

Progress Report – Fall Semester 2020

Research Title Water Treatments with Ratchet Based Ionic Pumps (RBIPs)
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Background

Estimates show that about two thirds of the world's population experience severe water scarcity at least one month every year[1]. Water desalination is already in widespread use in many parts of the world, however current industrialized technologies require extensive capital and energetic costs [2], making them unpractical in the developing world where access to clean drinking water is most needed. Pollution of ground and wastewater is also a major source of scarcity, for example heavy metal ions pollution (such as zinc, nickel, lead, etc.) due to advanced industrialization[3], or Arsenic pollution in developing countries[4]. Therefore, In the face of ever-growing demand, the need for small-scale, low cost and reliable water treatment technologies is of great importance.

Ratchet Based Ionic Pump (RBIP)

Electronic ratchets are devices that utilize modulations of a spatially non-symmetric electric field to drive a steady state current. Theoretical studies of the functionality of ratchets have shown that their efficiency can be very close to 100%[5]. We propose that the ratchet mechanism can be harnessed to pump ions in steady state, and that those Ratchet Based Ionic Pumps (RBIPs) can be used as building blocks for different water treatment devices.

The simplest design that creates a non-symmetric electric field in an electrolyte solution is shown in Figure 1(a). An insulating material with a nano-scale pores, is coated with two metal contacts on both sides forming a porous capacitor. When an alternating signal V_c is applied to the ratchet, an asymmetric potential distribution is formed in the solution near the contacts, as illustrated by the solid purple line in Figure 1(b). In the initial step, $t=t_0$ the cations flow to the potential minimum (and the anions are repelled).

After the potential switching at $t=t_1$, the cations disperse in both directions. However, since the potential drop to the right (outside the pore) is steeper than to the left

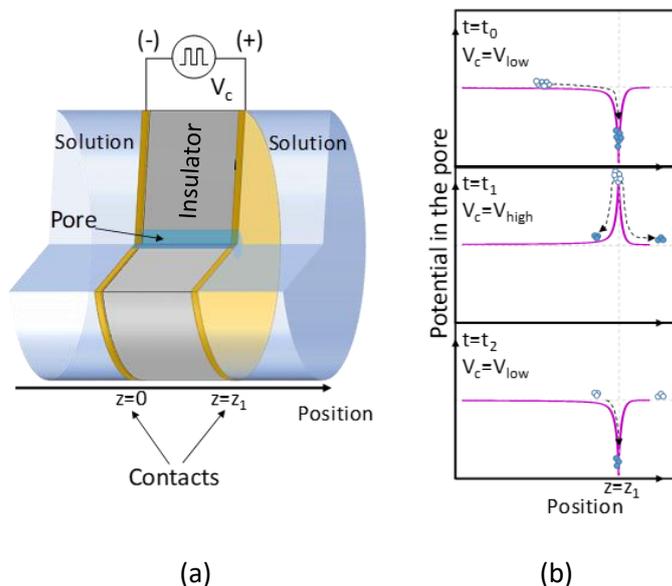


Figure 1. (a) Illustration of the basic structure of the RBIP. (b) Potential distribution in the pore at the vicinity of the left contact, and the consequent motion of cations.

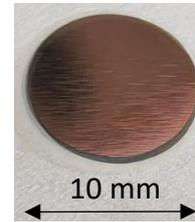
(inside the pore), the cations flowing to the right reach the potential plateau first, and when the potential is switched again at $t=t_2$, the cations on the right are hardly affected but those on the left will be driven back towards the contact. The overall result is a net particle flux to the right.

We have developed a fabrication process for a RBIP, based on a nano-porous Anodic Aluminum Oxide (AAO) wafer (purchased from InRedox). Annealing at 650°C is done to minimize permeance reduction due to water absorption in the pores, followed by E-beam physical vapor deposition of Ti/Au electrical contacts on both sides of the wafer. Figure 2(a) shows a fabricated RBIP membrane sample with the electrical contacts, and Figure 2(b) shows a SEM image showing the nano-pores. In order to test the operation of the RBIP, we have designed a test cell as shown schematically in Figure 2(c). The test cell is constructed of two chambers containing an aqueous electrolyte solution and are separated by the RBIP membrane. A square wave signal, with varying duty cycles, frequency and amplitudes is applied to the two sides of the RBIP using a signal generator, and the electrochemical potential difference, that is a measure of the driving force for Cl^- flux, is measured between two Ag/AgCl wires that are submerged in the solution.

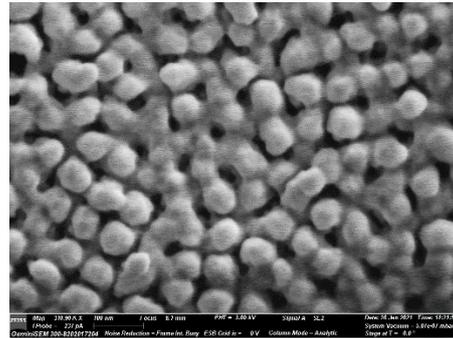
Initial Testing Results

Our initial testing was performed using a KCl solution with a concentration of 0.2mM. Figure 3(a) shows the measured response to a 100Hz square wave with an amplitude of 1.6Vpp and several duty cycles. The gray areas are periods in which the ratchet was off ($V_c=0$), and in the white areas the ratchet signal was on. The ratchet output voltage is calculated as the average difference between the on and off periods voltage (following an initial transient peak response right after an abrupt input voltage change) and is presented as a function of duty cycle for different ratchet amplitudes in Figure 3(b). It is evident that the response in the case of duty cycle 0% ($V_c=-0.8\text{V}$) and 100% ($V_c=+0.8\text{V}$) is a perturbation that quickly disappears, whereas for a square wave signal, the measured voltage tends to settle on a stable non-zero potential, that is the driving force for ion transport between the two chambers.

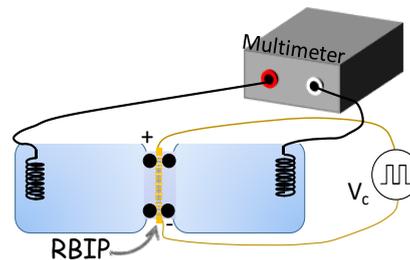
The nature of the response is highly dependent on the ratchet signal parameters, as can be seen by the shift in the duty cycle that leads to maximal output voltage, shown in Figure 3(b).



(a)



(b)



(c)

Figure 2. (a) RBIP membrane sample with contact layer. (b) SEM image of 40nm pore size, with Ti20nm/Au30nm contact. (c) Test setup schematic diagram.

This is also observed by the colormap in Figure 3(c), that shows the results of more recent testing in a large range of frequencies and duty cycles. We note here an interesting phenomenon, that by selecting certain signal parameters, we can flip the sign of the output voltage, which means we can change the transport direction. Figure 3(d) shows measurements done using a solution with a different cation (done at duty cycle 85%). This comparison suggests the ability to selectively pump different cations in opposite directions by changing the frequency from 100Hz to 2000Hz.

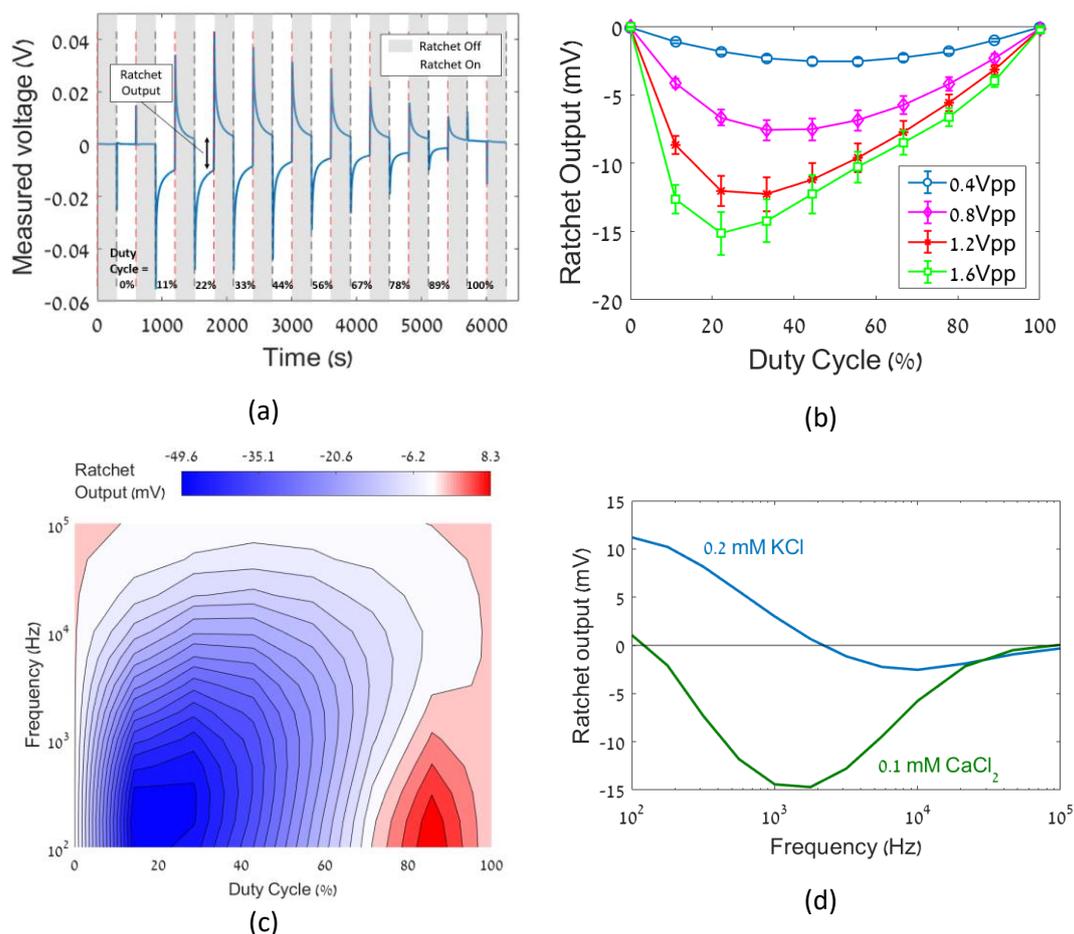


Figure 3. (a) Time response for a duty cycle sweep for 0.2mM KCl with a 100Hz, 1.6Vpp square wave signal. (b) Ratchet output voltage of 0.2mM KCl at 100Hz for different duty cycles and signal amplitudes. (c) Ratchet output voltage of 0.2mM KCl at 1.2Vpp for different duty cycles and frequencies. (d) Ratchet output voltage for 0.2mM KCl and 0.1mM CaCl_2 at duty cycle 85%, as a function of frequency.

Interim Conclusions and Future Work

These initial results confirm that ions can be pumped with a ratchet mechanism using the suggested RBIP design. However, much more work is needed to fully understand the effect of different parameters on transport outcomes, and in order to realize actual water treatment devices with high pumping efficiency. The next few months will be dedicated to understanding the underlying electrokinetic principles governing the potential distribution in the nano-pores (using COMSOL simulations), and by further testing of RBIP samples with different electrolyte solutions (such as HCl that will allow measuring PH to determine concentration changes), combinations of pore sizes, metal contacts, and treatments to affect the surface charge in the pores.

References

- [1] M. M. Mekonnen and A. Y. Hoekstra, "Four billion people facing severe water scarcity," *Sci. Adv.*, vol. 2, no. 2, p. e1500323, Feb. 2016, doi: 10.1126/sciadv.1500323.
- [2] C. Fritzmann, J. Löwenberg, T. Wintgens, and T. Melin, "State-of-the-art of reverse osmosis desalination," *Desalination*, vol. 216, no. 1–3, pp. 1–76, 2007, doi: 10.1016/j.desal.2006.12.009.
- [3] F. Fu and Q. Wang, "Removal of heavy metal ions from wastewaters : A review," *J. Environ. Manage.*, vol. 92, no. 3, pp. 407–418, 2011, doi: 10.1016/j.jenvman.2010.11.011.
- [4] World Health Organization, "Arsenic Pollution." <https://www.who.int/news-room/fact-sheets/detail/arsenic#:~:text=Arsenic is highly toxic in,cause cancer and skin lesions>.
- [5] J. M. R. Parrondo, J. M. Blanco, F. J. Cao, and R. Brito, "Efficiency of Brownian motors," *Europhys. Lett.*, 1998.