With the rapid expansion of desalination to address global freshwater shortages, particularly through reverse osmosis, seawater brine (SWB) is a significant byproduct. 1, 2 It is a potentially valuable resource rich in dissolved salts.3 Traditionally, direct discharge into the ocean will pose ecological risks, and cause resource waste.2, 4-7 In that case, recovering useful chemicals from SWB aligns with circular economy and improves the overall sustainability of desalination processes.3, 4, 8 Among the techniques to recover resources from SWB, bipolar membrane electrodialysis (BMED) has gained attention due to its ability to separate and convert ionic species without adding chemicals.7, 9-11 Moreover, it offers a direct route to produce high-value acid and base from SWB by integrating water dissociation at the bipolar membrane (BPM) interface.4, 12, 13 In that case, BMED is promising for integrated SWB management, enabling simultaneous desalination waste valorization and valuable chemical production.7, 14, 15

Although BMED shows potential in treating SWB, scaling that is induced by ions (such as Mg2+, Ca2+, HCO3- and SO42-) remains a critical problem in BMED. 16-19 During the operation of BMED stack, cations including Mg2+ and Ca2+ will transport through CEM and reach the base chamber. With the operation time increasing, OH- produced by water dissociation at BPM interface gradually accumulates in the base chamber. The high-pH environment promotes the precipitation of Ca(OH)2 and Mg(OH)2 in the chamber and on the membrane surface. 19, 20 The scaling on IEMs may further induce water splitting to aggravate scaling. 21-23 Scaling adversely affects BMED performance by reducing ion flux, increasing membrane resistance, and elevating energy consumption.17, 18, 23, 24 As scaling progresses, it can cause irreversible damage to membranes, especially increasing the risk of membrane rupture23. In-depth research on the causes of scaling can provide effective strategies to alleviate or avoid scaling, thereby achieving high efficiency.

Although scaling in electrodialysis (ED) has been extensively studied, 21-23, 25-29 there remains a significant lack of research specifically addressing scaling in BMED. While both ED and BMED share similar ion transport principles, that of BMED is more complicated due to additional BPMs. The changing pH in chambers poses additional risks of scaling. Existing BMED studies have primarily focus on the influence of scaling on overall system performance or have qualitative identification of scaling on IEMs. 16, 18, 20, 30-33 It shows a lack of comprehensive understanding of scaling formation across the entire BMED stack. It is essential to recognize that water dissociation and ion transport in BMED alter the ion concentration dynamically, leading to changes in local conditions that strongly influence scaling tendencies. Therefore, it is necessary to identify scaling formation in different parts of the stack.

The objective of this study is to elucidate the mechanism of scaling formation throughout the BMED process, with a focus on the interactions between ion transport and scaling development. The influence of scaling on BMED performance and efficiency was discussed to explain the significance of the study. The scaling in the chamber and on IEMs was characterized to ensure the location where scaling took place and its composition. In the BMED process, the system parameters were monitored to explain the scaling evolution. By providing a mechanistic framework, this study offers insights into future strategies for effective mitigation and operational optimization.

In conventional chemical processes, high-salinity wastewater often arises as a byproduct of acid-base neutralization reactions. The direct discharge of brine solutions not only damages the environment34-36 but also leads to the loss of valuable resources.35, 37-39 Therefore, the effective treatment of such waste brine solutions has become an urgent and critical issue. Among various treatment methods, electrodialysis (ED) has been widely employed to concentrate brine solutions, facilitating subsequent crystallization into solid salts.40-42 However, the economic viability of salt recovery via ED is not always favorable.43??? To address this limitation, bipolar membrane electrodialysis (BMED) has been developed as an advanced electrochemical separation technology that combines the principles of ED with the unique properties of bipolar membranes (BPMs).43-46 This approach enables the production of acids and bases from salt solutions, providing an efficient and environmentally sustainable alternative to conventional chemical processes. BMED has been applied in various biological and chemical industries.47-50 Many studies have shown that BMED has the potential to produce high-purity acids (e.g., HF,51 HNO3,10 HCl,52 H2SO4,53 H3PO4,54 acetic acid,55 citric acid56) and bases (e.g., NaOH, 54, 57 LiOH52) from salt solutions.

Scaling on ion exchange membranes (IEMs) is an urgent problem in BMED. 16, 17 Scaling adversely affects BMED performance by reducing ion flux, increasing membrane resistance, and elevating energy consumption.17, 18, 24 As scaling progresses, it can cause irreversible damage to membranes, especially increasing the risk of membrane rupture.58 In-depth research on the causes of scaling can provide effective strategies to alleviate or avoid scaling, thereby achieving high efficiency. Previous studies concluded that scaling is related to the solution composition, process parameters.21, 23, 26, 31, 59 Bazinet, Montpetit, Ippersiel, Amiot and Lamarche 30 and Wang, Yang and Cong 18 found scaling on cation exchange membranes (CEMs) when feeding solution contained Ca2+ and Mg2+. Casademont, et al. 60 found that an alkali feeding solution triggered scaling on CEMs. Therefore, pretreatment such as nanofiltration,61 chemical precipitation,61 ion exchange resins,52 pellet reactor 17 was introduced prior to BMED to remove scaling ions. 不用去讲pretreatment These studies informed that the presence of scaling ions (e.g., Ca2+, Mg2+ and OH⁻) in feeding solution predominantly resulted in sparingly soluble precipitates on IEMs in ED.16-18, 30 However, the transport of ions is more complicated in BMED: water dissociation happens on BPMs, and the increasing OH⁻ concentration in the base chamber is likely to result in scaling in the stack. Besides the solution composition, Mehran Aliaskari 20 concluded that flow rate and current densityplay key roles in scaling growth on BPM in BMED system. However, the research only focuses on the scaling on BPM without considering the scaling on CEMs and in chambers.

Some limitations of previous studies (e.g., only focusing on specific IEMs) result in a lack of comprehensive understanding of scaling formation across the entire BMED stack. It is essential to recognize that water dissociation and **selective** ion transport in BMED alter the ion concentration dynamically, leading to changes in local conditions that strongly influence scaling tendencies. Therefore, it is necessary to identify scaling formation in different parts of the stack. This understanding will support the development of targeted process modifications, novel membrane configurations, and advanced operational strategies to effectively avoid scaling. The objective of this study is to elucidate the mechanism of scaling formation throughout the BMED process, with a focus on the interactions between ion transport and scaling development. The influence of scaling on BMED performance and efficiency was discussed to explain the significance of the study. The scaling in the chamber and on IEMs was characterized to ensure the location where scaling took place and its composition. In the BMED process, the system parameters were monitored to explain the scaling evolution. By providing a mechanistic framework, this study offers insights into future strategies for effective mitigation and operational optimization.

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