Bipolar Membrane and Water Splitting in Electrodialysis

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Abstract

The traditional view of the conductivity of electrolytes is based on the mobility of ions in an electric field. A new concept of water conductivity introduces an electron–hole mechanism known from semiconductor theory. The electrolyte ions in the hydrogen bond network of water imitate the structure of a doped silicon lattice. The source of the current carriers is the electrode reaction generating H^+ and OH^- ions. The continuity of current flow is provided through the electron–hole mechanism, and the movement of electrolyte ions is only a side process. Bipolar membrane in the semiconductor approach is an electrochemical diode forward biased. Generation of large amounts of H^+ and OH^- has to be considered as a result of current flow and does not require any increase in the water dissociation rate. Bipolar membranes are essential in electrodialysis stacks for the recovery of acids and bases by salt splitting.

Keywords Semiconductors · Water splitting · Bipolar membrane

Water as a Conductivity Medium

Liquid water is an intermediate state between ice and vapor. It has a dual nature where most of the molecules form an ice-like ordered structure (85%); the rest are in a gas-like state [1, 2]. Gas-like gaps in the structure of water are readily filled by electrolyte ions or other water-soluble substances, and even by gases such as methane. Evidence of the porous structure of water is the formation of methane clathrates on the floor of the ocean, where crystalline forms are formed under low temperature and high pressure [3]. These forms contain approximately 200 m³ of methane in 1 m³ of water, which corresponds to the molar ratio of water to methane 6:1.

Simultaneously, methane completely displaces the salt contained in the water in an amount of 3.5% and occupies free space in the structure of water on a principle similar to reverse osmosis. Under normal conditions, there are the electrolyte ions that expel any gas from water and reinforce its ice-like structure. The equilibrium between ice-like structure of the solution and pure water reach with free gas-like

molecules is the cause of huge osmotic pressure at the interface. The osmotic pressure reaches a significant value of 22.4 bar/mol and meets the ideal gas law, which clearly indicates the existence of a hidden gaseous form in the water structure.

Pure water shows a poor electrical conductivity of 55 nS/cm (25 °C) despite the presence of H^+ and OH^- ions at a concentration of $10e^{-7}$ mol/L. Only the addition of small amounts of electrolyte causes an enormous increase in the conductivity.

It may seem that the conductivity of aqueous solutions is due to the movement of ions in the electric field, which is considered the main principle in electrochemistry since the nineteenth century. Already in 1806, Theodor von Grotthuss [4] presented the charge transfer model as a side-to-side transport in water treated as a continuum, even without knowing the exact chemical structure of water (Fig. 1).

Recently, this mechanism presented as a jumping of hydrogen ions or proton tunneling in the network of hydrogen bonds [6]. Now, all these hypotheses may be improved using the electron–hole mechanism known from semiconductor theory.

The fundamental condition for the conductivity of water is the presence of hydrogen bond network. Hydrogen bonds are weak (23 kJ/mol) compared to covalent bonds in water (492 kJ/mol), but form a dense ice-like network. In this network, all hydrogen atoms can be considered as equal being

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Fig. 1 Grotthuss mechanism of H^+ transport through hydrogen bonding (hop and turn mechanism of H^+ along a proton wire) [5]

in instantaneous exchange. This is evidenced by the formation of mixed HDO molecules in a mixture of water H_2O and deuterium oxide D_2O [7]. However, the network of hydrogen bonds does not provide conductivity due to the lack of free electrons.

There are certain similarities between the structure of water and the silicon crystal. Both substances are insulators, but a small addition of ions with excess or deficiency of electrons is enough to form a semiconductor. From this point of view, an electrolyte solution is similar to the silicon crystal doped with elements of valence 3 or 5 (e.g., antimony or boron). The assumption of the semiconductor nature of aqueous solutions has been known since the 1950s, but so far, no clear consequences for the conductivity of the electrolyte conductivity have been derived [8, 9].

Figure 2 shows schematic diagram of the p – n junction in a solid semiconductor known as diode and biased in the forward direction. Current flows from the n -type region containing electron excess to the p -type region with electron vacancy called “holes” in the crystal lattice [10]. The current can also be considered as an apparent movement of “holes” in the opposite direction, which is highlighted even by a traditional diode symbol from the nineteenth century, presented below.

Fig. 3 Formation of an electron “hole” **a** in an acid solution and **b** in a semiconductor (three electrons in the outer valence shell) [9]

Fig. 2 Hole and electron current in p – n junction of semiconductor

The Grotthuss mechanism indeed has many similarities with current conduction in semiconductors as shown in the example of acetic acid (HAc) and silicon crystal doped with boron (Fig. 3) [9].

The hydrogen ion (H^+) from acid dissociation should be considered as an equivalent of electron hole in hydrogen bond network, while the acid anion (Ac^-) is an electron carrier. Unlike a solid semiconductor, ions in an aqueous solution are mobile and can move along the electric field gradient produced by the current flow. Nevertheless, the proper current carriers are always the electrons by electron–hole mechanism and not the electrolyte ions traditionally considered as charge carriers. Meanwhile, the opposite process takes place on the electrodes, where virtual charge carriers are produced as a result of chemical reactions of water oxidation and reduction. Thus, in addition to gaseous products, H^+ and OH^- ions are also generated. These ions can be considered as the proper charge carriers providing constant current flow regardless of the electrolyte ion shift (Fig. 4).

In fact, the charge transport takes place according to the electron–hole mechanism. The hydroxyl ion OH^- is virtually located as a temporary excess of electrons, whereas the H^+ is an electron vacancy in the hydrogen bond network. The

Fig. 4 Principle of membrane electrolysis [11]

electrolyte ions present in the solution are not involved in charge transport, being only shifted along the gradient of electric field. The potential gradient is produced precisely by the current flow as a voltage drop according to Ohm's law. The electrolyte ions may even be immobilized in the polymer structure, e.g., in the form of ion exchange membrane, then also promote conductivity. In case of bipolar membrane, the current flow manifests itself spectacularly as the generation of large number of ions due to an apparent increase in water dissociation.

Bipolar Membrane

It is well known that salts in an aqueous solution dissociate to a greater or lesser extent, which can be considered as virtual salt splitting (Fig. 5). Hydration of charged ions, in turn, triggers a downstream process of increased water dissociation or virtual water splitting. As a result, the salt solution can be partially considered as a mixture of free acid and base. Therefore, salt dissociation also leads to partial water splitting (withdrawal of the neutralization reaction)

Fig. 5 Illustration of water and salt splitting as a result of salt solubilization in water

and an increase of the total ion concentration. Especially in the case of weak acid salts, the solution becomes a strong alkaline property.

If an ion-permeable barrier in the form of cationic or anionic membrane is placed into solution, the solution will split into acid and base as the current flows. If we put both of these membranes, we get deionized water with high electrical resistance between them. In turn, if we bring both membranes very closely together, we get a bipolar membrane with low electrical resistance and unusual properties of increased water dissociation. Therefore, bipolar membrane is a combination of two solid electrolytes containing immobilized ions with opposite sign. According to the Donnan exclusion principle, such a bipolar membrane is impermeable to cations and anions, but simultaneously, it is well known as a strong emitter of H^+ and OH^- ions from enhanced water dissociation (Fig. 6).

The principle of the bipolar membrane by analogy to the p–n junction of semiconductors has recently been described. Reference was made to the point of view of the corpuscular mode of charge transfer by autonomic ions, resulting from the dissociation of water in a catalyzed reaction [12]. Meanwhile, in the electron–hole mechanism, electrons are the current carriers, and all the so-called holes are virtual in nature and play the role of electron attractor in the current flow.

Figure 7 presents the analogy of the p–n junction in solid semiconductors and bipolar membrane. The structure of the depletion layer is similar in both cases, both systems show diode properties and a similar potential in depletion region of approximately 0.8–1.2 V [12]. Similar semiconductor properties can also be attributed to electrolyte solutions, although in this case, the virtual diodes produced by

Fig. 6 Bipolar membrane as „water splitting” device

Fig. 7 Comparison of *p-n* junction principle in **a** solid semiconductors, **b** bipolar membranes, and **c** hydrated ions in electrolyte solution

hydrated cations and anions are mixed at the nanoscale. It is noteworthy that the series of *p-n* junctions creates a transistor-like *p-n-p* junction, which opens a possibility of analyzing the role of electrolytes for the future.

The phenomenon of water splitting and generation of large amounts of H⁺ and OH⁻ ions by the bipolar membrane has been controversial for many years. The apparent dramatic rise in water dissociation has been recognized as one of the fundamental research problems open until now [13, 14]. For explanation, an extraordinary role was attributed to the boundary layer at the interface estimated as thin as 2–5 nm. The intensive dissociation of water was believed to be a special catalytic effect of ion exchange groups with opposite signs. Some researchers are even trying to change the inner structure of bipolar membrane. They introduce special additives such as graphene or graphene oxide in order to increase the catalytic activity of the intermediate layer. Indeed, some decrease in the electrical resistance of this modified membrane was achieved [15].

The H⁺ and OH⁻ ions produced by water dissociation should be transported in their hydrated form outside the membrane, but the dissociation constant of water supplied inside membrane should be 6 orders of magnitude higher as normally, because the ion production rate is enormous. The mass balance shows that the rate of diffusion of water into the membrane core is not high enough to secure such a large production of ions. Recently, enhanced water dissociation has also been postulated at the solution/membrane interface in the case of monopolar membrane, but the mechanism has been poorly understood [16]. The calculation of water

Fig. 8 Bipolar membrane according to the *p-n* semiconductor junction principle (OH⁻ as electron carrier, H⁺ as hole current)

splitting rate at membrane/solution interface or bipolar junction seems to be a quite complicated problem. A comprehensive solution taking into account both a chemical reaction and the presence of a space charge has not yet been found [17].

The regions with electron excess (cationic) and vacancy (anionic) in the bipolar membrane are separated by a very thin intermediate layer, which forms a potential barrier similar to the *p-n* junction in the semiconductor. Bipolar membrane acts like semiconductor diode, conducting the current only in one direction from cationic side to anionic one. The cationic layer corresponds to the *n-type* structure, and the anionic layer corresponds to the *p-type* structure in solid semiconductor. Instead of the hydrated ions moving outside the membrane, only the current flow according to the electron–hole mechanism is sufficient to provide the formation of H⁺ and OH⁻. The amounts of water in the membrane remain unchanged during the process (Fig. 8).

Current flow in the system is closely related to the production of OH⁻ ions at the cathode and H⁺ at the anode (gaseous products H₂ and O₂ are omitted). Seemingly, the bipolar membrane also produces H⁺ and OH⁻ ions, which are in fact the result of current flow. The ions produced by both bipolar membrane and electrodes recombine to form water and complete the electrical circuit. Even if an electrolyte such as NaCl is present in the solution, the pH of the solution will not change as it is not possible for the electrolyte ions to pass through the bipolar membrane.

It is clear that the required ion production in the bipolar membrane shown in Fig. 7 is not necessary to provide conductivity by the electron–hole mechanism. Therefore, the working principle of bipolar membrane is the current flow without any water splitting in the depletion layer (Fig. 8). The properties of bipolar membrane result directly from its semiconductor nature, and the apparent production of

H^+ and OH^- ions is simply a consequence of the current flow. OH^- ions serve as electron carriers moving towards the anode, and H^+ ions form “holes” and move in the opposite direction. The ions formally produced by the bipolar membrane do not reach the electrode surfaces but are successively recombined with the ions of the opposite sign produced by the electrodes.

The low resistance of bipolar membranes allows high current densities up to 4500 A/m^2 with a small voltage drop in the range of 1 V. However, in practical application of bipolar membranes, some shortcomings are mentioned such as low current efficiency, insufficient permselectivity, and short life time [18]. We hope that this new look at the operating principle of the bipolar membrane will provide a better understanding of electro dialysis processes.

Application of Bipolar Membranes

Bipolar membranes are used in electro dialysis systems to split salts into the appropriate acid and base. The main practical purpose is the recovery of carboxylic acids from the fermentation broths. Three different membrane configurations can be used here; their benefits and shortcomings are briefly outlined below.

Bipolar and Cationic Membranes

The simplest method of salt splitting is to use a cationic membrane in electro dialysis. The salt solution, e.g., sodium lactate, is introduced between the anode and the cationic membrane. The electric current transfers sodium ions to the cathodic compartment, while the remaining carboxyl anions react with H^+ ions generated at the anode, giving a weakly dissociated carboxylic acid. Simultaneously, the cathode produces OH^- ions as electron carriers

toward the anode. The cation exchange membrane does not constitute a barrier to OH^- transport, as is observed in the case of diffusion dialysis [19].

Extending a salt splitting electro dialysis stack requires the introduction of bipolar membranes on the cathode or anode side. Subsequently, a system of repeating separation units can be built in which the salt solution will always flow between the cationic membrane and the bipolar membrane with the cationic side facing the solution (Fig. 9). In this system, the metal cations are only shifted through the cationic membrane to meet the OH^- and form an alkaline solution. Acid anions remain in the feed and combine with H^+ ions to form carboxylic acid. A shortcoming of this arrangement is that all non-ionic components of the feed solution remain in the stream of carboxylic acid. For this reason, classical electro dialysis is often used to separate acid salts from the fermentation broth prior to salt splitting.

Bipolar and Anionic Membranes

The system is similar to that described previously, but in this case, salt solution is introduced between the cathode and the anionic membrane (Fig. 10). Salt splitting is determined by the transport of carboxylic anions through the anionic membrane. However, the progress of anions transport can be inhibited by an increasing gradient of NaOH in the feed solution. Replacing the ion-exchange sites with OH^- ions from an alkaline solution stops the transport of carboxylic anions, and the system completely turns into a generator of water electrolysis products. For this reason, the anionic membrane system is not recommended for the separation of carboxylic acids, even though the separated acid stream is then purified from nonionic impurities.

Fig. 9 Salt splitting with cationic membrane and two-compartment ED-BM stack (BP – bipolar membrane; MX – organic salt, MOH – base) [20]

Fig. 10 Schematic presentation of one step electrodialysis with anionic membrane and ED stack with bipolar membranes (BP – bipolar membrane; MX – organic salt, MOH – base) [20]

Three Chamber Electrodialysis with Cationic and Anionic Membranes

In a three-chamber system, the salt solution is dosed between the cationic and anionic membranes (Fig. 11). Both metal cations and acid anions are transported across the cationic and anionic membranes to form an alkaline and acidic solution, respectively.

Increasing the number of stages in the stack is possible simply by inserting bipolar membranes in place of the anode or cathode. Due to the increased electrical resistance, the number of stages in practice does not exceed 50.

Three-chamber system ensures complete separation of non-ionic impurities from the feed solution (e.g., sugars). In addition, there is no direct contact of the alkaline and acid solution, which prevents cation leakage. The main disadvantage of this system is a drop of conductivity in the feed chamber as the electrolyte concentration decreases.

During the electrodialysis process, oxygen in its radical, aggressive form is always released at the anode. For this

reason, in all systems, the anode space is usually separated from the supply stream by a cationic membrane to form an additional electrode cell filled with, e.g., 0.3 M H_2SO_4 .

Conclusions

A new, coherent concept of water conductivity based on some analogies to the electron–hole mechanism in semiconductors was presented. Pure water is a poor conductor of electricity, despite the large proportion of hydrogen bonds, approximately 85%. Only the addition of electrolyte drastically increases the conductivity of the solution, but it is not the electrolyte ions that conduct electricity. Charge carriers are produced in the electrode reactions of oxidation and reduction of water in the form of H^+ and OH^- ions. This implies the obvious semiconductor nature of electrolyte conductivity in hydrogen bond network using electron–hole mechanism.

The semiconductor analogy is particularly well suited to explain the principle of a bipolar membrane. The assumptions in the literature based on the physical production of H^+ and OH^- ions in the boundary layer collided with the problem of water deficit inside the membrane. Meanwhile, the current flow through the membrane in the electron–hole mechanism leaves electron vacancy on the cationic side as H^+ ions, and electron excess in the form of OH^- groups on the anionic side.

Different types of membranes, such as cationic, anionic, or both, can be used in electrodialysis systems for acid and base recovery. In each case, increasing the number of electrodialysis stages requires the use of bipolar membranes in place of the anode or cathode. Bipolar membranes form a barrier to electrolyte transport but simultaneously serve as apparent electrode system generating H^+ and OH^- to form acid and base from salt splitting.

Fig. 11 Three chamber system with cationic, anionic, and bipolar membrane for salt splitting [20]

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Declarations

Competing Interest The authors declare no competing interests.

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