

The Catalytic Interface Layer for Bipolar Membrane

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Bipolar membranes, a new type of composite ion exchange membrane, contain an anion exchange layer, a cation exchange layer and an interface layer. The interface layer or junction is the connection between the anion and cation exchange layers. Water is dissociated into protons and hydroxide ions at the junction, which provides solutions to many challenges in the chemical, environmental and energy fields. By combining bipolar membranes with electrodialysis technology, acids and bases could be produced with low cost and high efficiency. The interface layer or junction of bipolar membranes (BPMs) is the connection between the anion and cation exchange layers, which the membrane and interface layer modification are vital for improving the performance of BPMs.

Keywords: bipolar membrane ; water dissociation ; interface layer ; catalyst ; organic material ; inorganic materials

1. Overview of Bipolar Membranes

Bipolar membranes (BPMs) are one kind of special ion exchange membranes, which contain an anion exchange layer (AEL), a cation exchange layer (CEL) and an intermediate layer (IL). The intermediate layer is the junction of the anion and cation exchange layers. When the applied reverse bias potential causes the potential of the bipolar membranes reach or exceed 0.83 V, a large electric field is generated in the interface layer ^[1] to split water molecules into H^+ and OH^- . The generated H^+ and OH^- pass through the cation-exchange membrane and anion-exchange membrane of the bipolar membrane, together with cation and anion exchange membranes in an electrodialytic cell arrangement, forming acids and bases in the adjacent two compartments. The hydrolysis rate of the interface layer applied with a DC electric field is much higher than that of the general case ^{[2][3]}. During the electrolysis process, the water consumed by the dissociation of the water in the interface layer of bipolar membranes can be replenished in time by the water in the electrolyte on both sides of the membranes. Unlike the reactions on the electrodes during electrolysis, this process does not generate any gas ^{[4][5]} and can obviously reduce energy consumption.

This unique advantage of bipolar membranes has led to an increasing interest in it. The improvement of the bipolar membrane interfacial layer material accelerates the rate of water dissociation in the interface layer, decreases the hydrolysis voltage and reduces energy consumption. The effect of the performance of synthetic bipolar membranes can be explained by applying them in electrolysis experiments on brine in electrodialysis. In recent years, researchers have devoted much effort in regard to the interface layer materials for this purpose. Eswaraswamy et al. introduced a nanocomposite layer of graphene oxide and sulfonated polyether ether ketone the intermediate layer ^[6]. Montmorillonite nanoclay with a large surface area and containing alumina and silicate components was also demonstrated by Eswaraswamy et al. to be an efficient catalyst for water dissociation ^[7]. Celik et al. further explored that ferric chloride as an interface layer catalyst enhanced acid production and induced lower electrical resistance during bipolar membrane electrodialysis ^[8]. Nano-MoS₂ was synthesized by Rathod et al. because of its similar conductivity to that of graphene and carbon nanotubes ^[9]. However, these bipolar membranes are only used for electrodialysis experiments under laboratory conditions, and there are many problems to be overcome for industrial applications. Problems include energy consumption, current efficiency, membrane lifetime and optimization of equipment parameters. Poor resolution of these issues can lead to higher production costs and is not conducive to mass production.

2. Application of Bipolar Membranes

Bipolar membrane electrodialysis (BMED) is a new technology that combines the separation function of electrodialysis with the water dissociation at the interface layer of bipolar membranes, which can convert salts into the corresponding acids and bases. Therefore, the two combinations are often used in industry to produce acids and bases. **Figure 1** is an example of an electrodialysis device. BMED can be used for the clean production of organic acids, inorganic acid and bases, including succinic acid ^{[10][11]}, salicylic acid ^{[12][13]}, lactic acid ^{[14][15]}, amino acids ^[16], hydrochloric acid ^[17], sulfuric

acid [18][19], phosphoric acid [20] and choline hydroxide [21]. Sheldeshov et al. introduced ionic polymers with catalytically active phosphoric acid groups into bipolar membranes and studied the process of recovering nitric acid and sodium hydroxide from a sodium nitrate solution [22]. The use of bipolar membrane units for the production of nitric acid and sodium hydroxide containing phosphoric acid groups could achieve higher concentrations, current efficiencies, productivity and lower energy consumption and sodium nitrate contamination levels. Venugopal et al. functionalized and modified polysulfone (PSu) with resin and fiber reinforcement to prepare bipolar membranes containing Pt catalysts. The sodium chloride solution in brackish water with a concentration of 5–25 g/L was desalinated by electrodialysis desalination process. During the desalination treatment, the current efficiency was 82.5%, the energy consumption was 0.52 Wh, and the acid-base production was 0.006 mol/L acid and 0.006 mol/L base [23]. According to the unique hydrolysis mechanism and desalination effect of BMED, it could also be applied to the treatment of high-salt wastewater [24][25][26]. At the same time, bipolar membranes also play an irreplaceable role in the fields of the chemical industry, food processing, environmental protection, CO₂ emission reduction, photocatalytic hydrogen production, biotechnology and the pharmaceutical industry [27][28][29][30][31][32][33].

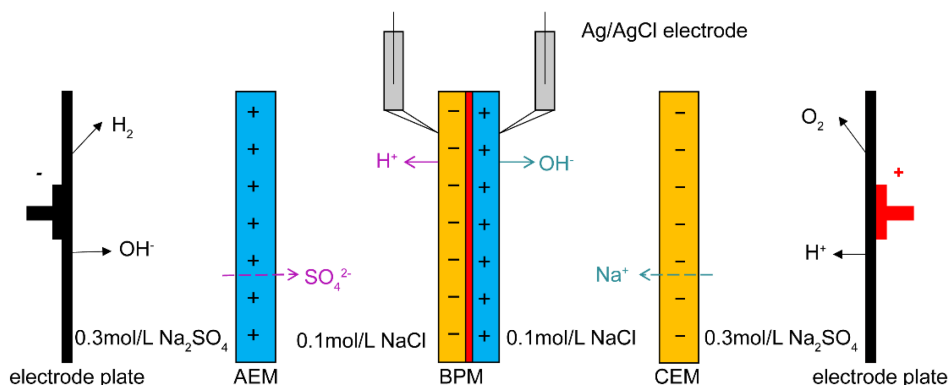


Figure 1. A bipolar membrane electrodialysis device and measurement principle of I-V curves.

The burning of fossil fuels and the convenient living of people produce large amounts of CO₂. The CO₂ contained in these waste gases cannot be directly utilized. Therefore, the combination of CO₂ capture and BMED technology can realize the utilization and regeneration of CO₂. CO₂ is captured using potassium hydroxide and sodium hydroxide solutions to produce the corresponding carbonate solution or bicarbonate solution [34][35][36]. The bipolar membrane electrodialysis technology electrolyzes the salt solution to produce pure CO₂ gas. This CO₂ regeneration process significantly reduces energy costs and is environmentally friendly. CO₂ capture can also be performed by passing the exhaust gas into organic reagents such as methionine salts [37] or aniline [38]. In addition, BMED technology can treat hazardous substances and recover other resources such as organic acids in industrial waste [39][40][41]. Noguchi et al. used multi-step BMED to concentrate a sodium borate solution with an initial concentration of 100 mg/L to a solution containing approximately 10,000 mg/L of boron [42]. In the discharged beverage industry, wastewater, a combination of concentration electrodialysis and BMED, Lameloise et al. successfully obtained L-malic acid recoveries of 93–97% [43].

3. Study of the Interface Layer Catalyst

The interfacial layer is the main place where water dissociation occurs in bipolar membranes. Assuming that this phenomenon was explained by the usual water dissociation mechanism, according to Simons' theory [44], the calculated fluxes of H⁺ and OH[−] were about 2×10^{-9} mol/m² s, while the actual fluxes in bipolar membranes were as high as 10^{-2} mol/m² s, the calculated value was inconsistent with the experimental value, indicating that the water dissociation of the bipolar membrane is not the same as the water dissociation in the normal state. Therefore, there is an effect of promoting water dissociation.

According to the studies of the water dissociation behavior of a bipolar membrane by many researchers, there are two main theoretical models to explain this phenomenon. The second Wien effect is a theoretical model based on the hydrolysis of weak electrolytes under high electric fields [45]. The theory holds that when the applied electric field is high enough, the conductivity of electrolyte increases rapidly with the electric field, causing Ohm's law to fail. Applying the second Wien effect to bipolar membranes, water dissociation occurs in a sharp depletion region between the anion and cation exchange layers, where water is broken down into H⁺ and OH[−] as a weak electrolyte. In Onsager's experiments, the electric field strength in the depletion region was as high as 10^8 V/m, and the water dissociation rate constant was 10^7 times higher than when no applied voltage was applied. Surprisingly, the theory cannot continue to be implemented in the

experiment for the electric field intensity higher than 10^8 V/m. To investigate the cause, other effects that high electric fields may bring are ignored.

Since then, Simons had conducted numerous experiments to investigate functional groups and proposed that the hydrolysis of water molecules into H^+ and OH^- generated a protonation and deprotonation reaction model by interacting with the membrane's fixed charge groups [44][46], i.e., the chemical reaction theoretical model (CHR). According to the CHR hypothesis, water dissociation is primarily driven by active group catalysis, i.e., protonation and deprotonation of the active group. The application of this model to the water dissociation mechanism of the bipolar membrane interface layer showed that the water dissociation depends on the properties of charged groups, and not all functional groups made a significant contribution to water dissociation. Other studies had found that protonation and deprotonation reactions were not limited to membrane fixed charge groups [47], and the role between other active points in the membrane (such as metal oxides, heavy metal impurities, and metal complexes) and water molecules might also be applicable.

The bipolar membranes currently used could not bear high temperatures with low mechanical strength and poor conductivity. New bipolar membranes which have good permeability, high permselectivity and good stability are urgently needed. Selectivity is an important parameter in the BMED process, if it is necessary to electrolyze ion solutions containing different valence states to produce a specific substance. Bipolar membranes with high selectivity improve the purity of the product. On the contrary, it not only reduces the product purity but also increases the energy consumption in the electrodialysis process [48]. Since water molecules in the interface layer are split to generate an acid-base solution, it is further required that the bipolar membranes need to have great resistance ability for acids and bases. The methods to improve the performance of bipolar membranes are mainly divided into the modification of the anion and cation exchange layers and the introduction of catalysts in the interface layer. **Figure 2** depicts the development process of the interfacial layer materials. The transmembrane voltage of bipolar membranes is an important factor affecting the performance of bipolar membranes, which mainly depends on the voltage drop of the interface layer. Catalysts are added to the interface layer to promote the water dissociation, reduce the activation energy of the water dissociation reaction, increase the water dissociation rate, reduce the membrane impedance, and make the BPM process more energy efficient. The basic principles for the selection of the interfacial layer materials are included in **Figure 3**.

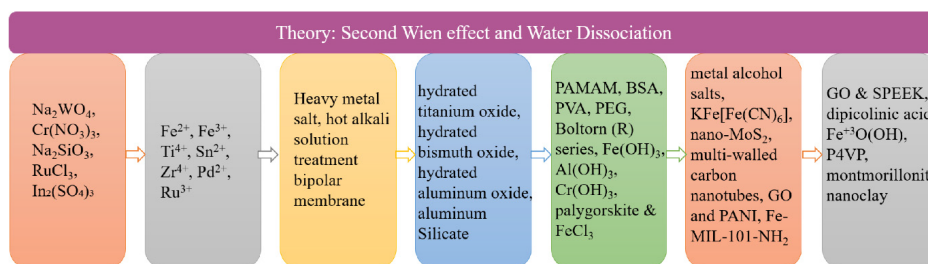


Figure 2. A schematic diagram of the development of intermediate layer materials. Polyamidoamine (PAMAM); bovine serum albumin (BSA); polyvinyl alcohol (PVA); polyethylene glycol (PEG); graphene oxide (GO); polyaniline (PANI); sulfonated polyether ether ketone (SPEEK); poly(4-vinylpyrrolidone) (P4VP).



Figure 3. The basic principles for selecting interlayer materials.

Previous research found that inorganic electrolytes with amphoteric properties ^[44] (such as sodium metasilicate, chromium nitrate, ruthenium trichloride, or indium sulfate) and heavy metal ions (Fe^{2+} , Fe^{3+} , and Ti^{4+} , etc.) on CEL/AEL catalyzed interface layer water dissociation and reduced bipolar membrane voltage. Moreover, weak acids, amino functional groups, carboxylic acids and pyridines had catalytic effects on the interface layer of the bipolar membrane, reducing the voltage of the bipolar membrane ^[49]. Although the expected results were obtained, these results did not fully describe the precise interface layer water dissociation process, and more research is still needed to properly understand the water dissociation behavior as well as the wider catalytic components.

The research on bipolar membranes mainly focuses on introducing suitable catalysts to improve the water dissociation rate. Catalysts that have been used could be classified as organic and inorganic materials. Newly designed materials with multiple components as catalytic intermediate layers are being studied more frequently.

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