Integration of Bipolar Membrane Electrodialysis with Ion-Exchange Absorption for High-Quality H₃PO₂ Recovery from NaH₂PO₂

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ABSTRACT: H₃PO₂ has emerged as an indispensable reducing agent for electroless nickel plating. Commercial preparation of H₃PO₂, with high purity and low cost, is a great challenge. In this work, a novel technique by the integration of bipolar membrane electrodialysis (BMED) with ion-exchange absorption was designed to prepare high-quality H₃PO₂ aqueous solution. The critical parameters, such as voltage drop, NaH₂PO₂ concentration, and different types of anion-exchange membranes, were systematically investigated. Continuous experiments indicated that a high yield of up to 80.06% with a low energy consumption of 4.99 kW h/kg was achieved under optimal operation conditions (voltage drop of 20 V, feed concentration of 15 wt % NaH₂PO₂, and anion-exchange membrane of AHA). Moreover, leakage of Na⁺ ions through the bipolar membrane was observed. By using T-52H cation-exchange resin, the final concentration of Na⁺ ions in H₃PO₂ aqueous solution was reduced to 20.91 mg/L. Subsequently, a long-term experiment was performed to evaluate the stability of the BMED stack, and the concentration of H₃PO₂ in the acid compartment reached 4.15 mol/L. Under optimal conditions, the H₃PO₂ production cost was estimated at $0.937 kg⁻¹, which was competitive and economically friendly for industrial application.

1. INTRODUCTION

Hypophosphorous acid (H₃PO₂) is a colorless water-soluble inorganic acid with strong reducibility, as two H atoms are directly attached to P.¹ The chemical structure of hypophosphorous acid is shown in Figure 1, revealing the presence of one acidic H atom and a monoprotic acid. H₃PO₂ has been widely applied in industries as a reducing agent in electroplating industry, as a catalyst in esterification and phosphated steel manufacturing, as refrigerants for cooling water-treatment manufacture, for the decolorization of polymers, and so forth.²,³ The H₃PO₂ products such as 50 wt % aqueous solution and industrial grade products are commercially available now.¹ Simultaneously, the purity of H₃PO₂ aqueous solution should be controlled strictly at a low grade of impurities.

Currently, the main techniques to prepare H₃PO₂ are electro-electrodialysis and ion-exchange.⁴ Electro-electrodialysis has proven to be a promising, high-efficient, and convenient method for the production of H₃PO₂.⁴,⁵ Conventionally, the principle of producing H₃PO₂ by electro-electrodialysis is mainly as follows: H⁺, which is generated from decomposed water in the anode, combines with hypophosphite ions (H₂PO₂⁻) to form H₃PO₂. Chen successfully applied electro-electrodialysis to prepare high-purity H₃PO₂.⁶ However, the drawbacks of the electro-electrodialysis technique are low yield and high energy consumption, which is mainly due to the oxidation of H₃PO₂.⁷ In addition, the large amounts of H₂ and O₂ generated from the electrodes is also a potential risk for industrial-scale H₃PO₂ production. For the ion-exchange technique, the cation-exchange resin characterized by unique functional groups was used to remove Na⁺ ions from high-concentration sodium hypophosphite (NaH₂PO₂) solution.⁸ Nevertheless, the ion-exchange technique has been demon-

Figure 1. Chemical structure of H₃PO₂.
studied the BMED technique for acids and bases production. 
This is mainly because the amount of resin is proportional to the concentration of the solution. The NaH₂PO₂ solution with a high concentration requires voluminous cation-exchange resins, and the time of resin regeneration would be prolonged accordingly. Furthermore, this process often generates a large amount of wastewater washed from the resin, which is a pollutant to the environment. Therefore, the treatment of high-concentration NaH₂PO₂ solution by ion-exchange technique would make H₃PO₂ a rather costly commodity, which is not suitable for large-scale industrialized production.

Bipolar membrane electrodialysis (BMED) is a well-developed, efficient, and environmentally friendly technology, which can be used to produce bases and acids from neutral salts. The BMED technique is an integration of bipolar membrane (BM) with conventional electrodialysis. Meanwhile, the BM comprises an anion-exchange layer, an intermediate catalytic layer, and a cation-exchange layer. When the voltage drop is applied on the BMED stack, water will be dissociated into H⁺ and OH⁻ ions because of the potential gradient bias in the middle layer of the BM. Hence, the acid and base can be produced from the salt without other additives through the BMED stack. Currently, owing to its unique advantage of low energy consumption, BMED technique is being successfully applied in various industrial productions, such as recycling of waste in the environmental protection industry, preparation of vitamin C and organic salt in the pharmaceutical industry, organic acids and bases production in the chemical industry, and so forth. Chen et al. investigated the BMED technique to produce alkali for CO₂ adsorption. Davis et al. studied the BMED technique for acids and bases production from dilute salt solutions. Yang et al. presented BMED to obtain high-purity NaOH and acid byproducts by treating Ca²⁺/Mg²⁺ brine. Unfortunately, the permeation of salts through the BM is still an inevitable problem, which significantly affects the purity of the product.

Herein, a novel process integrating BMED with ion-exchange absorption was adopted to produce high-quality H₃PO₂ aqueous solution. Specifically, a lab-scale BMED setup was used to treat high-concentration NaH₂PO₂ solution for the production of H₃PO₂. Our proposed method proved to be feasible, and various key parameters such as current density, H₂PO₂ concentration, energy consumption, yield, and current efficiency during the BMED process have been systematically investigated. The phenomenon of Na⁺ ions leakage through the BM was analyzed and processed. Moreover, a long-term experiment was conducted to investigate the stability of the BMED stack. Compared to the conventional ion-exchange technique for the production of H₂PO₂ from NaH₂PO₂, this study presented a cost-effective process by using T-52H cation-exchange resin to treat the interfering Na⁺ ions in the BMED effluent of H₂PO₂, which was demonstrated by the calculation of process economics.

2. RESULTS AND DISCUSSION

2.1. Impact of Voltage Drop. Voltage drop is a vital parameter in the BMED process because it determines the current efficiency, energy consumption, and yield. A series of constant voltage (CV) drops (10, 15, 20, and 25 V) were used to investigate the influence of voltage drop on H₃PO₂ production with BMED stack. FBM/AHA/CMB/FBM were used in the BMED stack as membrane pairs, and the initial NaH₂PO₂ concentration was 15 wt % in the feed compartment. The effect of voltage drop on the current density, concentration of H₃PO₂, energy consumption, current efficiency, and yield is illustrated in Figure 2.

Figure 2a shows the impact of current density on the BMED stack. The curves show an upward tendency during the first 10 min, which may be due to the migration of ions between different compartments. Specifically, the H₃PO₂⁻ ions migrate to the acid compartment and Na⁺ ions migrate to the base compartment, and thus the electrical resistance of the stack system decreases accordingly. According to Ohm’s law, the current density increases sharply at first and then approaches a maximum value. Afterward, when the H₂PO₂⁻ ions and Na⁺ ions in the feed compartment are exhausted, a sharp decrease of current density can be observed because of increase of electrical resistance in the BMED stack. In addition, the voltage drop is inversely proportional to the experimental time. According to the Second-Wien' effect, ionic mobility increases with the increase of voltage drop across the BMED stack. Therefore, higher voltage drop causes shorter experimental time. In contrast, the maximum current density at the voltage drop of 10 V maintains approximately for 120 min. This phenomenon suggests that the depressed voltage drop results in a sharp drop in the ionic mobility, and therefore a longer experimental time is obtained.

Figure 2b exhibits the change of H₃PO₂ concentration in the acid compartment. The curves are almost linear in the initial experiment, which is ascribed to the constant driving force by the voltage drop applied on the BMED stack. Moreover, the linear curves indicate that the migration rate of ions between the feed compartment and the acid compartment (H₃PO₂⁻ and H⁺ ions) could reach equilibrium state. This is due to the limited processing capacity of the ion-exchange membrane inside the BMED stack. Particularly, the ionic mobility is limited at the lower voltage drops, and thus the concentration curve of H₃PO₂ exhibits a smaller slope at the voltage drop of 10 V. The result is consistent with the previous report by Ji et al. Additionally, at higher voltage drops, the slope of the H₂PO₂ concentration curve increases, and therefore the experimental time is shorter. However, a slight decrease of...
the slope of curves is observed as the experiment progressed, which is mainly due to the change of the concentration gradient between the feed compartment and the acid compartment.\textsuperscript{23} Because the relatively high concentration gradient between the feed compartment and the acid compartment prevents the migration of H\textsubscript{3}PO\textsubscript{2}\textsuperscript{−}, the H\textsubscript{3}PO\textsubscript{2} concentration slowly increases and approaches a maximum value at the end of the experiment.

The effect of voltage drop on energy consumption is shown in Figure 2c. It suggests that the energy consumption increases with the increase of voltage drop, which demonstrates a proportional relationship between the energy consumption and the voltage drop. Furthermore, at higher voltage drops, there is higher loss of energy consumption on the nonreversible joule heat.

Figure 2d displays the effect of voltage drop on the yield and current efficiency. The measured current efficiency increases when the voltage drop is less than 20 V. At the voltage drop of 25 V, the current efficiency slightly drops. The main reason is that the protons with a small hydroradius transport through the AHA anion-exchange membrane (AM), and thus the current efficiency is on the decline.\textsuperscript{24,25} Simultaneously, the change of H\textsubscript{3}PO\textsubscript{2} yield at different voltage drops is consistent with the current efficiency. This is because the selectivity for counterions of the AM decreases with the increasing voltage drop. Furthermore, the increase of voltage drop accelerates the generation of H\textsuperscript{+} ions by the BM, leading to more leakage of H\textsuperscript{+} ions through the cation-exchange membrane (CM). Considering all factors described above, an appropriate voltage drop of 20 V was selected in the following experiment to maintain a higher current efficiency and yield.

2.2. Influence of NaH\textsubscript{2}PO\textsubscript{2} Concentration. The concentration of NaH\textsubscript{2}PO\textsubscript{2} solution is a critical factor that may affect the preparation of H\textsubscript{3}PO\textsubscript{2} from NaH\textsubscript{2}PO\textsubscript{2} by the BMED stack. To investigate the influence of NaH\textsubscript{2}PO\textsubscript{2} concentration, a series of concentrations of NaH\textsubscript{2}PO\textsubscript{2} (10–30 wt %) were applied to the feed compartment with a CV drop of 20 V. FBM/AHA/CMB/FBM were used in the BMED stack as the membrane pairs. The changes in the current density, concentration of H\textsubscript{3}PO\textsubscript{2}, energy consumption, current efficiency, and yield at different concentrations of NaH\textsubscript{2}PO\textsubscript{2} solution are shown in Figure 3.

Figure 3a shows that the current density increases with the concentration of NaH\textsubscript{2}PO\textsubscript{2} during the first 10 min of the experiment. The curves display a similar maximum current density with the NaH\textsubscript{2}PO\textsubscript{2} concentration of 15, 20, 25, and 30 wt %. However, the maximum value of current density is achieved at different times. This is mainly ascribed to the different conductivities in the initial feed compartment and the increase of feed concentration, which causes the current density to be stable for a longer time. In short, with a higher NaH\textsubscript{2}PO\textsubscript{2} concentration, a longer experimental time is required at the same voltage drop. Additionally, when the NaH\textsubscript{2}PO\textsubscript{2} concentration is 10 wt %, the maximum value of current density is the lowest. It may be due to the extremely lowest contents of H\textsubscript{3}PO\textsubscript{2}− and Na\textsuperscript{+} ions in the feed compartment, resulting in the highest electrical resistance.

As shown in Figure 3b, the concentration of H\textsubscript{3}PO\textsubscript{2} increases with the experimental time. At the end of the experiment, the concentration of H\textsubscript{3}PO\textsubscript{2} approaches a maximum value, which can be ascribed to the existence of concentration diffusion that hinders the migration of H\textsubscript{3}PO\textsubscript{2}− and Na\textsuperscript{+} ions. Simultaneously, a similar trend of energy consumption is observed in Figure 3c. This is due to the increase of concentration of H\textsubscript{3}PO\textsubscript{2}− and Na\textsuperscript{+} ions in the feed compartment, which causes longer experimental time for the migration of H\textsubscript{3}PO\textsubscript{2}− and Na\textsuperscript{+} at the same voltage drop of 20 V. Furthermore, the slope of the curves gradually decreases over time, which is due to the decrease of electrical resistance of the BMED stack with the increase of NaH\textsubscript{2}PO\textsubscript{2} concentration.

Figure 3d presents the effect of NaH\textsubscript{2}PO\textsubscript{2} concentration on the current efficiency and yield. The current efficiency decreases when the concentration of NaH\textsubscript{2}PO\textsubscript{2} is higher than 20 wt %. The possible reason is that the protons pass through the AM into the feed compartment. The highest yield reaches over 80% with a NaH\textsubscript{2}PO\textsubscript{2} concentration of 15 wt % because a higher concentration (20, 25, and 30 wt %) of NaH\textsubscript{2}PO\textsubscript{2} promotes a higher concentration of H\textsubscript{3}PO\textsubscript{2}. At the end of the experiment, reverse osmosis of H\textsuperscript{+} ions will occur, and there is a higher degree of H\textsuperscript{+} ion leakage from the acid compartment to the feed compartment through the AM, which reduces the yield of H\textsubscript{3}PO\textsubscript{2}.\textsuperscript{26} As a consequence, it can be confirmed that the NaH\textsubscript{2}PO\textsubscript{2} concentration of 15 wt % is optimal for further explorations.

2.3. Effect of AM Type. The AM is a crucial factor for the migration of H\textsubscript{3}PO\textsubscript{2}− ions. Therefore, a suitable AM should be selected to evaluate the performance of the BMED stack. In this section, three different AMs (AHA, FAB, and JAM-II-05) were investigated to prepare H\textsubscript{3}PO\textsubscript{2} with the BMED stack. On the basis of the experimental results described in Sections 2.1 and 2.2, the voltage drop of 20 V and the NaH\textsubscript{2}PO\textsubscript{2} concentration of 15 wt % were used in this experiment. The purpose was to study the effect of AM on the current density, H\textsubscript{3}PO\textsubscript{2} concentration, energy consumption, current efficiency, and yield.

As shown in Figure 4a, all curves exhibit a similar trend over time. However, it can be observed that the current density of the AHA membrane stack is higher than those of the other two membrane stacks, which is mainly due to the lowest membrane resistance of the AHA membrane. Therefore, the increase of H\textsubscript{3}PO\textsubscript{2} concentration with the AHA membrane stack is higher than the other two membrane stacks throughout the experiment, as shown in Figure 4b. Conversely, the H\textsubscript{3}PO\textsubscript{2} concentration curve with the FAB membrane stack presents a
relatively smaller slope in the first 25 min. The possible reason is that the ion-exchange capacity of FAB membrane is lower than those of AHA and JAM-II-05 membranes. Figure 4c displays the effect of AHA, FAB, and JAM-II-05 membrane stacks on energy consumption. It suggests that the energy consumption of AHA membrane stack is lower than those of other membrane stacks. This is possibly due to the relatively higher membrane resistance of FAB and JAM-II-05 leading to a higher electrical energy loss.

Figure 4d presents the comparison of yield and current efficiency with the AHA, FAB, and JAM-II-05 membrane stack. It is obvious that the current efficiency of the BMED stack with the AHA membrane is higher than those with the other two membrane stacks. This is ascribed to the higher membrane resistance of the FAB and JAM-II-05 membranes. However, the H$_3$PO$_2$ yield of the BMED stack with the FAB membrane is the highest, which is mainly due to the higher transport number of the FAB membrane. Through the comprehensive comparison between energy consumption, current efficiency, and yield, the AHA AM is selected for the production of H$_3$PO$_2$.

2.4. Integration of BMED with Ion-Exchange Absorption. According to the configuration of the BMED stack, the Na$^+$ ions may diffuse from the feed compartment into the acid compartment, which greatly reduce the quality of H$_3$PO$_2$ aqueous solution. Therefore, the migration of Na$^+$ ions needs to be further investigated. In this section, FBM/AHA/CMB/FBM was used as the BMED stack membrane pairs; a voltage drop of 20 V and a NaH$_2$PO$_2$ concentration of 15 wt % were used in this experiment.

Figure 5a shows the variation of Na$^+$ ion content in the acid compartment. It indicates that the content of Na$^+$ ions increases with the experimental time, however, an inflection point occurs at 20 min. This is mainly due to the leakage of Na$^+$ ions from the electrode compartment in the initial 20 min. Subsequently, when the Na$^+$ ion content in the base compartment increases, it may migrate into the acid compartment through the BM leading to a higher slope of the curve.

Figure 5b reveals the content of Na$^+$ ions existing in the column effluent, which is comparable to commercial H$_3$PO$_2$ aqueous solution in the electroplating industry. Taking into consideration the removal rate of 90.12% for Na$^+$ ion content, the T-52H resin is promising for H$_3$PO$_2$ aqueous solution purification. After the adsorption of T-52H resin, the recycled H$_3$PO$_2$ aqueous solution was concentrated to 51.86 wt % by vacuum evaporation.

2.5. Long-Term Evaluation. Considering the performance variation of the BMED stack in practical applications, a long-term experiment was conducted to investigate the stability of the BMED stack. In this section, the acid tank and base tank were filled with 500 mL of deionized water before the experiment. NaH$_2$PO$_2$ solution with a concentration of 15 wt % and volume of 500 mL was used as the feed solution under the batch mode (feed and bleed). The experiment was operated at a CV drop of 20 V by using FBM/AHA/CMB/FBM as the membrane pairs.

As illustrated in Figure 6a, the curve exhibits a sharp increase in the first 20 min, which is ascribed to the deionized water in the acid compartment and base compartment. Therefore, the migration rates of H$_3$PO$_2^-$ and Na$^+$ ions are extremely high at the beginning of the experiment. Simultaneously, the electrical resistance of the BMED stack gradually decreases with the increment of the solution concentration in each compartment, and thus the current density curve shows a continuous increase with time. However, the voltage drop is maintained at a relatively stable value in the last stage of the experiment. This is due to the high concentration gradient between the feed compartment and the acid and base compartments inside the BMED stack, resulting in the extremely slow migration of H$_3$PO$_2^-$ and Na$^+$ ions. As shown in Figure 6b, the curves are nearly linear with time in the first 140 min, which suggests that the BMED stack was running under an almost stable state. Subsequently, the curves tend to be stable at the end of the experiment, which is mainly due to the phenomenon of the concentration gradient. Additionally, the concentration of NaOH is higher than the concentration of H$_3$PO$_2$ over the

![Figure 4](image1.png)

Figure 4. Effect of AHA, FAB, and JAM-II-05 AMs on the (a) current density of the BMED stack, (b) concentration of H$_3$PO$_2$, (c) energy consumption, and (d) current efficiency and yield.

![Figure 5](image2.png)

Figure 5. (a) Variation of Na$^+$ ion content in the acid compartment. (b) Comparison of the Na$^+$ ion content existing in the BMED effluent and the column effluent.
course of the experiment. This is due to the intrinsic mobility of $H^+$ ions higher than $OH^-$ ions, resulting in the higher leakage of $H^+$ ions. Furthermore, the concentration of $H_3PO_2$ in the acid compartment reached 4.15 mol/L, whereas the concentration of NaOH in the base compartment was 4.32 mol/L at the end of the experiment. The above results suggest that the CMB and AHA membranes exhibit superior permselectivity under extreme base/acid circumstances.

2.6. Process Economic Evaluation. The cost of $H_3PO_2$ production can be estimated from the proposed experimental design. As summarized in Table 1, an estimation of the overall total process cost was listed, including the energy cost and investment cost. Meanwhile, the energy consumption consists of the BMED setup and vacuum evaporation. The process cost was lower in the BMED, and a part of the calculation refers to Wang et al.15

### Table 1. Total Process Cost of BMED Integrating with Ion-Exchange for $H_3PO_2$ Production

| operation conditions | quantity |
|----------------------|----------|
| repeat unit          | 5        |
| membrane configuration| FBM/AHA/CMB |
| practical membrane area (cm²) | 297 |
| effective membrane area (cm²) | 189 |
| voltage drop (V)     | 20       |
| experiment time (min) | 60      |
| the concentration of NaH$_2$PO$_2$ (wt %) | 15 |
| fluid flow rate (L/h) | 20      |
| current efficiency (%) | 58.41  |

#### Energy Cost

- energy consumption (kW h/kg) | 6.19 |
- process capacity (t/year) | 95.40 |
- electricity charge ($/kW h) | 0.10 |
- energy consumption for $H_3PO_2$ production ($/kg) | 0.62 |
- energy consumption for peripheral equipment ($/kg) | 0.31 |
- total energy cost ($) | 0.93 |

#### Investment Cost

- membrane life-time (years) | 3 |
- BM price ($/m²) | 1540 |
- AM price ($/m²) | 770 |
- CM price ($/m²) | 770 |
- membrane cost ($) | 503.12 |
- membrane stack cost ($) | 754.68 |
- peripheral cost ($) | 1132.02 |
- total investment cost ($/kg) | 1886.70 |
- total fixed cost ($/year) | 628.90 |
- total fixed cost ($/kg) | 0.0066 |
- total process cost ($/kg) | 0.937 |

The physical and chemical properties of T-52H resin are given in Table 4. NaH$_2$PO$_2$ (analytical grade) was purchased from Solvay-Hengchang specialty chemical Co., Ltd., Zhangjiagang, China. Other reagents such as NaOH, HCl, and Na$_2$SO$_4$ (analytical grade) were supplied by Shanghai Lingfeng chemical reagent Co., Ltd., Shanghai, China. Deionized water was used in all experiments.

3. CONCLUSIONS

A novel technique by the integration of BMED with ion-exchange absorption was established for producing high-quality $H_3PO_2$. The performance of BMED stack was evaluated by the current density, $H_3PO_2$ concentration, energy consumption, current efficiency, and yield. The experimental conditions were optimized, such as the voltage drop, concentration of NaH$_2$PO$_2$, and AM. Under optimal conditions, a high yield of $H_3PO_2$ up to 80.06% with a low energy consumption of 4.99 kW h/kg was achieved. Furthermore, the concentration of Na$^+$ ions in the $H_3PO_2$ aqueous solution decreased to 20.91 mg/L by using T-52H cation-exchange resin. The BMED stack exhibits superior stability during the long-term experiment, and the concentration of $H_3PO_2$ in the acid compartment approached 4.15 mol/L. The total process cost was estimated to be approximately $0.937 kg$–$^2$ with the lab-scale equipment, demonstrating the economic feasibility of $H_3PO_2$ production by using BMED in combination with ion-exchange.

4. EXPERIMENTAL SECTION

4.1. Materials. The CMs used in the experiment were NEOSEPTA CMB (ASTOM Co., Japan). The AMs used in the experiment were Neosepta AHA (ASTOM Co., Japan), Fumasep FAB (Fuma-Tech Co., Germany), and JAM-II-05 (Beijing Tingrun Membrane Technology Development Co., China). The BM used in the experiment was Fumasep FBM (Fuma-Tech Co., Germany). The major properties of the membranes used in the experiments are listed in Table 3.
The BMED stack consisted of air bubbles trapped on the membrane surface.30 All solutions tank and the compartment of the BMED stack, the solution of deionized water in the initial experiment. Between the solution both acid tank and base tank were fed with 500 mL of NaH2PO2 aqueous solution was added into the feed tank. of Na+ ions was determined by inductively coupled plasma mass spectrometry (Elan DRC-e, PerkinElmer, USA). The current across the BMED stack was directly recorded from the CV/CC regulated power supply.

4.4. Data Processing. The current efficiency was calculated by eq 1

$$
\eta_{\text{el}} = \frac{z(C_i V_t - C_0 V_0)E}{NIt \times 100}
$$

(1)

where $C_0$ and $C_i$ (mol/L) correspond to the molar concentration of H₃PO₂ at time 0 and $t$, respectively; $V_0$ and $V_t$ (L) represent the recirculated volume of H₃PO₂ in the acid compartment at time 0 and $t$, respectively; $F$ is the Faraday constant (96 485 C/mol); $N$ is the number of repeating units ($N = 5$); and $I$ (A) is the current applied.

The energy consumption was calculated by eq 2

$$
E = \int_0^t \frac{U_i dt}{C_i V_t M}
$$

(2)

where $U_i$ refers to the voltage drop across the BMED stack at time $t$; $V_t$ (L) is the volume of H₃PO₂ in the acid compartment at time $t$; and $M$ represents the molar weight of H₃PO₂ (65.99 g/mol).

The production yield was calculated by eq 3

$$
Y = \frac{n_i}{n_0} \times 100%
$$

(3)

where $n_i$ (mol) is the molar mass of H₃PO₂ at time $t$ and $n_0$ (mol) represents the molar mass of NaH₂PO₂ at time 0.

Na₂SO₄ solution (500 mL, 3 wt %) was used as the supporting electrolyte in the electrode tank. The feed solution of 500 mL of NaH₂PO₂ aqueous solution was added into the feed tank. Both acid tank and base tank were fed with 500 mL of deionized water in the initial experiment. Between the solution tank and the compartment of the BMED stack, the solution of each compartment was circulated for 20 min to eliminate the air bubbles trapped on the membrane surface.30 All solutions were circulated at a constant flow rate of 40 L/h.

Figure 7b presents the scheme of a three-configuration BMED stack. The BMED stack consisted of five repeating units, each unit installed with a BM, an AM, a CM, and a BM in series. A spacer with 0.7 mm thickness was used to separate each membrane. The dimension of each membrane area was 297 cm² with an active membrane area of 189 cm². The electrodes were made of a graphite cathode and an anode of titanium coated with ruthenium. Moreover, a CV/constant current (CC) regulated power supply (WYL3010S, from Hangzhou Siling Electrical Instrument Ltd., China) was connected to the electrodes. Driven by the CV drop applied to the BMED stack, H₃PO₂⁻ ions migrated through the AM and combined with H⁺ ions in the acid compartment. Simultaneously, Na⁺ ions migrated through the CM and combined with OH⁻ ions in the base compartment.31,32

To further optimize the purity of H₃PO₂ aqueous solution, a certain amount of cation-exchange resins was used to absorb the interfering Na⁺ ions. Figure 7c shows the schematic diagram of the column mode system. The height of the exchange layer was 40 cm, and the setup was equipped with 200 mL of T-52H resin. H₃PO₂ aqueous solution (500 mL) obtained from the BMED effluent was pumped into the inlet of the column through a peristaltic pump (BT600-2J, Baoding Longer peristaltic pump, China). Moreover, the H₃PO₂ aqueous solution was controlled at a rotational flow rate of 2 BV/h (bed volume per hour) to maintain the liquid level constant. The Na⁺ ions in the H₃PO₂ aqueous solution were replaced by H⁺ ions released from the resin reactive groups. After the experiment, the purified H₃PO₂ aqueous solution was collected from the outlet of the column. Then, the resin was washed by deionized water and followed by regeneration using 4 wt % HCl solution.

4.3. Analytical Methods. A conductivity meter (S220 type, Mettler-Toledo, Switzerland) was used to measure the conductivity of the samples from the BMED stack compartment. The concentration of the acid and base was titrated with NaOH and HCl standard solutions, respectively. The content of Na⁺ ions was determined by inductively coupled plasma—mass spectrometry (Elan DRC-e, PerkinElmer, USA). The current across the BMED stack was directly recorded from the CV/CC regulated power supply.
The removal rate was calculated by eq 4

\[ Q = \frac{C_m - C}{C_m} \times 100\% \]  

where C (mg/L) is the content of the Na⁺ ions in the column effluent and \( C_m \) (mg/L) is the content of the Na⁺ ions in the BMed effluent.

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LY16B060013).

This research was supported by the Natural Science Foundation of China (no. 2016726249), the National Key research and development program (no. 2017YFC0403701), and the Natural Science Foundation of Zhejiang Province (no. LY16B060013).

**ACKNOWLEDGMENTS**

This research was supported by the Natural Science Foundation of China (no. 2016726249), the National Key research and development program (no. 2017YFC0403701), and the Natural Science Foundation of Zhejiang Province (no. LY16B060013).

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This research was supported by the Natural Science Foundation of China (no. 2016726249), the National Key research and development program (no. 2017YFC0403701), and the Natural Science Foundation of Zhejiang Province (no. LY16B060013).

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