

Batteries Made From Water

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This paper largely comprises a draft chapter of my forthcoming book, **The Fourth Phase of Water: Beyond Solid, Liquid and Vapor** [1]. I preface it by providing some background.

School children learn that water has three phases: solid, liquid and vapor. But we recently uncovered what appears to be a fourth phase. This phase occurs next to water-loving (hydrophilic) surfaces. It is surprisingly extensive, projecting out from the hydrophilic surface by up to millions of molecular layers. A principal attribute of this phase is that it excludes particles and solutes because of its liquid crystalline nature. We have therefore labeled this phase the “exclusion zone” or EZ for short. Of particular significance is the observation that the EZ is charged; and, the water just beyond is oppositely charged. This creates a battery that can produce current. We found that light recharges this battery. Thus, water can receive and process electromagnetic energy drawn from the environment – much like plants. The material below outlines the evidence that water acts as a battery.

1. Introduction

A flash of lightning from the skies above – hundreds of thousands of volts of raw energy unleashed to the earth as the clouds release their pent up negative charge. Sounds familiar, but have you ever thought about where those pent-up charges finally wind up?

According to atmospheric scientists the charges spread over the earth’s surface. So many lightning flashes strike the earth each second that those charges can hardly dissipate; therefore, they persist, leaving the earth’s surface with a net negative charge. The negativity is substantial. It creates a vertically oriented electric field of 100 volts per meter pointing downward to the earth’s surface. If you’re standing on the earth, this leaves your nose about 200 volts more positive than your toes [2]. Imagine that!

While lightning and its electrical consequences are not the subjects of this paper, charge definitely is. The EZ contains concentrated charge. Pent up charges confer potential energy, exactly as in the cloud. The clouds’ potential energy is deliverable in the form of awesome lightning bolts, whereas in the case of the EZ, more modest mini-discharges are anticipated. Even modest discharges, however, can be consequential in the right setting.

Consider, for example, the biological setting. Charged biomolecules such as membranes, proteins, and DNA interface with water; hence, exclusion zones should envelop every one of them. Those zones contain concentrated charge. This charge is deliverable electrical energy, which is abundantly distributed throughout the cell. Since nature rarely discards bounties of free energy, this energy will likely find use in driving all kinds of cellular processes ranging from chemical reactions all the way to fluid flows. Opportunity abounds. Thus, EZ charge may be every bit as “powerful” as cloud charge.

On the other hand, isolated bodies of charge are rare birds. More naturally, bodies of charge are paired with bodies of opposite charge – like plates of a charged capacitor or poles of a chemical battery. The EZ system could manifest similar separation: a concentration of charge lying within the EZ, and a concentration of opposite charge lying outside.

So let us consider whether the EZ might have a companion pole of opposite charge, and what consequence any such pairing might have.

2. Beyond the Exclusion Zone

In considering whether there are two poles instead of one, we need to bear in mind that the exclusion zone builds from plain old water, which is neutral. If a charged EZ is borne out of a neutral substance, then an equivalent opposite charge must lie somewhere else; otherwise, the law of conservation of charge would be violated. Violating laws cannot lead us anywhere useful.

We guessed that the zone of opposite charge might build just beyond the exclusion zone: as the negative charge builds within the EZ, corresponding positive charge zone would build nearby. The region beyond the EZ would then acquire many protons. A high proton concentration means a low pH, so we suspected that a low pH region might be found in water beyond the EZ.

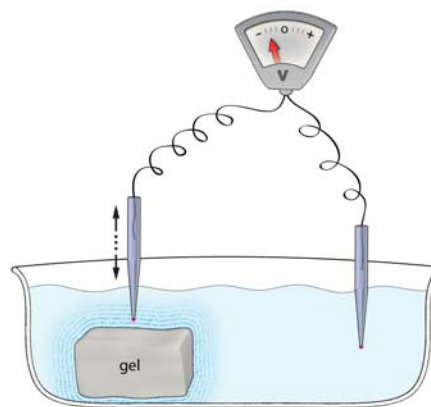


Fig. 4.5. Experimental setup used for measuring the electrical properties of the exclusion zone. Reference electrode at right.

To test for this possibility we dropped a gel into a beaker of water and immersed a pH probe just beyond the gel’s EZ (see Fig. 4.5). We would have been excited by a drop of one pH unit, which would mean a proton-concentration increase of ten times, but we got a more dramatic result. Next to the polyacrylic-acid

gel's EZ we found that the pH level dropped by up to three or four units and occasionally more – a ten-thousand-times increase of proton concentration. This result amazed us.

We could change the magnitude of the pH drop by altering the experimental setup in various ways. For example, the pH drop depended on the size of the beaker. With a beaker very much larger than the gel, we saw only a modest pH drop; but, when we used one that was barely larger than the gel, so that the protons had nowhere to go, we obtained the more impressive pH drop that I mentioned.

Little in classical chemistry could explain what we observed. Nevertheless, the results were so unexpected and so dramatic that the more conservative thinkers in the laboratory became uneasy. One bright lad well versed in classical chemistry simply could not believe it and moved onto another project. I wasn't absolutely convinced myself.

One lingering concern was whether those protons really accumulated as a consequence of EZ buildup. A less interesting alternative is that they leaked from the gel, which is known to contain protons. We soon figured out how to test for this: If the protons came from the gel, then their contribution could not exceed some fixed number, for the gel could not supply infinite protons. We found that pre-immersing the gel into a succession of water baths to draw out those protons did not make much difference for subsequent trials: the protons built up with similar dynamics. It seemed, therefore, that the protons really did come as a result of EZ buildup after all, as we had suspected.

This conclusion made sense because of water's neutrality. If neutral water contributed negative charge to the EZ it had to contribute positive charges elsewhere, and we found those charges. That result was satisfying – like a cool drink on a hot summer's day. It was also reassuring, for evidence of high positivity lent credence to the high negativity proposed for the EZ. To some physicists that substantial charge concentration had seemed unfathomable, for it lacked common precedent. Finding opposite charges elsewhere reassured us that we were on a productive track.

3. Proton Buildup beyond the Exclusion Zone

To nail down the dynamics of proton buildup, we used a miniature pH probe. The probe was small enough that we could track the local pH change at each of a series of distances from the EZ-nucleating sample (Fig. 5.1). For the sample we used a sheet of Nafion, secured to the bottom of a chamber. We filled the chamber with water and then observed the proton buildup.

The right panel of Fig. 5.1 shows records of pH change detected at each of several distances from the sample. At 1 mm distance the pH began to drop within a few seconds, reaching a low point in 15 seconds and then recovering modestly as protons spread to more distant regions. At a 5-mm the pH change began later; and at 10 mm it began still later. Eventually, the pH attained roughly the same final value in all regions, which was lower than the initial value.

The successive delays shown in Fig. 5.1 imply a wave of protons originating from somewhere in the vicinity of the sample and then dispersing away. Eventually, the disparate pH values equilibrate. We can anticipate this equilibration because protons repel one another and eventually distribute more or less uni-

formly – at least those protons beyond the attractive grip of the EZ's negativity.

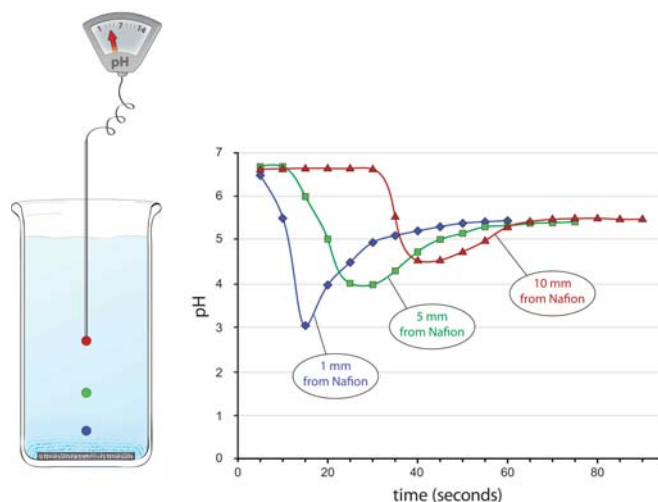


Fig. 5.1. Time course of pH change following the addition of water to a sheet of Nafion. The pH was measured at three points, as indicated at left. The pattern shows a wave of protons progressing upward.

The wavelike progression affirms that the protons are generated somewhere near the sample, presumably at the EZ's growing boundary (Fig. 5.2). Proton generation transiently diminishes the local pH value. Some of those protons will spread because they repel one another. The extent of spread and the depth of the transient pH dip should both depend on the chamber's size, as earlier noted. The main point, however, is that the protons do appear to come from the EZ's leading edge. As the exclusion zone builds, it releases protons.



Fig. 5.2. Wave of protons generated at the leading edge of growing exclusion zone. [Instead of Nafion, put "hydrophilic surface"]

4. Long Range Proton Distribution: pH Sensitive Dyes

Because the proton issue seemed so critical, we employed an additional proton-detection vehicle: pH-sensitive dyes. These dyes are similar to the ones used in litmus paper – they change color depending on pH.

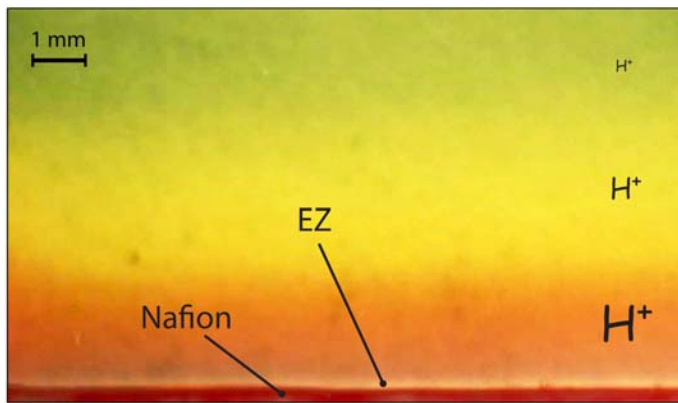


Fig. 5.3. Proton distribution beyond the exclusion zone. View is perpendicular to the wide face of a narrow chamber. Image was obtained 5 min after pouring water with pH-sensitive dye solution into the chamber. The EZ excludes the dye. The pH value immediately beyond the EZ is 3 or below (red-orange), indicating numerous protons. Expectedly higher proton concentration immediately adjacent to EZ is beyond the dye's detection range.

Fig. 5.3 shows a representative example of the color distribution observed beyond the exclusion zone. The red-orange color near the EZ, according to the calibration chart, indicates a pH value of three or below. At greater distances, the pH was also lowered, but less dramatically; and so on. In other words the pH-dye technique confirmed largely what the pH probe showed: abundant protons accumulating in the water beyond the exclusion zone. This was a reassuring result.

We tried to take it a step further and actually measure the number of protons, but this could be only crudely estimated. The reason is the undetectable protons immediately adjacent to the EZ: the exclusion zone's negative charge draws many or most of the positive protons to its vicinity, and the expected high concentration lies beyond the measurement capability of the dye (see Fig. 5.3).

Undaunted, we set up a chamber similar to that of Fig. 5.3 to measure what we could measure. We found 1015 to 1016 protons. For comparison, we estimated the number of EZ electrons. This was computed from the lattice structure and the measured potential distribution. The number was 1018 to 1019, which is substantially higher than the measured proton count. Whether the unmeasured protons in the near field could make up the difference depends on one's choice of proton-distribution model. Hence, the question could not be definitively answered, although it seemed to be roughly in the ballpark.

Later, we augmented these quasi-static measurements with one that continuously refreshes the near-EZ water. We used a Nafion tube, whose inner surface nucleates an annular EZ within. When fresh water was passed through the tube, the exiting water's pH was consistently lower than the entering water. The drop was 1 to 2 units, and never diminished even after 30 minutes of continuous passage [5]. Evidently, the passing water continued to receive many protons.

We could even find evidence of released protons in suspensions of microspheres. As hydrophilic entities, those spheres ought to build exclusion zones, presumably in the form of shells. Although such shell zones might be too small to be detectable microscopically, what should be detectable is the corresponding

water-pH change. Fig. 5.4 confirms that such pH changes are indeed observable.

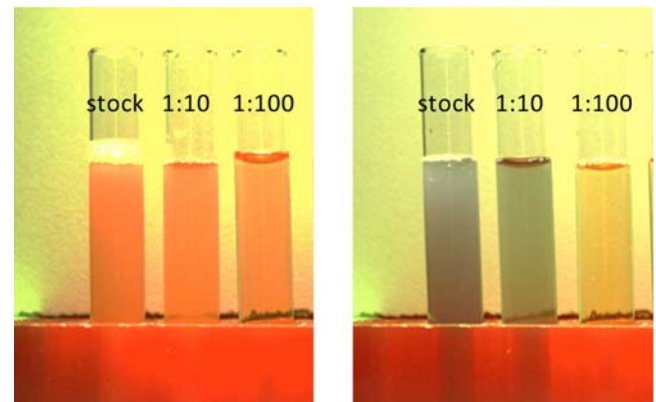


Fig. 5.4. Addition of microspheres alters water's pH. Stock solutions: 109 microspheres per mL 1- μ m diameter. Left stock: Negatively charged carboxylate microspheres lower the water's pH (red). Right stock: Positively charged amino microspheres elevate the water's pH (blue-green). The altered pH persists to some extent even in dilutions.

The collection of results above confirms the separated charges: Bulk water's free charges consistently juxtapose next to the EZ's opposite charges. The water molecule's internal charges have effectively been split up between EZ and bulk, creating something that looks suspiciously like a battery – a chemical factory with separated, deliverable charges.

Battery-like charge separation remains evident even when the exclusion zone builds in odd configurations. Fig. 5.5 shows an example. This image came from the same experimental setup as Fig. 5.3, but we obtained it later. The EZ had grown in the form of dendritic projections extending more or less perpendicular to the plane of the original EZ. It looked like fingers sticking up. Red color surrounds each finger; this indicates that protons juxtapose not only in the standard case when the EZ remains adjacent to the nucleating surface, but also when it grows far into the water.

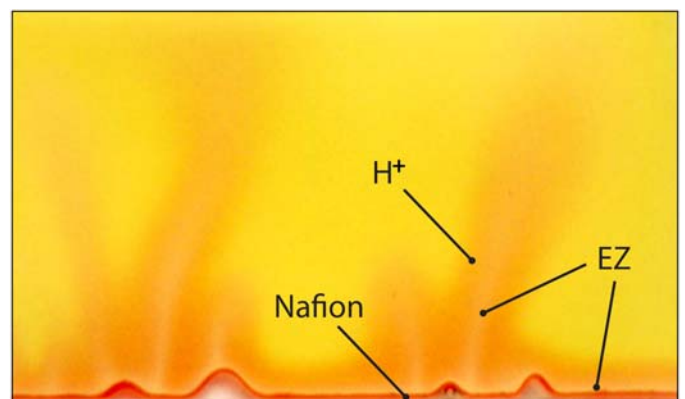


Fig. 5.5. Similar to 5.3, except taken at a later time and at lower magnification. Note zones of low pH (red) surrounding each vertical EZ projection. Bumps in Nafion arise as hydration induces buckling, and are not relevant here.

In other words, wherever an EZ is present, so are battery-like features. Charge separation is an ever-present feature of exclusion zones. You might even call it a fingerprint.

5. Energy from the EZ Battery

If the separated charges really act like a battery, then the stored electrical energy should be deliverable. If you place one electrode in the EZ, the other in the zone beyond, and connect those electrodes through a resistor, then you should obtain current flow. And, that's what's found: the stored charges can flow as current (Fig. 5.6).

Hence, those separated charges are not merely non-functional byproducts of EZ formation, but something real that can be delivered to a load. This is much like what happens with standard batteries, but here the internal construction is simpler: an exclusion zone bearing negative charge juxtaposed to bulk water zone with positive charge.

Think of it. Within a short time after dumping a hydrophilic material into water, the EZ builds and charges separate. They want to recombine, but they stay separated because the EZ's dense honeycomb lattice keeps the free charges from penetrating back in. The charge separation maintains the potential difference. Its magnitude may be only 100 to 200 mV, but the respective zones are nevertheless packed with charge; thus, the amount of deliverable energy is substantial.

A water-based battery of this kind exists wherever hydrophilic surfaces interface with water, i.e., virtually everywhere. I already mentioned, for example, that the solid materials inside the living cell mainly contain hydrophilic surfaces and therefore order the surrounding water into EZs. Hence, the cell will contain numerous nano-batteries. The batteries also exist within the clouds' aerosol droplets. Particles nucleate the buildup of cloud droplets. Ordinary nucleating particles such as dust, sand, and salt contain hydrophilic surfaces, which build EZ layers; hence, the droplet may contain separated charges, just like the cell and other water-containing entities.

Water batteries should even exist in simple aqueous solutions or suspensions (Fig. 5.4). Whenever molecules dissolve or particles suspend, EZs will form and separate charge. Even the container itself can nucleate charge separation. All of these scenarios create batteries, which are intimate manifestations of water's fourth phase. They are virtually everywhere.

Within the framework of conventional thinking these batteries are unexpected, and may even sound weird. We will soon see, however, that this simple concept has broad explanatory power. Its impact will become evident as we deal with numerous water-related phenomena, ranging from osmosis all the way to ice formation.

6. Extracting Energy from the Water Battery

To understand how the batteries' energy might be consumed, it is necessary to bear in mind the species carrying the charge. This depends on the zone. In the exclusion zone, electrons carry the charge; they reside in the electronegative oxygen atoms distributed throughout the EZ lattice. The larger the number of oxygen atoms, the larger the number of negative charge carriers.

Although the electrons lodge at distinct loci, there is no reason to think they could not move from point to point through the lattice. Any such charge movement amounts to current flow (Fig. 5.6). In fact, charge movement through the EZ occurs so easily that the EZ's electrical conductivity measured parallel to the nu-

clearing surface is 100,000 times higher than through bulk water [3]. Hence, the electron charges can move about as readily through the EZ lattice as physicists know they move through n-type semiconductor lattices.

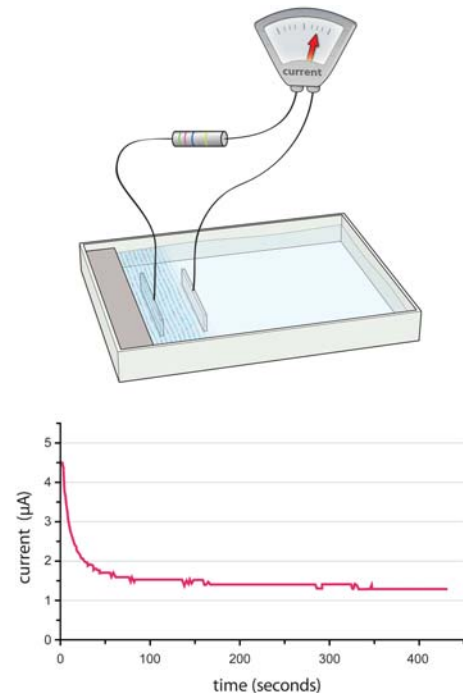


Fig. 5.6. Current flow from separated charges in EZ and the water beyond. Current begins flowing immediately after immersing electrodes, and maintains a non-zero plateau value for an extended period of time.

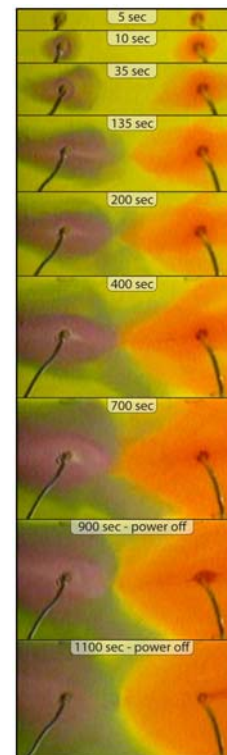


Fig. 5.7. Time course of pH-dye distribution as current flows between wire electrodes immersed in a water bath containing pH-sensitive dye. Orange corresponds to low pH, purple to high pH.

The positive charge carriers are free protons – or more accurately hydronium ions. Naked protons seek out negativity, and the nearest prospects are the water molecules’ electronegative oxygens. They are all over. Protons quickly latch on to the nearest water molecule to form hydronium ions. You might think of the hydronium ion as a positively charged water molecule (H_3O^+). These molecules carry the battery’s positive charge, intermingled among ordinary water molecules.

Positively charged water is packed with potential. Since like-charged molecules repel, the hydronium ions have high potential to disperse to remote locations. This creates flow. At the same time, any negatively charged sites situated remotely should draw those ions, creating additional motivation for flow. Later, we will see how such attractive and repulsive forces constitute the most primitive drivers of natural water movement.

In other words, both the EZ’s electrons and the bulk water’s hydronium ions have considerable potential for doing work. The electrons can shift through the EZ lattice for delivery to juxtaposed sites hungry for high-energy electrons. The hydronium ions can drive flows, and can also drive reactions requiring positive charge. Both of those charged species can do work and deliver energy.

7. Extracting Energy from Artificial Water Batteries

As you have just seen, electrical energy can be extracted from water by placing electrodes into the water battery’s oppositely charged zones.

A related question is whether we can separate charge by some other means, store that charge, and then collect the electrical energy. This question arose from a conversation with Andrey Klimov [6], a Russian colleague who first introduced me to the subject of water electrolysis. Andrey suspected that electrolysis might create long-term energy storage in water, and he was right.

In the electrolysis experiment, platinum electrodes are inserted at two positions in a water-filled chamber, and a few volts (DC) are imposed between the electrodes. Nothing obvious happens you happen to crank up the voltage to a high enough level; then it’s clear that something is happening because gas bubbles form. Even at lower voltages, however, charge must still flow between electrodes and thus into and out of the water.

obvious did happen (Fig. 7.12). Near the cathode the color change indicated high pH, while near the anode it indicated low pH. The difference was easily six pH units. The respective colors spread progressively toward the chamber midline, and before you knew it, a large part of the chamber was one color, another part a different color. The chamber’s water looked like a color chart: one region positively charged with low pH, another negatively charged with high pH (Fig. 7.12).

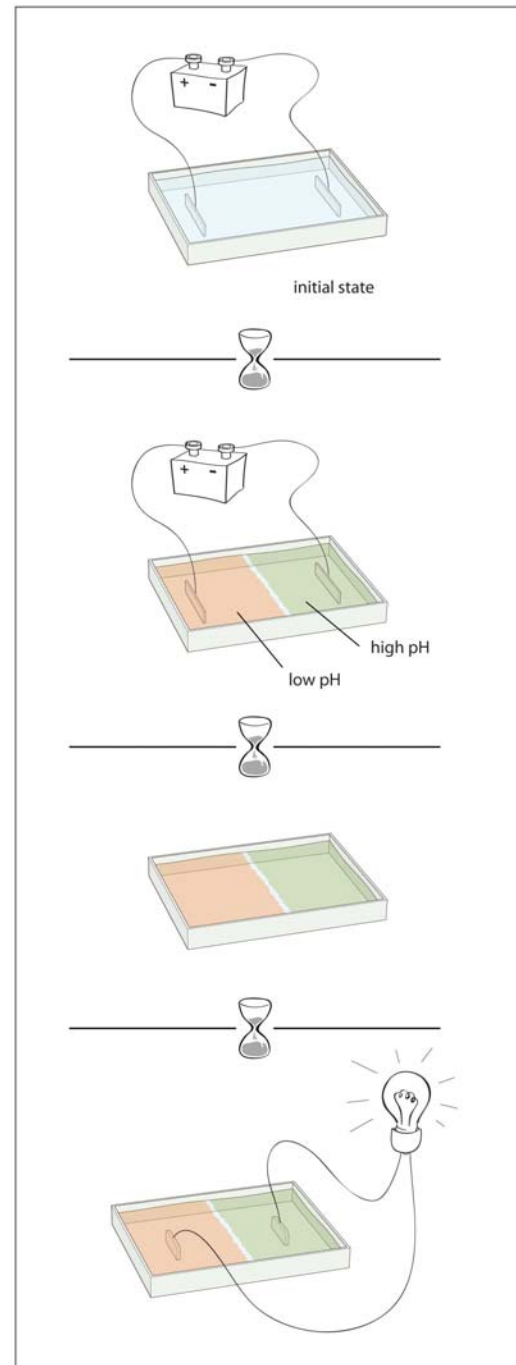


Fig. 5.8. Charge storage and extraction in water. pH-sensitive dyes indicate charge separation. Separation is sustained, and is later extractable using freshly immersed electrodes. [light bulb glow yellow]

When the power supply was disconnected, the color blocks remained in evidence easily for tens of minutes (Klimov and Pol-

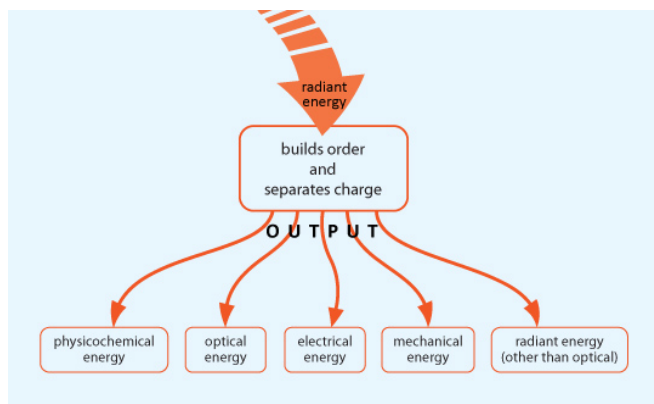


Fig. 7.12. Water as a transducer of energy.

To determine what might be happening during this charge transfer, we added pH-sensitive dyes to the water. Something

lack, 2007). During that time you could extract current from the electrodes lodged in the respective zones. Thus, charges were evidently concentrated in those two zones.

To determine how much current could be extracted we designed a follow-up experiment (Fig. 5.8). Here the electrodes were systematically positioned at the two ends of the chamber. A few volts were applied, and the color production more regularly distributed. We found again that current could be drawn off through a load. It could be drawn either from the same electrode pairs used for charging, or from fresh electrodes positioned at any of a series of separate points around the chamber's centerline [4]. Up to 70% of the input charge could be recovered.

The storage mechanism here almost certainly resides in EZ-like matrices. If the charges were free, they would immediately coalesce and annihilate one another. That does not happen: the lower panels show that the separated colors persist, implying that the charges lie in structural matrices.

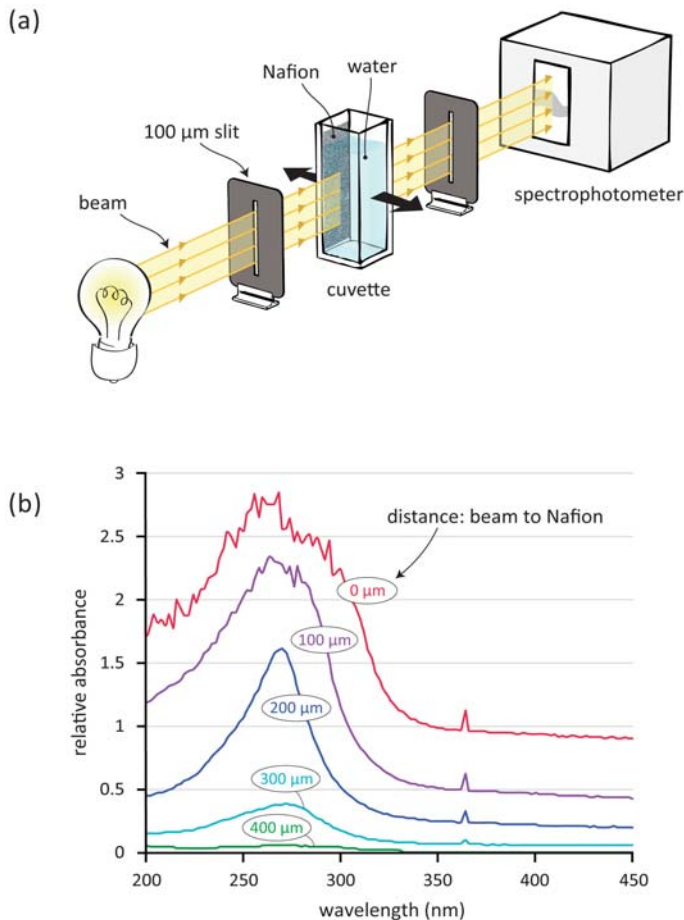


Fig. 3.9. (a) UV-VIS spectrometer setup. Moving the cuvette laterally allowed us to interrogate water at various distances from the Nafion surface. (b) Absorption spectrum measured at various distances from the Nafion-water interface, denoted by numbers above each curve.

In fact, we could confirm the presence of structured matrices in another way. Do you remember the 270-nm absorption peak that characterizes exclusion-zone matrices (Fig. 3.9)? Both zones of the chamber showed this absorption. Thus, the relevant charges are embedded in structural matrices, and this accounts for the separation's long-term persistence.

Thus, EZ-batteries are capable energy suppliers. They can store energy for substantial periods of time, and can then deliver that energy for use in driving processes ranging from chemical reactions to hydraulic flows. Perhaps it is evident that the EZ battery could be a versatile supplier of much of nature's energy.

8. Conclusion

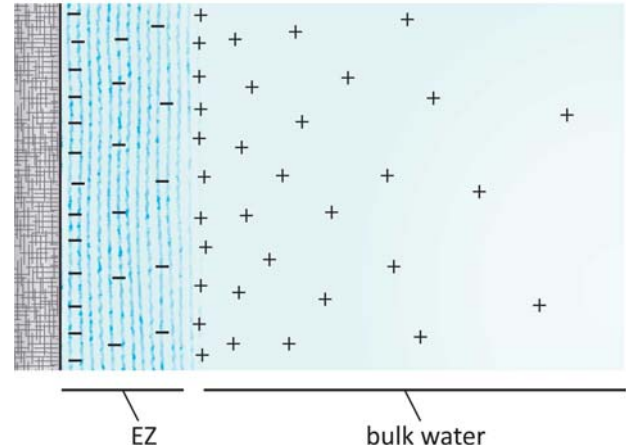


Fig. 5.9. Diagrammatic representation of the EZ water battery. The separated charges are deliverable.

Aqueous regions next to hydrophilic surfaces contain exclusion zones. Those EZs separate charges. The separated charges constitute a battery (Fig. 5.9).

One pole of the battery is the exclusion zone, which is typically negative as a result of abundant electronegative oxygen atoms. The other pole lies in the bulk-water zone just beyond the EZ; it typically comprises hydronium ions, which can disperse freely according to the standard rules of electrostatics. Most of them accumulate near the EZ boundary.

While the separation mechanism may be clear, the maintenance mechanism is not. Like your cell-phone battery, the water battery will slowly run down as charges trickle back together. It will need recharging. The wall socket that recharges your phone is an unlikely option; hence, some other source of energy must be at hand.

That source had eluded us for several years — until a chance discovery finally set us on the right track. We turn to that next.

References

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