Desalination

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ABSTRACT

Recent progress in ionic rectifier technology suggests that elementary devices based on microholes (5 to 40 μm diameter in 5 μm thick poly-ethylene-terephthalate or PET) are feasible based on, for example, highly conducting ionomers such as Nafion[®]. The main component to consider is the ionic diode (as “cationic diode” or “anionic diode”). The mechanism for the rectification effect can be traced back to a combination of ionomer conductivity (in the “open diode” state) and geometry-induced concentration polarization (in the “closed diode” state). This report describes state-of-the-art devices and it explores potential for applications of ionic rectifiers in water purification.

Keywords: ionic rectifier, diode, electrochemistry, water, energy

1 INTRODUCTION

Ionic rectification phenomena are well known and have been reported in nano-channels and at hydrogel/hydrogel interfaces. In particular nano-channel devices have been highlighted recently due to similarity to natural ion channels [1,2]. Applications of nano-channels have been proposed for example in analytical detection and DNA sequencing [3-5]. The surface charge in these channels is important to induce semi-permeable properties and therefore ion-selectivity into the double layer region [6,7]. Engineered materials with similar nano-channel diodes could be useful for example in energy harvesting [10] and in “iontronics” [11], the development of technology equivalent to “electronics” but based on ions.

Most work on nano-channel devices is currently being pursued with “track etch” membranes [12] or glass capillaries with nano-orifices [13]. Gating effects can be induced by surface functionalisation [14] as well as by exploitation of a conical geometry [15]. Hydrogels have been embedded as ionomers into conical channels [16], but also employed directly in junctions [17] or in “ionic transistors” [18,19].

Instead of using hydrogels, we have recently started using polymers with intrinsic microporosity [20] or PIMs. PIMs provide a molecularly rigid backbone structure and are therefore simple to process and to cast into thin layers

and membranes. When deposited onto a substrate of poly-ethylene-terephthalate (PET) with 20 μm diameter microhole, we observed “ionic diode” and “ionic flip-flop” effects [21,22]. Similarly, we observed that zeolitic imidazolium framework materials such as ZIF-8 or also cellulose can be used for ionic diode applications [23,24]. Here, we report that a commercial fluoropolymer (Nafion[®]), an intrinsically porous ion-channel containing material, provides excellent current rectification and ionic diode characteristics, when fabricated into the appropriate micro-structure [25].

A mechanism responsible for the “open” and “closed” diode has been proposed [25] and we have been able to observe both cationic diodes (Nafion) and anionic diodes (PIM). Figure 1 contrasts the functionality with cationic diodes allowing uni-directional cation flow and anionic diodes allowing uni-directional anion flow. In combination the cationic and anionic diode can be switched to allow salts to be transported only in one direction (here to the left compartment, Figure 1). The resulting desalination process could be employed with external potential applied as the driving force and without any moving parts such as pumps.

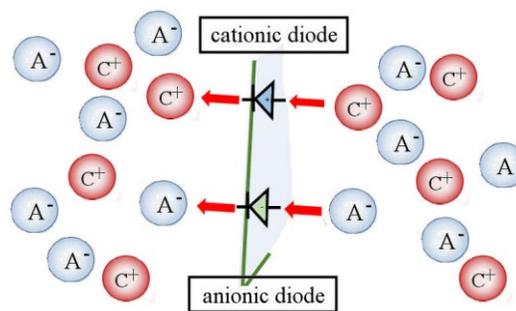


Figure 1. Schematic drawing of the effect of “cationic diodes” and “anionic diodes” on electrochemically driven ion flow across a membrane.

This report describes operational principles for the case of a Nafion-based cationic diode and the parameters that are responsible for the desalination process to be effective.

2 EXPERIMENTAL METHODS

Chemical Reagents: Nafion®-117 (5 wt. % in a mixture of lower aliphatic alcohols and water) and concentrated hydrochloric acid (37%) were obtained from Sigma-Aldrich and used without further purification. Solutions were prepared under ambient conditions in volumetric flasks with ultra-pure water of resistivity 18.2 MΩ cm from an ELGA Purelab Classic system.

Instrumentation: Electrochemical data were recorded at $T = 20 \pm 2^\circ\text{C}$ on an Ivium compactstat potentiostat system. A 4-electrode electrochemical cell (see Figure 2A) was used. The membrane separates two tubular half-cells (15 mm diameter), one with the Pt wire working and saturated calomel (SCE) sense electrode and the other with the SCE reference and Pt wire counter electrodes.

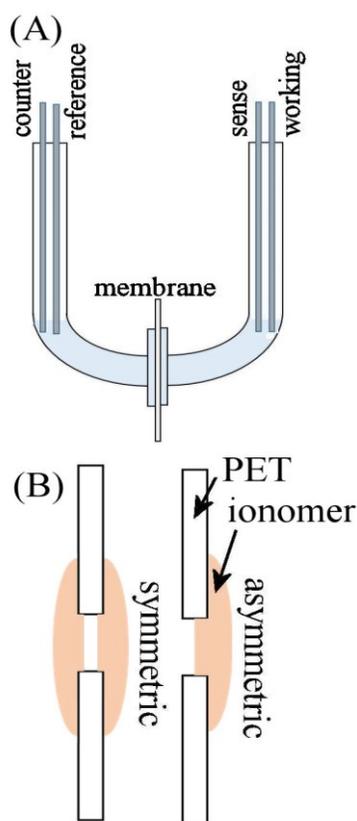


Figure 2. (A) Drawing of the membrane cell assembly based on two glass half-cells with potentiostatic potential control. (B) Drawing of the poly-ethylene-terephthalate film (PET, 6 μm thick) with ionomer deposited either on both sides (symmetric) or on one side (asymmetric).

Procedure for Membrane Preparation: In order to form films of Nafion® on the PET substrate with 10 μm diameter microhole in a 6 μm thick PET film (from Laser-Micro-Machining Ltd., Birmingham, UK) 10 μL Nafion solution was applied to a PET film on a glass substrate (pre-coated with a thin layer of 1% agarose gel to avoid Nafion

passing through the microhole) by solution-casting. With a glass rod the Nafion® solution was spread evenly over the PET to give a 1 cm² film, which after drying produced a thin uniform coating of typically 5 μm thickness (confirmed by fluorescence microscopy [25]). When peeled off the substrate, asymmetric Nafion deposits on the PET microhole are achieved (see Figure 2B). These are mounted in the electrochemical cell with Nafion deposit facing the working electrode (see Figure 2A). For symmetric deposits the deposition was repeated on the opposite side.

3 RESULTS AND DISCUSSION

Initial investigation of the Nafion ionic diode membranes was performed with cyclic voltammetry. Figure 3A shows a typical SEM image for a 10 μm diameter microhole in a PET film with Nafion partially inside of the microhole and forming a layer below the PET film. The Nafion film is observed both before and after use in electrochemical measurement confirming that the film assembly is robust and stable even at applied voltages of up to +/- 4 V.

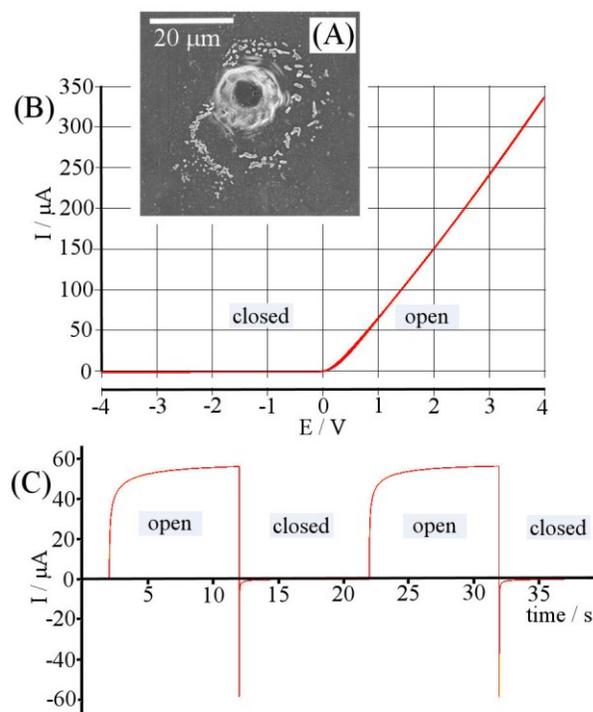


Figure 3. (A) Scanning electron micrograph (SEM) showing a 10 μm diameter microhole in a 6 μm thick PET film covered from the back with Nafion. (B) Cyclic voltammogram (scan rate 10 mVs⁻¹) for the ionic diode membrane placed between two half-cells with 10 mM HCl electrolyte solutions. (C) Chronoamperometry data for switching of the diode between “open” (+1 V) and “closed” (-1 V) states.

Figure 3B shows typical steady state cyclic voltammetry data obtained with a scan rate of 10 mVs⁻¹ and over a potential window of +/- 4V. In the positive potential range significant current can flow and the behaviour is essentially resistive. The observed resistance, 14.3 kΩ, is in first approximation given by the specific conductivity κ of the Nafion and the radius of the microhole, *r* (equation 1 [26]).

$$R = \frac{1}{\kappa} \left(\frac{1}{2r} + \frac{L}{\pi r^2} \right) \quad (1)$$

In this equation the first term describes the access resistance to the microhole and the second term describes the resistance of the cylindrical central part. Although the Nafion ionomer is not fully occupying the space around the microhole, it is likely to dominate the conductivity in the open state of the diode. When operating the “empty” microhole without Nafion in the same electrolyte solution, only a much lower current (due to higher resistance) is observed [25].

When scanning the potential into the negative potential range, a “closed” state can be observed from about 0 to -2 V. It has been shown that this “closed” state is actually dominated by diffusion-migration in the electrolyte solution phase. The diffusion-migration access for a 1:1 electrolyte such as HCl can be predicted (at least approximately) based on theory developed for microelectrode voltammetry [27] (equation 2).

$$I_{lim} = 4ZFDr c \quad (2)$$

Here, the limiting current, *I*_{lim}, is given by a constant *Z* (here *Z* = 2 for a 1:1 electrolyte [27]), the Faraday constant *F*, the diffusion coefficient here either for protons *D* = 9.0 × 10⁻⁹ m²s⁻¹ [28], or for chloride, *D* = 2.1 × 10⁻⁹ m²s⁻¹ [29], the microdisc radius *r*, and the bulk concentration *c*. Assuming, that the diffusion-migration process is dominated by the slower chloride diffusion coefficient, the estimated current is *I*_{lim} = 81 nA. The measured value is 61 nA in reasonable agreement and therefore confirming the limiting region as dominated by concentration polarisation in the electrolyte phase. A further potential region from -2 v to -4 V exists where the current is higher due to onset of convection. This region is termed over-limiting in accordance with work by Yossifon [30] and by Rubinstein [31].

Next, chronoamperometry experiments are performed switching the applied potential between +1 V and -1 V (see Figure 3C). Both opening and closing of the diode happens with approximately 1-2 s switching time. The closed state appears to be reached slightly faster. It is interesting to explore the rectification ratio which is defined here as the current at +1 V (open) divided by the current at -1 V (closed). The value of approximately 1000 is consistent with very high rectification ratios quoted in the literature

for example for nano-channel devices [32]. The implications from this are a readily accessible new type of ionic diode for robust high performance applications. The scheme in Figure 4 summarises the observed diode effect for the asymmetrically deposited Nafion.

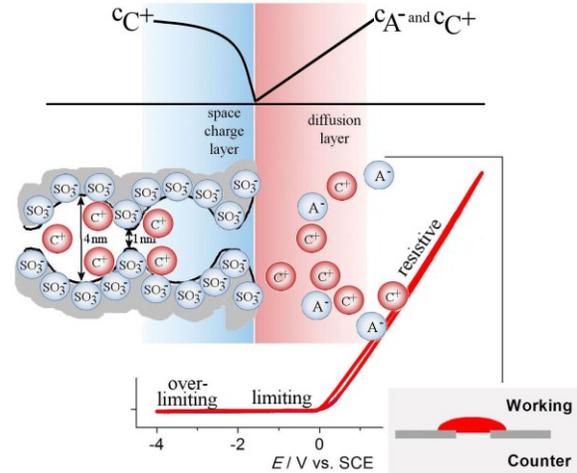


Figure 4. (A) Schematic drawing of the ionic diode membrane when operating in the closed state. Transport of cation through the ionomer membrane and concentration polarisation at the ionomer|electrolyte interface are proposed. Also shown are the three regions resistive, limiting, and over-limiting, that occur in open and closed diode regimes.

By placing a cationic diode (Nafion) in conjunction with an anionic diode (with a corresponding anion conducting material) into a membrane (see Figure 5), uni-directional transport of salt can be achieved for AC potential driven two-compartment cells. This is a simple concept for desalination (or energy harvesting) systems devoid of problems with electrolytic side products.

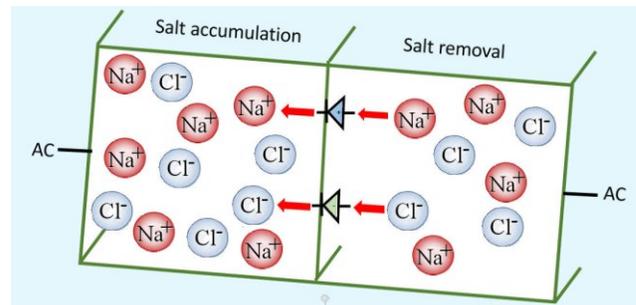


Figure 5. Schematic drawing of the ionic diode membrane cell assembly with both cation diode and anionic diode switched into the same direction. With external AC polarisation this allows salt to be “pumped” uni-directionally into the left compartment to give desalination effects.

4 CONCLUSIONS

A concept for a desalination system based on combination of cationic and anionic diodes has been developed. The principle of the cationic diode is explained with a device based on a Nafion film cast asymmetrically onto a thin PET film with a 10 μm diameter microhole. Although proof-of-principle data are provided, there is substantially more work required (i) to find better ionic diode materials, (ii) to improve and optimise the geometry and design, (iii) to improve the switching time, and (iv) to combine and study diodes into single membrane substrates. Better understanding of the mechanism will be possible with the help of appropriate computer models.

In addition to desalination applications, these ionic diode devices will provide access to a wider range of rectification-based processes (sensing, energy harvesting, pumps for charged or neutral species) with improved ionomer materials and switchable molecular layers. In contrast to the nano-engineering approach to nano-fluidic diodes, here a materials approach is chosen to lead to new technologies.

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