멤브레인(Membrane Journal)
Vol. 33 No. 3 June 2023, 87-93

총 설

Print ISSN: 1226-0088
Online ISSN: 2288-7253
DOI: https://doi.org/10.14579/MEMBRANE_JOURNAL.2023.33.3.87

전기투석 공정에 의한 알칼리 회수: 총설

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(2023년 2월 23일 접수, 2023년 4월 28일 수정, 2023년 6월 7일 채택)

Alkali Recovery by Electrodialysis Process: A Review

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(Received February 23, 2023, Revised April 28, 2023, Accepted June 7, 2023)

요 약: 전기투석(ED)은 이온교환막을 통한 이온의 분리에서 중요한 과정이다. 해수담수화로 발생하는 염수 처리는 환경적으로 큰 문제이며 막분리 기술을 통한 재활용 효율이 높다. 마찬가지로 알칼리는 가죽, 전기도금, 염색, 제련 등과 같은 여러 화학 산업에서 생산된다. 폐기물의 고농도 알칼리는 부식성이 높고 화학적 산소 요구량(COD) 값이 높기 때문에 환경에 방출하기 전에 처리해야 합니다. 칼슘과 마그네슘의 농도는 염수의 거의 두 배이며 주요 환경 오염 물질인 이산화탄소의 흡착에 완벽한 후보입니다. 수산화나트륨은 양극성 막 전기투석 공정으로 쉽게 생산되는 금속 탄산화 공정에 필수적입니다. 역삼투압(RO), 나노여과(NF), 초여과(UF), ED 등 다양한 공정을 통해 회수가 가능하다. 본 검토에서는 알칼리 회수를 위한 이온교환막에 의한 ED 공정에 대해 논의한다.

Abstract: Electrodialysis (ED) is essential in separating ions through an ion exchange membrane. The disposal of brine generated from seawater desalination is a primary environmental concern, and its recycling through membrane separation technology is highly efficient. Alkali is produced by several chemical industries such as leather, electroplating, dyeing, and smelting, etc. A high concentration of alkali in the waste needs treatment before releasing into the environment as it is highly corrosive and has a chemical oxygen demand (COD) value. The concentration of calcium and magnesium is almost double in brine and is the perfect candidate for carbon dioxide adsorption, a major environmental pollutant. Sodium hydroxide is essential for the metal carbonation process which, is easily produced by the bipolar membrane electrodialysis process. Various strategies are available for its recovery, like reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and ED. This review discusses the ED process by ion exchange membrane for alkali recovery are discussed.

Keywords: *electro dialysis (ED), ion exchange membrane (IEM), bipolar membrane (BPM), anion exchange membrane (AEM)*

1. Introduction

Environmental pollution and global warming lead to changes in weather patterns, resulting in severe scarcity of freshwater. Desalination of seawater is one of the alternatives to fullfill the global freshwater demand [1-3]. However, this process generates a large amount of brine, and its disposal becomes a critical issue. One

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way to address this is through the recycling of seawater brine, and achieving zero liquid discharge (ZLD), which is one of the vital goals of recently developing concepts. Recovery of salt from the brine is done by thermal and membrane processes. In thermal process, water present in the brine is evaporated, and the solid salts are recovered. In the second case, nanofiltration (NF), reverse osmosis (RO), and electrodialysis (ED) are the major process.

Several industries, such as textile, leather, paper, and mineral ore processing, discharge large amount of wastewater with alkali into the environment. Conventionally, the alkali is treated with acid for neutralization. The diffusion dialysis process is an alternative method of recovering alkali from wastewater instead of destroying it. ED process is the most efficient one used in several applications. In the ED process, an ion exchange membrane is used to separate selectively ions based on their charge. Although this is a very efficient process, the presence of a large number of components and the high concentration of the brine makes the membrane prone to scaling and makes it difficult to separate the impurity salt. Bipolar membrane (BPM) is based on electro dialysis in which cation exchange membrane (CEM) and anion exchange membrane (AEM) are sandwiched together and known as bipolar membrane electrodialysis (BMED)[4-9]. When current is applied, the water dissociates, and the cation and anion are exchanged through CEM and AEM, respectively, in order to maintain the ionic current. There are several advantages of BMED such as no generation of byproducts and efficient energy utilization.

AEM with high selectivity of hydroxyl ion is one of the critical electrodialysis membranes used for selective recovery of alkali[10-13]. Both stability and selectivity of the AEM membrane is the key parameter for an efficient ED process. In this review, both BPM and AEM membranes are discussed in detail for the recovery of alkali.

2. Electrodialysis

Capturing carbon dioxide with a powerful alkali group like sodium hydroxide is one of the possible applications to reduce carbon dioxide amount[14]. The Bipolar membrane electrodialysis (BMED) process was used for the recovery of sodium hydroxide from neutralized liquor glyphosate, which can also be used as sorbent for carbon dioxide catch. A solution of sodium hydroxide was prepared, which had ~ 96.5% of purity with a concentration of ~1.45 mol/L^{-1}. The optimum efficiency of BMED process was obtained at 2.15 $kW\ h\ kg^{-1}$ in which 98.2% of glyphosate was recovered. The net CO_2 captured by this BMED process was 530.65 g per kg of alkali. Carbon dioxide capture and utilization is one of the critical needs of the hour to control environmental pollution[15]. Baena-Moreno *et al.* utilized potassium and calcium present in the waste to capture carbon dioxide and prepare their respective carbonates, which has industrial importance. The effect of the concentration of potassium in the formation of calcium carbonate is studied in detail.

2.1. Bipolar membrane

Recycling brine from seawater is one of the ways to recover resources effectively[16]. The system of hydride selective electrodialysis (HSED) with improved selectivity bipolar membrane electrodialysis (SBMED). HSED is used to recover divalent anions and cations from brine simultaneously by increasing the concentration of sodium chloride. The mixture with a high concentration of salt was passed through the SBMED process to prepare acid/base by skipping purifying pretreatment. By analyzing the HSED case, it revealed that an increased voltage value from ~2.33 to 2.67 V, increases better removal of divalent magnesium, calcium, and sulfate ions.

Lithium carbonate (Li_2CO_3) is an essential raw chemical for lithium batteries[17]. The growing demand for clean energy, leads to a rapid increase in the price of lithium carbonate. Extraction of lithium carbo-

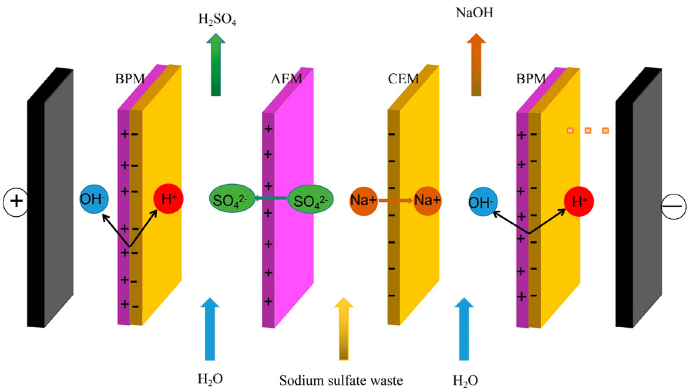

Fig. 1. Schematic diagram of the BMED membrane reactor used in the experiment (Reproduced from Gao *et al.*[17], MDPI).

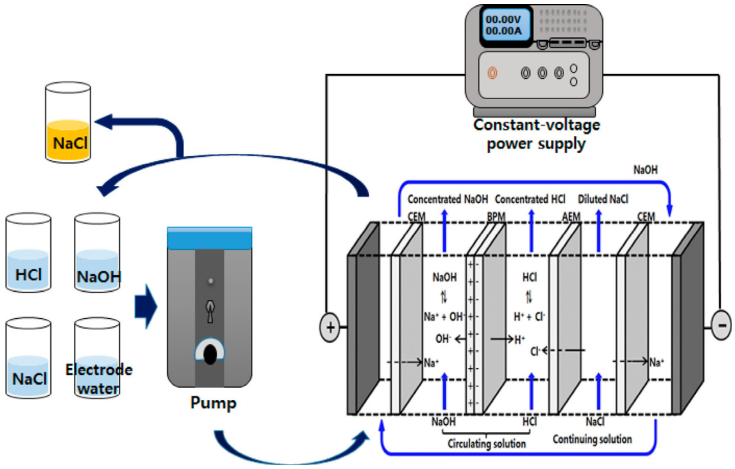

Fig. 2. Schematic diagram of the overall experimental apparatus and the internal structure of the cell (Reproduced with permission from Kwon *et al.*[18], Copyright 2018, American Chemical Society).

nate is not economical due to the production of sodium sulfate waste. BMED process was used to convert the waste sodium sulfate to valuable sulfuric acid and sodium hydroxide economically with minimum energy consumption of 1.4 kWh.kg^{-1}. Fig. 1 represents the schematic of BMED process.

The bipolar membrane was prepared by hot pressing sulfonated polyether ether ketone and aminated polysulfone[18]. Experimental measurement of the bipolar membrane setup schematic is presented in Fig. 2. How pH changes with time is presented in Fig. 3.

The properties of the synthesized bipolar membrane were compared with commercial ASTOM membranes. The formation of acid and base in the synthesized membrane is the same or more than the commercial

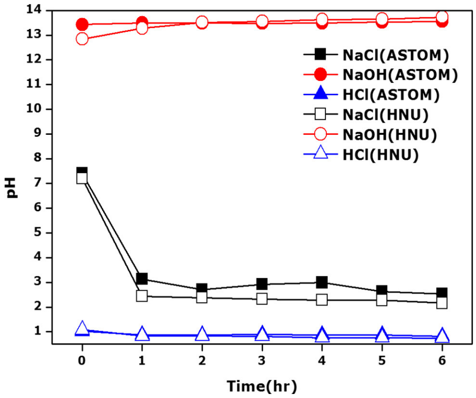

Fig. 3. Changes of pH in each solution (HNU: self-prepared BPM, SPEEK/APSf 4:1) (Reproduced with permission from Kwon *et al.*, 18, Copyright 2018, American Chemical Society).

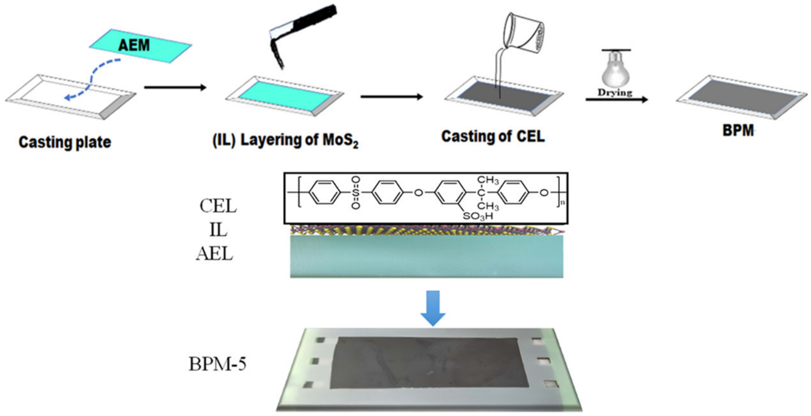

Fig. 4. Schematic representation of BPM preparation (Reproduced with permission from Rathod *et al.*[20], Copyright 2020, American Chemical Society).

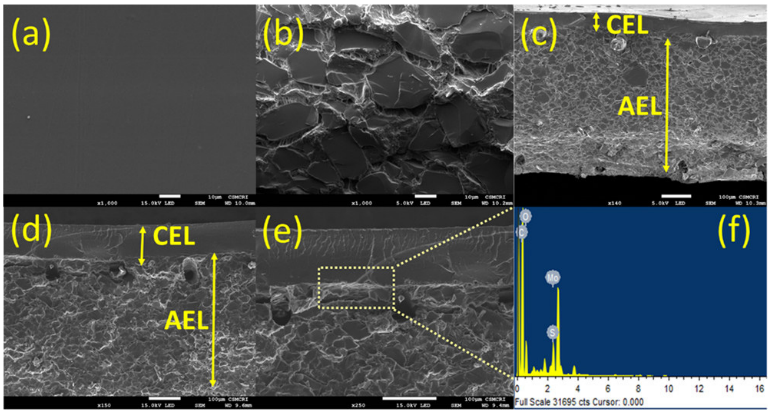

Fig. 5. SEM images of BPMs: (a) surface image of BPM-5 from the CEL side, (b) surface image of BPM-5 from the AEL side, (c) cross section of BPM, (d, e) cross section of BPM-5 with an interfacial layer at different resolutions, and (f) EDX analysis of the interfacial layer at membrane cross section (Reproduced with permission from Rathod *et al.*[20], Copyright 2020, American Chemical Society).

membrane depending on the percentage of sulfonation and quaternization of CEM and AEM, respectively.

Bismuth oxychloride, a photoactive material, was sandwiched in between the interlayer of a bipolar membrane (BPM) to fabricate BiOCl/ BPM for sodium hydroxide regeneration[19]. Newly prepared composite bipolar membrane, operated under sunlight irradiation and reverse bias condition consume lower energy leading to efficient product generation. Current efficiencies increased due to separation of hole-electron separation.

An efficient bipolar membrane (BPM) was fabricated through layer-by-layer staking of cation and anion exchange polymer[20]. Sequence of deposition on the support layer is presented in Fig. 4. MoS_2 is the intermediate layer (IL) sandwiched in between anion exchange layer (AEL) and cation exchange layer (CEL). SEM image as well as elemental composition is presented in Fig. 5.

For the development of salt hydrolysis, the interfacial layer of the membrane was tested in terms of nano-MoS_2 catalyst characteristics. Membranes were characterized by their uptake of water, ion conductivity, and ion exchange capacity. The difference was found in the presence of nano-MoS_2, which had better efficiencies in comparison to ones without it. BPM with specific composition has the highest power consumption of 2.16 kWh kg^{-1} for ionization of 0.4 M sodium chloride solution.

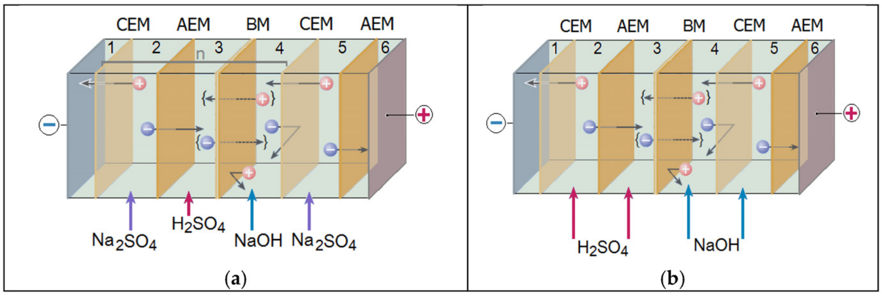

Fig. 6. Diagram of an electrodialysis apparatus with a three-chamber unit cell for obtaining sulfuric acid and sodium hydroxide solutions: (a)—for the first and second variants of the experiment; (b)—for the third variant of the experiment. CEM, cation-exchange membrane, AEM, anion-exchange membrane, BM, bipolar membrane; n is an elementary repeating fragment (Reproduced from Kozaderova *et al.*[26], MDPI).

Compared to seawater, brine has double calcium and magnesium concentration, which are ideal candidates for the reduction of carbon dioxide[21]. The specific interest of this work is to use sodium hydroxide for carbonation which is generated by the BMED process that contains divalent ions. Anion exchange membrane used the proton leaked from it to prepare NaOH. 147 mg/L of divalent magnesium ion containing brine generates 2.0 mol/L sodium hydroxide. Yao *et al.* reported bipolar membrane electrodialysis to utilize and separate industrial waste into acid and base for further applications[22].

2.2. Anion exchange membrane

Two different composite anion exchange membranes were prepared with polyvinyl alcohol (PVA), followed by crosslinking with formaldehyde. In the first case, quaternized graphene oxide (QGO) was incorporated, and in the other case, quaternizedpolyethylene imine (QPEI)[23]. PVA/QGO have lower ion exchange capacity (IEC) as well as water uptake. PVA/QPEI/QGO membrane has higher IEC resulting in lower area resistance. The alkali resistance of the synthesized membrane is better than the commercial AMV membrane. Recovery of NaOH from the Na_2WO_4 mixture through the ED process by the synthesized membrane is much better than the commercial one. A new cross-linker copolymer named acrylonitrile-vinyl imidazole (PVACN) was synthesized and used to crosslink polysulfone (PSCr) which, is used as AEM for caustic soda recovery by ED[24]. This polymer is highly stable in the alkali medium due to the lower presence of the hydroxyl group. The optimized membrane showed lower swelling and good IEC which, is excellent for the ED process. The length of the side chain in the polysulfone AEM are varied to prepare different polymer with variation in ion exchange capacity[25]. The optimized membrane has a low swelling ratio, and good hydroxyl conductivity along with retention of IEC. It shows good performance even after the ED test five times, which is about 96.4% retention. Fig. 6 represents the electrodialysis process to obtain sodium hydroxide solutions through a bipolar ion exchange membrane.

3. Conclusions

IEM based process for sea water desalination is far more advantageous than the traditional process. Desalination of seawater to generate drinking water is one of the effective alternatives but brine or concentrated salt water generated in this process is very difficult to dispose of. Ion exchange membranes are used in harsh chemical conditions, and their stability in the ED process is crucial. More specifically, the anion exchange membrane is prone to degradation during alkali recovery. Grafted functional groups like quaternary ammonium ions are unstable in at high pH. In order to overcome these demerits, cross-linking is another alternative method to improve ion exchange efficiency. But in order to enhance the membrane stability, new approaches like functional inorganic filler incorporated mixed matrix membrane may enhance the stability much better.

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