Short Communication

Mitigating external and internal cathode fouling using a polymer bonded separator in microbial fuel cells

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ABSTRACT

Microbial fuel cell (MFC) cathodes rapidly foul when treating domestic wastewater, substantially reducing power production over time. Here a wipe separator was chemically bonded to an activated carbon air cathode using polyvinylidene fluoride (PVDF) to mitigate cathode fouling and extend cathode performance over time. MFCs with separator-bonded cathodes produced a maximum power density of $190 \pm 30\,mW\,m^{-2}$ after 2 months of operation using domestic wastewater, which was ~220% higher than controls ($60 \pm 50\,mW\,m^{-2}$) with separators that were not chemically bonded to the cathode. Less biomass (protein) was measured on the bonded separator surface than the non-bonded separator, indicating chemical bonding reduced external biofouling. Salt precipitation that contributed to internal fouling was also reduced using separator-bonded cathodes. Overall, the separator-bonded cathodes showed better performance over time by mitigating both external biofouling and internal salt fouling.

1. Introduction

A microbial fuel cell (MFC) is a sustainable technology that can be used to harvest electricity from organic matter in wastewater (An et al., 2016; Tan et al., 2017; Zhang et al., 2017). In an MFC, exoelectrogenic bacteria on the anode degrade organic matter and release electrons to the anode, which are then transferred to the cathode where oxygen reduction takes place (Wang et al., 2017). Commercial applications of MFCs have been partly hindered by high material costs, half of which results from the cost of cathode materials (Sleutels et al., 2012). The development of low cost oxygen reduction cathode catalysts, such as activated carbon (AC), has proven to be one of the most promising solutions, as AC is much less expensive ($1.4\,kg^{-1}$) than platinum ($> \$150,000\,kg^{-1}$) (Yang et al., 2014).

Another requirement for using MFCs for wastewater treatment is extending the lifetime of the cathode (Yang et al., 2016). External and internal fouling of the cathode can greatly reduce the performance of the cathode over time, and result in either the need for frequent cathode cleaning or cathode replacement (He et al., 2016; Oliot et al., 2016). MFCs operated for one year using only an acetate substrate had a 40% decrease in performance (Zhang et al., 2011). Removing the biofilm on the cathode surface recovered only 12% of the original cathode performance, suggesting the existence of both external and internal fouling (Zhang et al., 2011). External fouling is due primarily to biofilm growth

on the cathode surface, which reduces mass transfer to and from the cathode. A reduction in external biofouling has been obtained using antimicrobial polymer coatings or biocidal particles blended into the cathode catalyst layer, but this can increase the cost and complexity of making the cathode, and the effectiveness of these chemicals can decrease over time (Li et al., 2016; Liu et al., 2015). The factors that contribute to internal fouling have been less investigated, especially for AC cathodes, due to the difficulties of probing the cathode internal structure. Sulfide and phosphate ions can deactivate the platinum catalyst (Santoro et al., 2016; Savizi and Janik, 2011). For AC cathodes, adsorption of humic acids in AC catalyst layer led to a 14% decrease in MFC power generation (Yang et al., 2016), suggesting other reasons are responsible for the much larger decreases in cathode performance over time. Salt precipitation within AC cathodes was recently found to contribute to decreased cathode performance, likely due to chemical precipitation occurring as a result of the localized pH increases in the cathode from hydroxide ion production (An et al., 2017). To date, there have been few studies on methods to mitigate internal cathode fouling. In addition, most studies on reducing cathode fouling were tested using only acetate and buffered solutions, rather than real wastewaters.

In this study, a cloth separator was chemically bonded to the cathode to better maintain cathode performance over time, and compared to a control containing a non-bonded separator, using AC cathodes. Low cost cloth separators ($1.7\,m^{-2}$) are commonly used in MFCs

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to reduce cathode oxygen transfer into the anolyte and cathode fouling (Ahn and Logan, 2012). The use of separator is necessary in preventing short circuiting between electrodes when they are placed close to each other to reduce ohmic resistance for high power output (Fan et al., 2007). Separators are usually placed adjacent to the cathodes, which can result in electrolyte accumulation on both sides of the separator (Zhang et al., 2009). Such a free standing separator can provide more attachment sites for bacteria on both sides of the cathode, and water accumulation between the separator and cathode can reduce performance due to retention of the hydroxide ions released during oxygen reduction. It was hypothesized here that chemical bonding of the separator to the cathode could provide a simple solution to reduce biofilm growth. Moreover, direct chemical bonding to the cathode should facilitate better hydroxide ion diffusion from the cathode, which could provide a more neutral pH near the cathode, potentially alleviating salt precipitation within cathode. To chemically bond the separator to the AC cathode, a simple phase inversion process used to make AC cathodes (Yang et al., 2014) was modified to include the cloth separator in the process with the other cathode materials during cathode fabrication, and thus no additional preparation steps were needed. MFCs with chemically bonded separator cathodes were compared to controls that had a separator that was held against (but not bonded to) the cathode. MFCs with these cathodes were fed domestic wastewater for over two months, with performance evaluated by the change of power production over time. The biofilm growth on separator and cathode surface was quantified via a protein analysis, and acid cleaning was used to alleviate internal fouling.

2. Methods

2.1. Cathode fabrication

Separator bonded cathodes were fabricated by modifying a phase inversion method (Yang et al., 2014) to include a cloth separator. Briefly, 300 mg of AC powder (Norit SX plus, Norit Americas Inc., TX), 30 mg of carbon black (CB: Vulcan XC-72, Cabot Corporation, USA) and 1.1 mL of 10% (w/v) polyvinylidene (PVDF, ∼534,000 Da; Sigma Aldrich) in dimethylacetamide (anhydrous, 99.8%, Sigma Aldrich) were mixed together in a beaker at the mass ratio of AC:CB:PVDF = 30:3:11 to form a paste. The mixture was then spread onto a circular stainless steel mesh (50 × 50, type 304, McMaster-Carr, USA) with an area of 11.3 cm^2 using a spatula. A pre-cut wipe cloth (PZ-1212, Contec, USA) with the same area of 11.3 cm^2 was then applied onto the carbon surface and wetted by the excess PVDF solution from the carbon mixture. The whole cathode was then transferred to a petri dish filled with distilled water for phase inversion process to take place at room temperature. After 15 min, the cathode was taken out and dried in a fume hood at room temperature for 24 h. The non-bonded cathodes were made by preparing the cathode, and then placing the separator next to the cathode as a control for the separator bonded cathode.

2.2. MFC construction and operation

The separator bonded and non-bonded cathodes were both tested in cubic single-chamber reactors constructed from Lexan blocks 4 cm in length with an inside diameter of 3 cm, in duplicate (Yang et al., 2017). The anodes were graphite fiber brushes (2.5 cm in both length and diameter) heat treated at 450 °C in air for 30 min (Feng et al., 2010). Anodes were fully acclimated by operating at 1000 Ω external resistance in a constant temperature room (30 °C) for one month to ensure anode stability. Domestic wastewater, collected from the primary clarifier of the Pennsylvania State University Wastewater Treatment Plant (State College, USA), was used as the inoculum and medium. The total chemical oxygen demand (tCOD) and soluble chemical oxygen demand (sCOD) of domestic wastewater were determined in duplicate before each polarization test.

Single cycle polarization tests were conducted to obtain data for MFC power curves by decreasing the external resistance from 1000 through 500, 200, 150, 100 and 50 Ω at 20 min intervals (Yang et al., 2014). Polarization tests were conducted on day 3, 35 and 65 for the MFCs with separator bonded and non-bonded cathodes. After the polarization tests on day 65, both cathodes were removed from the MFCs for further analysis.

To analyze cathode internal fouling, the separators were gently peeled off from the cathode surface using a tweezer. Only the cathodes were put back into the MFCs on day 75 (no separators) and single cycle polarization tests were conducted with domestic wastewater to determine performance of only the used cathodes (without separators). To examine the effect of acid wash on cathode internal fouling, 10 mL of 0.01 M HCl solution was used to clean each cathode by immersing the cathodes in the HCl solutions for 1 h at room temperature (He et al., 2016). After acid cleaning, the cathodes were rinsed with deionized (DI) water and then put back into the MFCs. On day 78, another single cycle polarization test was conducted for MFCs installed with the bonded and non-bonded cathodes (still without separators).

2.3. Cathode characterization

Linear sweep voltammetry (LSV) was used to evaluate the electrochemical performance of the separator bonded and non-bonded cathodes in an electrochemical cell (2 cm length, 3 cm diameter) containing two chambers separated by an anion exchange membrane (AEM; AMI-7001, Membrane International Inc., USA) (Yang et al., 2016). A circular platinum plate with projected area of 7 cm^2 was used as the counter electrode. An Ag/AgCl reference electrode (RE-5B, BASi, West Lafayette, IN; +0.209 V vs. SHE) was placed close to cathode and fixed by a rubber O-ring. A potentiostat (VMP3 Multichannel Workstation, Biologic Science Instruments, USA) was used for the LSV tests, and all measurements were conducted in a constant temperature room at 30 °C. The electrolyte was 50 mM phosphate buffer solution (PBS; Na$_2$HPO$_4$, 4.58 g L^{-1}; NaH$_2$PO$_4$·H$_2$O, 2.45 g L^{-1}; NH$_4$Cl, 0.31 g L^{-1}; KCl, 0.31 g L^{-1}; pH = 6.9; conductivity of κ = 6.9 mS cm^{-1}). The cathode potentials were scanned 7 times from +0.509 to −0.209 V at a scan rate of 0.1 mV s^{-1} versus SHE to reach steady state.

Biomass on the separators and cathodes were measured based on total protein concentrations using a bicinchoninic acid protein assay kit (Sigma Aldrich) (Ishii et al., 2008). Protein was extracted from the separator or cathode with 0.2 N NaOH. The separators were gently peeled off the cathode surface with a tweezer, placed in a test tube containing 5 mL of 0.2 N NaOH at 4 °C for 1 h, and vortexed every 15 min for 10 s. The extracted solution was collected, and the separators were further rinsed with 5 mL of DI water, which was also collected in the test tube. The final volume of extracted solution was 10 mL with a concentration of 0.1 N NaOH. The extracted solution was then frozen at −20 °C, and thawed at 90 °C. This freeze–thaw cycle was repeated three times and 0.1 mL of the extracted solution was used for protein analysis. To prevent damage to the cathode, proteins on the cathode were extracted only by rinsing with 5 mL DI water (no vortexing). The rinsing water of 5 mL was then mixed with 5 mL of 0.2 N NaOH to prepare the extracted solution and followed through the same freeze-thaw cycle for protein analysis.

3. Results and discussion

3.1. Fresh cathode performance in wastewater powered MFCs

The MFCs with the separator bonded cathodes initially (day 3) had similar performance to those with non-bonded cathodes. The maximum power density was 380 ± 30 mW m^{-2} for MFCs with separator bonded cathodes, which was not different from 340 ± 20 mW m^{-2} for MFCs with non-bonded cathodes (Fig. 1A). These values are similar to those obtained in a previous study using wastewater from the same source
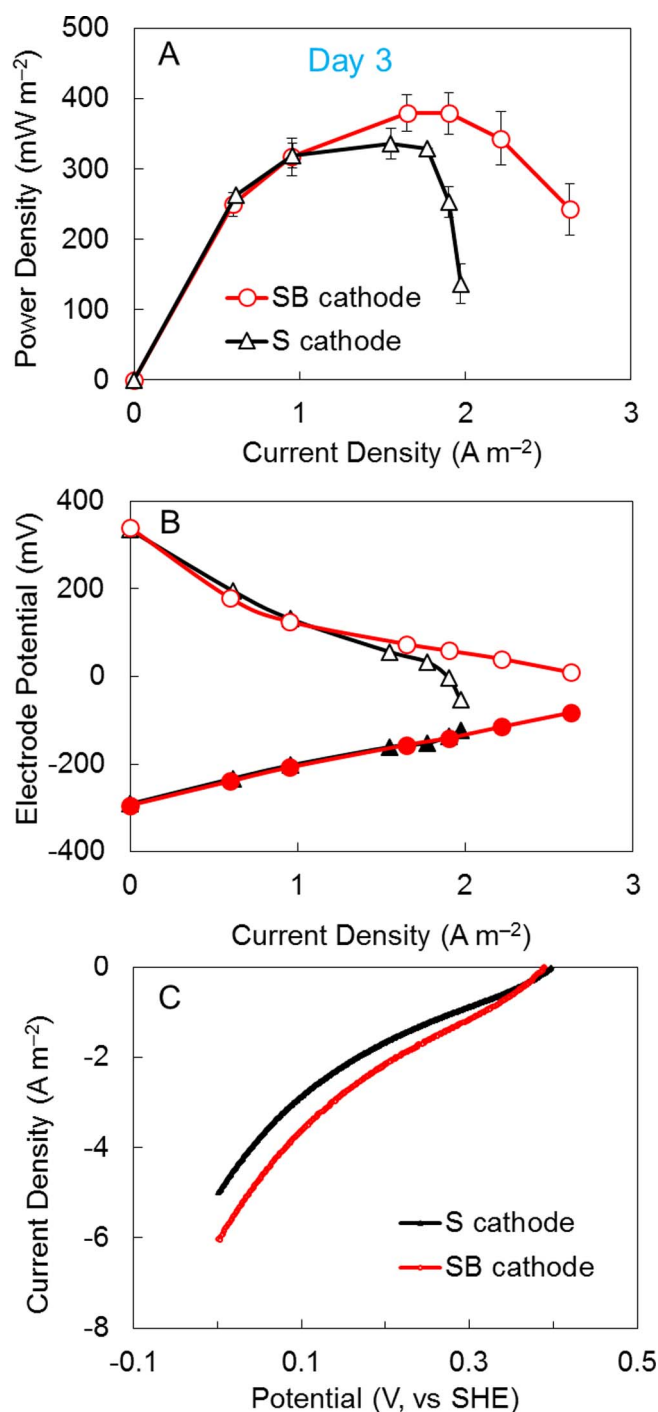
Fig. 1. MFC tests: (A) power density curves for separator bonded cathodes and non-bonded cathodes at day 3; (B) electrode potentials (solid symbols, anode potentials; open symbols, cathode potentials). (C) Current-voltage (polarization) curves for the same cathodes in an abiotic electrochemical cell. (SB cathode: separator bonded cathode; S cathode: separator non-bonded cathode)

(Yang and Logan, 2016). However, the non-bonded cathode potentials became substantially more negative than those of the separator bonded cathodes at current densities > 1.5 A m^{-2} (Fig. 1B). This decrease in cathode potential might have been due to hindered ion transport, due to electrolyte buildup between the free standing separator and cathode.

Better performance of separator bonded cathodes compared to non-bonded cathodes was more clearly observed in abiotic LSV tests than in the MFC polarization tests. For example, at a current density of 1.6 A m^{-2}, which is the current of the maximum power for the

separator bonded cathodes, the bonded cathodes had a more positive potential of 0.26 V compared to the non-bonded cathodes (0.21 V) (Fig. 1C). The differences in potential became larger at higher current densities, demonstrating the better catalytic activity of the separator bonded cathodes.

3.2. Fouled cathode performance in wastewater powered MFCs

After about one month (35 d) of operation using wastewater, MFCs with separator bonded cathodes had a maximum power density of 200 ± 60 mW m^{-2}, which was similar to 220 ± 30 mW m^{-2} for MFCs with non-bonded cathodes (Fig. 2A). Both separator bonded and non-bonded cathodes showed decayed performance at day 35 compared to day 3 mainly due to cathode fouling, as the CODs did not significantly change for these comparisons (450 ± 10 mg L^{-1} at Day 3 and 420 ± 20 mg L^{-1} at Day 35) (Supplemental information). The current density where maximum power density was obtained was also lower, at ∼0.8 A m^{-2} (Fig. 2A) at day 35 compared to 1.6 A m^{-2} at day 3 (Fig. 1A).

After about two-months (65 d) of operation, the power densities of the MFCs equipped with the non-bonded cathodes continue to diminish while the maximum power densities of the MFCs with separator bonded cathodes were remained comparable to those obtained in the previous month. A maximum power density of 190 ± 30 mW m^{-2} was obtained after 65 d with the separator bonded cathodes, which was ∼220% higher than the non-bonded cathodes (60 ± 50 mW m^{-2}) (Fig. 2C). The significant drop in power performance of the non-bonded cathodes was due to the decay of cathode potentials (Fig. 2D). At the maximum current density (0.28 A m^{-2} for non-bonded cathodes and 1.8 A m^{-2} for separator bonded cathodes), the cathode potential of the non-bonded cathodes was −211 mV compared to −74 mV for the separator bonded cathodes. This lack of a decline in the performance of the separator bonded cathodes indicated better antifouling properties of these cathodes with the separator bonded to the cathode surfaces.

3.3. Cathode surface biomass analysis

To characterize the extent of biofouling, protein was extracted from the separators as an estimate of total bacterial biomass. Separators from the non-bonded cathodes had greater biofouling, as shown by a protein content of 370 ± 60 mg cm^{-2} (n = 2) on the separators, which was ∼150% higher than that on the separators of the separator bonded cathodes (150 ± 100 mg cm^{-2}, n = 2). The differences in protein loading indicated that the non-bonded separator provided better conditions for bacterial attachment and growth compared to the bonded separator, which was consistent with visual observations of a denser biofilm formation on the non-bonded separators compared to the bonded separators (Supplemental information). The protein concentrations on both cathode surfaces were below the detection limit, suggesting that separators were effective in blocking extensive bacterial growth on the cathode surface.

3.4. Cathode internal fouling and acid wash

After removing the separators for all cathodes, both bonded and non-bonded cathodes were put back into the MFCs to examine performance with the two cathodes without fouled separators. A maximum power density of 290 ± 40 mW m^{-2} was obtained for the bonded cathode, which was 32% higher than 220 ± 10 mW m^{-2} for the non-bonded cathode (Fig. 3A). At the current density of 0.9 A m^{-2}, the bonded cathodes had a cathode potential of 118 mV, which was ∼320% higher than 28 mV for non-bonded cathodes, indicating that the power difference was mainly due to cathode performance difference (Fig. 3B). Both of these maximum power densities are lower than those obtained at the start of the experiments (day 3) using with new separators. Therefore, it was concluded that the decline in performance
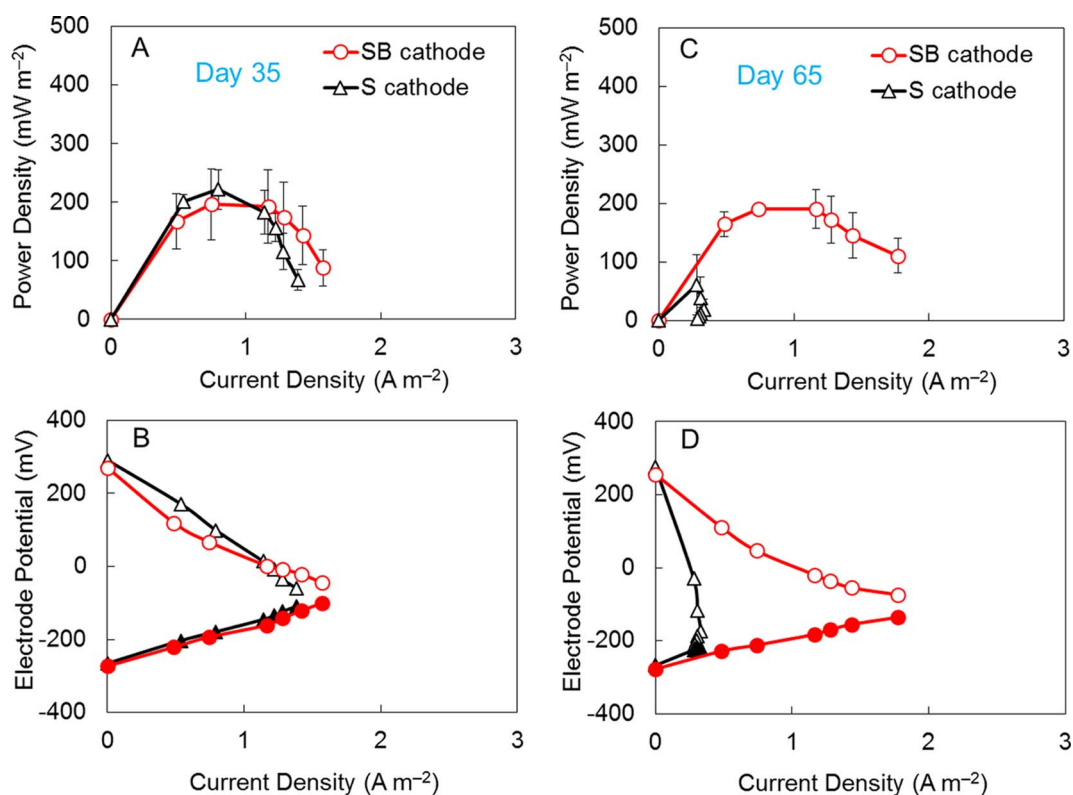
Fig. 2. MFC tests: (A) power density curves for separator bonded and non-bonded cathodes at day 35; (B) electrode potentials (solid symbols, anode potentials; open symbols, cathode potentials); (C) power density curves for separator bonded and non-bonded cathodes at day 65; (D) electrode potentials (solid symbols, anode potentials; open symbols, cathode potentials). (SB cathode: separator bonded cathode; S cathode: separator non-bonded cathode)
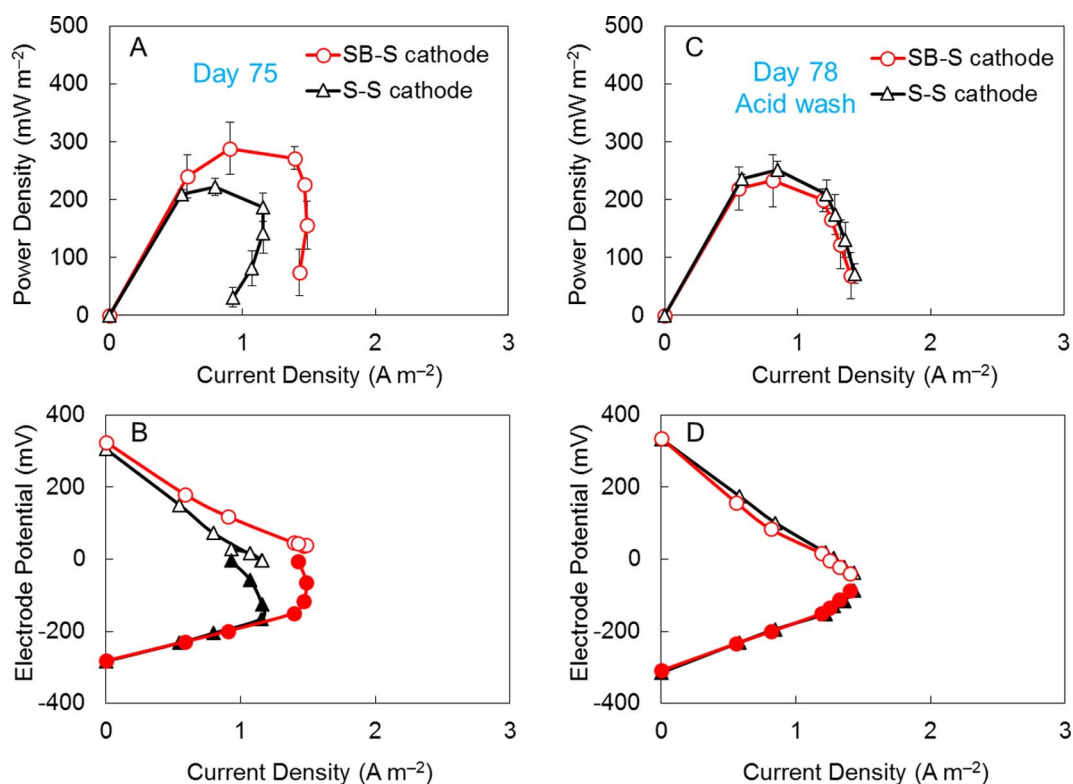

Fig. 3. MFC tests: (A) power density curves for separator bonded and non-bonded cathodes without separator at day 75; (B) electrode potentials (solid symbols, anode potentials; open symbols, cathode potentials); (C) power density curves for same cathodes without separators after acid wash at day 78; (D) electrode potentials (solid symbols, anode potentials; open symbols, cathode potentials). (SB–S cathode: separator bonded cathode without separator; S–S cathode: separator non-bonded cathode without separator)

when the separators were removed was due to internal fouling of the cathodes, as external fouling was not a factor due to the lack of appreciable biomass on the cathode surface.

To investigate a possible reason for the lower power production from non-bonded cathodes after removing the separators, the cathodes were cleaned using an acid wash (0.01 M HCl) to try to regain cathode performance. Similar power densities with the cleaned cathodes was obtained for the MFCs with bonded ($230 \pm 50\,\mathrm{mW\,m^{-2}}$) and non-bonded cathodes ($250 \pm 40\,\mathrm{mW\,m^{-2}}$) after acid washing (Fig. 3C), demonstrating that acid washing had improved the activity of the non-bonded cathodes. As no bacteria was identified on the surface of the non-bonded cathode, it is likely that the acid removed accumulated salts in the cathodes, which had been previously observed that salt precipitation did occur on activated carbon cathodes after 6 months operation (An et al., 2017) and platinum cathodes after 1 month operation (Santoro et al., 2013). Cathode electrode potentials of the non-bonded cathodes were also shown to be similar to that of the bonded cathodes (Fig. 3D). With a bonded separator, cathodes likely have less pH changes and thus less salt precipitation compared to cathodes with non-bonded or free standing separators.

4. Conclusions

Separator bonded cathodes showed better antifouling over time compared to cathodes with non-bonded separators. A maximum power density of $190 \pm 30\,\mathrm{mW\,m^{-2}}$ was obtained for separator bonded cathodes after two months of operation, which was ~220% higher than $60 \pm 50\,\mathrm{mW\,m^{-2}}$ for non-bonded cathodes. Bonding the cathode to the separator minimized the interstitial volume between the cathode and separator that could have allowed for biofilm growth or accumulation of higher pH solutions due to oxygen reduction at the cathode.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2017.10.109.

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