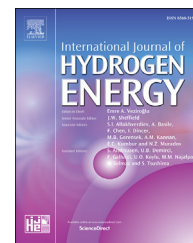


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# The importance of OH<sup>−</sup> transport through anion exchange membrane in microbial electrolysis cells

Yaoli Ye, Bruce E. Logan<sup>\*</sup>

Department of Civil and Environmental Engineering, The Pennsylvania State University, University Park, PA, 16802, USA

## ARTICLE INFO

### Article history:

Received 21 September 2017

Received in revised form

9 December 2017

Accepted 11 December 2017

Available online 11 January 2018

### Keywords:

Hydrogen

Microbial electrolysis cell

Anion exchange membrane

Anolyte pH

Buffer retention

Polymeric buffer

## ABSTRACT

In two-chamber microbial electrolysis cells (MECs) with anion exchange membranes (AEMs), a phosphate buffer solution (PBS) is typically used to avoid increases in catholyte pH as Nernst equation calculations indicate that high pHs adversely impact electrochemical performance. However, ion transport between the chambers will also impact performance, which is a factor not included in those calculations. To separate the impacts of pH and ion transport on MEC performance, a high molecular weight polymer buffer (PoB), which was retained in the catholyte due to its low AEM transport and cationic charge, was compared to PBS in MECs and abiotic electrochemical half cells (EHCs). In MECs, catholyte pH control was less important than ion transport. MEC tests using the PoB catholyte, which had a higher buffer capacity and thus maintained a lower catholyte pH (<8), resulted in a 50% lower hydrogen production rate (HPR) than that obtained using PBS (HPR = 0.7 m<sup>3</sup>-H<sub>2</sub> m<sup>−3</sup> d<sup>−1</sup>) where the catholyte rapidly increased to pH = 12. The main reason for the decreased performance using PoB was a lack of hydroxide ion transfer into the anolyte to balance pH. The anolyte pH in MECs rapidly decreased to 5.8 due to a lack of hydroxide ion transport, which inhibited current generation by the anode, whereas the pH was maintained at 6.8 using PBS. In abiotic tests in EHCs, where the cathode potential was set at −1.2 V, the HPR was 133% higher using PoB than PBS due to catholyte pH control, as the anolyte pH was not a factor in the performance. These results show that maintaining charge transfer to control anolyte pH is more important than obtaining a more neutral pH catholyte.

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## Introduction

Microbial electrolysis cells (MECs) are devices which can achieve simultaneous degradation of organic matter in wastewater and conversion of the chemical energy into hydrogen gas [1], with an additional voltage input by power supply (0.5–1.0 V) [2]. A separator, such as an ion exchange

membrane, is usually placed between the electrodes to reduce hydrogen consumption by microbes on the anode that results in hydrogen cycling (consumption of hydrogen produced on the cathode by microorganisms on the anode), and loss of hydrogen due to methanogenesis [3,4]. In previous two-chamber MEC studies [5,6] where different ion exchange membranes have been compared, better performance was obtained with anion exchange membranes (AEMs) than with

<sup>\*</sup> Corresponding author.

E-mail address: [blogan@psu.edu](mailto:blogan@psu.edu) (B.E. Logan).

<https://doi.org/10.1016/j.ijhydene.2017.12.074>

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cation exchange membranes (CEMs). However, the addition of a membrane increases internal resistance and creates pH differences between the electrolyte chambers, with the anolyte becoming more acidic and the catholyte more basic. The anolyte should be kept above a pH = 6 so that pH does not inhibit current generation by the exoelectrogens. An increase in the catholyte pH is not desirable because it increases the voltage needed to evolve hydrogen gas at equilibrium [5], which according to the Nernst equation is:

$$E_{eq} = E_{cat}^0 - \frac{RT}{zF} \ln \frac{a_{red}}{a_{oxi}} - E_{an} \\ = -0.414 \text{ V} - \frac{RT}{2F} \ln p_{H_2} [OH^-]^2 - (-0.289 \text{ V}) \quad (1)$$

assuming an equilibrium anode potential of  $-0.289 \text{ V}$  (acetate as substrate at pH 7 [7]), where  $E_{cat}^0$  is the cathode potential at equilibrium ( $-0.414 \text{ V}$ ),  $R$  the ideal gas law constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ),  $F$  the Faraday's constant ( $96485 \text{ C mol}^{-1}$ ),  $T$  the absolute temperature (K),  $z$  the number of electron transferred per mole of hydrogen produced (2),  $p_{H_2}$  the hydrogen partial pressure and  $[OH^-]$  the concentration of hydroxide ions. Even in MECs lacking a membrane, the local pH near the electrodes can vary, with the anolyte becoming more acidic and the catholyte more alkaline [8], leading to concentration overpotential [9]. To avoid large pH changes, buffers such as phosphate [10,11] or bicarbonate buffers [12] are usually used in MECs.

Buffers improve the performance of the MEC by reducing the overpotential of the hydrogen evolution reaction (HER) on the cathode, as predicted by the Nernst equation, as long as the pH is near the pKa of the buffer. The minimum overpotential for the hydrogen evolution reaction (HER) can range from  $0.05 \text{ V}$  to  $0.09 \text{ V}$  for a variety of buffers (PBS, BBS, ammonia, Tris, or Hepes;  $50 \text{ mM}$ , at  $15 \text{ A m}^{-2}$ ) when the pH is near the buffer pKa [13]. Buffers in MEC catholytes also increase the solution conductivity [14] and serve an additional function of shuttling charge between the electrolyte chambers, primarily through the transport of negatively-charged buffer ions through the AEM [5]. The importance of ion transport in an MEC, relative to pH changes, cannot be assessed using the above Nernst calculation approach, and thus it is not clear whether pH control or charge balance by the buffer is more critical for hydrogen gas production. For example, it was shown that MECs with a highly conductive, but non-buffered saline catholyte solution ( $68 \text{ mM NaCl}$ ), had a higher hydrogen production rate (HPR) of  $1.6 \text{ m}^3\text{-H}_2 \text{ m}^{-3}\text{-d}$  than MECs using a phosphate buffer solution (PBS,  $\text{HPR} = 1.0 \text{ m}^3\text{-H}_2 \text{ m}^{-3}\text{-d}$ ) in the catholyte for MECs with an AEM [15]. This finding suggested that solution conductivity was more important than pH for HER in MECs, which conflicts with the calculation based on the Nernst equation which shows the importance of pH.

To separate the impacts of pH and ion transport on MEC performance, we synthesized a polymer buffer (PoB) that produced a high solution conductivity and had a pKa similar to that of PBS, but was restricted from passage through the AEM due to its high molecular weight (MW,  $30 \text{ kDa}$ ) and positive charge. The PoB are polycations that deprotonate at basic pHs or gain protons at acidic pHs [16]. It was reasoned based on past studies showing the importance of catholyte pH that

the HPR would be improved by better pH control, by preventing the loss of the buffer, compared to low MW buffers such as PBS. However, the charge would not be balanced by buffer ion transport between the chambers as the transport of PoB is restricted by its large MW from transport through the AEM into the anolyte, and thus the importance of charge transfer could be separated from that of pH. The two buffers (PoB or PBS) were initially compared by demonstrating their different transport through the AEM, and by measuring their solution conductivities and buffer capacities at the selected concentrations. The performance of MECs using PoB or PBS was compared in terms of current densities and hydrogen production, while monitoring electrolyte conductivity and pH. In addition, hydrogen production was examined using PoB and PBS in abiotic electrochemical half cells (EHCs), with a set cathode potential, to separate the impact of the catholyte pH on HER from the impacts of pH changes of the anodes observed in MECs. Hydrogen production in MECs was also evaluated over many cycles without catholyte replacement. The differences in the performance of the MECs and EHCs were used to support findings that the transport of  $OH^-$  through AEM was more important than buffer capacity, solution conductivity, and buffer transport through AEM in MECs.

## Material and methods

### PoB synthesis and preparation

Poly (2-(dimethylamino) ethyl methacrylate) (PDMAEMA), a water soluble cationic polymer [17,18], was synthesized as reported by others [19]. Briefly,  $1 \text{ g}$  of 2-(dimethylamino)ethyl methacrylate (DMAEMA),  $19 \text{ mg}$  2,2'-bipyridine, and  $9.14 \text{ mg}$  of copper (I) bromide were mixed and degassed using pure  $N_2$  gas. Then,  $1 \text{ g}$  of degassed deionized (DI) water was added, followed by the addition of methyl 2-bromopropionate as the initiator. The reaction was carried out at  $20^\circ \text{C}$ . After PDMAEMA was collected and dissolved in  $10 \text{ mL}$  of DI water, the solution was purified by dialysis (Sigma-Aldrich, average flat width  $35 \text{ mm}$ ,  $12 \text{ kDa}$  MW cut off) to remove copper ions and small-MW compounds. The dialysate was used as the PoB after adjusting pH to  $7.0$  by adding hydrochloric acid.

The MW distribution of PoB was measured using an ultrafiltration method [20]. Briefly, PoB was first diluted and then passed in parallel through several ultrafiltration membranes with different MW cutoffs of  $2$ ,  $10$ ,  $30$  and  $100 \text{ kDa}$  (Ultrafiltration membrane disc,  $62 \text{ mm}$ , Amicon, US) in a stirred cell ( $200 \text{ mL}$ , Amicon, US). The concentration of total organic carbon (TOC) was measured (Shimadzu TOC-V, Shimadzu Corp., Japan) of the original PoB and at several different times of the permeate solution. The MW distribution was obtained with the permeate concentration data using the permeate coefficient model [20] (detailed protocol given in the SI).

### Buffer retention and buffer capacity tests

A side-by-side test of buffer retention using PBS ( $4.58 \text{ g Na}_2\text{HPO}_4$ ,  $2.45 \text{ g NaH}_2\text{PO}_4$ ,  $0.31 \text{ g NH}_4\text{Cl}$  and  $0.13 \text{ g KCl}$  in  $1 \text{ L}$ ,  $50 \text{ mM}$ ) and PoB was compared using a diffusion test. The

concentration of 50 mM was chosen based on previous studies [10,11]. The AEM (AMI-7001, Membrane International Inc.) was placed in the middle of an MEC reactor (without electrodes, Fig. S1A) which had a cylindrical chamber with 3 cm in diameter and 4 cm in length (a total volume of 26 mL), to separate it into two chambers. Buffer solution (PoB or PBS) was put in one of the chambers (buffer chamber), while DI water was added to the other one (water chamber). The water chamber was emptied and refilled with DI water every two days. The two chambers were sealed to prevent liquid evaporation. Samples (0.2 mL) were collected from the buffer chamber every four days. The concentration of PoB was monitored based on concentrations of TOC (Shimadzu TOC-V, Shimadzu Corp., Japan), while the concentration of PBS was obtained using a phosphate analysis kit (total phosphorus TNT reagent set, Hach, US). Buffer losses were monitored based on the change of the percentage of buffer in the chamber. A minimum buffer retention curve was calculated by assuming that half of the buffer in the buffer chamber was lost within two days before the water chamber is refilled, using

$$r = (0.5)^{0.5t} \times 100\% \quad (2)$$

where  $r$  is the percentage of buffer retained, and  $t$  is time in day.

Titration of the two buffer solutions, PoB and 50 mM PBS, were conducted to determine their buffer capacities. Concentrated NaOH (1.7 M) was added into the buffer solution (20 mL) with constant mixing until a pH of 12 was reached, with the amount of NaOH used measured as a function of pH during titration.

### MEC operation and hydrogen test

A schematic of the MEC used in this study is shown in Fig. S1A. The anode (carbon felt) and cathode (stainless steel mesh, #60, SS mesh) were placed in a cubic reactor 3 cm in diameter with two 2-cm long chambers separated using an AEM. The anode was pushed next to the endplate, while the cathode placed next to the membrane, resulting in an electrode spacing of 2 cm. An anaerobic culture tube with the bottom cut off (Bello Glass, Inc., US) was epoxied so that the open bottom covered a hole on the top of the cathode chamber to collect hydrogen gases produced during the tests. A thick butyl rubber stopper (20 mm diameter, Chemglass Inc., Vineland, NJ) and aluminum crimp top was used to seal the top of the tube, with the produced hydrogen gas collected using a gas bag (Calibrated Instruments, Inc, US) connected to the tube using a needle pierced through the rubber stopper. The reference electrode (Ag/AgCl, RE-5B, BASi, West Lafayette, IN; +0.209 V vs. Standard hydrogen electrode, SHE) was placed in the anode chamber to measure the anode potential every 10 min.

The anodes of MECs were initially inoculated and acclimated in microbial fuel cells (MFCs) using the effluent from other MFCs operated for more than six months. After the current of the MFCs stabilized, the feed solution was switched to the synthetic wastewater, which consisted 10 mM sodium bicarbonate, 2 g L<sup>-1</sup> of sodium acetate, vitamin and mineral solution [15]. The pH of the synthetic wastewater was

adjusted to 7.5 using hydrochloric acid and the conductivity was increased to 7.0 mS cm<sup>-1</sup> by adding sodium chloride. The low anolyte buffer concentration (10 mM) used here was intended to mimic the low buffer capacity of municipal wastewater with alkalinity reported to be 100–300 mg-CaCO<sub>3</sub> L<sup>-1</sup> [21]. MFCs were then converted into MECs, which were then operated with same synthetic wastewater as anolyte and PBS or PoB as catholyte for two months at an applied voltage of 1.1 V to ensure a stable biofilm. The voltage adopted in this study was consistent with a previous study on single-chamber MECs [22]. The pH for both PBS and PoB was 7.0, while the conductivity for PoB was 12.0 mS cm<sup>-1</sup> compared to 7.0 mS cm<sup>-1</sup> for PBS. The conductivity of PoB was increased by adding sodium chloride. A higher conductivity for PoB was chosen to compensate the conductivity decline when pH increases.

Hydrogen production in the MECs was evaluated daily in 3-cycle tests, by replacing the anolyte each cycle (daily) with fresh medium, but not replacing catholyte, in order to study changes of the catholyte over time. The anolyte and catholyte pH and conductivity were also monitored daily. The hydrogen produced was measured using a gas chromatograph (SRI 301c, SRI instruments) with the gas bag method [12]. Total phosphate concentrations in the catholyte were measured using the phosphate analysis kit (total phosphorus TNT reagent set, Hach, US) to calculate buffer losses. Long-term performance of MECs with a high catholyte pH was evaluated after 15 cycles (no catholyte replacement) for MECs with PoB.

### Electrochemical tests

Hydrogen production using the PoB was compared to that obtained with PBS in electrochemical half cells (EHCs) with a Pt plate as counter electrode, and SS mesh as working electrode. The reactor structure of the EHCs was similar with those used as MECs, except that the electrode spacing was increased to 4 cm and a reference electrode (Ag/AgCl, +0.209 V vs SHE) was inserted close to the cathode and outside current path, as recommended in a previous study (Fig. S1B) [23]. The same anolyte solution, 10 mM sodium bicarbonate solution with 2 g L<sup>-1</sup> sodium acetate (pH, 7.0 and conductivity, 7.0 mS cm<sup>-1</sup>) was added to the anode chamber, while one of the buffer solutions, PoB or PBS, was tested as the catholyte. The cathodic potential was set and fixed at -1.2 V (vs. Ag/AgCl). The hydrogen production test was carried out in a similar fashion with that in MECs in a 3-cycle test, with replacement of the anolyte every daily cycle but not the catholyte. The pH and conductivity of the anolytes and catholytes were monitored each day. Chloride ion concentrations in the anolyte were monitored using ion chromatography (AS 18 column, ICS-1100, Dionex Corporation, Sunnyvale, CA, US).

Solution resistance was compensated in EHCs using a current interrupt technique with a potentiostat (BioLogic model; software version = 10.23; 80% compensation based on the average of 10 measurements). Both MEC and EHC tests were conducted in duplicate, and all tests were conducted in a constant temperature room (30 °C). All potentials were reported versus the Ag/AgCl reference electrode.

## Calculations

The overpotential due to the bulk solution pH increase,  $\eta$  [5], was calculated as

$$\eta = \left| \frac{RT}{F} \ln \left( \frac{10^{-7}}{10^{-\text{pH}}} \right) \right| \quad (3)$$

The overpotential reported here only accounts for the bulk pH change, but the overpotential of HER can also be due to the specific response of the electrode material (SS mesh) to pH changes, as noted by others [24]. The cathodic coulombic efficiency (CCE) is used to evaluate the conversion of electrons to hydrogen gas, and it was calculated from current and hydrogen production using Simpson's rule as

$$e_{\text{cathode}} = \frac{n\rho FV_m}{m \int_{t=0}^{t_{\text{end}}} i dt} = \frac{n\rho FV_m}{m \left\{ \frac{\Delta t}{3} \left[ i_0 + i_{\text{end}} + 2 \sum_{j=1}^{\frac{1}{2}-1} i_{2j} + 4 \sum_{j=1}^{\frac{1}{2}} i_{2j-1} \right] \right\}} \quad (4)$$

where  $V_m$  is the measured hydrogen production,  $n$  the number of electrons transferred per mole of hydrogen (2),  $m$  the molar weight of hydrogen,  $\rho$  the density of hydrogen at 30 °C,  $i$  the current (A),  $t$  the time (s),  $\Delta t$  is the time interval between current sampling,  $i_0$  the initial current (A),  $i_{\text{end}}$  the end current (A),  $l$  the total current sampling points, and  $i_j$  is the  $j^{\text{th}}$  current sampling point.

The average current was calculated based on the time for accumulation of 90% of charge ( $I_{\text{avg},90}$ ) to minimize the impact of low current at the end of the cycle on the calculation of the average [25]. It was calculated as:

$$I_{\text{avg},90} = \frac{0.9 Q}{t_{90}} = \frac{0.9 \int_{t=0}^{t_{\text{end}}} i dt}{t_{90}} \quad (5)$$

where  $Q$  is the charge accumulated calculated by integral the current over time period, and  $t_{90}$  the time for accumulating 90% of charge.

## Results and discussion

### Characterization of PoB and buffer retention test

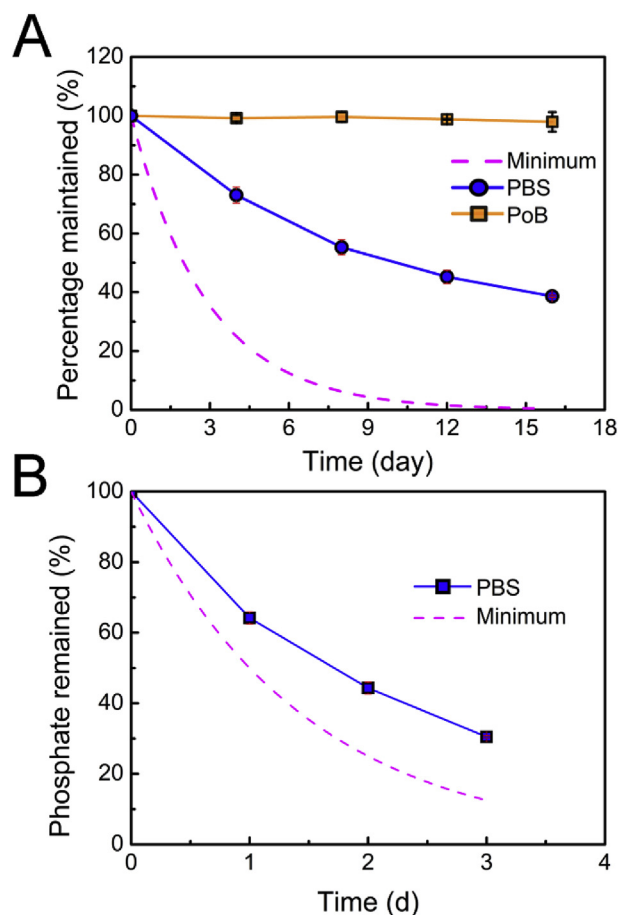
The MW distribution obtained from the ultrafiltration method showed that 60% of PDMAEMA had a MW between 30 kDa and 100 kDa. A small portion (6%) of PDMAEMA had a MW in the range of 2 kDa–30 kDa, with the remaining material (34%) < 2 kDa. This < 2 kDa fraction likely consisted of monomers that were not polymerized or removed by dialysis. The MW distribution obtained in this study was consistent with a previous study using the same synthesis method [19].

Based on titration results from a pH of 7–10, the buffer capacity of the PoB (pKa ~ 7.5) was 2.2 times as high as that of 50 mM PBS (pKas of 7.2 and 12.3) commonly used in MECs [10,11] (Fig. S2). At the start of the titration for the PoB there was a slow increase in pH from 7 to 9, and then a rapid increase in pH from 9 to 10 indicating loss of the buffer capacity. The polymer functioned differently than the small-MW PBS buffer in response to base addition due to the complexity of

ionization of the polymer monomers and electric repulsion between adjacent charged monomers [26,27]. This repulsion was reported to contribute to better deprotonation under high pHs. The titration curve of PoB (pKa ~ 7.5) obtained in this study was consistent with the titration of PDMAEMA in deionized water reported by a previous study [28]. The buffer capacity of PoB and PBS were similar when the pH increased from 7 to 12.

The PoB was effectively retained using an AEM (Fig. 1A), with  $98 \pm 2\%$  of the buffer retained in the passive diffusion test (no current). The small loss of buffer was likely due to the diffusion of the <2 kDa fraction of the PoB through the membrane. However, the PBS retention of only  $39 \pm 0.4\%$  was obtained with AEM after 16 days, indicating appreciable loss of buffer through AEM driven by a concentration gradient. Compared with the minimum curve calculated (Fig. 1A), the PBS was better retained by AEM, indicating equilibrium was not reached before water replacement (2 days).

Linear sweep voltammetry (LSV) was conducted for SS mesh cathode buffered with PoB (data not shown). No extra



**Fig. 1 – The percentage of PoB or phosphate (PBS) buffers retained in (A) diffusion tests using an AEM (without current) and (B) in MECs. The dashed line (minimum) shows the result that would be based on equilibrium between the two chambers each time the counter electrolyte solution was changed (eq. (2)). (B) The retention of PBS in MECs with AEM.**



peaks were found for PoB solutions indicating negligible electrochemical interactions between PoB and the cathode.

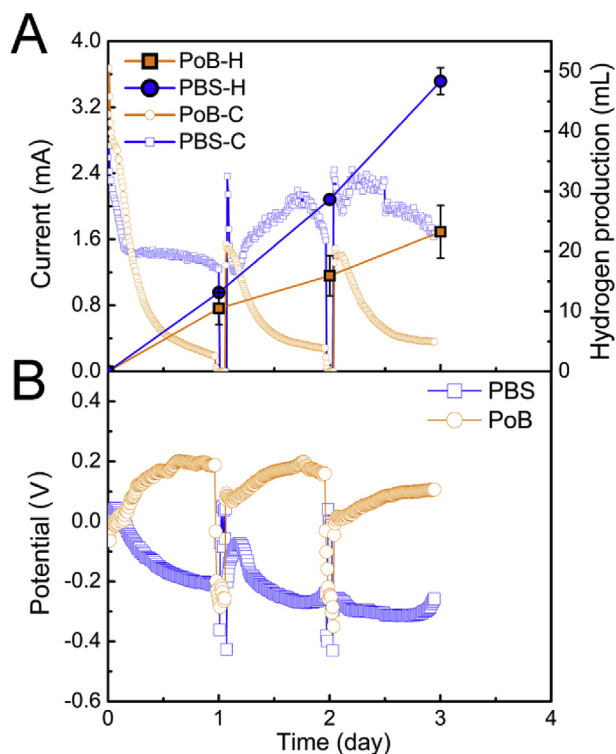
### Hydrogen production in MECs for a single cycle

Hydrogen production in the MECs with PBS were 25% higher ( $\text{HPR} = 0.5 \pm 0.1 \text{ m}^3\text{-H}_2 \text{ m}^{-3} \text{ d}^{-1}$ ), and current was 26% higher ( $I_{\text{avg},90} = 1.5 \text{ mA}$ ) than that with PoB ( $\text{HPR} = 0.4 \pm 0.1 \text{ m}^3\text{-H}_2 \text{ m}^{-3} \text{ d}^{-1}$ ,  $I_{\text{avg},90} = 1.2 \text{ mA}$ ) on day 1 (Fig. 2A). These higher rates were obtained with the PBS even though the buffer capacity (Fig. S2) and conductivity of the PoB solutions were both higher than those of the PBS. Thus, having a better buffered catholyte with a higher conductivity was not sufficient to ensure better electrochemical performance.

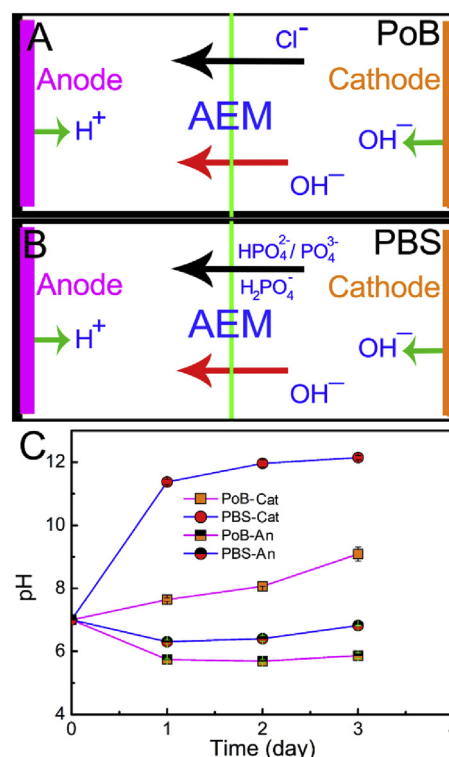
The MECs with the PoB had less of a change in pH than those with PBS. The pH with PBS substantially increased ( $\text{pH} = 11.4 \pm 0.1$ ) after the first cycle (day 1), consistent with pH changes reported in a previous study using this concentration of PBS [29]. There was much less of a rise in pH with PoB after the first day ( $\text{pH} = 7.6 \pm 0.1$ ). The higher pH of PBS than PoB resulted in a higher overpotential of 0.2 V (eq. (3)). The much more rapid rise in pH of the PBS was due to a combination of loss of phosphate ions (36%) due to transport through the membrane, and decreased buffer capacity with  $\text{OH}^-$  ion

production at the cathode. In contrast, little PoB would be transported across the membrane due to its high MW, and it had twice the buffer capacity of PBS, so the pH change with the PoB was relatively smaller than that of PBS. Based on these changes in the pH, it was reasoned that on day 1, charge was balanced with the PoB primarily by transport of chloride ions through AEM (Fig. 3A), while for PBS the main ions transported were negatively charged phosphate ions (Fig. 3B). Therefore, though the calculated overpotential using the Nernst equation at the final pH conditions was calculated for the PBS to be 0.2 V higher than that of the PoB ( $\text{pH} = 11.4$  for PBS vs  $\text{pH} = 7.6$  for the PoB), the electrochemical charge balance by phosphate ions that could pass through the AEM was more important for improving current and hydrogen production than maintaining low catholyte pH. This indicated that the ion transport played a more important role than buffer capacity or conductivity in the MECs.

The differences in hydrogen production (day 1) with the two different buffers was consistent with the measured anode potentials (Fig. 2B). The anode potential with PBS became more negative, while the PoB anodes became more positive. Since the applied voltage was constant as 1.1 V, the more negative anode potential for PBS would result in a more negative cathode potential, and therefore a higher current according to the Butler-Volmer equation. The more positive anode potential in MECs with PoB was likely due to the low anolyte pH of  $5.7 \pm 0.1$ , compared to the anode potential with



**Fig. 2 – (A) Current (C, open symbols) and hydrogen production (H, filled symbols) using PoB or phosphate (PBS) buffers in MECs with AEMs in three, one-day cycles. The anolyte was replaced daily, while the catholyte was not. (Data for the current is from one experiment, while the hydrogen production is based on four experiments with replicate reactors). (B) The anode potential of the MECs with PoB and PBS.**



**Fig. 3 – Schematic showing the main ions that are expected to be transported through the AEM with (A) PoB and (B) PBS. (C) Changes in the pH of the anolytes (-An) and catholytes (-Cat) in MECs with AEMs.**

PBS (pH of  $6.3 \pm 0.1$ ) (day 1, Fig. 3C). A pH of  $\sim 6.0$  or lower is known to inhibit current generation by exoelectrogenic bacteria [30–32]. The higher anolyte pH in MECs with PBS was due to the transport of phosphate ions from the catholyte through the AEM (Fig. 3B), which contributed to a more stable anolyte pH. The higher HPR obtained here with PBS compared to PoB due to a higher anolyte pH was consistent with a two previous studies showing that a stable anolyte pH was more beneficial for hydrogen production than controlling the catholyte pH [33,34].

### Hydrogen production in MECs over 3 cycles

Hydrogen gas production was also evaluated over 3 cycles in order to study the impact on gas production when the catholyte was not replaced, and thus there was little buffering capacity of both PoB or PBS. In addition, most of the PBS would have been transported out of the catholyte as well. The rates of hydrogen production with PBS increased over the second and third cycles (days 2 and 3), with a  $0.6 \text{ m}^3\text{-H}_2 \text{ m}^{-3} \text{ d}^{-1}$  (day 2,  $I_{\text{avg},90} = 1.7 \text{ mA}$ ) and  $0.8 \text{ m}^3\text{-H}_2 \text{ m}^{-3} \text{ d}^{-1}$  (day 3,  $I_{\text{avg},90} = 2.1 \text{ mA}$ ). In contrast, the rates of hydrogen production decreased for PoB to  $0.2 \text{ m}^3\text{-H}_2 \text{ m}^{-3} \text{ d}^{-1}$  (day 2,  $I_{\text{avg},90} = 0.6 \text{ mA}$ ) and  $0.3 \text{ m}^3\text{-H}_2 \text{ m}^{-3} \text{ d}^{-1}$  (day 3,  $I_{\text{avg},90} = 0.7 \text{ mA}$ ). Overall, based on four tests using replicate reactors, the average hydrogen production was  $48 \pm 3 \text{ mL}$  using PBS, and  $23 \pm 5 \text{ mL}$  using PoB. The conversion of current into hydrogen gas was high for tests with both buffers, with CCEs of  $98 \pm 2\%$  for PoB and  $88 \pm 1\%$  for PBS, indicating that loss of hydrogen was not a decisive factor in the differences in the HPRs.

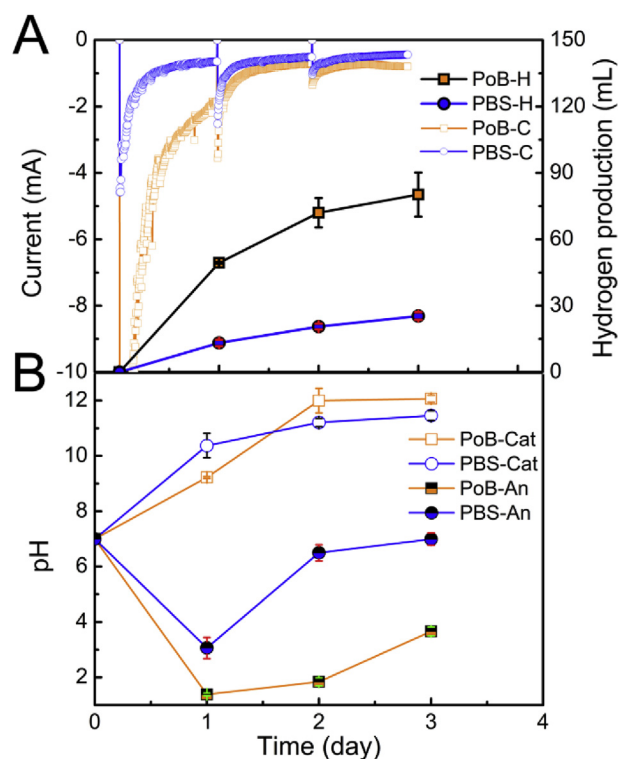
For PBS, the rapid rise in catholyte pH, combined with the loss of phosphate ions ( $\sim 70\%$ , Fig. 1B) meant that charge would have to be balanced by  $\text{OH}^-$  ion transport, as these ions were now present at a bulk concentration of  $16 \text{ mM}$  when the pH reached 12.2. The conclusion of dominant transport of  $\text{OH}^-$  ions through the AEM at high catholyte pH was consistent with that in another study proposing that the dominance of  $\text{OH}^-$  transport under steady conditions [35]. For the PoB solution, chloride ions likely dominated ion transport due to the lower pH of  $\sim 9$  ( $0.01 \text{ mM}$  of  $\text{OH}^-$ ) (Fig. 3B). The different ions transported with the PBS and PoB therefore can explain why the pH of the anolyte was higher with PBS (pH = 6.8, day 3) than with PoB (5.8), even though proton production would have been higher in the MECs with PBS than PoB due to the higher current.

The anolyte pH of the MECs with PBS continued to increase in days 2 and 3 due to the hydroxide ion transport (Fig. 3B), leading to more negative anode potentials (Fig. 2B), consistent with an increase in HPRs and current. The MECs with PBS on days 2 and 3 started with larger pH gradients between anode and cathode ( $\Delta\text{pH} = \sim 5.6$ ) than they had on day 1, resulting in additional overpotential of  $0.3 \text{ V}$  ( $0.06 \text{ V}$  of overpotential per pH unit [36]). This suggested that stabilizing anolyte pH was more important than the overpotential produced by the pH gradient. Even though the previous studies [13,14] suggested that lowest cathode overpotential of  $0.05 \text{ V}$  was achieved at pH 6.2 for PBS due to a weak acid catalysis effect, the increased HPR corresponded to increased anolyte pH indicating that  $\text{OH}^-$  ion transport that stabilized anolyte pH was more important than weak acid catalysis.

### Hydrogen production tests in EHCs with AEM

In order to examine the impact of the buffer on HER in the absence of adverse conditions that impacted current generation by the biotic anode, hydrogen production was measured using the two buffers in abiotic EHCs at a fixed cathode potential ( $-1.2 \text{ V}$ ). Under these conditions, current and hydrogen generation are limited only by performance of the cathode and not ion transport or anode potentials. The average rate of hydrogen production with the PoB was  $0.7 \pm 0.1 \text{ m}^3\text{-H}_2 \text{ m}^{-3} \text{ d}^{-1}$  ( $I_{\text{avg},90} = 2.6 \pm 0.2 \text{ mA}$ ) in EHCs, which was 1.3 times higher than that for PBS ( $0.3 \pm 0.1 \text{ m}^3\text{-H}_2 \text{ m}^{-3} \text{ d}^{-1}$ ,  $I_{\text{avg},90} = 0.9 \pm 0.1 \text{ mA}$ ) (Fig. 4A). This result was different with the hydrogen production obtained in MECs, where twice as high HPR was achieved by using PBS ( $0.7 \pm 0.1 \text{ m}^3\text{-H}_2 \text{ m}^{-3} \text{ d}^{-1}$ ) compared to PoB. There was nearly complete recovery of hydrogen gases with both PoB (CCE =  $96 \pm 4\%$ ) and PBS (CCE =  $90 \pm 5\%$ ), consistent with the results from MECs, indicating that a large loss of hydrogen gas was not a factor in the HPR.

In EHCs, the higher buffer capacity of PoB than PBS accounted for the increased HPR, as the pH remained lower using PoB ( $9.2 \pm 0.2$ ) than using PBS ( $10.4 \pm 0.2$ , day 1) (Fig. 4B). The higher HPR for PoB is consistent with a weak acid catalysis effect [13,14]. The different results for the MECs and EHCs further supported the conclusion that the low anolyte pH of  $<6$  was the primary reason for the lower HPR ( $0.3 \text{ m}^3\text{-H}_2 \text{ m}^{-3} \text{ d}^{-1}$ ) in the MECs with PoB, compared to that with PBS (HPR of



**Fig. 4 – (A) Hydrogen production (-H, filled symbols) and current (-C, open symbols) in an EHC, with PoB or PBS catholytes, at a fixed cathode potential of  $-1.2 \text{ V}$ . The negative current indicates a reduction reaction. (B) Changes in pH of the anolytes (-An) and catholytes (-Cat) in electrochemical half cells with PoB or PBS.**

$0.7 \text{ m}^3\text{-H}_2 \text{ m}^{-3} \text{ d}^{-1}$ ). The lower HPR in EHCs with PBS than that with the MECs with PBS was due to the more positive cathode potential in EHCs ( $-1.2 \text{ V}$ ) than  $-1.4 \text{ V}$  (MECs, an anode potential of  $-0.3 \text{ V}$ ).

There was a decrease in the current and HPR for EHCs with both PoB and PBS in days 2 and 3, likely due to the increase in catholyte pH (PoB, 7 to 12.1 and PBS, 7 to 11.4). The increase in the bulk pH (Fig. 4B) resulted in an increase in overpotential, calculated using the Nernst equation, to be as high as  $0.3 \text{ V}$  with the pH increase from 7 to 12.

The conductivity of anolyte of EHCs with PoB was four ( $\sim 42 \text{ mS cm}^{-1}$ , day 1) and two ( $\sim 21 \text{ mS cm}^{-1}$ , day 2) (Fig. 5A) times as high as the corresponding anode conductivity in MECs ( $\sim 11 \text{ mS cm}^{-1}$ ) (Fig. 5B). With hydroxide and chloride ions as the anions in the cathode chamber, this increase in anolyte conductivity indicated that chloride ions likely dominated the transport of ions through the AEM in EHCs with PoB (Fig. 3B). Separate tests, which showed an accumulation of chloride concentration (178 mM in day 1 and 112 mM in day 2, Fig. S3) in anolyte, support the dominant transport of chloride ions under these conditions, consistent with the schematic shown for ion transport using PoB (Fig. 3A).

#### MECs with PoB without catholyte over 15 cycles

To examine the impact on hydrogen generation after loss of the buffering capacity of the PoB (due to the rise of the pH),

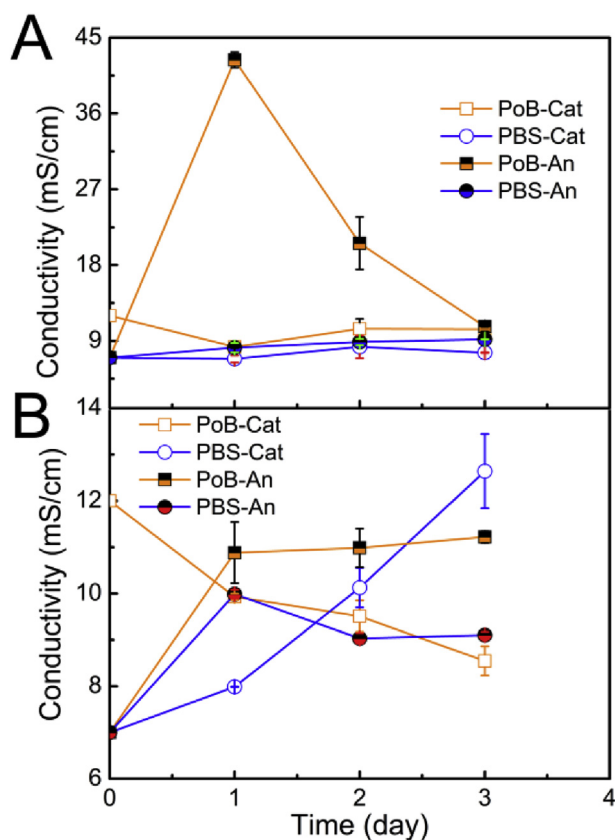


Fig. 5 – Conductivities of the anolytes (-An) and catholyte (-Cat) over three days with one day cycles, with the anolyte replaced daily in (A) EHCs and (B) MECs.

hydrogen generation was studied in a daily batch cycle after a long period of time (15 cycles) without catholyte replacement. The HPR reached  $0.7 \pm 0.1 \text{ m}^3\text{-H}_2 \text{ m}^{-3} \text{ d}^{-1}$  ( $I_{\text{avg},90} = 1.4 \pm 0.3 \text{ mA}$ , Fig. 6), which was similar to that produced in the MECs with PBS on day 3 ( $0.8 \text{ m}^3\text{-H}_2 \text{ m}^{-3} \text{ d}^{-1}$ ) and 166% higher than the HPR of MECs with PoB at a lower pH (day 1–3,  $0.3 \text{ m}^3\text{-H}_2 \text{ m}^{-3} \text{ d}^{-1}$ ). The high catholyte pH ( $12.2 \pm 0.3$ ) and conductivity ( $17.4 \pm 0.4 \text{ mS cm}^{-1}$ ) measured at the start of this test were maintained over the batch cycle, with a final pH of  $12.3 \pm 0.2$  and conductivity of  $17.6 \pm 0.3 \text{ mS cm}^{-1}$ , indicating a steady state was reached for MECs catholyte. This final pH was five pH units above the measured pKa, so the buffer capacity of the PoB was negligible.

The anolyte pH was also higher here ( $6.9 \pm 0.1$ ) in the cycle than that with PoB in days 1–3 ( $\sim 5.8$ ), and this higher pH was comparable with that ( $\sim 6.8$ ) in MECs with PBS after 3 days. The high anolyte pH obtained after many cycles indicated that hydroxide ion transport from the catholyte was able to better maintain the pH in the anolyte pH, which is consistent with the more negative anode potentials (Fig. 6), which indicated better anode performance.

#### Outlook

The different effects of the PoB buffer in the EHCs, which had improved hydrogen generation with the PoB compared to PBS, and in the MECs where the anolyte pH was not well maintained and hydrogen production was low compared to PBS, help to explain different observations among some previous MEC studies. For example, electrochemical tests, such as cyclic voltammetry [14,37], chronopotentiometry [13] and resistance analysis [5] consistently show that addition of buffer can enhance cathode performance by reducing overpotential through weak acid catalysis, increasing conductivity and serving as charge carrier. However, these conclusions were different from those of an MEC study which showed a non-buffered saline catholyte solution had a higher hydrogen production than a buffered catholyte solution using PBS [15]. Although the mechanism for better performance with saline solution was not well understood in that study, our results suggest that the MEC result was likely due to a favorable anode

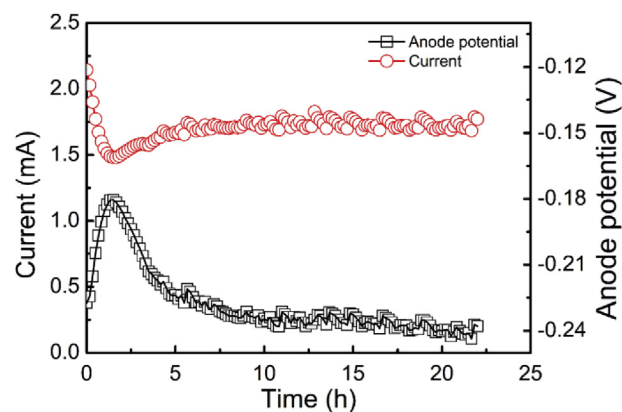


Fig. 6 – Current and the anode potentials of MECs with PoB over a single, 24-h cycle after 15 cycles without catholyte replacement.



pH due to hydroxide ion transport as a result of the high pH of the catholyte with NaCl. In another study, MECs were studied without catholyte (100 mM PBS) replacement over 10 cycles but using CEMs, which would not facilitate hydroxide ion transport [29]. They observed a reduction in HPR from 0.2 to  $0.1 \text{ m}^3\text{-H}_2 \text{ m}^{-3} \text{ d}^{-1}$  over time, different from the result of increase in HPR in this study. Their result of reduction in HPR was likely due to a lack of  $\text{OH}^-$  or negatively charged buffer ions transport through the CEM compared to the AEM.

The importance of the hydroxide ion transport for buffering the anolyte pH suggests that catholyte buffer replacement may not be needed. If PBS or other negatively charged buffers are used with AEMs, the loss of the buffer will occur unless it is constantly replenished. This loss of buffer capacity was clearly shown here. Moreover, buffering the catholyte can impair  $\text{OH}^-$  ion transport into the anolyte resulting in a lower HPR, as shown here by a 38% decrease in HPR with PBS (pH = 7) at day 1 compared to 70% loss of PBS and a high catholyte pH at day 3 in MECs. When the buffering capacity was lost in the MECs with PoB (catholyte pH of 12.3) without catholyte replacement (after 15 cycles), the HPR of  $0.7 \pm 0.1 \text{ m}^3\text{-H}_2 \text{ m}^{-3} \text{ d}^{-1}$  was comparable to that with PBS (pH = 12.2) on day 3. These two observations support that operating MECs using high catholyte pH strategy would be more favorable than maintaining catholyte pH at a neutral pH when a poorly buffered solution, such as an actual domestic wastewater, is treated in MECs. The cost of a PBS buffer in batch-mode MECs was estimated to be  $3.39 \$ \text{ m}^{-3}\text{-H}_2$  in a previous study, almost 8 times as high as the value of hydrogen gas ( $0.42 \$ \text{ m}^{-3}\text{-H}_2$ ) produced [29]. In addition, using PBS in the catholyte would result in its undesirable loss into the wastewater, leading to potential environmental issues.

## Conclusions

The effect of buffer capacity and ion transport were examined in this study by comparing MECs and EHCs with either a large-MW PoB, which was well retained by an AEM ( $98 \pm 2\%$ ), or PBS which readily passed through the AEM. A hydrogen production of  $0.7 \pm 0.1 \text{ m}^3\text{-H}_2 \text{ m}^{-3} \text{ d}^{-1}$  was produced in MECs with PBS, which was twice as high as that with PoB, despite the higher buffer capacity of the PoB. It was concluded that the poorer performance of the PoB was due to the decrease in the anolyte pH with the PoB. In abiotic EHCs, however, where current was generated by setting the cathode potential, the HPR was 133% higher for PoB than PBS. The increased hydrogen production for PoB in EHCs was due to the better buffer capacity and retention of the PoB. Hydroxide ion transport at high catholyte pH was needed to stabilize anolyte pH and avoid an adverse impact on the anode activity in MECs, while increasing buffer capacity and conductivity can enhance cathode performance by weak acid catalysis when the anode performance did not constrain current generation in EHCs. In addition, the catholyte pH ( $12.2 \pm 0.3$ ) and conductivity ( $17.4 \pm 0.4 \text{ mS cm}^{-1}$ ) reached a steady state in MECs with PoB after long term without catholyte replacement (15 cycles), producing a high hydrogen production of  $0.7 \pm 0.1 \text{ m}^3\text{-H}_2 \text{ m}^{-3} \text{ d}^{-1}$ . This indicated that the catholyte buffer solution replacement was not needed in the MECs examined here,

which could lower the costs and simplify operational conditions.

## Acknowledgements

This work was supported by Award OSR-2015-SEED-2450-01 from the King Abdullah University of Science and Technology (KAUST).

## Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.ijhydene.2017.12.074>.

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