Dangers of Using Tap Water with Nafion™ Polymer: Discussing The Ion Exchange Properties of Nafion

The Mechanism of Ion Exchange and Nafion™ Polymer.

Chemical bonds in nature are of the primary types: covalent bonds and ionic bonds. Covalent bonds form are non-polar (do not involve exchange of electrical charge) and occur in organic molecules. They are not relevant to this discussion.

Ionic bonds form when two or more atoms with different affinities for electrons form a bond. Atoms "needing electrons" will accept electrons from another atom, becoming negatively charged in the process. Atoms "with excess electrons" will donate electrons to another atom, becoming positively charged in the process. Once this process occurs, the two atoms are attracted to each other by their positive and negative charges. Water is called the "universal solvent" because it will dissolve most ionic bonds. As a result atoms or groups of atoms are released into solution.

Very pure water contains only water molecules (H2O) which are electrically neutral, with a very small proportion of the water molecules broken down into two fragments, one positive hydrogen ion (H+) and one negative hydroxyle ion (OH-). The concentration of these ions in very pure water is 0.0000001 gm per liter. This is 10 to the minus 7. The pH for this pure water is the negative logarithm of 10 to the minus 7. The pH for this pure water is the negative logarithm of 10 to the minus 7, or simply 7. Because there is only a very low concentration of charged particles in this water (0.0000001 gm per liter), there are very few charged particles to conduct an electrical charge. For this reason, pure water is actually a pretty good insulator. The purity of water can be measured by measuring its electrical resistance, and water purification systems typically target 10 to the minus 18 megaohms as representing good purity.

Because water is the universal solvent, when it is exposed to chemical compounds containing ionic bonds, it dissolves them. Tap water contains high concentrations of various dissolved ions because when the ionic bonds are broken, the fragments retain the number of electrons they contained in the original compound. Common elements like sodium, potassium, calcium, magnesium, and iron all are routinely found in tap water at relatively high concentrations. All of these elements form positive ions in solution because they have “excess electrons” that they donate during ionic bonding. So-called ion exchange resins are commonly used to purify water by removing dissolved ions and replacing them with another ion. In water softeners used in the home this replacement ion is quite often sodium. Sodium salts are used to regenerate these ion exchange resins used in home water softeners.

Nafion™ tubing can serve as an ion exchange resin. In its form supplied by Perma Pure, the ion to be donated is a hydrogen ion. We supply Nafion™ tubing with a hydrogen ion attached to the tip of the sulfonic acid groups because the hydrogen ion is very small (only a single proton) so it does not interfere. Water is bound to the sulfonic acid as part of the water permeation process. When Nafion™ tubing is exposed to water solutions containing other positively charged ions at higher concentrations than the hydrogen ion concentration in the solution, there is a tendency for the hydrogens in the Nafion™ tubing to be released and the other ions to replace them. Ultimately this means that the concentrations of the hydrogen ions evens out between the Nafion™ tubing and the surrounding solution, and that the concentrations of the other positive ions even out between those bound to the Nafion™ tubing and those still in solution. When the hydrogen atoms bound to the sulfonic acid in Nafion™ tubing are replaced by other, larger atoms (hydrogen is the smallest element so all other atoms are larger), these larger atoms interfere with the access of water to the sulfonic acid groups. As a result, Nafion™ tubing loses some of its ability to bind and to permeate water.
For this reason, exposure of Nafion™ tubing to tap water will “denature” the Nafion™ tubing. Substitution of other cations (positively charged ions) for the hydrogen ions bound to Nafion™ tubing will reduce its ability to permeate water. Depending upon the size and chemical nature of the other cations, this reduction in water permeability will be severe.

The good news is that while ionic bonds freely dissociate into separate ions when dissolved in water, ionic bonds are difficult to break in the gas phase. To break ionic bonds and form free ions in the gas phase, chemical compounds must be heated to more than 500 deg C (most to much higher temperatures still). At these very high temperatures, Nafion™ tubing has long since melted, so there is no danger of denaturing Nafion™ tubing by exposure to free ions as long as Nafion™ tubing is exposed only to gases. It has been the experience of Perma Pure that when Nafion™ tubing is exposed to typical tap water, the Nafion™ tubing loses 2/3 of its water permeability within a few hours. However, eventually the Nafion™ tubing permeability stabilizes at this new, lower level. Since the water permeability is the property exploited in the products of Perma Pure, exposure to tap water should be avoided whenever possible. If exposed to tap water, the Nafion™ tubing device will likely suffer loss of 2/3 of its expected performance.

With regard to a chemical formula, the sulfonic acid contained at the terminal end of the Nafion™ tubing side-chains is the only area of importance in this reaction. The chemical formula for these sulfonic acid groups is R-SO3H, where R represents the remainder of the organic molecule of the copolymer side-chain. There are a great many sulfonic acid groups in Nafion™ tubing. The sulfonic acid groups clump together in long chains, extending from one side of the Nafion™ tubing wall to the other side. Under normal circumstances, each sulfonic acid can bind up to 13 water molecules, attracting them as water-of-hydration. Water molecules move very rapidly from one sulfonic acid group to the next along the chain. This is how water permeates very quickly through Nafion™ tubing. Proper formation of these chains with many interconnecting branches is what makes Nafion™ tubing permeate water particularly well, and what distinguishes Nafion™ polymer performance from competing polymers.

When undergoing ion exchange the sulfonic acid exchanges its hydrogen for a positively charged ion in solution. That ion may be an ion of sodium, potassium, calcium, magnesium, iron, or virtually any element that forms positive ions. If the ion has a positive charge higher than one, then multiple hydrogens will be exchanged for it to balance the charge. For the purposes of this discussion, we will assume a singly-charged positive ion such as sodium. We will designate the atom generically as X, where X = lithium, sodium, potassium, or other singly-charged ions. In this case, the chemical formula for the ion exchange reaction with Nafion™ polymer is:

$R\text{-}SO_3\text{-}H + X^+ \rightarrow R\text{-}SO_3\text{-}X + H^+$

As may be seen, the singly-charged ion formerly in solution is now bound uncharged to the sulfonic acid in Nafion™ tubing, and its place in solution has been taken by a hydrogen ion.

The Regeneration of Nafion™ polymer membranes

The reason that Nafion™ polymer exchanged its hydrogen for ions in solution is because the concentration of hydrogen ions in the original solution was relatively low while the concentration of other positive ions was relatively high. Chemical reactions attempt to balance these concentrations of these ions between those bound in Nafion™ and those free in solution by the exchange of ions.

This process can be reversed simply by soaking Nafion™ tubing in any strong acid (nitric, sulfuric, hydrochloric, etc.). Under these circumstances, the hydrogen ions in the acid solution will substitute for the other positive ions that have bound to the sulfonic acid in Nafion™ tubing . If sufficiently strong acid solutions are used, virtually all of the sulfonic acid groups will recover their terminal hydrogen, and the water permeability of Nafion™ polymer will be completely restored.

This process does require strong acid concentrations. Perma Pure uses 40% nitric acid to soak the Nafion™ tubing. The exact quantity and concentration of acid needed will vary depending upon how concentrated the ions were in the tap water or other solution exposed to the Nafion™ tubing originally.