1	Supporting information		
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3	The importance of OH <sup>-</sup> transport through anion exchange membrane		
4	in microbial electrolysis cells		
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6	Y. Ye and B. E. Logan*		
7	Department of Civil and Environmental Engineering, The Pennsylvania State University,		
8	University Park, PA, 16802, USA		
9	*Corresponding author: Phone: 814-863-7908, Fax: 814-863-7304, Email: blogan@psu.edu		
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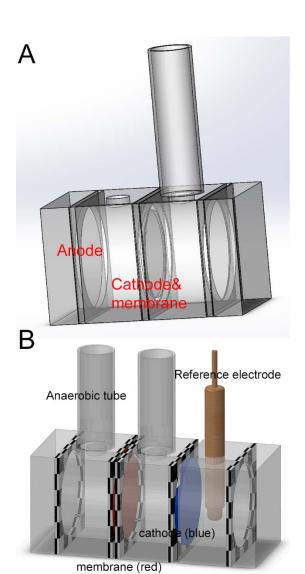


Fig. S1 (A) the structure for MEC (4 cm wide) with 2 cm electrode spacing, resulting in anode and cathode volume of 13 mL; (B) electrochemical half cells with anode chamber of 13 mL and cathode chamber of 26 mL. The cathode was incised to ventilate produced hydrogen gas from reference electrode chamber to the chamber with anaerobic tube for gas sample collection. A Pt plate was used as counter electrode, and SS mesh as working electrode, leading to an electrode spacing of 4 cm. The anolyte was a 10 mM sodium bicarbonate solution with 2 g/L sodium acetate (pH = 7 and conductivity of 7 mS/cm). The cathode potential was fixed at -1.2 V

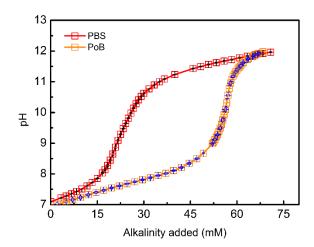


Fig. S2 Titration curves showing the buffer capacities of the PBS and PoB solutions.

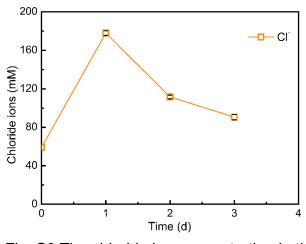


Fig. S3 The chloride ion concentration in the analyte in EHCs with PoB

## 33 Details for MW distribution test of the polymer buffer

- 34 The MW distribution test was carried out using the protocol below (Bruce E. Logan, Environmental Transport
- 35 *Process, John Wiley & Sons, 2012, p.71*):
- 36 1. The concentration of the original polymer buffer solution was tested as  $C_0$ . The total volume was  $V_0$ .
- 37 2. Permeate was collected from the ultrafiltration cell with different ultrafiltration membranes with cut-off of
- 2 K, 10 K, 30 K and 100 K. The volume and its TOC concentration was monitored. A set of volume and TOC
- can be obtained as  $V_1$ ,  $V_2$ ,  $V_3$ , .... (L) and the corresponding TOC concentration of  $C_1$ ,  $C_2$ ,  $C_3$ , .... (mg L<sup>-1</sup>)
- 40 3. The cumulative mass of TOC can be calculated using the volumes and the TOC concentration as:
- $41 M_i = \sum_{i=1}^{i} V_i C_i$
- 42 (1)
- 4. The cumulative volume of permeate can be calculated as:
- $V_{a,i} = \sum_{1}^{i} V_{i}$
- 45 (2)
- 46 5. The TOC concentration could pass through the ultrafiltration  $C_{r,0}$  can be obtained by non-linear fitting using
- 47 cumulative masses and volumes:
- 48  $M_i = \frac{C_{r,0}}{V_0^{P_c-1}} [V_0^{P_c} (V_0 V_f)^{P_c}]$
- 49 (3)
- where  $C_{r,0}$  is the original concentration that can pass through the membrane,  $P_c$  is filtration coefficient, and
- V<sub>f</sub> is the filtrate volume.
- 52 6. The percentage of the chemicals has MW smaller than the membrane pore size is:
- $p_{smaller} = \frac{c_{r,0}}{c_0} \times 100\%$
- 54 (4)
- 7. The percentage of the chemicals has MW larger than the membrane pore size is:
- 56  $p_{larger} = \left(1 \frac{C_{r,0}}{C_0}\right) \times 100\%$
- 57 (5)

8. With a set of membranes with different cut off, the distribution can be obtained.

59 60

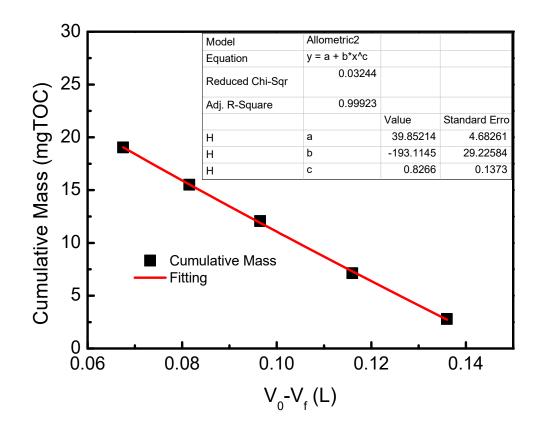
An example of 100 K membrane:

61 V<sub>0</sub>=151 mL, C<sub>0</sub>=260 mg/L, V<sub>0</sub>=151 mL

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Filtrate volume, V <sub>f</sub> (mL)	TOC (mg/L)	Cumulative mass (mg)	
15	186	2.8	
30	217	7.1	
49.5	253	12.1	
64.5	229	15.5	
78.5	252	19.0	

62 The data were plotted using Cumulative mass vs. (V<sub>0</sub>-V<sub>f</sub>), and then fitted using non-linear fitting

63 method, Allometric2, in the Origin 8.5 pro.



64

The P<sub>c</sub> and C<sub>r,0</sub> obtained from fitting:

66 C<sub>r,0</sub>=268 mg/L

67 Pc=0.83

The percentage (<100 KDa) is:

69 
$$p_{smaller} = \frac{c_{r,0}}{c_0} \times 100\% = 100\%$$