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New bipolar membrane setup for high current densities

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ABSTRACT

Limited affordable current density of ca. 0.2 A cm^{-2} is a major drawback in bipolar membrane (BPM) electrodialysis technology. At higher current densities, the diffusion of water into the BPM interface between the anion and cation exchange layers becomes the rate-limiting step for the water dissociation process. The extended use of the BPM setup at such high current densities, however, results in dehydration of the membrane, an increase in its resistance, and irreversible damage to the BPM. A new experimental setup intended to enable high current densities to be safely used is described. The setup comprises a BPM made of a commercial anion exchange membrane to which a thin (<60 μm) sulfonated polyphenyl sulfone layer (TCL) is glued. Between the TCL and an adjacent commercial cation exchange membrane, a solution of polystyrene sulfonic acid (PSSA) is circulated through a net. This setup enables water to diffuse at a high rate through the TCL into the interface where the dissociation process occurs. The composition of the circulating solution prevents the excessive leakage of anions through the TCL into the solution of the basic product. Current densities of 0.4–0.5 A cm^{-2} were achieved with comparatively low voltage drops on the BPM and without limiting the rate of water diffusion.

Keywords: Bipolar membrane; Electrodialysis; Water dissociation; Dehydration; Electroosmosis

1. Introduction

The bipolar membrane (BPM) is a laminate comprising an anion exchange layer and a cation exchange layer (AEL and CEL, respectively). By applying a direct current to the BPM, water molecules can be split at the interface between the anion and CELs into protons and hydroxide ions that migrate out of the BPM and are then replenished by fresh water that diffuses from the outer solution into the BPM (Fig. 1).

The current–voltage dependence for a BPM, illustrated schematically in Fig. 2, is characterized by four voltage ranges [1–5]. In the first, which extends to point (a) in Fig. 2(A), the current rises linearly with the voltage, a process supported by the migration of counter-ions out of the BPM. The incomplete permselectivity of the ion-exchange layers means that they are somewhat permeable to co-ions. As the current increases, the concentration of the salt ions across the ion-exchange layers gradually drops, becoming zero at the interface, at which point the maximal rate of diffusion is attained. In Fig. 2(A), this point (a) is called the first limiting current density, which generally is in the range of few mA cm^{-2}. Because a decrease in the BPM permselectivity will result in an increase in the first limiting current density, the latter is therefore an indicator for the former.

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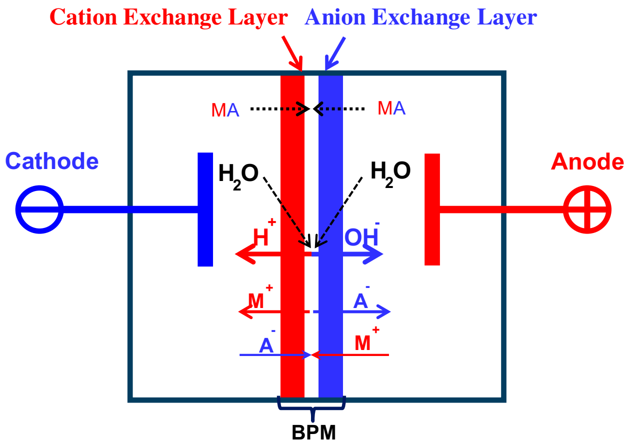

Fig. 1. Schematic representation of BPM and fluxes during water dissociation.
Note: Migration—Solid arrows; Diffusion—Dashed arrows.

The distance between points (a) and (b) represents the second voltage range, where the current density increases only slightly since this increase is supported exclusively by co-ion migration (Fig. 1). This range, which extends up to about 0.83 V, represents the theoretical drop in potential sufficient for water dissociation to take place [6]. With the start of water dissociation, current density increases sharply between points (b) and (c). This is the third range, which represents the desired current for water dissociation and the optimal range for conventional BPM operation. Indeed, at current densities larger than about 200 mA cm^{-2} (point (c), the fourth range), the current vs. voltage slopes of most BPMs decrease. The inflection point at (c), referred to as the second limiting current density, is caused by an insufficient supply of water to the BPM to replace the water consumed during the dissociation process [2,7,8]. A BPM that functions continuously in this range is subject to dehydration that may lead to its irreversible damage [9], a phenomenon that ranks among the major drawbacks in BPM electrodialysis technology.

Research to develop BPMs that can work at high current densities, which lead to better current efficiency and product purity and lower operational costs, is therefore of practical importance [6,9,10]. Several works have shown that the use of an asymmetric BPM characterized by a thin AEL and a regular CEL enabled high water transport rates [5,8]. In those works, the CEL was highly selective toward cations, whereas the thin AEL was of low anion permselectivity, and therefore, that setup may result in a basic product of low purity. A theoretical study that analyzed the problem of dehydration showed that a thermodynamic parameter that expresses the dependence of water content on osmotic pressure has a major influence on the rate of water transport [11], a conclusion that has yet to be tested experimentally.

Within the framework of the EU project NEW-ED [12], two prospective solutions to overcome the current operational limitations of BPM design—the insertion of a thin porous ion-exchange layer between the AEL and the CEL and the incorporation of microchannels in the BPM by using a corrugated CEL—were tested. Both setups involved forcing the water through the BPM interface. The pressure applied to force the water into the interface can cause the layers constituting the BPM to separate. In principle, in both cases, the net consumption of water during the electrodialysis process could be assessed by measuring the amounts of water entering and exiting the BPM.

In the present work, we tested a new method for increasing the rate of water transport and working continuously at high current densities. Our new setup

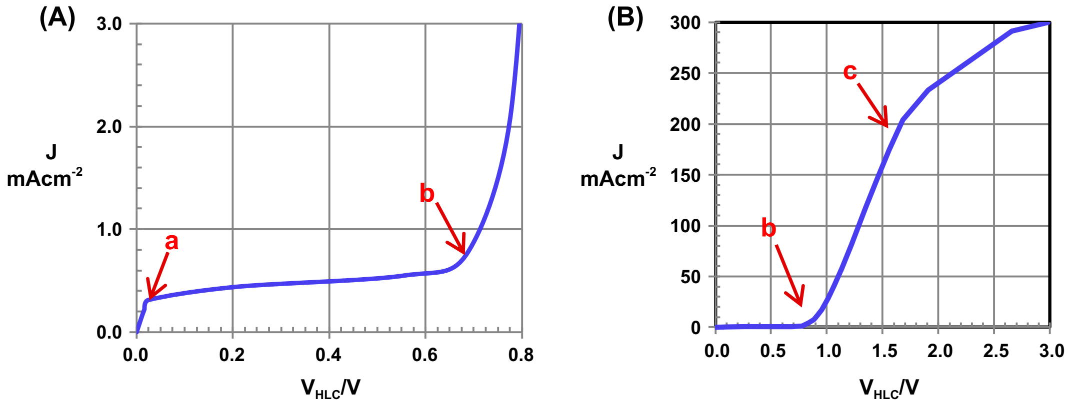

Fig. 2. Current density vs. voltage drop dependence (schematic) for a BPM. (A) Initial range and (B) Overall range.

supported high permselectivity toward both counter-ions, thus enabling the production of pure basic and acidic solutions.

2. Experimental setup

The experiments were carried out in a test system comprising six compartments and equipped with a new BPM setup (schematically depicted in Fig. 3). The BPM contained a commercial anion exchange membrane (AEM) to which was attached a thin cationic layer (TCL) of sulfonated polyphenyl sulfone that measured 40–60 μm thick. Two Haber-Luggin capillaries (HLCs) situated facing the cation exchange membrane (CEM) and AEM surfaces enabled the voltage drop (V_{HLC}) to be measured as a function of the applied current. The AEM component of the BPM was adjacent to the solution in compartment 4, and the TCL was aligned parallel to a porous net (NET) through which an auxiliary solution was circulated. On the left side of the NET, a commercial CEM separated the auxiliary solution from compartment 3. The solutions in all six compartments were individually circulated through Perspex containers with volumes of approximately 2 L.

The defining characteristics of this BPM setup include:

(1) The TCL enabled high rates of water transport from the auxiliary solution to the BPM interface between the anion and CELs where the dissociation reaction takes place, and therefore, high current densities were possible.

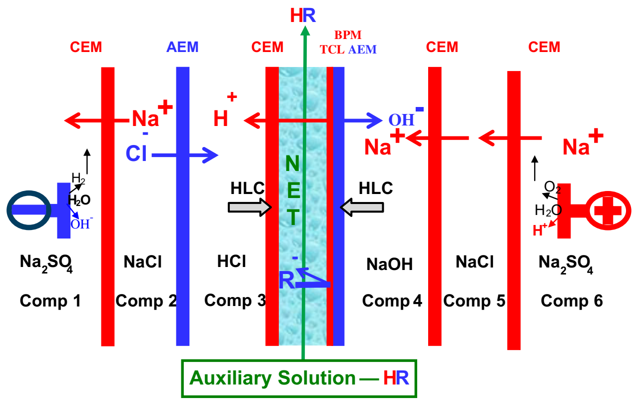

Fig. 3. A six-compartment test system equipped with the new BPM setup. The BPM comprised an AEM and a TCL. Two HLCs, one each adjacent to the CEM and to the AEM surfaces, enabled the voltage drop (V_{HLC}) to be measured. Auxiliary solution was recirculated through the NET.

(2) Although the TCL was of low selectivity, excessive anion transport from compartment 3 to compartment 4 was prevented by the adjacent CEM.

(3) The voltage drop between the TCL and the CEM was minimized by the presence of a thin NET (~0.5 mm) and an auxiliary electrolyte solution of high conductivity. Anion transport through the TCL was prevented using a high molecular weight poly-acid, e.g. polystyrene sulfonic acid (PSSA, MW~75,000).

3. Results and discussion

The new BPM setup was tested with HCl and PSSA auxiliary solutions. The same experimental setups, including membranes, were used for both solutions. The results are presented in Figs. 4–5. V_{HLC} values, which were obtained using reference electrodes of Ag/AgCl/3 M KCl, were corrected for the IR-drop that occurred on the solution layers between

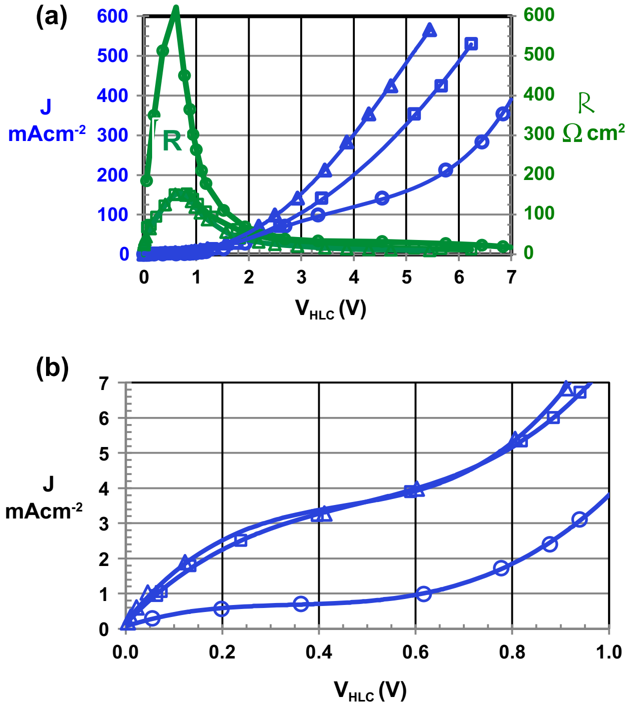

Fig. 4. (a) Current–voltage dependence for experiments carried out with various HCl auxiliary solutions, (Δ—0.3 M, 106 mScm^{-1}; □—0.2 M, 62 mScm^{-1}; ○—0.05 M, 16 mScm^{-1}). BPM resistances, calculated as V_{HLC}/J are shown on the secondary (right) vertical axis. (b) Initial current–voltage dependence, for experiments carried out with various HCl auxiliary solutions (Δ—0.3 M, 106 mScm^{-1}; □—0.2 M, 62 mScm^{-1}; ○—0.05 M, 16 mScm^{-1}).

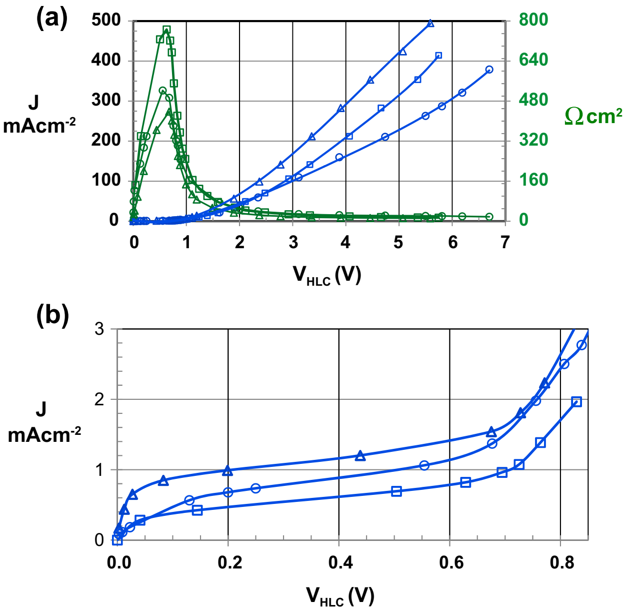

Fig. 5. (a) Current–voltage dependence for experiments carried out with various PSSA auxiliary solutions. (Δ—PSSA 12%, 31 mM Cl^-, 106 $mScm^{-1}$; □—PSSA 12%, 10 mM Cl^-, 94 $mScm^{-1}$; ○—PSSA 4%, 10 mM Cl^-, 31 $mScm^{-1}$). Values of BPM resistance, calculated as V_{HLC}/J, are shown on the secondary (right) vertical axis. (b) Initial current–voltage dependence, for experiments carried out with various PSSA auxiliary solutions (Δ—PSSA 12%, 31 mM Cl^-, 106 $mScm^{-1}$; □—PSSA 12%, 10 mM Cl^-, 94 $mScm^{-1}$; ○—PSSA 4%, 10 mM Cl^-, 31 $mScm^{-1}$).

the HLC tips and the membrane layers. The active area of the BPM was 7.0 cm^2. All measurements were carried out at room temperature without temperature control. Nominal BPM resistance, calculated as V_{HLC}/J and given in units of Ωcm^2, is presented in Figs. 4(a) and 5(a). The peak signifies the V_{HLC} at which water dissociation began, and in all cases it appeared at about 0.8 V.

In Figs. 4(b) and 5(b), the initial J vs. V_{HLC} dependence is presented. The figures show the first limiting current density, which is governed by salt leakage through the BPM. Higher values of the first limiting current density are indicative of lower BPM permselectivity and lower dissociation reaction efficiency.

3.1. HCl auxiliary solutions

The results of the experiments carried out with HCl auxiliary solutions are shown in Fig. 4(a) and (b). At 0.2 and 0.3 M HCl solutions, current densities above 0.5 A cm^{-2} were reached at 5–6 V, without any signs of limitation, meaning that no dehydration of the BPM occurred. However, the first limiting current density (see Fig. 4(b)) was high, over 3 mA cm^{-2}, and the efficiency of water dissociation is expected to be low. Indeed, as will be shown in Section 3.3, measurements of the efficiency of water dissociation with PSSA auxiliary solutions have revealed that the higher the chloride concentration, the lower the efficiency. At 0.05 M HCl solution, the first limiting current was very low but to achieve high rates of dissociation, prohibitively high values of V_{HLC} were needed.

3.2. PSSA auxiliary solutions

A solution of PSSA (MW ~75,000, 18 wt% in H_2O) purchased from Sigma–Aldrich was dialyzed with a Cellu•Sep H1 membrane to exclude low MW chains. During the dialysis, the solution was diluted by osmosis to 12 wt%. Experiments were carried out with the 12% PSSA solution and with a solution further diluted to 4% (Fig. 5(a) and (b)). In all experiments with the PSSA auxiliary solutions, high current densities were attained without any limitation, meaning that the BPM did not undergo any dehydration.

The first current densities, which were less than 1 mA cm^{-2}, were low compared with those achieved with the HCl auxiliary solutions. This finding is the result of the low permeability of the TCL component of the BPM to the polystyrene sulfonate ions. The higher chloride concentration of 31 mM Cl^- in the run with 12% PSSA, however, led to a higher limiting current density of more than 1 mA cm^{-2}.

3.3. Water dissociation efficiency

Water dissociation was measured during electrolysis at a constant current of 2 A (285 mA cm^{-2}) by monitoring the change in the OH^- concentration in compartment 4, in which 1 L of neutral 1-M NaCl solution was loaded at the start of these experiments. The experiments were run using PSSA auxiliary solutions, two of which contained low concentrations of chloride and one whose chloride concentration was high: 0.25 M (Fig. 6). There was no significant difference between the two experiments with the low chloride concentrations, although they were run with different PSSA concentrations. In contrast, the experiment with the high chloride concentration exhibited a considerably lower efficiency of 65 vs. 84%. It should be mentioned that in previous seven experiments done with regular BPM setups at a constant current of either 2 or 3 A, the average efficiency was 84 ± 2%.

3.4. Water transport

During electrodialysis with the BPM, water is consumed by the dissociation process; however, the

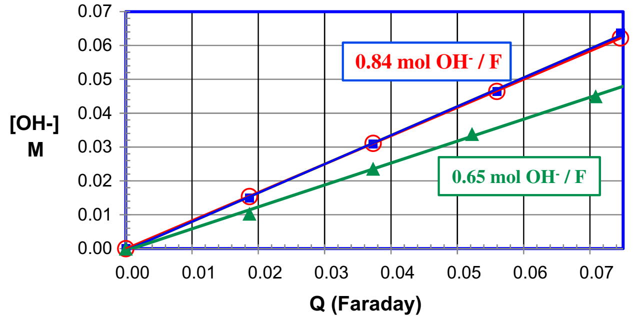

Fig. 6. Dependence of OH^- concentration in compartment 4 (1 L) on the amount of charge during electrolysis at 2 A using various PSSA auxiliary solutions. (○—PSSA 12%, 0.02 M Cl^-, ■—PSSA 4%, 0.04 M Cl^-, ▲—PSSA 6%, 0.25 M Cl^-).

migration of H^+ and OH^- ions is accompanied by water molecules, which form their hydration shell, i.e. electroosmotic transport. At steady state, therefore, the amount of water that diffuses into the interface between the anion and CELs must be equal to the total amount of water consumed by dissociation and by the electoosmotic transport into compartments 3 and 4. One study [13], in which the electrotransport of water that accompanied the H^+ ion migration was included in a theoretical model, was based on the assumption that one molecule of H_2O was transported for each H^+ ion, and calculated and experimental values were compared.

Although it is important to know the total amount of water transported into the BPM and not only that consumed by dissociation, to the best of our knowledge no such information exists in the literature. We calculated the total amount of water involved by measuring the change in weight of the circulating auxiliary solution during electrodialysis and neglecting the amount of water that diffused through the comparatively thick AEL. An average value of 6.2 ± 0.6 mol H_2O/F was found, which shows that in addition to the amount of water consumed in the dissociation process, transport by electroosmosis—through the TCL and CEM into compartment 3 and through the AEM into compartment 4—accounted for about 5 mol H_2O/F of the total (Fig. 3).

4. Conclusions

The use of BPMs at high current densities, which typically cause membrane dehydration, has been largely unsuccessful. In this study, we showed that at high current densities, the new BPM setup did not undergo dehydration, which was prevented by the high water transport rate. Moreover, this finding was especially true when the electrolyte in the auxiliary solution was 12 wt% PSSA in the presence of a low Cl^- concentration. The combined effects of the TCL and of the large polystyrene sulfonate ion not only enabled the high rate of water transport necessary to prevent dehydration, it also apparently did not allow transport of the anion through the BPM, thus ensuring the purity of the product. Furthermore, the high conductivity of 12 wt% PSSA auxiliary solutions enabled the use of a high current density with a low voltage drop.

Future research should evaluate the potential to improve the performance of the new BPM setup by the addition of suitable catalysts to the interface between the anion and CELs of the BPM.

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