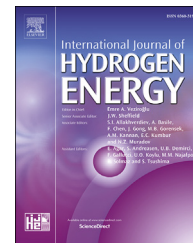




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Short Communication

Comparison of cathode catalyst binders for the hydrogen evolution reaction in microbial electrolysis cells



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ABSTRACT

Nafion is commonly used as a catalyst binder in many types of electrochemical cells, but less expensive binders are needed for the cathodes in microbial electrolysis cells (MECs) which are operated in neutral pH buffers, and reverse electro dialysis stacks (RED), which use thermolytic solutions such as ammonium bicarbonate. Six different binders were examined based on differences in ion exchange properties (anionic: Nafion, BPSH20, BPSH40, S-Radel; cationic: Q-Radel; and neutral: Radel, BAEH) and hydrophobicity based on water uptake (0%, Radel; 17–56% for the other binders). BPSH40 had similar performance to Nafion based on steady-state polarization single electrode experiments in a neutral pH phosphate buffer, and slightly better performance in ammonium bicarbonate. Three different Mo-based catalysts were examined as alternatives to Pt, with MoB showing the best performance under steady-state polarization. In MECs, MoB/BPSH40 performed similarly to Pt with Nafion or Radel binders. The main distinguishing feature of the BPSH40 was that it is very hydrophilic, and thus it had a greater water content (56%) than the other binders (0–44%). These results suggest the binders for hydrogen evolution in MECs should be designed to have a high water content without sacrificing ionic or electronic conductivity in the electrode.

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Introduction

Many new types of microbial electrochemical technologies (METs) are being developed for the generation of useful products, including electricity, biofuels, desalinated water, and high value chemicals [1,2]. Microbial fuel cells (MFCs) use exoelectrogenic microorganisms on the anode to oxidize different organic and inorganic chemicals, and catalysts on the cathode for oxygen reduction for spontaneous electricity production. Microbial electrolysis cells (MECs) also use exoelectrogenic bacteria on the anode, but an additional voltage must be applied to drive hydrogen production on the cathode. Due to the favorable anode potential, only ~0.2 V is needed for hydrogen evolution in an MEC, compared to >1.2 V in a conventional electrolyzer with water splitting at the anode [3]. Microbial reverse electro dialysis cells (MRECs) incorporate both exoelectrogenic bacteria on the anode and reverse electro dialysis (RED) stacks to simultaneously capture energy from chemicals in the anolyte and energy from salinity gradients in the RED stack [4]. The cathode reaction in an MREC can be either oxygen reduction, for the production of electricity [5,6], or hydrogen evolution [4]. Natural salinity gradients (e.g. freshwater and seawater) can be used in the RED stack, or engineered salinity gradients can be used to capture energy in waste heat using thermolytic salts such as ammonium bicarbonate [7].

Inexpensive materials are needed in order to make electricity or hydrogen production economically viable for these different METs [8–11]. Platinum is an excellent catalyst for oxygen reduction or hydrogen evolution, but it is too expensive for use in METs [12–14]. Examples of inexpensive alternatives that have been developed include activated carbon for oxygen reduction [15,16], and Mo-based catalysts for hydrogen evolution [17,18]. Binders are needed to hold the catalysts in close contact with the current collector and to establish favorable mass transport conditions for all involved species (ionic conductivity, water and gas permeability, etc.) in the three-dimensional architecture of the electrode assembly. Nafion is often used as a catalyst binder due to its long history in fuel cell applications, its high performance in many types of electrochemical cells, and its wide availability, but the cost of this binder can be quite expensive relative to other polymers, and therefore METs must be developed that use less expensive binders [9]. For oxygen reduction catalysts in MFCs, binders that have better oxygen reduction rates are typically composed of hydrophilic polymers [19]. The best performing binder in an MFC had a high water uptake of 50% [polystyrene-*b*-poly(ethylene oxide)], but this block copolymer binder would be too expensive for MFC applications. In hydrogen fuel cells, where the only positively charged species are protons, increasing the ion exchange capacity (IEC) of the binder should improve performance [20]. However, in MFC tests with phosphate buffers, increasing the IEC by sulfonating Radel to facilitate cation transport resulted in decreased cathode performance [21].

Relatively little work has been conducted on cathode binders for hydrogen gas evolution in MECs. The main difference between these MFC and MEC systems is that the binder for a MFC must enable a three phase reaction due to the

need for gas-phase oxygen transfer to the catalyst, but in MECs only a two phase reaction occurs between the solid catalyst and water. In order to determine the more optimal properties of a binder for use in MECs, several different binders were examined based on their differences in ion exchange properties and hydrophilicity (Table 1). For the cation exchange polymers, two different biphenyl poly(arylene ether sulfone) (BPSH) samples (BPSH 20, 20 mol % disulfonated comonomer; and BPSH 40, 40 mol % disulfonated comonomer) were chosen based on their high hydrophilicity [22,23], while S Radel (poly(sulfone) Radel[®]) and Nafion[®] were examined based on their previous use in MFCs [24]. Radel[®] and BAEH [poly(bisphenol A-co-epichlorohydrin)] were tested as examples of non-ionic polymers [19], while Q Radel (quaternary ammonium-functionalized Radel[®]) was used as a representative anion exchange polymer [25]. The performance of cathodes with the different binders was examined in single electrode experiments, whereby steady-state polarization curves were extracted from chronoamperometry, which has been shown to provide good agreement with subsequent performance in MECs [19,21,26]. Three different Mo-based catalysts were then examined as alternatives to Pt in abiotic steady-state experiments, and the best performing Mo-catalyst and binder were compared in both abiotic electrochemical tests and in MECs.

Methods

Cathode construction

The catalyst for each cathode was applied with 60 mg of carbon black with 10 wt% of the catalyst and 10 wt% of the binder, in 200 μ L of dimethylacetamide. After extensive mixing and ultrasonication, the catalyst ink was diluted with 200 μ L of additional solvent to achieve uniform coatings by paint brushing. The binders had different charges, ion exchange capacities (IEC), and water uptake (UP), and were purchased or made as previously described as indicated for each binder. The negatively charged binders were: BPSH20 (IEC = 1.2 meq/g, UP = 17%) [22] and BPSH40 (IEC = 1.7 meq/g, UP = 56%) [23]; S Radel (IEC = 1.8 meq/g, UP = 32%) [25]; Nafion[®] perfluorinated resin solution 5 wt. % (Sigma–Aldrich, 274704, IEC = 0.91 meq/g, UP = 30%) [21]. Q Radel (R-5500, M_w = 63 kg/mol, kindly donated by Solvay Advanced Polymers, LLC) was a positively charged binder [27]. The neutral binders were Radel (IEC = 0, UP = 0%) [21], and BAEH (IEC = 0, UP = 24%) [19]. Cathodes

Table 1 – Table of Binder properties.

Polymer	Charge	IEC (meq/g)	Water uptake (%)	Reference
Q Radel	+	2.0	44	[25]
Radel	0	0	0	[21]
BAEH	0	0	24	[19]
BPSH 20	–	1.2	17	[22]
Nafion	–	0.91	30	[21]
S Radel	–	1.8	32	[25]
BPSH 40	–	1.7	56	[23]

(12 cm², with an exposed surface area of 7 cm²) were made by applying the catalyst to a stainless steel mesh (type 304, mesh size 50 × 50; McMaster-Carr) current collector. A diffusion layer (commonly applied in MFCs) was added to the other side (air-facing) of the cathode for single electrode tests, made of polydimethylsiloxane (PDMS) to avoid water leakage and to block the outer side surface in order to achieve a defined working area [28].

Electrochemical tests

Cathode performance was examined in abiotic tests using a single-chamber, cube-shaped reactor with an electrolyte chamber 3 cm in diameter, and 4 cm long, a Pt mesh (6.25 cm²) counter electrode, and Ag/AgCl reference electrode (3 M KCl, 0.209 V versus a standard hydrogen electrode). Two different electrolytes were tested: a phosphate buffer used in many MFC and MEC tests (100 mM, 4.90 g NaH₂PO₄·H₂O, 9.16 g Na₂HPO₄) [29–33]; and 1 M ammonium bicarbonate (AmB), which has been used as the catholyte in MRECs [6,7]. Prior to single electrode experiments, the cathodes were conditioned with cyclic voltammetry for 10 cycles at 20 mV/s, over a range of –1.5 V to 0.5 V for tests in PBS, and from –1.2 V to 0.2 V in AmB, in order to ensure reproducibility of electrochemical response in subsequent steady-state tests with the final cycle shown as a representative scan. Scans (triplicate tests) were then collected at set potentials of –0.4 V to –1.5 V at 0.1 V increments for 3 min each in order to eliminate the contribution of capacitive currents. Three different Mo-based catalysts were compared to Pt: MoB, MoS₃ and Mo₂C [34,35] in the electrochemical cell using a standard Nafion binder [18].

MEC tests

Cathodes with the best alternative catalyst and binder were examined for performance in MECs (duplicate tests) for hydrogen production compared to a Pt catalyst with three different binders (BPSH 40, Nafion and S Radel). The anodes were graphite fiber carbon brushes that were first heat treated, and then acclimated in MFCs with air cathodes for multiple cycles, as previously described [36–38]. MFCs and MECs were fed an acetate (1 g/L) in a 50 mM phosphate buffer solution (PBS) medium containing (per liter): 2.45 g NaH₂PO₄·H₂O, 4.58 g Na₂HPO₄, 0.31 g NH₄Cl, 0.13 g KCl, 12.5 mL metal salts and 5 mL vitamins (pH 7; conductivity = 7.5 mS/cm) [39]. The MECs electrolyte chamber was 4 cm long and 3 cm in diameter, with a 5 mL tube anaerobic tube (sealed with a thick rubber stopper and an aluminum crimp top) connected to a gas bag as previously described [40]. A single chamber MEC was used here although two-chamber designs, which have a membrane between the two electrodes, can avoid hydrogen gas recycling [41,42]. Improvements in the cathode performance identified here will be applicable to either single- or two-chamber designs. The MEC electrolyte chamber was purged with N₂ gas prior to experiments.

MECs were operated with an applied potential of 0.9 V using a power supply (3646A DC Power Supply, Circuit Specialists Inc.), with the voltage measured across a 10 Ω resistor to determine the current. Performance was evaluated based on current, coulombic efficiency (CE) and treatability rate (TR).

CE was calculated as $CE = n_p/n_c$, where $n_p = F^{-1} \int_0^t I dt$ is the moles of electrons for the produced current (I), and n_c is the moles of electrons converted based on the acetate removal measured in terms of the change in the chemical oxygen demand of the solution (ΔCOD), calculated as $n_c = (\Delta COD N_e V_r) / M_s$, where $N_e = 4$ is the moles of electrons per mole of COD, V_r the volume of the reactor, and M_s the molecular weight of oxygen (32 g/mol). The treatability rate (TR) was used to evaluate the current relative to the energy consumption, where $TR = I_{AVG} / W_{el} = V_r \Delta COD / U_{app} t$, I_{AVG} is current averaged over the cycle [42], W_{el} the electrical energy input normalized to the COD removal, U_{app} the applied voltage, and t the cycle time. While hydrogen gas production was not measured, the maximum energy efficiency based on energy input, using an applied potential of 0.9 V, would be 137% if all the hydrogen gas was recovered [3]. Typical hydrogen gas recoveries and efficiencies for this type of reactor have been well described in previous studies [3,40,43].

Results and discussion

Electrochemical performance of different binders with Pt catalyst

The electrodes with different binders and a Pt catalyst had similar performance in 50 mM PBS in the low current region (<5 A/m²), but differences were appreciable at the higher current densities with the best performance obtained with Nafion or the BPSH40 binder (Fig. 1A). The lowest currents were produced using the non-charged Radel and BAEH binders. The QRadel and S Radel, which had opposite charges, had similar performance but both had high water uptake.

The same general trends in current production with the different binders were obtained using AmB at the different set potentials, although the currents were much larger than those in PBS (Fig. 1B). BPSH40 had slightly higher current densities on average than Nafion, but there were large deviations in the currents based on repeated experiments. The higher current in AmB compared to PBS was expected due to the deprotonation of ammonium ions, which contributes to high faradaic currents and increased hydrogen production [4,6,7,44]. The difference between the hydrophobic Radel and the rest of the binders was even more apparent in AmB than in PBS. For instance, electrodes prepared with Radel generated –20 mA (2.9 mA/cm² based on the exposed projected cathode area) at –1 V vs. Ag/AgCl, while all other binders resulted in currents between –55 and –95 mA.

Comparison of Mo-based catalysts to Pt

Of the three different Mo-based alternative catalysts, MoB produced the highest current, with slightly lower current produced with MoS₃ and Mo₂C, which were similar to one another (Fig. 2a). Pt had the highest current at potentials more negative than –0.7 V, with about double the current (27 vs. 13 mA) at –1 V than the MoB. In the higher currents region, MoB had between 100 and 200 mV higher overpotential than Pt, which was similar to previously reported results for RED stacks [4,5,45].

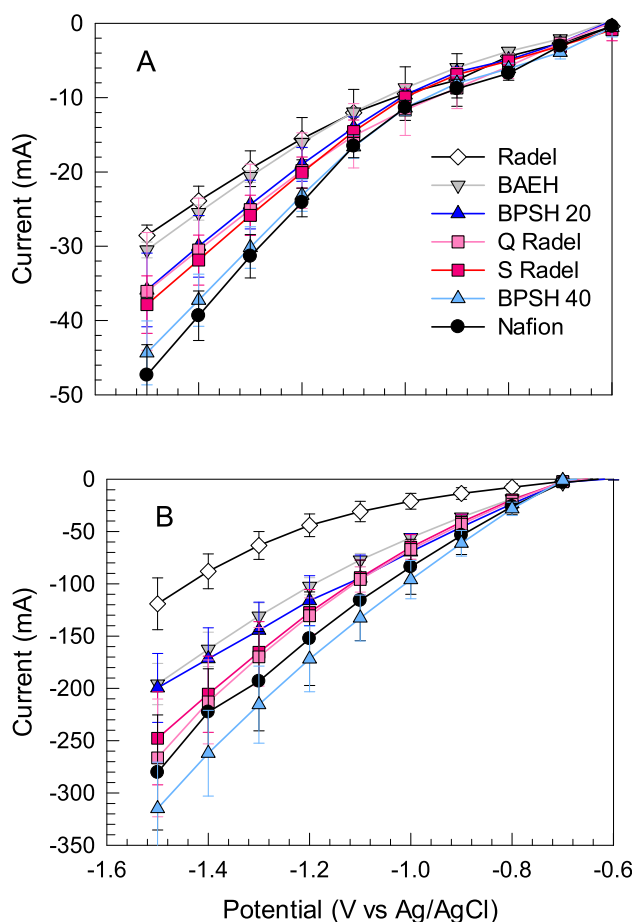


Fig. 1 – Comparison of binders in (A) 0.1 M phosphate buffer and (B) 1 M ammonium bicarbonate using steady-state polarization curves extracted from chronoamperometry tests.

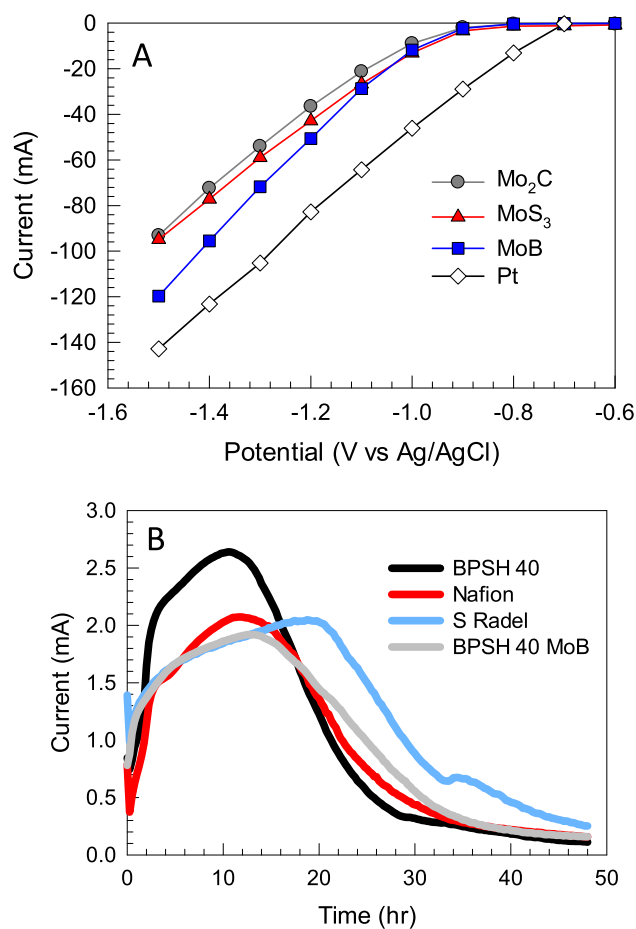


Fig. 2 – (A) Comparison of catalysts with Nafion binder in 0.5 M ammonium bicarbonate using steady-state polarization curves extracted from chronoamperometry tests. (B) Comparison of binders in MECs showing representative current profiles for a single batch cycle using the different binders.

MEC tests

The performance of cathodes with the best catalyst (MoB) and the best alternative binder to Nafion (BPSH40) was compared to cathodes with the Pt catalyst and three different binders (Nafion, BPSH40, and S Radel). The MECs were operated for 14 cycles to achieve steady cycles of current generation, with each cycle lasting around 48 h. Based on current generation over a cycle, MoB with the BPSH40 binder produced similar performance to Pt with a Nafion binder or the S Radel binder (Fig. 2b). The highest current was produced using the Pt catalyst and the BPSH40 binder, with lower current after ~20 h resulting from the more rapid consumption of the acetate. Note that in the abiotic electrochemical tests, the performance of Nafion and the S Radel binders was similar at the low currents produced in the MECs of up to only ~2.7 mA.

The total coulombs produced from the acetate exceeded that theoretically possible from stoichiometric conversion of acetate to current, as shown by CEs larger than 100%. The CEs were close to 100% for MoB/BPSH40 ($105 \pm 6\%$) and Pt/Nafion ($107 \pm 6\%$), but much larger for the other two cathodes ($122 \pm 13\%$, Pt/BPSH40 and $121 \pm 5\%$, S Radel). CEs larger than

100% result from hydrogen cycling, whereby H_2 evolving from the cathode is used by bacteria on the anode. Thus, on the basis of net current generation, no difference could be found between the cathode materials and binders due to hydrogen cycling. The TR, an alternative approach to evaluate the performance of an MEC, was used to evaluate the substrate removal rate relative to the applied voltage [46]. Based on the TRs, the performance of the cathodes with the different binders were all similar ($5.6 \pm 0.1 \text{ mg day}^{-1} \text{ V}^{-1}$, MoB/BPSH40 and $5.8 \pm 0.2 \text{ mg day}^{-1} \text{ V}^{-1}$, Pt/Nafion), which indicated the feasibility of using alternative catalysts even though they may result different current densities and thus hydrogen gas production rates.

Implications of the different electrode performance characteristics

Previous electrochemical tests and tests in MFCs with oxygen reduction at the cathode have found improved performance with unsulfonated and hydrophobic polymers such as bare

Radel, with the main improvement ascribed to charge shielding due to the charged binders [21]. However, in those tests current production was dependent on oxygen transfer to the cathode. In tests with PEM fuel cells, it was shown that increasing the IEC decreases oxygen permeability, which increases the concentration overpotential [47]. In MECs, however, hydrogen evolution proceeds through direct reduction of water (at neutral to more alkaline pH), and there is no need for diffusion of a gas-phase reactant to the cathode. This suggests that hydrogen production from the cathode in MECs will be more efficient when the accessible catalytic area for the cathodic reaction is increased. Thus, the binder with the highest water content and IEC would have the highest activity in MECs, but not in MFCs. Both the BPSH polymers tested had moderately high IECs of 1.2 meq/g (BPSH20) or 1.7 meq/g (BPSH40), and they both outperformed S Radel which had an IEC of 1.8 meq/g. The BPSH40 binder had a very large water uptake of 56%, suggesting water uptake was more critical to performance than IEC. However, binder chemistry is still relevant, as S Radel had a higher IEC and similar water content to Nafion, but Nafion performance was much better than S Radel. Although binder performance for hydrogen evolution is a result of several factors, the best performing binders in MECs are concluded to be different than those for MFCs.

The cost of cathodes is difficult to estimate given large uncertainties in the cost of materials in bulk compared to the small quantities used here. However, with some assumptions, the materials cost for the MoB catalyst and binder would be $\$42 \text{ m}^{-2}$ (8 g^{-1} for MoB, and $\$0.3 \text{ g}^{-1}$ for a typical aromatic polymer binder), compared to $\$830 \text{ m}^{-2}$ for Pt and Nafion (163 g^{-1} for Pt, and $\$3.6 \text{ g}^{-1}$ Nafion). The cost of the carbon black would be negligible ($\$0.1 \text{ m}^{-2}$), and a stainless steel current collector or carbon mesh or cloth could be used ($\$10 \text{ m}^{-2}$ for mesh, $\sim \$500 \text{ m}^{-2}$ for cloth). Thus, a MoB/BPSH40 layer on carbon mesh or stainless steel would provide a relatively inexpensive cathode configuration compared to those based on Pt and Nafion.

Conclusions

BPSH40 was the best alternative to Nafion as an electrode binder, likely due to its very high water uptake and IEC. MoB with the BPSH40 produced similar performance in MECs compared to electrodes containing Pt with Nafion, although the highest current densities were achieved using Pt with BPSH40. Thus, high water content is a favorable property for an alternative electrode binder to Nafion in MECs, and BPSH40 is an excellent low cost alternative to the other binder materials examined in this work.

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