SYNTHESIS AND CHARACTERIZATION OF NANOPOROUS ION-CONDUCTIVE MEMBRANES FOR ENERGY CONVERSION PURPOSES

In my research I work on synthesizing membranes that can be used in electrokinetic energy conversion (EKEC) which is the process of converting a pressure into electrical energy. In the next sections I will give a short introduction to ion exchange membranes, EKEC, and my own field of research.

Ion exchange membrane

The word membrane can in general be used to described anything that is somewhat porous and seems to separate two solutions, gasses or a mix of these. A membrane is often put to use when we want to be able to control the transport of material like the sift we use to separate pasta and boiling water. In this case we are interested in keeping the pasta but not the hot water which will require a membrane with large enough pores to remove the water relatively fast but small enough to prevent the pasta to pass through. In this example the membrane used discriminates based on size (water molecules vs. pasta) but there are also membranes that can separate species based on different shapes (spheres vs. rods) or charges (positive ions vs. negative ions). Ions are species that carries and overall charge and always occur in pairs so that the two charges balance each other out and the total charge is 0, this is known as electroneutrality. An example of this is NaCl (regular kitchen salt) which contains the two ions Na+ and Cl- with the overall charge balance of +1 + (-1) = 0 since each ions have a charge of 1.

The charge discriminating membrane is referred to as an ion exchange membrane

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which often is a nanoporous (pores diameters in range of 10-9m = 1 nm, to put that in perspective bacteria are in the size of 1000 nanometers) material that contains functional groups (e.g. the sulfonic group SO3H). When such membrane is placed in water it will start to swell and absorb water (like a sponge) since the SO3H groups like to be surrounded by water and this creates water filled pores. Being surrounded by water the SO3H group will separate into two ions; one negative (SO3 -) that will still be attached to the surface of the pore and is referred to as the fixed charge and one positive ion (H+) which no longer is attached to the membrane but freely can move throughout the whole pore network, this ion is referred to as the counter-ion. The now mobile counter-ion can move along the pore and even be exchanged with another positive ion as long as electroneutrality is met; meaning that at every point in time every negative fixed charge is balance by a positive counter-ion in solution.

The ability of exchanging ions has given name to this kind of membranes, ion exchange membranes, and in the case of a negative surface charge (positive counter ions) the membrane is known as a cation exchange membrane or an anion exchange membrane if the surface charge is positive (negative counter ions). Cation and Anion are other names for a positive or a negative ion, respectively.

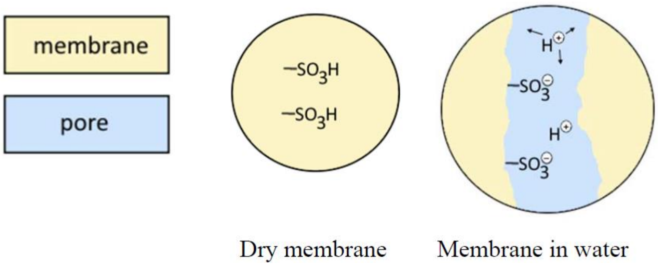

Figure 1 Shows the difference between a dry ion exchange embrane and a membrane that have been placed in water. In the dry membrane no pores are present and the membrane is rather dense. On the other hand, in the wet membrane water is absorbed and the membrane swells (like a sponge) resulting in the formation of pores containing water. In contact with water the functional groups (SO3H) on the pore walls will break into the two charged species, SO3- and H+, where the SO3-ions still are attached to the rest of the membrane and are referred to as the fixed charges. On the contrary the H+ ions are no longer attached but are free to move throughout the pore network (have been shown with arrows on the figure) and have been given the name of the counter-ions since they balance out the fixed charges to reach electroneutrality.

Electrokinetic energy conversion

Electrokinetic energy conversion (EKEC) is the process of converting a pressure across a membrane into electrical energy. In the experimental setup a cation exchange membrane separates to identical aqueous solution containing the two ions Li+ and Cl-. When pressure is applied across the cation exchange membrane the solution is forced from the high pressure side to the low pressure side but because of the fixed charges on the pore walls of the membrane the negative Cl- ion will be repelled when it approaches and only the positive Li+ can cross (see Figure 2). This ill result in an accumulation of negative charges on the high pressure side and positive charges on the low pressure side, this difference in concentrations across the membrane results in something called a chemical potential and is a type of stored energy (potential energy). It can be compared with a dam of water and a turbine placed far below it, in that case the water contains large amounts of potential energy due to the difference in height between it and the turbine and this energy can be converted into electrical energy by letting the water flow though the turbine. In the case of EKEC the potential energy is stored as a difference in concentrations across the membrane and can be converted into electrical energy by using silver/silverchloride electrodes (Ag/AgCl, see Figure 2). In this process the excess of Cl- ions on the high pressure side undergoes a chemical reaction with the Ag/AgCl electrode and electrons are released. The released electrons will be transported in a circuit connecting the high pressure side and low pressure side and hence create a flow of electrons also known as a current that e.g. can make a bulb light up (see Figure 2). On the low pressure side the electrons will react again with the Ag/AgCl electrode and release Cl- ions into the solution. These ions will balance out the excess of Li+ ions so electroneutrality can be restored.

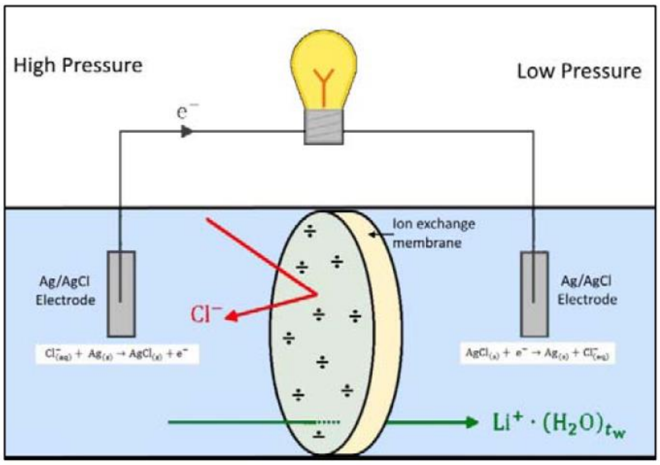

Figure 2 Schematic representation of the electrokinetic energy onversion principle. A pressure is applied to one side of an ion exchange membrane that separates two identical solution of LiCl. Because of the negative fixed charges in the pores of the membrane the negative Cl- ions are repelled and only the positive Li+ can cross. This difference in mobility creates a concentration difference across the membrane which can be converted into electrical energy.

The process can also be reverse, in this case an electrical potential is applied across the membrane and a pressure difference is created as a results of pumping solution from the positive side to the negative side. The electrical potential is applied to the setup through the Ag/AgCl electrodes resulting in one electrode being positive and the other negative. The Li+ ions in the solution will move toward the positive electrode and in their movement across the membrane they will push some of the water molecules in the solution along with them thereby creating a pumping effecting. The amount of water being transfer per Li+ ion is referred as the water transport number tw (see Figure 2) and describes the number of molecules that is dragged along with each ion and can vary from a couple up to thousands of water molecules. In this case pore size plays a crucial role, if the pores are big there will be more water present in the pores and hence more water molecules which will result in a larger tw compared to a smaller pore with more restricted space. It is though still required that only the Li+ ions are allowed to cross the membrane.

My research

The aim of my research is to synthesized cation exchange membranes for EKEC but also to explore and through this get a general understanding of the effects of the different membrane properties such as pore size and surface charge density (the amount of fixed charges per m2 pore surface) on the transport in these types of membranes and hence the efficiency in converting pressure to electrical energy. The main focus of my research has been synthesis and optimization of the cation exchange embrane used to separate the two solutions in the EKEC setup. The optimum will be a membrane that only allows Li+ to cross and repels Cl- , the two ions in the solution; such ion exchange membranes are called permselective. It should also have relative large pores so large amounts of water will be able cross when ressure is applied since this flow of water, called the hydraulic permeability, is somewhat proportional to the power we can get out of the system and is expressed in Watt per m2 of membrane surface. If the power output is low we need a huge membrane surface area if we want high or maybe even reasonable power outputs which will result in enormous setups. As an example, at the moment the largest power output I have achieved is 13 W/m2 which will require a membrane surface area of 170 m2 (corresponding to two badminton courts) with a pressure difference applied across the membrane of ten times the normal atmospheric pressure (this is faily high, the pressure we live under on Earth is 1 atmosphere) to run one water kettle. A setup like is clearly not rentable so for it to be we need a much higher efficiency and power output.

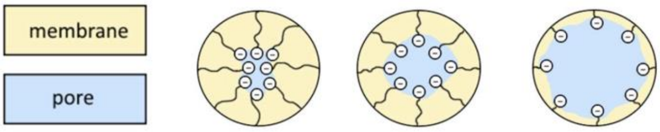

Figure 3 the goldilocks principles. The membrane to the left have a high permselectivity but because the pore is tiny a very low hydraulic permeability whereas the embrane on the right has the opposite trade with big pores and low surface charge density resulting in low permselectivity and high hydraulic permeability. In both cases the efficiency or the power output will be low. The membrane shown in the middle has just the right amount of surface change and pore size to achieve high efficiencies and power outputs in EKEC and it is these membrane characteristics that I am trying to accomplish in my research.

The requirements to pore size and permselectivity of the membrane result in a somewhat Goldilocks situation though (see Figure 3), if the pores are too small and the surface charge density high (many fixed charges on the pore wall) the membrane will have a high permselectivity but the hydraulic permeability will be low, on the hand if the pores are large and the surface charge density low (few fixed charges on the pore wall) a high hydraulic permeability can be achieved but the membrane will lose its permselectivity since the repelling forces will diminish in the middle of pores and thereby allow the Cl- to cross, in both cases this will result in a low efficiency and power output. My research is to find that optimum between the pore size and the charge density so we can get a high efficiency and a high power output.

There are two ways of making the ion exchange membranes; one way is to have a material which contains the sulfonic groups (SO3H) and make a membrane from this material only. The other way is to combine two materials, one material that contains the sulfonic group but might have pour stability so it is mixed with another material that can work as the membrane scaffold and contribute to the stability but not the functionality of the membrane.

To get a better understanding of EKEC and the role of the membrane properties, membranes have been synthesized, using both the one-material and the two-material synthesis approach, with different pore sizes and charge densities. Unfortunately, it is not as simple as just varying the surface charge density but at the same time keeping the pore size constant and analyze how this affects the efficiency. Because the increase in surface charges leads to an increase in swelling since the SO3H groups likes water which will induce an increase in pore size. The change in membrane geometry when only changing one parameter will affect the other membrane characteristics, which makes it difficult to fully understand the effects of the properties such as surface charge density and pore size on the EKEC efficiency and therefore makes it more difficult to optimize these membranes.

In the characterization of the membranes we measure the swelling and how much water is absorbed when the membrane is placed in water compared to the dry mass and dimensions. We measure the ion exchange capacity which is a measure of the amount SO3H groups present in the membrane pores as a function of the mass of the dry membrane. We can also measure the permselectivity which gives an indication of the ratio of surface charge and pore size. The pore size both in the wet (swelled) but also in the dry state can be determined.

In the experimental EKEC setup we can measure the hydraulic permeability which is the flow of water across the membrane as a function of time and pressure applied. The streaming potential is the measure of the chemical potential difference that occurs when a pressure is applied across an ion selective membrane as described earlier. Lastly we measure how well the membrane conducts ions when we apply an electrical potential. These three measurements can be combined to calculate the theoretical electrokinetic energy conversion efficiency and power output.

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