



Investigation of ionic polymer cathode binders for microbial fuel cells

Tomonori Saito^{a,b}, Matthew D. Merrill^b, Valerie J. Watson^b, Bruce E. Logan^b, Michael A. Hickner^{a,*}

^a Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, United States

^b Department of Civil and Environmental Engineering, The Pennsylvania State University, University Park, PA 16802, United States

ARTICLE INFO

Article history:

Received 6 October 2009

Received in revised form

30 December 2009

Accepted 6 January 2010

Available online 15 January 2010

Keywords:

Sulfonated polysulfone

Nafion

Microbial fuel cell

Cathode

Catalyst binder

ABSTRACT

Microbial fuel cell (MFC) air cathodes examined here were made using poly(phenylsulfone) (Radel®) binders sulfonated to various ion exchange capacities (IECs). We examined the effect of increasing the IEC of poly(phenylsulfone) Radel binders from 0 to 2.54 meq/g on cathode performance using linear sweep voltammetry (LSV), impedance, and single chamber air-cathode MFC tests. Unsulfonated Radel, which is a non-ionic, hydrophobic polymer, showed the highest current in LSV tests and the lowest charge transfer resistance. Increasing the binder IEC resulted in a decreased current response in LSV tests and an increased charge transfer resistance from 8 to 23 Ω . It is proposed that the presence of sulfonate groups in the cathode binder impeded the oxygen reduction activity of the cathodes by adsorption of the sulfonate to catalytic sites and by impeding proton diffusion to the catalyst surface. The unsulfonated Radel binder produced the most stable performance, and eventually the highest power density, in MFCs operated over 20 cycles (55 days). These results suggest that the use of a non-ionic binder is advantageous in an MFC cathode to facilitate charge transfer and stable performance in the neutral pH conditions found in MFCs.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

Microbial fuel cells (MFCs) represent a promising renewable energy-production technology using a microbe-laden anode to liberate electrons from organic compounds [1]. Electricity-generating microbes (exoelectrogens) that are abundant in domestic wastewater, ocean sediments, and animal wastes, may afford a powerful approach for electricity production from excess organic substrates that promote microbial growth. The application of MFC technology to wastewater treatment could alter a wastewater treatment plant from an energy consumer to an energy producer. One wastewater plant in Toronto contained 9.3 times more energy in its wastewater compared to the energy needed for treatment of the wastewater [2] and various wastewaters in the US holds 17 GW of power, approximately the same amount of power currently used for the entire water infrastructure in the US [1].

One type of MFC constitutes an exoelectrogen-attached anode and a cathode containing an inorganic electrocatalyst, such as platinum. Exoelectrogens oxidize organic matter at the anode to liberate electrons to the electrical circuit. At the cathode, an electron acceptor (i.e. oxygen) is reduced on the surface of the electrocatalyst. In addition to the bacterial anode, the cathode plays a

crucial role in MFC performance. The electrochemical reactions to reduce oxygen to water at the cathode involve the impingement of electrons, protons, and oxygen at a catalytic site [1]. Nafion, a cation-conducting polymer, has typically been used to good effect as a binder for the cathode catalyst in MFCs to hold the catalyst in place on the current collector and to allow good wetting of the catalyst surface by the electrolyte buffer. However, there are few studies of other polymer binders in air-cathode MFCs and the ideal properties for cathode binder materials are not known.

Nafion has been the standard ion transport material, in both the membrane and electrode binder, for proton-exchange membrane fuel cells (PEMFC) due to its good proton-transport properties and its chemical and mechanical stability. Researchers have been seeking alternative membrane materials for PEMFCs because of Nafion's high cost and low temperature resistance. Among the many candidates for alternative inexpensive membranes for PEMFCs, sulfonated poly(sulfone) has shown promising water uptake, ion conductivity, and mechanical stability, and much research has been directed towards understanding its performance as an ion transport polymer in PEMFCs [3–5].

In this work, we investigated sulfonated and non-sulfonated poly(sulfone) as catalyst binders for the MFC cathode as an alternative to Nafion. Our group previously reported the use of PTFE, a non-ionic hydrophobic polymer, as an alternative binder to Nafion, a sulfonated, hydrophilic polymer [6], and similar performance was obtained with either material. From past work, it is not clear what type of material is most advantageous as a cathode binder in the unique environment of an MFC and what binder properties may

* Corresponding author at: 310 Steidle Building, Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, United States. Tel.: +1 814 867 1847; fax: +1 814 865 2917.

E-mail addresses: hickner@matse.psu.edu, mah49@psu.edu (M.A. Hickner).

Table 1
Properties and reaction conditions of sulfonated Radel R-5500.

	ClSO ₃ Si(CH ₃) ₃ /monomer unit (mol/mol)	Reaction time (h)	DS	IEC (meq/g)	Water uptake (%)	IEC _v (wet) (meq/cm ³)
Nafion	–	–	–	0.91	20	1.59
Radel	–	–	–	0	0	0
sRadel-0.34	0.5	24	0.14	0.34	3	0.43
sRadel-1.05	2.0	24	0.46	1.05	10	1.23
sRadel-1.59	1.5	96	0.73	1.59	22	1.68
sRadel-1.95	2.5	96	0.93	1.95	37	1.83
sRadel-2.54	5.5	96	1.28	2.54	70	1.93

¹H NMR condition: Bruker-Spectrospin, 400 MHz, *d*-DMSO. Water uptake was measured at room temperature without boiling treatment.

lead to the highest-performing and most stable cathodes. If MFCs follow the trends observed in PEMFCs [7], sulfonated poly(sulfone) binders with higher IECs would result in improved proton conductivity and better MFC cathode performance. It should be noted, however, that very different operational conditions exist between MFCs and PEMFCs. The MFC cathode interfaces with a millimolar buffer solution at pH 7, whereas a PEMFC cathode interfaces with a proton-exchange membrane at approximately pH 0 with an equivalent ion concentration in the solid polymer membrane of about 1 mol/L, based on the IEC of the membrane. Both the large pH and electrolyte ion concentration differences between PEMFCs and MFCs may result in quite different needs for cathode binders in each system. It is this difference in cathode characteristics that we explored in the reported work.

To measure the detailed effects that a series of binders with systematic property variations had on MFC cathode performance, we fabricated cathodes with poly(sulfone) catalyst binders that had a range of ion contents (IEC = 0–2.54 meq/g) and measured their electrochemical performance using linear sweep voltammetry (LSV), electrochemical impedance analysis (EIS), and MFC performance in single chamber air-cathode MFCs. Through these studies we seek to systematically understand the impact of ionic binders on the basic performance attributes of MFC cathodes and to determine how changes in the cathode materials affect overall cell performance. Characterization of sulfonated poly(sulfone)s with varying ion content will help to elucidate the most desirable balance of properties for binder materials including water uptake, ion content, and ionic conductivity for MFC cathodes. Additionally, we desire an inexpensive material for construction of MFC cathodes to replace Nafion.

2. Experimental

2.1. Synthesis of sulfonated poly(phenylsulfone) and its properties

Poly(phenylsulfone) (Radel R-5500, *M_w* 63 kg/mol) was kindly donated by Solvay Advanced Polymers, LLC. A series of sulfonated Radel R-5500 (sRadel) samples was prepared through post-sulfonation with trimethylsilyl chlorosulfonate (Aldrich, 99%) in tetrachloroethane (Aldrich, >98%) using a modified reference procedure [8]. Reaction conditions and properties of the prepared sRadels are summarized in Table 1. The degree of sulfonation (DS) and IEC were determined using ¹H NMR with *d*-DMSO solvent. Water uptake and IEC on a volumetric basis under wet conditions after immersion in liquid water (IEC_v(wet) (meq/cm³)) were measured following the reference procedure [9].

The membranes of the synthesized sRadels were obtained by casting polymer solution on glass plates from dimethylformamide (DMF, Mallinckrodt Analytical) and drying at 60 °C for 2 h, then 80 °C for 2 h in an atmospheric environment followed by drying in a vacuum oven at 80 °C for 5 h. The proton conductivities of the membranes were measured by two-probe electrochemical impedance spectroscopy (EIS) using a Solartron 1260A frequency

response analyzer coupled to a Solartron 1287 potentiostat. EIS was performed in water at 30 °C as previously described [10]. The proton conductivities in water (Fig. S1 in supporting information) demonstrated that the higher IEC sRadels possessed higher proton conductivity.

2.2. Cathode construction

Care was taken to produce cathodes with similar characteristics for this study, with the only change being the polymer binder for the cathode catalyst. The cathodes were fabricated via brush application of the binder solution containing platinum catalyst (0.5 mg/cm² Pt) with carbon black on wet-proofed carbon cloth (type B-1B, E-TEK) with four PTFE diffusion layers as previously described [11]. The catalyst (10% Pt on Vulcan XC-72, BASF Fuel Cell Inc.) was applied to each cathode with 400 μL of 5 wt% polymer solution per cathode. The Nafion solution (Aldrich) was composed of a methanol and water solvent mixture, and the other polymer solutions in this study were from DMF solvent. The applied binders were Nafion, Radel, sRadel-0.34, sRadel-1.05, sRadel-1.59, sRadel-1.95 and sRadel-2.54, where the number after sRadel denotes the corresponding IEC of the sample in units of meq/g.

2.3. Electrochemical measurements

Linear sweep voltammetry (LSV) of oxygen reduction was performed at 1 mV/s (Gamry Instrument model PC4/750, Warminster, PA) on the cathodes at 30 °C in an atmospheric environment. The reactor (13 mL volume) was filled with 200 mM phosphate buffer (PBS) (pH 7) without other nutrients and equipped with 7 cm² platinum disc counter electrode and an Ag/AgCl reference electrode (RE-5B, Bioanalytical Systems Inc.). The charge transfer resistance, *R_{ct}*, of each cathode was measured using electrochemical impedance spectroscopy (EIS) with the same potentiostat and reactor configuration as for LSV. Impedance measurements were conducted at 0.3 V (vs. NHE) over a frequency range of 10⁵–0.004 Hz with sinusoidal perturbation of 10 mV amplitude.

The log-linear portions of the LSV scans were fitted via linear regression to the Butler–Volmer equation

$$\log J = \log J_0 + \frac{\alpha n F}{2.303 RT} (E - E_0), \quad (1)$$

where *J* (A/cm²) is the measured current density, *J*₀ (A/cm²) is the exchange current density, *α* is the cathodic transfer coefficient, *n* is the number of electrons per reaction, *E* (V) is the working potential and *E*₀ (V) is the equilibrium potential. The equilibrium potential *E*₀ (V) of the oxygen reduction reaction was calculated according to

$$E_{O_2} = 1.228 - 0.0602 \text{ pH} + 0.0150 \log(p_{O_2}) = 0.796 \text{ V} \quad (2)$$

where *T* = 30 °C, pH 7, and the partial pressure for oxygen (*p*_{O₂}) was 0.2 atm.

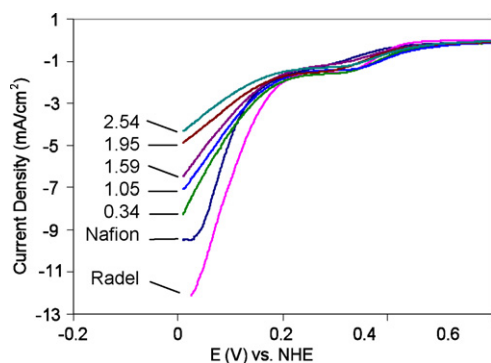


Fig. 1. LSV for cathodes with binders made from sulfonated Radel (numbers indicate IEC), Radel and Nafion (200 mM PBS, pH 7, 30 °C).

2.4. MFC measurements and calculations

Cube-shaped single-chambered MFC reactors machined to contain a cylindrical chamber (4 cm length and 3 cm diameter; liquid volume 28 mL) [12] were used to examine the MFC performance. All MFC reactors were equipped with ammonia-treated graphite brushes (25 mm diameter \times 25 mm length, 0.22 m² surface area) prepared as previously described [11]. Reactors were inoculated with the anode solution from another acetate-fed MFC reactor which had been running for several months with sodium acetate (1 g/L) in 50 mM PBS solution (4.576 g/L Na₂HPO₄, 2.452 g/L NaH₂PO₄·H₂O; pH 7.0). After several cycles of inoculation, the medium was switched from 50 mM PBS to 100 mM PBS solution (9.152 g/L Na₂HPO₄, 4.904 g/L NaH₂PO₄·H₂O; pH 7.0), consisting of 0.31 g/L NH₄Cl and 0.13 g/L KCl. The reactors were operated via fed-batch mode and the temperature was maintained at room temperature around 25 °C. Sodium acetate (0.5 g/L as acetate) was fed to reactors in each cycle.

The produced voltage (V) was monitored across a fixed resistance using a multimeter data acquisition system (2700 Keithley, USA). The electrode potentials were measured using a digital multimeter (22-813, Radioshack, USA) and Ag/AgCl reference electrode. The polarization and power density curves as a function of current density were taken after 15 min at each external resistance, 100–1000 Ω . Current ($I = V/R$), power ($P = IV$), and coulombic efficiency (CE) based on total input of acetate were calculated as previously described [13,14].

3. Results

3.1. Oxygen reduction performance of the cathodes

Significantly different electrochemical responses were observed among the samples with different binder compositions (Fig. 1), which suggests that the chemistry of the Pt catalyst boundary region as controlled by the polymer binder affected the electrochemical performance. In general, increased IEC of the sulfonated Radel binder produced a decrease in current density in the LSV. Two linear regions were observed in all Tafel plots, where the first linear slope was measured between 0.34–0.49 V vs. NHE (line 1) and the second linear portion occurred from 0.05–0.2 V vs. NHE (line 2) (Fig. 2). In the kinetic region (line 1), α and J_0 values of Nafion and sRadel cathodes were similar (Table 2). The unsulfonated Radel cathode had significantly larger α and smaller J_0 values indicating that cathodic transfer was facilitated with unsulfonated binder, but the surface area available for reaction was lower than in the sulfonated samples. In the higher current density region of line 2, there was a trend of decreasing α and increasing J_0 with increased sulfonation of the sRadel samples.

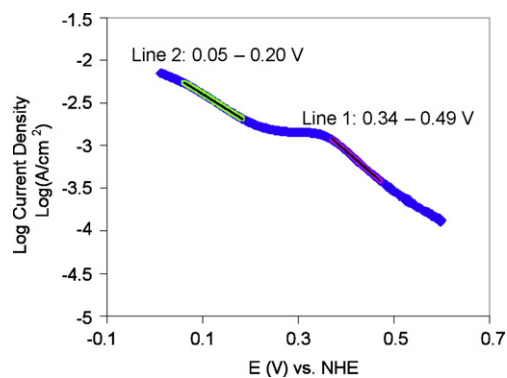


Fig. 2. Tafel plot for sRadel-1.05 from LSV (200 mM PBS, pH 7, 30 °C).

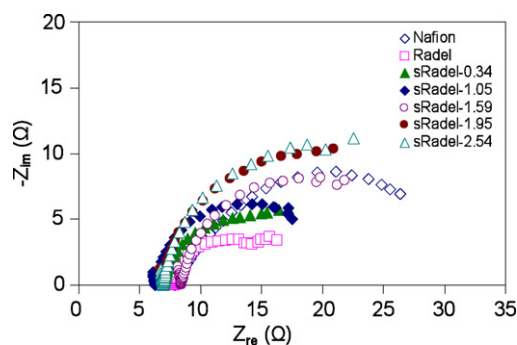


Fig. 3. EIS for cathodes with different binders at 0.3 V (vs. NHE) (200 mM PBS, pH 7, 30 °C).

3.2. Charge transfer resistance

The R_{ct} , obtained from the charge transfer loop in Nyquist impedance plots (Fig. 3), increased with increasing IEC of the binder. The R_{ct} correlated well to the ionic concentration in the hydrated polymer, $IECv(\text{wet})$ (Fig. 4). Unsulfonated Radel gave an R_{ct} of 8 Ω , which increased with IEC to an R_{ct} of 23 Ω for sRadel-2.54. The R_{ct} of the Nafion cathode, which has a completely different polymer structure than the sRadel samples, was in agreement with this relationship between R_{ct} and $IECv(\text{wet})$, indicating that $IECv(\text{wet})$, or the local ionic concentration at the catalyst surface as imposed by the binder properties, had a direct influence on R_{ct} . Increased R_{ct} in the impedance measurements indicates that polymer binders with a higher volumetric ion concentration ($IECv(\text{wet})$) impeded ions from reaching the catalyst surface, regardless of an increase in conductivity with $IECv(\text{wet})$. Given that the ions traveling to the

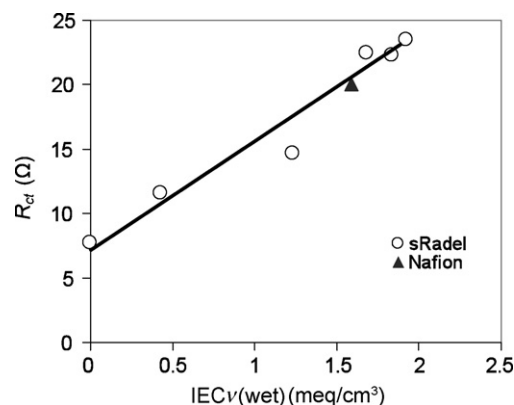


Fig. 4. Charge transfer resistance (R_{ct}) measured using EIS at 0.3 V (vs. NHE) as a function of $IECv(\text{wet})$.

Table 2
Tafel parameters, α and J_0 , from LSV (200 mM PBS).

	Line 1 (0.34–0.49 V)		Line 2 (0.05–0.2 V)	
	α	J_0	α	J_0
Nafion	0.074	4.46E–06	0.076	1.71E–06
Radel	0.183	7.25E–09	0.081	1.19E–06
sRadel-0.34	0.083	5.03E–06	0.054	1.35E–05
sRadel-1.05	0.074	9.86E–06	0.053	1.39E–05
sRadel-1.59	0.073	6.05E–06	0.052	1.37E–05
sRadel-1.95	0.081	4.10E–06	0.041	3.84E–05
sRadel-2.54	0.081	4.55E–06	0.039	4.05E–05

Table 3
Voltages (mV) produced by MFCs (100 mM PBS, pH 7, 1000 Ω , 0.5 g/L acetate) (\pm S.D. based on first 24 h of the cycle).

Cycle	Nafion	Radel	sRadel-0.34	sRadel-1.05	sRadel-1.59	sRadel-1.95	sRadel-2.54
2	616 \pm 5	561 \pm 4	613 \pm 4	621 \pm 4	619 \pm 4	609 \pm 8	589 \pm 5
3	615 \pm 5	562 \pm 2	607 \pm 4	614 \pm 4	616 \pm 5	602 \pm 4	591 \pm 5
4	614 \pm 4	562 \pm 3	605 \pm 4	612 \pm 4	612 \pm 5	591 \pm 6	580 \pm 3
5	611 \pm 4	561 \pm 2	600 \pm 4	608 \pm 4	609 \pm 3	588 \pm 5	570 \pm 4
6	612 \pm 4	562 \pm 3	613 \pm 4	609 \pm 3	610 \pm 4	587 \pm 4	571 \pm 3
11	603 \pm 4	561 \pm 3	588 \pm 3	593 \pm 3	597 \pm 3	580 \pm 4	568 \pm 2
16	598 \pm 4	562 \pm 3	586 \pm 3	592 \pm 2	592 \pm 2	569 \pm 4	564 \pm 3
20	595 \pm 5	557 \pm 3	582 \pm 4	587 \pm 4	588 \pm 4	562 \pm 3	535 \pm 2

Table 4
Maximum power density and CE for cycle 2 (after 3 days) and cycle 18 (after 50 days).

	Maximum power density (mW/m ²)		CE (%)	
	Cycle 2	Cycle 18	Cycle 2	Cycle 18
	Nafion	1790	1190	46
Radel	1470	1200	40	43
sRadel-0.34	1520	1050	54	50
sRadel-1.05	1590	1070	50	51
sRadel-1.59	1660	1090	52	41
sRadel-1.95	1510	1050	54	34
sRadel-2.54	1270	960	58	31

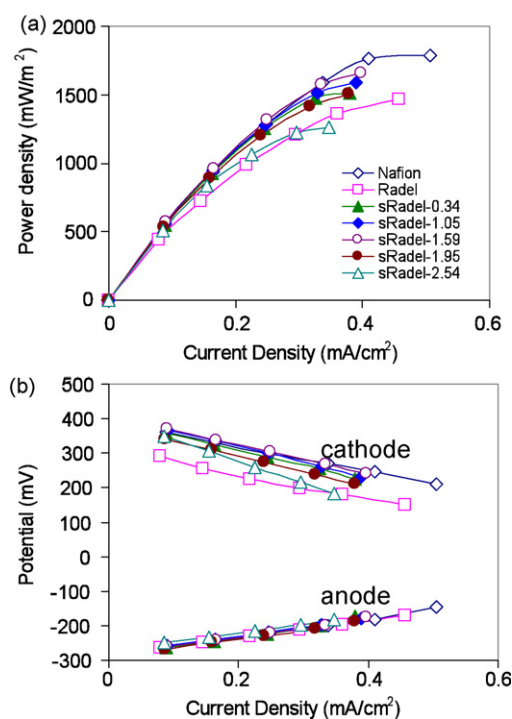
cathode must cross the MFC buffered electrolyte-catalyst binder interface where a liquid–liquid junction may be formed, this data is reasonable and helps to explain the MFC performance of the different cathodes.

3.3. MFC performance

Each MFC cycle lasted 2.5–3 days and data were recorded and analyzed over 20 cycles (Fig. S2 in supporting information). The maximum voltage output across a 1000 Ω resistance decreased slowly over successive cycles, consistent with previous reports (Table 3) [6]. The decreasing trend of voltage with each cycle was more pronounced in cathodes with higher IEC sRadel binders, while the unsulfonated Radel binder cathode showed the most stable performance over time.

MFCs with Nafion, unsulfonated Radel, sRadel-0.34, and sRadel-1.05 cathodes had coulombic efficiencies (CE) between 40 and 50% that varied only about 3 to 4% over 20 cycles (Table 4 and Fig. S3). However, a decrease in CE with cycle number was observed for binders with IECs of 1.59 meq/g and higher. The MFCs with sRadel-1.59, sRadel-1.95, and sRadel-2.54 cathodes had CEs between 55 and 65% at cycles 1 and 2, but they declined to 30–45% at cycle 20. It should be noted here that binders with greater IECs tend to have higher water uptake and are softer materials when hydrated, which may influence the CE as a function of time as the cathode's exposure to the cathode biofilm is prolonged.

At cycle 2, Nafion (IEC = 0.91 meq/g) and sRadel-1.59 showed the highest power densities (Fig. 5). The power density decreased for the Radel binders at higher or lower IEC than 1.59 meq/g as summarized in Table 4. The trend in cathode potential (Fig. 5) followed the

**Fig. 5.** (a) Polarization curves and (b) cathode and anode potentials (vs. NHE) after cycle 2 (3 days of operation; 100 mM PBS, pH 7, 0.5 g/L acetate).

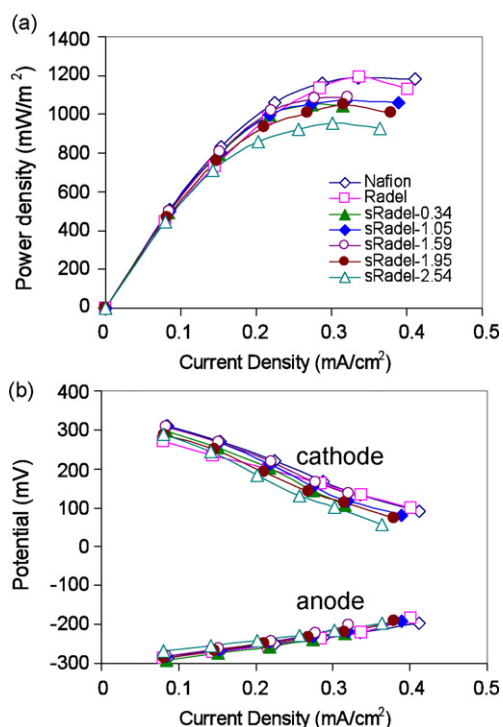


Fig. 6. (a) Polarization curves and (b) cathode and anode potentials (vs. NHE) after cycle 18 (50 days of operation; 100 mM PBS, pH 7, 0.5 g/L acetate).

corresponding polarization curves, indicating that the measured differences in cathode performance were the origin of the changes observed in the MFC performance as the cathode binder was varied.

At cycle 18, sRadel binders showed similar power densities except for sRadel-2.54, which had significantly lower power (Fig. 6). This trend corresponded well with the trend observed in a voltage output over time (Table 3 and Fig. S2(b)). All cathode binders showed a similar change in current with respect to overpotential except for the unsulfonated Radel, which is the only non-ionic binder except the unsulfonated Radel, which is the only non-ionic binder.

4. Discussion

4.1. Electrochemical performance of the cathodes

Electrochemical kinetics as measured by LSV showed that increasing the binder IEC resulted in decreased current response of the corresponding cathodes at high overpotentials for oxygen reduction. The high current displayed by the non-ionic Radel binder

in LSV could be ascribed to either intrinsically enhanced oxygen reduction kinetics due to the absence of sulfonate groups at the catalyst surface, or increased proton diffusion to the catalyst surface. Enhanced cathodic transfer coefficients, α , and low charge transfer resistance, R_{ct} , in the unsulfonated sample can be rationalized by considering the environment which protons encounter as they move from the buffer solution towards the platinum catalyst surface. For the hydrophobic, unsulfonated Radel binder, a significant portion of the catalyst particles could have been covered by polymer and therefore rendered inaccessible to the PBS and ion transport, causing the low catalytic surface area as reflected in J_0 (Fig. 7). For the hydrophilic sulfonated binders, there was more catalyst surface accessible to the ions as indicated by higher J_0 values, but the protons must travel from the buffer solution, through the polymer binder, to the catalyst surface. The polymer binder had an ion concentration that was determined by its IEC_{wet}. For example, sRadel-1.95 binder possesses 1.83 mol/L (=meq/cm³) of sodium sulfonate (Table 1). Since the ionic concentration was low in the PBS buffer, an ionic concentration gradient was present from the sulfonated polymer binder toward the PBS buffer, which in effect, created a liquid–liquid junction at the PBS-binder interface that the protons had to traverse. The data imply that the sulfonated polymer binders prevented proton transport from the PBS solution into the binder and to the Pt catalyst surface. With the non-ionic binder, there may have been less catalytic surface area (since the non-ionic binder is hydrophobic), but charge transport to the catalyst surface was greatly facilitated for a non-ionic binder polymer where ionic concentration gradients were not possible. R_{ct} from EIS correlated well with IEC_{wet} (Fig. 4), which demonstrated that higher ionic concentration in the binder caused deleterious effects to cathode performance. Increased charge transfer resistance as a result of increased ionic concentration in the catalyst layer binder polymer may be unexpected, given that the ionic conductivity increases with ion concentration, which could be expected to lower the charge transfer resistance in a conventional fuel cell. However, this data supports the thin-film model of the polymer binder in contact with the liquid MFC electrolyte where an ionic concentration gradient was formed near the surface of the catalyst and thus impacted the observed charge transfer resistance and played a role in the MFC performance of the various binders. The specific adsorption of sulfonate groups on the catalyst surface may also factor into the higher R_{ct} values and lower cathodic transfer coefficients observed for the cathode samples with sulfonated binders.

4.2. Influence of polymeric binders on MFC performance

Nafion and sRadel-1.59 had the highest power densities of all the cathodes in polarization curves at cycle 2 (Fig. 5). The performance of the Radel-based cathodes declined with decreasing IEC

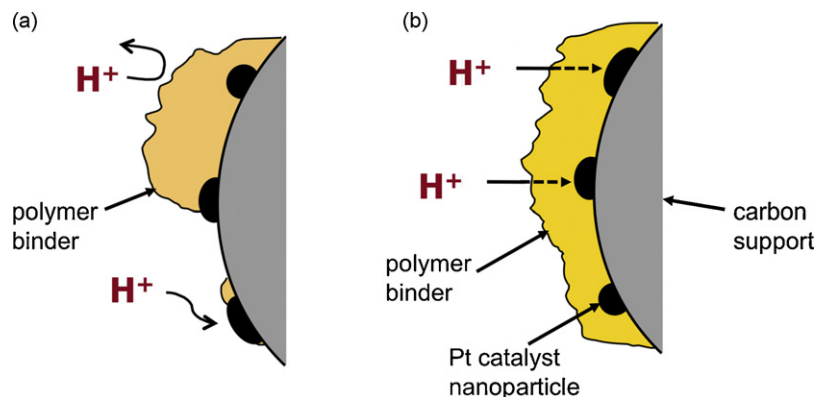


Fig. 7. MFC cathode diagrams with (a) non-ionic binder and (b) ionic binder.

and binder water uptake, probably due to less catalytic surface area being available with less water-swelling binders. For the high water uptake samples of sRadel with IECs greater than 1.59 meq/g, the proton concentration is also high, which hindered ion transport to the catalyst surface as discussed above. The water uptake and IEC_{wet} of Nafion were similar to that of sRadel-1.59, which suggests why these two materials showed similar performance in polarization experiments. Thus, it appears as though there is an optimum balance of water uptake and sulfonate content in the cathode binders that gives the maximum MFC performance.

In polarization curves at cycle 18 (Fig. 6), Radel binder cathode showed the highest power density and the most stable performance over the test period (Table 3 and Fig. S2(b)). The higher current density at a given overpotential for the non-ionic Radel cathode suggests that not having an ionic species tethered to the binder polymer improved the electrochemical performance of the catalyst in the cathode. The lower cathode overpotential for the Radel cathode is also supported by a large α value from line 1 in Tafel plots (Table 2), where the current density range of line 1 corresponds to the current density range relevant to MFC operation. The large α value of the Radel cathode contributed to lower the cathode potential slope, while similar α values of the other cathodes (sulfonated binder cathodes) resulted in the similar slopes of the cathode potential decrease. The small J_0 value from line 1 in Tafel plots (Table 2) for the Radel sample also correlated with the smaller voltage output of Radel sample versus the other cathodes at low current densities. Thus, the Tafel analysis of the cathodes from the *ex situ* LSV characterization correlated well with the observed *in situ* MFC cathode performance.

At cycle 18, unsulfonated Radel and low IEC sRadel binders (0.34, 1.05, and 1.59) showed similar power density and CE to Nafion. The high CE maintained for the lower IEC polymers could have been due to their low water uptake values, while cathodes constructed from sRadel samples with higher water uptake showed appreciable declines in CE with cycle number.

Considering its power density (Figs. 5 and 6) and voltage output stability (Table 3 and Fig. S2(b)), Nafion remains an attractive binder for MFCs, but the performance of poly(sulfone) based binders is also reasonable. Unsulfonated Radel poly(sulfone) showed good stability over the test time and high power density output, especially in later cycles. Radel R-5500 costs \$44.40/kg (25 kg lots) and DMF costs \$23.27 for 4 L. Thus, the binder solution for one cathode using Radel costs \$0.00326, compared to \$1.29 for Nafion (\$323 per 100 mL of 5 wt% Nafion solution). This significant difference of the cost makes Radel binder (~1/400 of Nafion's cost) very attractive for large-scale use.

In summary, non-ionic binder, Radel, showed the highest performance in LSV tests and the lowest R_{ct} . The addition of sulfonate moieties around the Pt catalyst increased the accessible surface area for oxygen reduction, but interfered with the electrochemical performance in MFC cathodes. The non-ionic, hydrophobic nature of Radel likely covered Pt reaction sites in the cathode and rendered them inaccessible for electrocatalysis, but electrochemical kinetics were enhanced by a lack of sulfonate groups in the polymeric cathode binder. These results may point to the use of non-ionic binders in MFC cathodes with some degree of hydrophilic character as alternatives to sulfonated polymers by eliminating liquid–liquid junction potentials at the PBS-binder interface while allowing good access to the Pt catalyst sites in the cathode.

Acknowledgments

This research was supported by the National Science Foundation (CBET-0803137). We thank Solvay Advanced Polymers for the donation of Radel polymer, and Dr. Shaoan Cheng for his insights into experimental procedures.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.electacta.2010.01.009.

References

- [1] B.E. Logan, *Microbial Fuel Cells*, John Wiley & Sons, Inc., Hoboken, New Jersey, 2007.
- [2] I. Shizas, D.M. Bagley, *Journal of Energy Engineering-Asce* 130 (2004) 45.
- [3] W.L. Harrison, M.A. Hickner, Y.S. Kim, J.E. McGrath, *Fuel Cells* 5 (2005) 201.
- [4] M.A. Hickner, H. Ghassemi, Y.S. Kim, B.R. Einsla, J.E. McGrath, *Chemical Reviews* 104 (2004) 4587.
- [5] M.A. Hickner, B.S. Pivovar, *Fuel Cells* 5 (2005) 213.
- [6] S. Cheng, H. Liu, B.E. Logan, *Environmental Science & Technology* 40 (2006) 364.
- [7] S. Sambandam, V. Ramani, *Electrochimica Acta* 53 (2008) 6328.
- [8] A. Dyck, D. Fritsch, S.P. Nunes, *Journal of Applied Polymer Science* 86 (2002) 2820.
- [9] Y.S. Kim, B. Einsla, M. Sankir, W. Harrison, B.S. Pivovar, *Polymer* 47 (2006) 4026.
- [10] R.C.T. Slade, J.R. Varcoe, *Solid State Ionics* 176 (2005) 585.
- [11] S. Cheng, H. Liu, B.E. Logan, *Electrochemistry Communications* 8 (2006) 489.
- [12] B. Logan, S. Cheng, V. Watson, G. Estadt, *Environmental Science & Technology* 41 (2007) 3341.
- [13] S. Cheng, H. Liu, B.E. Logan, *Environmental Science & Technology* 40 (2006) 2426.
- [14] B.E. Logan, B. Hamelers, R. Rozendal, U. Schrorder, J. Keller, S. Freguia, P. Aelterman, W. Verstraete, K. Rabaey, *Environmental Science & Technology* 40 (2006) 5181.