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Exfoliated MoS₂ nanosheets loaded on bipolar exchange membranes
interfaces as advanced catalysts for water dissociation

Jian Li^a, Sofie Thage Morthensen^b, Junyong Zhu^a, Shushan Yuan^a, Jing Wang^{a,c},
Alexander Volodine^d, Jiuyang Lin^e, Jiangnan Shen^f, Bart Van der Bruggen^{a,g}

^a Department of Chemical Engineering, KU Leuven, Celestijnenlaan 200F, B-3001
Leuven, Belgium

^b Department of Chemical and Biochemical Engineering, Technical University of
Denmark, Søltofts Plads Building 229, 2800 Kongens Lyngby, Denmark

^c School of Chemical Engineering and Energy, Zhengzhou University, Zhengzhou
450001, China

^d Laboratory of Solid State Physics and Magnetism, Celestijnenlaan 200d - box 2414
3001 Leuven

^e School of Environment and Resources, Qi Shan Campus, Fuzhou University, No.2
Xueyuan Road, University Town, 350116 Fuzhou, Fujian, China

^f Center for Membrane Separation and Water Science & Technology, Zhejiang
University of Technology, Hangzhou, 310014, China

^g Faculty of Engineering and the Built Environment, Tshwane University of
Technology, Private Bag X680, Pretoria 0001, South Africa

* Corresponding author.

E-mail address: shenj@zjut.edu.cn (J. Shen)

bart.vanderbruggen@cit.kuleuven.be (B. Van der Bruggen)

Abstract: Over the last few decades, ion exchange membranes have evolved from a laboratory tool to industrial products with significant technical and commercial impacts. Electrodialysis with bipolar membranes (EDBM) is a technology that can produce acids and bases from the corresponding salt solutions. Bipolar membranes are key factors for splitting water at the interface of a cation and anion exchange layer in an electric field. The ideal bipolar membrane should have a low energy consumption, a high current efficiency and long-term stability. In order to investigate the catalytic effect of a monolayer of MoS₂, the bipolar membranes were prepared by introducing monolayer MoS₂ to the interface of bipolar membranes. The resulting bipolar membrane was found to have lower potential drop, which clearly demonstrates the applicability of the MoS₂ layer to act as catalyst. Enhanced acid production confirmed this prediction. Furthermore, a bipolar membrane prepared at 90°C had a low swelling ratio of about 7.5% while maintaining a high water uptake of 71.6%. From the calculation of current efficiency and energy consumption, the bipolar membrane with a monolayer of MoS₂ has a higher current efficiency (45%) and a lower energy consumption (3.6 kW/h·kg) compared to a current efficiency of 24% and an energy consumption of 6.3 kW/h·kg for a bipolar membrane without MoS₂. This study proves the catalytic function of MoS₂, which lays a foundation for further research on catalytic bipolar exchange membranes.

Keywords: Bipolar exchange membrane; MoS₂; water dissociation; catalyst; electrodialysis

1. Introduction

Electrodialysis with bipolar membranes (EDBM) is a technology that integrates solvent and salt dissociation, thus inherently has economical and environmental benefits. It has found many interesting applications in the chemical industry [1], in food processing [2], in biochemical industry [3], and in environmental protection [4]. The principle of EDBM lies in the use of a bipolar membrane, which is a laminar structure composed of a cation exchange layer to which an anion exchange layer is added in series. As the electric current passes through, protons and hydroxide ions are generated at the intermediate layer of a bipolar membrane and migrate to the cathode and anode chamber, respectively. The water dissociation observed in bipolar membranes is about 7 orders of magnitude higher than in free solutions [5]. Nevertheless, the actual mechanism of water splitting is still controversial [6].

The ideal bipolar membrane should have a high permselectivity, a low electrical resistance and water splitting voltage drop, a high current efficiency, a good chemical and mechanical stability, long lifetime, and no “ballooning” [7]. However, limitations such as the high membrane cost, insufficient recognition of the importance roles in sustainable development and industrialization, and scarce operation experience still restrict its development. Recently, the chemical composition and structure of the transition region between the anion and the cation exchange layer were modified to improve the water splitting capability. Zhou et al. [8] added nano-ZnO-CeO coupled semiconductors to the anion exchange membrane layer to prepare bipolar membranes, and showed that nano-composites have a better photocatalytic activity for water splitting. Abdu et al. [9] introduced molecularly thin catalyst groups at the interface of the ion exchange layers of a bipolar membrane using the consecutive dipping layer-by-layer (LbL) deposition technology; the outcomes revealed that an additional highly charged thin intermediate layer helps to enhance water splitting. Chen et al. [10] modified the anion and cation layers of a bipolar membrane with copper phthalocyanine tetrasulfonic acid (CuTsPc) and copper tetraaminophthalocyanine (CuTAPc), respectively. As the catalytic centers of water splitting in the intermediate layers, CuTsPc and CuTAPc speed up the water splitting into hydrogen ions and hydroxyl ions, which lowers the membrane impedance and the voltage drops of the bipolar membranes. With catalyst immobilization, the high activation energy of water dissociation can be reduced by catalytic activity.

Molybdenum disulfide (MoS_2) has recently demonstrated its functionality as a non-noble metal hydrogen evolution reaction (HER) catalyst with high catalytic efficiency, based on both theoretical and experimental studies [11, 12]. An indirect bandgap for thick MoS_2 layers becomes a direct bandgap of 1.8 eV in monolayer MoS_2 , consisting of two sulfide atomic layers and a layer of sandwiched Mo atoms [13]. This indirect-to-direct band gap transition leads to interesting phenomena in MoS_2 monolayers, opening new possibilities for optoelectronic applications [14]. However, a number of studies have revealed that the electrocatalytic HER performance of nanoscale MoS_2 mainly arises from its edge states, while the basal

plane is inert, which leaves a large area of basal planes useless [15]. Ghuman et al. [16] investigated the catalytically active sites for adsorption of H_2O , H and OH species on MoS_2 edges, and found that water dissociation can proceed by splitting into adsorbed OH and H species; the Mo -edge was the most favorable for adsorption of all species. One explanation of the mechanism of water splitting is the proton transfer reaction. According to the reaction model, the proton and hydroxyl ions are believed to be a result of protonation and deprotonation reactions between water molecules and the fixed charge groups according to the following equations:

where A^- and BH^+ are the catalytic sites. Following the mechanism of proton transfer, modifying the chemical composition and structure of the transition region is essential in order to improve the water splitting capability of bipolar membranes. The presence of MoS_2 enhances the adsorption of OH and H species, so that the rate of water dissociation is enhanced. As a result, the high activation energy of water dissociation is reduced. This method can provide an alternative reaction path for bipolar membranes.

So far the hydrophilic/hydrophobic behavior of MoS_2 has been discussed without coming to a clear convergence: MoS_2 is described as both hydrophilic and hydrophobic [17]. MoS_2 is thermally and mechanically stable, featuring a melting point reaching $1185^\circ C$. Aqueous dispersions of two-dimensional MoS_2 has shown a low cytotoxicity and high biocompatibility, which renders it suitable for water application [18]. Metal oxides or silicon groups, as well as metal hydroxides, have been examined as possible catalysts to enhance the water-splitting capability of bipolar membranes [19]. However, this is no report on MoS_2 to tailor the interface of bipolar membranes.

In this work, polyepichlorohydrin (PECH) with an inherent chloromethyl group is employed as the polymer matrix of an anion exchange membrane. Due to the inherent chloromethyl groups, the reaction steps can be reduced. In order to obtain high performance bipolar membranes with good mechanical stability and to maintain a certain ion exchange capacity, polyvinylidene fluoride (PVDF) was adopted as supporting material. PVDF is a widely used membrane material with antioxidation activity, great chemical resistance, thermal stability, high mechanical strength, and suitable membrane-forming characteristics [20]. The addition of PECH into a PVDF polymer matrix can improve the thermal properties, dimensional stability, and mechanical strength. The PVDF/PECH composite polymer membrane was obtained by directly blending PVDF polymer and PECH polymer in solutions. As sulfonated polyethersulfone (SPES) contains many polar groups along the back-bone chain [21] and is stable under acidic conditions [22], it was chosen as the cation exchange layer. To evaluate the advantages of this strategy, bipolar membranes were fabricated through conventional multi-layer casting and the performance was compared with the membranes having a MoS_2 layer at the interface.

2. Experimental

2.1. Materials

Polyepichlorohydrin (PECH, average molecular weight: 700 000 Da) was purchased from J&K Scientific Ltd. (Beijing, China). Polyvinylidene fluoride (PVDF) (grade Solefs 6020) was purchased from Solvay. Trimethylamine (TMA) was purchased from Sigma-Aldrich. Dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) were purchased from Sigma-Aldrich. MoS₂ was purchased from Chempur (Germany). Commercial CEM (FKS-PET-130), AEM (Fumaseps FAB) membranes and bipolar membranes (Fumaseps FBM) were purchased from FuMA-Tech (Germany). These membranes were selected because of their high permselectivity, low resistivity and very high mechanical stability. All other chemicals were commercially obtained and used without further purification.

2.2. Preparation of Bipolar Membranes

The bipolar membranes with MoS₂ were prepared by casting in a four steps method: (1) cation exchange layer preparation; (2) MoS₂ layer preparation; (3) anion exchange layer preparation; (4) amination.

1. Cation exchange layer preparation. 3 g SPES was fully dissolved in 17 g DMF. After degassing by ultrasound, it was casted onto a clean glass plate and kept in a 60 °C vacuum drying oven for 24 h to remove the solvent.
2. MoS₂ layer preparation. 2D MoS₂ flakes were prepared from MoS₂ bulk powder using a grinding-assisted liquid-phase exfoliation technique, which was similar to a method reported elsewhere [23, 24]. 10 gram of MoS₂ powder was added to 5 mL H₂O and 5 mL ethanol solution and stirred for 30 min. The slurry was then sonicated for 120 min and finally centrifuged for 45 min at 4000 rpm. The supernatant containing 2D MoS₂ nanoflakes was collected. The collected supernatant was tipped on the surface of SPES membranes. The supernatant containing the MoS₂ was dried in a vacuum oven for 12 h to remove the solvent.
3. Anion exchange layer preparation. 2 g PECH and 2 g PVDF were dissolved at 80 °C in 25 mL DMSO in a round bottom flask until the mixture dissolved completely. After the mixture was cooled to room temperature, the solution was cast on the surface of the former membrane with MoS₂. The assembled bipolar membrane was then placed in an oven at 60 °C for 12 h and then the membrane was peeled off from the glass plate.
4. Amination. The membrane was immersed in TMA solution (2 mL 24% TMA in 100 mL) at different temperature for different times. Afterwards, the obtained membrane was fully washed by water to remove the rest TMA and

finally stored for further use. The reaction process can be seen in Fig. 1.

Fig. 1 The amination reactions as well as the interpenetrating polymer networks of anion-exchange layers

In comparison with bipolar membranes with MoS_2 , the preparation method of blank experiments was similar to the previous procedure, except that step 2 was not included.

2.3. Characterization of MoS_2

Samples for AFM were prepared by drop-casting 10 μ L of each suspension onto a cation exchange membrane and heating at 40 $^{\circ}C$ to evaporate the solvent. Conductive AFM images were obtained using a Bruker MultiMode with an installed Peak Force TUNA module (MM8-PFTUNA for MultiMode8 AFM system, Germany).

2.4. Characterization of bipolar membranes

The physical morphologies and structures of nanofiber mats and bipolar membranes (the cross-sections and surfaces) were observed using high resolution scanning electron microscopy (Sirion 200, Philips). All specimens were sputter-coated with Au before testing.

The characteristic functional groups of bipolar membrane surface were recorded by Fourier transform infrared (FTIR). Membrane samples were scanned from 750 to 4000 cm^{-1} by using a Nicolet-6700 spectrometer with a resolution of 4 cm^{-1} .

Water uptake was based on the water retention inside the membrane (dry membrane as a reference) and determined at the room temperature. The membranes were dried at 60 $^{\circ}C$ in an oven and then weighed accurately followed by immersing in deionized water for at least 24 h to ensure complete equilibrium and then reweighed after removing surface water. The water uptake was calculated as follows:

$$\text{Water uptake} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\%$$

where the W_{wet} and W_{dry} are the weights of the membrane sample under wet

condition and dry condition, respectively.

The linear swelling ratio (LSR) was calculated based on the change of length of membranes (1 cm in width and 4 cm in length) before and after immersing in water at 25 °C for 24 h. It was calculated by the following equation:

$$\text{LSR} = \frac{l_w - l_d}{l_d} \times 100\%$$

where l_w and l_d are the membrane's length under wet condition and dry condition, respectively.

The static contact angles of the membrane surface were measured by a contact angle goniometer (OCA-20, Data-physics, Germany) at ambient temperature. The water droplet morphologies and contact angles were analyzed by an optical contact angle meter. At least five drops at different positions on the membrane surface was measured.

The ion exchange capacity (IEC) of the membrane was determined by titration. Before the measurement, the membrane was soaked in 1 mol/L HCl solution for 24 h to reach the final dilation. Then, it was taken out of the solution and carefully wiped with absorbent paper. Finally, the membrane was immersed in 100 mL 1 M NaCl solution for 24 h. The solution was titrated against 0.01 mol/L NaOH using phenolphthalein as indicator. The IEC of a cation exchange membrane was calculated from the following formula [10]:

$$\text{IEC} \left(\frac{\text{mmol}}{\text{g}} \right) = \frac{n_{\text{HCl}}}{W_{\text{dried}}}$$

where n_{HCl} is the milli-equivalent of H^+ ions determined by NaOH. W_{dried} was the mass of dried membrane sample (g). The IEC of anion exchange membrane was determined in the same way but the soaked solution was alkaline and titration solution was acid.

The mechanical properties of bipolar membranes were investigated using a tensile testing equipment (Type 4505, Instron, Nordwood, U.S.) at room temperature at a constant crosshead speed of 1 mm/min. The samples were cut into two strips with 2 mm width. Measurements were performed with membranes dried at room temperature for 3 hours. Load extension graphs were obtained and converted to stress-strain curves by applying the following equations:

$$\text{Stress } (\sigma) = \frac{F}{A}$$

$$\text{Strain } (\varepsilon) = \frac{\Delta l}{L}$$

where F is the applied force (N), A is the cross sectional area (m^2), Δl is the change in length (mm) and L is the length between clamps (40 mm).

The determination procedure of the ion transport rate of a bipolar membrane was as follows: a cation exchange membrane was fixed between the cathode chamber and the anode chamber as a separator. The catholyte was 1 mol/L Na_2SO_4 solution, and the anolyte was 0.5 mol/L H_2SO_4 solution. The volumes of the catholyte and the anolyte were 200 mL. A constant current was supplied by a direct current source (DF1720SB5A, Zhejiang Zhongce Electronic Co., Ltd. in China). The current density

was 10 mA cm^{-2} . The H^+ concentration in the cathode chamber was measured after 1 h transport.

To determine the ion transport rate of an anion exchange membrane, the process was similar as the procedure of a cation exchange membrane: an anion membrane was fixed between the cathode chamber and the anode chamber as a separator. The catholyte was 1 mol/L NaOH solution, and the anolyte was 1 mol/L Na_2SO_4 solution. The OH^- concentration in the anode chamber was measured after 1 h [10].

The current-voltage curves of bipolar membranes were recorded at 25°C through a two-compartment measuring technique (Fig. 2). The effective bipolar membranes area was 13.84 cm^2 and the working electrolytes of electrode were 0.5 mol/L NaCl solutions. The current was supplied by a programmable DC power system (DF1720SB5A, Zhejiang Zhongce Electronic Co., Ltd. in China) and applied into the cell by two carbon electrodes. The voltage drop was measured using a voltmeter (ZW1418, Qingdao Qingzhi Instruments Co., China) by two platinum filaments located approximately 1.0 mm away from each membrane surface. The membrane sample was inserted between two half-cells.

Fig. 2 The experimental setup for I-V curves: current electrodes, silver electrode, and bipolar membrane

The water dissociation performance of bipolar membranes was determined using a simple four-compartment electrodialysis stack as shown in Fig. 3. The effective membrane area was 7.07 cm^2 and all the four compartments were filled with 0.5 mol/L Na_2SO_4 solution as the electrolytes at constant current (20 mA/cm^2). The water dissociation time was 1 h and the yield of acid and base was determined by classical acid-base titration.

Fig. 3 The electrodesialysis stack to detect acid production

The current efficiency was calculated as:

$$\text{Current efficiency} = \frac{N}{nIt/F} \times 100\% = \frac{NF}{nIt} \times 100\%$$

where N is the equivalent of sulfuric acid, n is the number of bipolar membranes ($n = 1$ in this research), and F is the Faraday constant ($96,500 \text{ C mol}^{-1}$), I is the current, and t is the experimental time.

The energy consumption E (kW h kg^{-1}) was calculated as:

$$E = \int \frac{UI dt}{C_t VM}$$

where U is the voltage drop across the EDBM stack, I is the current, C_t is the concentration of sulfuric acid at time t , V is the volume of the acid cycle (0.25 dm^3), and M is the molar mass of sulfuric acid (98.08 g mol^{-1}).

3. Results and discussion

3.1 SEM

The surface morphology of the prepared composite membranes was observed by SEM as shown in Fig. 4a, b and d. A cation exchange membrane made by SPES shows smooth and uniform surfaces. For an anion exchange membrane composed by PECH/PVDF, a surface morphology without any obvious phase separation can be observed, indicating that PECH and PVDF are compatible. The surface of the prepared anion exchange membrane had pores, which may have two reasons: first, interpenetrating polymer networks cast on a substrate and coagulated to form pores [25]; second, during amination, membranes become more hydrophilic, and the solvent locally remained on the internal copolymers. Then the solvent was removed from the

copolymers; therefore, macro-pores remained at the location of the removed solvent [26].

The cross section of bipolar membranes is shown in Fig. 4e and f. A blurred inter layer was observed in the two layer bipolar membranes, this is because the anion exchange polymer dissolved and mixed with the cation exchange polymer during the casting process. For three layer bipolar membranes, a sharp junction between the anion- and the cation-exchange layers was formed, which is because the occurrence of MoS_2 hinders the contact between the two polymers. The MoS_2 nanostructure morphology was preserved in Fig. 4c after exfoliation: from the SEM images of the membrane after step 2, a full coverage of monolayer MoS_2 was found. The exfoliated nanosheets were disordered and compressed onto the membrane surface. From the SEM images, it can be concluded that exfoliation of MoS_2 was successful. For all the membranes, no bubbles and cracks at the inter layer were observed.

Fig. 4 SEM images of bipolar membranes and cross-section (a: cation exchange layer surface; b and d: anion exchange layer surface; c: MoS_2 images after step 2; e: cross-section image of bipolar membrane without MoS_2 ; f: cross-section image of bipolar membrane with MoS_2)

3.2 AFM of MoS_2

To further confirm the morphology and thickness of the exfoliated MoS_2 , atomic

force microscopy (AFM) topography images of these nanostructures were analyzed (Fig. 5). The AFM images shown in Fig. 5a and b demonstrate the uniformity of MoS₂ sheet coverage on mica substrates. A thickness of about 18 nm of vapor-deposited MoS₂ was obtained on the substrate, which corresponds to the thickness of the inter layer of bipolar membranes. Further analysis of the monolayer MoS₂ were exhibited at Fig. 5c, d and e, indicating that a mean longest diagonal of 100 nm with an average thickness of 4 nm was obtained.

Fig. 5 Atomic force microscopy (AFM) micrograph of MoS₂ nanosheets

3.3 FT-IR spectra

The FT-IR spectra of the bipolar membrane are shown in Fig. 6. The absorption peaks at approximately 1,026 cm⁻¹ are characteristic of the aromatic SO₃H symmetric stretching vibrations, with those of 1,235 cm⁻¹ for the asymmetric O=S=O and 1,080 cm⁻¹ for the symmetric O=S=O stretching vibrations [21]. The strong absorption appearing around 1106 cm⁻¹ for the SPES membrane is due to the presence of the aromatic ring [27], while the strong absorption appearing around 1297 cm⁻¹ for the two membranes is assigned to the presence of O=S=O ester sulfone [28].

For the opposite side, the strong peak appearing at 1402 cm⁻¹ corresponds to CF stretching vibrations. The C–C band of PVDF is clearly observed at 1165 cm⁻¹ [29]. Compared with the pure PVDF membrane, the composite membranes exhibited some new peaks. The peaks at 2878 and 2923 cm⁻¹ were attributed to the stretching vibration of the aliphatic C–H bond on the methyl or methylene groups of PECH [30]. The peak at 976 cm⁻¹ was assigned to the C–N vibration of the quaternary ammonium groups [31]. The characteristic peak at 1560 cm⁻¹ represents the typical stretching vibration of C–N peaks. All the observations confirmed successful blend of PECH-PVDF and successful introduction of functional groups for the bipolar membranes.

Fig. 6 FTIR spectra of bipolar membranes

3.4 Contact angle, water uptake, swelling ratio and ion exchange capacity

The water uptake and swelling ratio of the ion exchange membranes can greatly influence the performance when used in electrodialysis. Membranes with a higher water uptake tend to have a high ionic conductivity while an excessively high water uptake would reduce the dimensional and thermal stability. After amination by TMA solution, bipolar membranes have a low swelling ratio at about 7.5% while maintain a high water uptake of 71.6% at room temperature. The contact angles of anion exchange membranes decrease remarkably after amination as can be seen in Fig. 7. This indicates that the increase of the functional groups on the surface would elevate the hydrophilic properties. The ion exchange capacity for anion exchange layer after amination and cation exchange layer is 1.05 and 0.93 mmol/g, respectively. Obviously, amination reaction has a fundamental effect on bipolar membranes properties.

Fig. 7 Contact angle and IEC of bipolar membranes

3.5 Mechanical strength and ion transport rate of bipolar membranes

For bipolar membrane prepared at 90°C with MoS₂, a typical stress-strain curve was shown in Fig. 8. It can be seen that the stress-strain curves display an elastic behavior with continuously applied stress until the membrane break. The prepared bipolar membrane presented a break stress of approximately 20 MPa but with only 2.5 % of elongation at break. Consequently, the above results suggest that the bipolar membrane possess robust mechanical strength with high water uptake.

Fig. 8 Stress-strain curves of the prepared bipolar membrane with MoS₂

Protons migrate from the anode chamber to the cathode chamber through anion exchange membranes with the assistance of the electrical field. The concentration change of H⁺ in the cathode chamber within 1 h was 0.19 mol/L. Similarly, the concentration change of OH⁻ in the anode chamber within 1 h was 0.23 mol/L. The high concentration change was attributed to the high ion exchange capacity and the pores in the membrane matrix.

3.6 Current-voltage curves

Fig. 9 illustrates the effect of MoS₂ addition and amination temperature on the I-V curves of the prepared bipolar membranes. In comparison to the I-V curve of the bipolar membrane prepared without MoS₂, the membrane with an extra MoS₂ interface has a dramatically lower voltage drop. This indicates that MoS₂ is an excellent electrocatalyst that can catalyze water dissociation. In addition, mono-layer MoS₂ as inter-layer catalyst increased the junction electric field. The variations of amination temperature significantly affect the voltage drop across the bipolar membranes. Compared with bipolar membranes prepared at lower temperature, the voltage drop at 90 °C was 4.23 V, which is 18% lower than the blank one at the current density of 57.7 mA/cm². Since a higher temperature can enhance the amination reaction, the junction electric field is increased. Thus, the efficiency of water dissociation is promoted, and the membrane resistance is reduced. On the other hand, the hydrophilic groups on the surface of the anion exchange membranes enhance the hydrophilicity of the bipolar membranes. Consequently, more water molecules transfer into the inter-layer to compensate for the water consumption in the interlayer and further promote water dissociation to OH⁻ and H⁺ ions. Finally,

although quaternary ammonium groups have a very weak catalytic activity for water dissociation, they can degrade to tertiary and secondary amines in a high electric field in alkaline conditions, and become more reactive [32]. However, the voltage drop is still slightly higher compared to the commercial bipolar membranes.

Fig. 9 The I-V curves of the bipolar membranes (BPMs: bipolar membranes)

3.7 Water dissociation performance of bipolar membranes

To investigate the water dissociation of the new bipolar membrane with MoS₂ as the intermediate layer, a water dissociation test was conducted at a current density of 20 mA/cm². Fig. 10 shows the yields for water dissociation using bipolar membranes prepared by different methods. Obviously, the concentration of acid increased with time. However, as the reaction temperature increased, membranes exhibit a better acid yield. Furthermore, the bipolar membrane with MoS₂ produces much more acid than the blank membrane, suggesting that the water dissociation is enhanced after introducing MoS₂ as intermediate layer.

Fig. 10 Variations of the hydrogen ion concentration $[H^+]$ in the acid compartment (BPMs: bipolar membranes)

Fig. 11 shows the voltage drop as a function of time. A lower voltage drop was obtained at higher temperature; however, two-layer membranes have a lower voltage drop than three-layer bipolar membranes. This is because when no MoS_2 exists in the interfacial layer, the leakage of co-ions will reduce the voltage drop. Therefore, MoS_2 could efficiency promote the water dissociation.

Fig. 11 The change of voltage drops across the bipolar membranes with time (BPMs: bipolar membranes)

Fig. 12 shows the current efficiency and energy consumption of bipolar membranes prepared in different conditions. It can be concluded that amination at higher temperature tends to improve the current efficiency, with a decreased energy consumption. This is mainly because at higher temperature, the amination reaction occurs easily, and the electric field strength at the interface layer was enhanced. At lower temperature, the current efficiency for the membranes with MoS_2 increased while the energy consumption was similar. By introducing MoS_2 , although water splitting was enhanced, the resistance of bipolar membranes was also increased, which results in a higher energy consumption. For the method applied at higher temperature, the same phenomenon with respect to the current efficiency can be seen, but the energy consumption was reduced. This can be explained by two reasons. First, co-ion leakage reduced the energy consumption; second, protons generated by water splitting can compensate the current to some extent. From the view point of current efficiency and acid production, MoS_2 can be a good catalyst for bipolar membranes in water dissociation. Although the acid production and current efficiency is not as high as the commercial membranes, further improvement is underway to change the concentration and size of MoS_2 , the thickness and materials of the anion and cation exchange layer.

Fig. 12 Current efficiency and energy consumption of different membranes during water dissociation (BPMs: bipolar membranes)

To further analyse the influence of current density over acid production, bipolar membranes prepared with MoS_2 at 90°C were used at current densities of 20, 30, 40 and 50 mA/cm². As presented in Fig. 13, the production of acid is dependent on the current density, the higher the applied current density, the higher concentration of the produced acid, because the mass transport rate of SO_4^{2-} will become higher when the current density increases. At the same time, the water dissociation rate is accelerated with an increase in current according to the Second Wien effect. However, the current

efficiency decreased, which is caused by co-ion leakage and diffusion through the ion exchange membranes. The relationship between the energy consumption and current density revealed that the energy consumption increases as the current density increases. The increase in the energy consumption was attributed to energy consumed to overcome the electrical resistance while the current density increases. The current efficiency increases and energy consumption decreases as the current density decreases. As a result, the lower current density is more appropriate when considering the efficiency and consumption of energy.

Fig. 13 Comparison of the current efficiency and energy consumption at various current densities

4. Conclusions

Novel sandwiched bipolar membranes composed of SPES/MoS₂/PECH-PVDF were successfully fabricated. The optimal bipolar membranes have been tested for different properties such as ion exchange capacity, voltage drop, acid production and energy consumption. A bipolar membrane with IEC of 0.96 mmol/g for cation exchange layer and 1.03 mmol/g for anion exchange layer, showed high ion transport rate for both cation exchange layer (0.19 mol/L) and anion exchange layer (0.23 mol/L). In addition, a high water uptake of 71.6% and comparatively lower contact angle provide a super hydrophilic environment necessary for water transfer from membrane surface to inter layer. The prepared bipolar membranes with MoS₂ at 90 °C exhibit an outstanding performance with a higher current efficiency of 45% and a lower energy consumption of 3.6 kW/h • kg compared to a bipolar membrane without

MoS₂. As a consequence, a monolayer of MoS₂ on the inter layer of the bipolar membrane can serve as a good catalyst to reduce the high activation energy of water dissociation. In a broader context, further study of MoS₂ as catalyst should be studied referring to optimization of conditions and industrial applications.

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Highlights

1. MoS₂ as advanced catalysts was introduced to the interface of bipolar exchange membranes to enhance water dissociation.
2. Enhanced acid production, higher current efficiency and lower energy consumption was obtained after introducing MoS₂ layer catalyzes.
3. High water uptake of membrane provide a super hydrophilic environment necessary for water transfer from membrane surface to inter layer.