Journal of Power Sources 210 (2012) 122–128

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Microbial fuel cell biofilm characterization with thermogravimetric analysis on bare and polyethyleneimine surface modified carbon foam anodes

Jessica Kramer[a], Souren Soukiazian[b], Sky Mahoney[b], Jocelyn Hicks-Garner[b,*]

[a] Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095-1600, USA
[b] HRL Laboratories, LLC, 3011 Malibu Canyon Rd., Malibu, CA 90265, USA

ARTICLE INFO

Article history:
Received 23 December 2011
Received in revised form 21 February 2012
Accepted 9 March 2012
Available online 21 March 2012

Keywords:
Microbial fuel cell
Thermogravimetric analysis
Polyethyleneimine

ABSTRACT

Thermogravimetric analysis (TGA) of microbial biofilms on bare and polyethyleneimine (PEI) surface modified carbon foam is described. PEI-modified carbon foam was incorporated into a microbial fuel cell (MFC) as the anode, inoculated with electrogenic bacteria, and the voltage and power outputs were monitored over five weeks. The results were compared to MFCs containing unmodified carbon foam anodes. Biofilm formation was investigated by scanning electron microscopy and TGA. TGA is presented as a new method to assess the relative amounts of biofilm on an electrode surface.

1. Introduction

The energy field has recently developed a strong interest in renewable and alternative energy sources that are capable of reducing dependence on petroleum based energy. Microbial fuel cells (MFCs) are bio-electrochemical energy systems that provide new opportunities for environmentally friendly energy production to help meet the growing demand for energy. In MFCs, microorganisms oxidize organic materials and produce electrons that can be harnessed and routed through an electrical circuit where they can perform work [1–4]. While the energy density of MFCs is currently on par with traditional hydrogen based proton exchange membrane fuel cells, the power derived from MFCs remains relatively low [5]. Despite the relatively low power output, MFCs have successfully been used to power small scale buoys equipped with environmental monitoring devices (sediment/benthic MFCs) [6,7], demonstrating the benefit of their application in remote and unattended environments. The most promising initial large-scale application appears to be in the area of wastewater treatment where MFCs have been used to remove organic matter from waste streams while generating electricity [8–10]. MFC development is still at an early stage, and there is tremendous potential to increase power output through electrochemical, microbiological, and systems engineering improvements. With such improvements, the application space for this technology will broaden tremendously.

One strategy to increase MFC power output is optimization of the anode material with consideration of the surface area, porosity, and affinity for the microbes. In MFC systems, the electrical current scales with both the available surface area and the amount of metabolically active microbial biofilm [11]. Increasing the electrode surface area available for biofilm formation can result in increased power output, however, porosity and fluid flow inside the anode must be considered [11,12]. The electrode structure must allow for circulation of biological media (a mixture of water, food/fuel, trace nutrients, etc.) to the entire microbial population, and diffusion of waste byproducts away from the biofilm. If fuel and waste cannot be transported throughout the biofilm, cell viability and current production will be variable. The anode material requires an ability to accommodate a ~40 μm thick biofilm comprised of electrogenic bacteria typically 1–2 μm in length [11], with adequate room for fluid flow. Affinity of electrogenic bacteria to the anode material will also impact the rate of biofilm formation, and subsequently current production [11].

Carbon foam anodes address the surface area and porosity requirements of MFC anodes by combining extensive three-dimensional surface area with porosity that provides voids for biofilm growth and fuel/waste circulation. Electrogenic bacteria are naturally attracted to materials that can serve as an acceptor or sink for the electrons generated as part of their metabolic cycle [2]. Conductive carbon in such forms as graphitic cloth, vitreous carbon foam, and carbon felt, has proven capable of supporting bacterial biofilms in laboratory MFCs while conducting current [10,11,13].

Though research has demonstrated that electrogenic bacteria readily couple with and colonize on conductive carbon anodes,

* Corresponding author. Tel.: +1 310 317 5544; fax: +1 310 317 5840.
E-mail address: jhicks-garner@hrl.com (J. Hicks-Garner).

0378-7753/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2012.03.022

straightforward and readily available methods to characterize these biofilms are lacking. Confocal microscopy is often used for precision analysis of biofilm properties, but the technique requires expensive equipment as well as considerable time and training to obtain quality data. Thermogravimetric analysis (TGA) is an analytical tool which measures the rate and amount of mass loss of a sample as its temperature is raised. TGA is routinely used to analyze materials ranging from small molecules to polymers, to determine physical characteristics such as decomposition temperature, or levels of inorganic or organic components. TGA is also useful in observing the mass effect of surface functionalization of a material. The technique is simple, rapid, inexpensive, and requires little training. Adhesion of a bacterial biofilm to an MFC anode is analogous to surface modification and affects the mass of the anode. We have investigated the use of TGA as an analytical tool to observe trends in biofilm formation on carbon foam anode surfaces. We have correlated the trends in TGA data to our observations of cell voltages and the appearance of biofilms by scanning electron micrographs (SEM).

We have also investigated the use of carbon foam anodes that have been covalently surface modified with polyethyleneimine (PEI) in an effort to enhance the affinity of a mixed colony of electrogenic bacteria to the electrode. Currently, there has been little work done to increase the rate of biofilm formation or biofilm stability on MFC anode surfaces by enhancing attraction of the bacteria to the anode. Branched PEI is a polycationic organic polymer that has a high density of primary, secondary, and tertiary amino groups. PEI has been extensively used as a nonviral DNA transfection agent both in cell culture applications and in vivo [14,15]. PEI has also been used as an attachment factor for culturing both eukaryotic [16,17] and prokaryotic [18] cell lines. The cationic polymer is an effective bacterial flocculating agent and has been used to aid construction of both artificial biofilms [19] and artificially constructed microbial consortia [20] on electrode surfaces. Goncalves and Govind recently reported that PEI coating a gold electrode surface improved the biofilm formation of wastewater bacteria [21]. In this case, electrode surfaces were coated with PEI, polylysine, or collagen, and biofilm formation was compared to untreated electrodes. The PEI coated surface was reported to give the highest increase in biofilm spread. It is noteworthy that in this study, biofilm growth was observed via changes in electrode impedance and capacitance, noting that confocal microscopy is often time consuming and difficult. Given the reported benefits of PEI electrode coating on wastewater bacterial biofilm formation, we applied this to an MFC.

Herein, the MFC application of carbon foam anodes, PEI-modified carbon foam anodes, and biofilm characterization with TGA are described. Carbon foam anodes were covalently surface modified with PEI, then characterized by infrared spectroscopy (IR), TGA, and SEM. Biofilm formation was observed on PEI-modified versus unmodified carbon anodes in functional MFCs. Cell voltages and power densities were observed over five weeks, and biofilms were then examined by TGA and SEM. To our knowledge, this is the first application of anode surface modification with PEI in an MFC application, and the first use of TGA as a method for evaluating biofilm formation.

2. Experimental

2.1. General materials and methods

All chemicals were purchased from commercial sources unless otherwise noted. Water was purified in a Nanopure(R) water system.

2.2. Electrogenic microorganisms

A mixed colony was obtained as anaerobic digester sludge from the Tapia Wastewater Treatment Facility (Malibu, CA). The colony was propagated in a biological medium containing 10 mM acetate (electron donor) and 40 mM fumarate (electron acceptor).

2.3. Microbial fuel cell assembly

The MFCs used in these experiments were constructed from two pieces ($7 \times 7 \times 1.1$ cm) of machined acrylic glass, one having the anode compartment with dimensions $1.9 \times 1.9 \times 0.8$ cm, and the other having the cathode compartment with dimensions $3.2 \times 3.2 \times 0.8$ cm. Two pieces of butyl rubber, each with a 1 in. square opening in the middle, served as the gaskets. A piece of exchange membrane (Nafion® 117) soaked in 0.5 M H_2SO_4 was placed between the rubber gaskets to electrically separate the anode and cathode compartments while permitting proton transport.

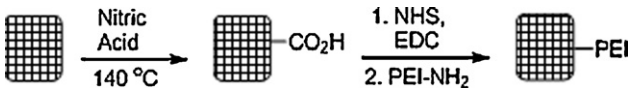
Reticulated vitreous carbon foam (20 ppi density, 3% density) from ERG Materials and Aerospace Corp., Oakland, CA, was used as the anode and a 3.0×3.0 cm piece of graphite cloth (0.3 mm thick GC-14, Electrolytica, Amherst, NY) was used as the cathode. A piece of platinum (Pt) mesh pressed to the carbon foam anode and a piece of Pt wire woven through the cloth were used to provide external electrical contact to the electrodes. The wire and mesh were secured outside of the cell to an electrical post with a screw and washer. All MFC materials were sterilized prior to use by autoclave, bleach, or ethanol treatment, and the cell components were assembled under sterile water.

2.4. Microbial fuel cell operation

Assembled MFCs were inoculated with 20 mL of propagated anaerobic digester solution, which was added anaerobically to 200 mL of media that was continuously circulated through the anode chamber at a flow rate of 20 mL min^{-1}. Anolyte (media) and catholyte were contained in sealed 250 mL bottles and continuously circulated through the anode and cathode compartments at a rate of 20 mL min^{-1} using a peristaltic pump. The anolyte consisted of anaerobic freshwater media [22] with 10 mM acetate as the electron donor, which was continuously purged with an 80/20 mixture of N_2/CO_2. A solution of 50 mM potassium ferricyanide in TRIS buffer [22] served as the electron acceptor. After the bacteria attached to the surface of the anode (as evidenced by the cell voltage) the anode and cathode were connected through a 500 Ω resistor.

2.5. Anode surface modification procedure

Carbon foam anodes were surface oxidized by immersion in concentrated nitric acid followed by heating for 4 h at 140 °C. Anodes were carefully removed from the acid solution and washed with copious distilled water until neutral. The carboxylic acid functionalized anodes were then submerged in 25 mL of an aqueous solution of 100 mM N-hydroxysuccinimide (NHS) and 100 mM 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride. Anodes were incubated for 4 h to allow formation of NHS esters, and then 1 mL of a 50 wt% solution of branched PEI (Mn = 1200, Sigma–Aldrich) was added. Anodes were incubated in this solution overnight at room temperature and then removed from the solution and washed with copious distilled water.



Scheme 1. Preparation of PEI-modified carbon anodes.

2.6. Infrared spectroscopy (IR) and thermogravimetric analysis (TGA)

IR samples were prepared by first oven drying at 120 °C overnight to remove water, and then grinding with dry KBr at 1 wt% sample. Samples were pressed into thin discs and analyzed on a Nicolet 6700 FT-IR spectrophotomer under N_2 with a dry KBr background. TGA samples (10–15 mg) were analyzed on TA Instruments Q500, thermogravimetric analyzer, at a heating rate of 15 °C min^{-1} in an atmosphere of N_2.

2.7. Scanning electron micrograph imagng (SEM)

Samples were prepared for SEM imaging by drying overnight at 75 °C in atmosphere oven. Prior to imaging, an electronically conductive coating was applied to the sample to reduce charging in the SEM. Images were taken on a Hitachi S-4800.

2.8. Electrochemical characterization

Fuel cell voltages were monitored periodically with a high impedance multimeter. Current–voltage curves were generated using a Solartron SI 1287 Electrochemical Interface.

3. Results and discussion

3.1. Preparation of PEI-modified carbon foam anodes

Carbon foam anodes for MFC applications were surface modified with branched PEI to investigate the polymer's effect on biofim formation. Various forms of carbon, such as nanotubes [23,24], and graphitic nanofibers [25], have been surface oxidized using heat and acid to bear carboxylic acid groups. The reported procedures were adapted for carbon anodes in this publication, which we oxidized by heating in nitric acid. Treatment with PEI under standard peptide coupling conditions with aqueous NHS and EDC, allowed formation of covalent amide bonds with the carbon surface (Scheme 1). This method of anode surface modification is rapid, simple, and applicable to the covalent attachment of any polymer or small molecule with a free amine.

3.2. Characterization of PEI-modified carbon foam anodes

Anodes were examined by FT-IR and TGA before surface modification, after oxidation to bear carboxylic acid groups, and finally after attachment of PEI. The FT-IR spectrum of the oxidized carbon anodes revealed two new absorptions with maxima at 1730 cm^{-1} and 1620 cm^{-1} when compared to the unmodified anodes (Fig. 1). These absorptions can be attributed to the carbonyls of the acid groups. It was also noteworthy that after oxidation the carbon anodes became much more hydrophilic and could be immersed in water. The unoxidized anodes are highly hydrophobic and float in water. The FT-IR spectrum of the PEI-modified anodes also revealed two absorptions in the carbonyl region, with maxima at 1730 cm^{-1} and 1577 cm^{-1}. The slight downshift in absorbance from 1620 cm^{-1} to 1577 cm^{-1} is characteristic of amide bonds (Fig. 1, inset). Peaks observed between 3500 and 3300 cm^{-1} in both modified anode spectrums are most likely due to water adhered to the hydrophilic surfaces.

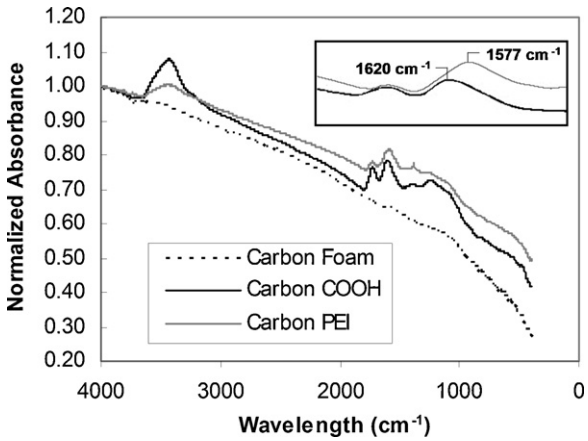


Fig. 1. IR spectrum of anodes before modification (carbon foam), after oxidation (carbon COOH), and after PEI modification (carbon PEI).

Anodes were also examined by TGA before surface modification, after oxidation to bear carboxylic acid groups, and finally after attachment of PEI. Distinct changes in overall mass loss were observed for both the acid and PEI-modified anodes (Fig. 2). Water adhered to the anode surfaces is likely to have contributed to mass losses from 25 to 100 °C and so only losses between 100 °C and 1000 °C were considered significant. The unmodified carbon foam showed a 16.06% total weight loss from 100 to 1000 °C. A slight increase to 17.96% was observed for the carboxylic acid modified carbon, whereas a significant increase to 22.46% loss was observed for the PEI-anodes. Two distinct mass loss events were observed

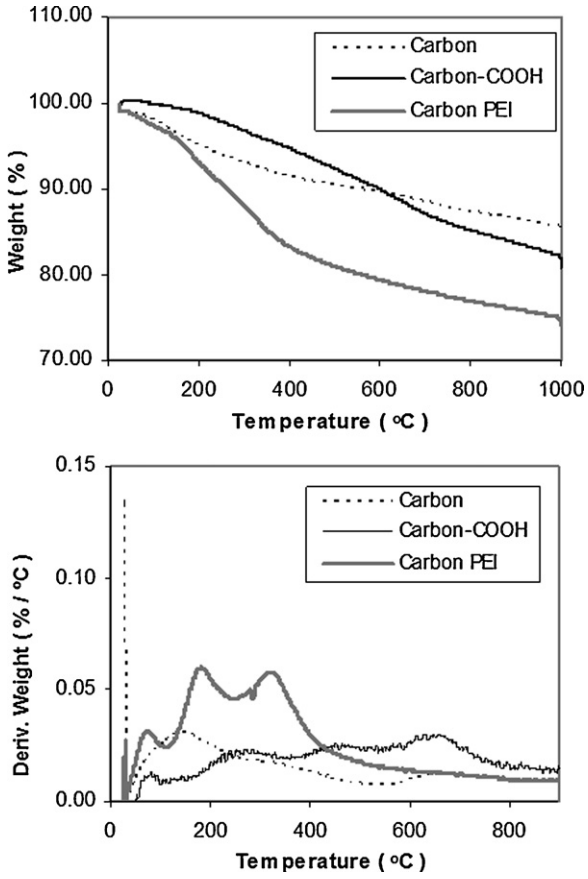


Fig. 2. TGA spectrum of anodes before modification (carbon), after oxidation (carbon COOH), and after PEI modification (carbon PEI).

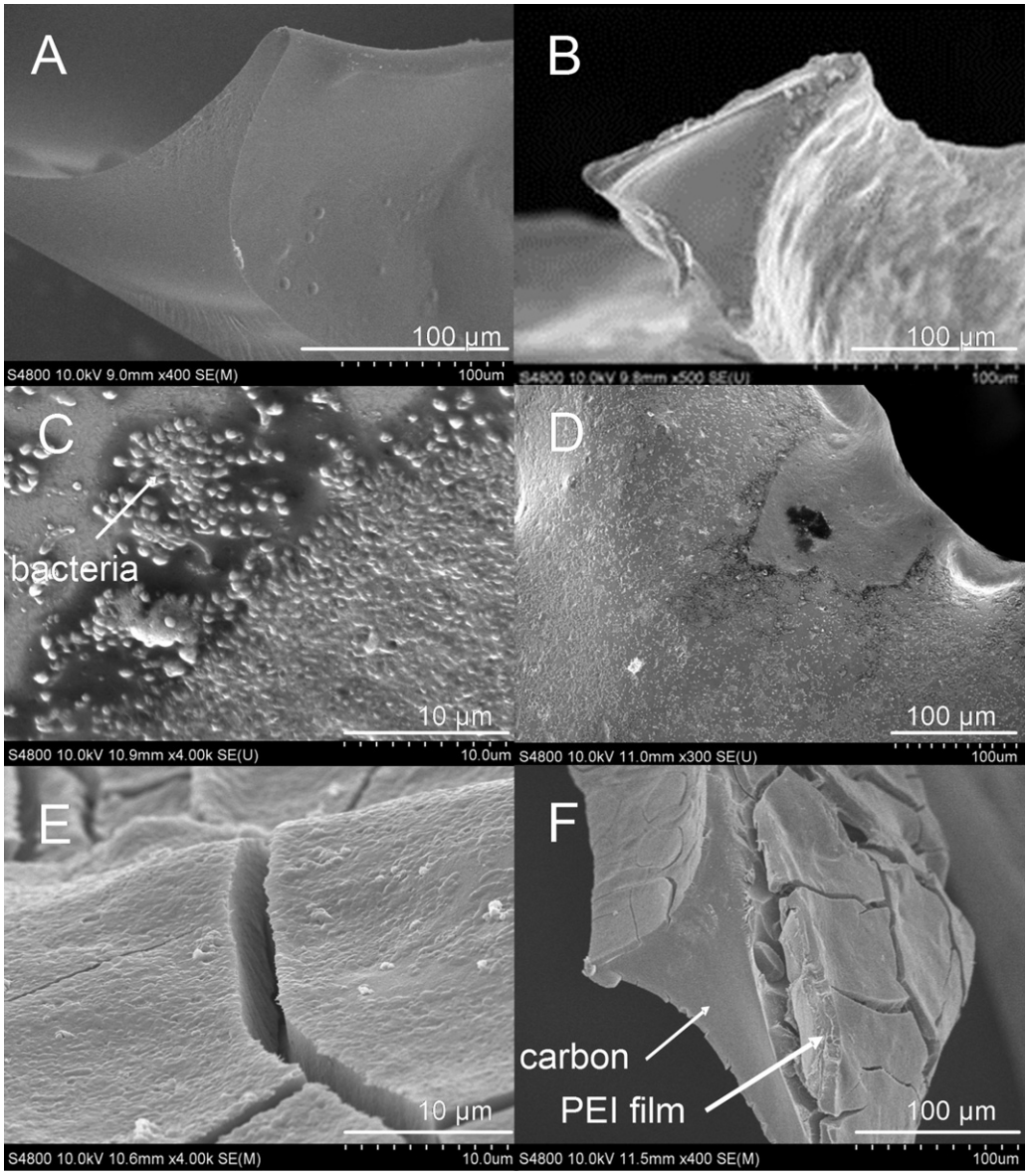


Fig. 3. Scanning electron microscopy images (SEM) of unmodified carbon foam anode (A), PEI-modified carbon foam anode (B), unmodified carbon anode after 5 weeks in an MFC (C, D), PEI-modified anode after 5 weeks in an MFC (E, F).

during PEI-anode heating, 3.75% from 100 to 200 °C and 7.99% from 200 to 375 °C. The distinct changes in TGA profiles can be attributed to the increased amount of volatile organic matter in the PEI chains and support the success of the surface modification chemistry.

PEI-modified anodes were examined by SEM and compared to unmodified anodes (Fig. 3A and B). Imaging revealed that the foam anode surface was coated with a film, presumably the polymer coating. Visible film formation was an unexpected result of the PEI modification, however, it is plausible given the highly charged nature of the polymer. The cationic polymer is likely to have a large hydrodynamic radius due to inter-chain charge repulsion, which could cause the polymer to swell, resulting in the observed film.

3.3. PEI-modified carbon anodes in MFC applications

To observe if PEI surface modification has an effect on biofilm formation, modified anodes were incorporated into MFCs and inoculated with a mixed colony of anaerobic digester bacteria. For comparison, MFCs containing unmodified carbon foam anodes were simultaneously inoculated with the same anaerobic bacteria sample. MFC cell voltages and power outputs were monitored over a period of approximately five weeks. Acetate was used as the oxidant and fuel source to initiate the bacterial metabolic cycle. Ferricyanide was used as the reductant and therefore the cell voltages reported are the difference in the oxidation potential of acetate and the reduction potential of ferricyanide, minus any contribution from internal cell resistance [22]. As expected, the voltage of the fuel cell with the unmodified anode gradually increased from 0.18 V to 0.58 V over a 40 day period (Fig. 4). However, the voltage of the system with the PEI-modified anode did not increase within the observation period.

Fig. 4 shows the change in power output over the same 40 day period. A substantial increase in power output was observed for the MFC containing the unmodified anode. The fuel cell's peak power output after approximately four weeks of biofilm growth was 0.08 mW at 0.45 V, characteristic of metabolically active bacteria populating the MFC anode surface. The power output of the MFC with the PEI-modified anode was negligible, which is expected given the low cell voltage. This data indicates that the bacteria originally inoculated into the MFCs were metabolically active and

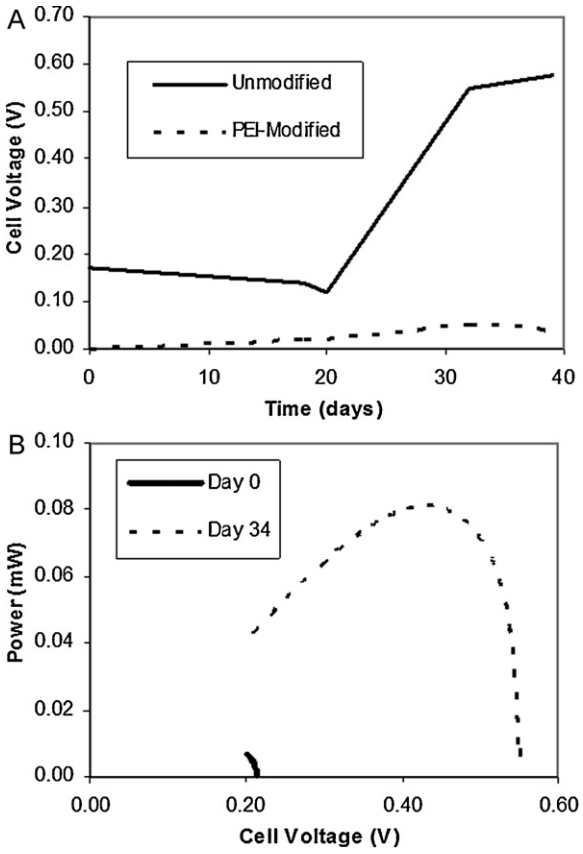


Fig. 4. (A) Fuel cell voltages of PEI-modified and unmodified carbon foam anodes. A 500 Ω resistor was placed in series with the anode and cathode at day 20. (B) Unmodified MFC polarization curve, PEI-modified MFC curve not pictured due to low voltage. Electron donor: 10 mM acetate. Electron acceptor: 50 mM potassium ferricyanide.

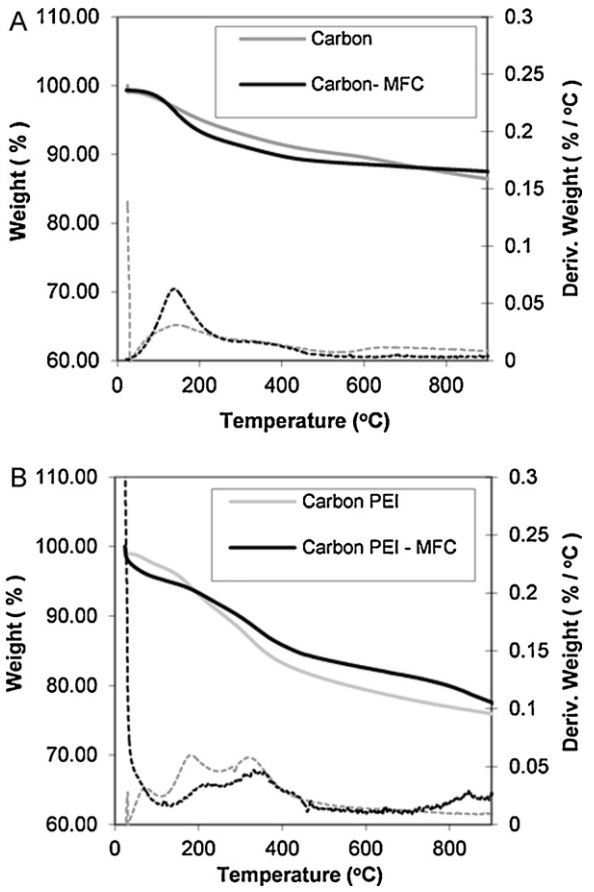


Fig. 5. (A) TGAs of unmodified carbon foam anode before and after use in an MFC. (B) TGAs of PEI-modified carbon foam anode before and after use in an MFC. Solid lines (—) are % weight loss and dashed lines (—) are the derivative of this loss with respect to temperature.

capable of biofilm formation, but that PEI modification either does not support biofilm growth, or that the PEI coating prevents electrochemical observation of the biofilm.

3.4. Characterization of biofilms on anode surfaces

Biofilms on the carbon foam anodes and PEI-modified carbon foam anodes were examined by both SEM and TGA after five weeks in MFCs. Carbon foam anodes are known to support biofilm growth [10,11,13] and thicker anode biofilms have been associated with higher MFC power outputs [11]. Though SEM is not capable of measuring depth, the technique is useful for a qualitative examination of the presence and quality of the biofilms. SEM imaging of the unmodified carbon anode surface clearly revealed bacterial populations (Fig. 3). Common electrogenic bacteria such as Geobacter and Shewanella species are typically on the order of 1 μm in length. At the 10 μm scale (Fig. 3C), rod-like individual bacteria were observed populating the anode surface. At the 100 μm scale (Fig. 3D), the unmodified carbon foam anode surface appeared to be covered with a layer of bacteria and seemed to support a healthy biofilm. Although there appeared to be some structures on the PEI-anode after use in an MFC (Fig. 3E and F), it was not clear whether they were live bacteria composing a biofilm. The presence of a biofilm is possible but the structures are not as uniformly rod-like as those observed on the unmodified anode, and could be cellular debris instead of live bacteria. It is difficult to measure depth with SEM so it is unclear whether the film on the anode surface is thicker after use in the MFC, which could indicate the presence or absence of a biofilm. In the MFC environment, electrostatic interactions with negatively charged organic compounds in the buffered nutrient media and debris from the charged bacterial cell wall are likely to further contribute to film formation. Further work is underway to elucidate the nature of the PEI coating.

In an effort to quantitate the differences in biofilm formation, we investigated TGA as a method to observe differences in the mass loss profiles. To our knowledge, this is the first application of TGA in biofilm characterization. Biofilm thickness is typically characterized by confocal microscopy, [10] which is a highly effective method, but requires expensive equipment and considerable training to obtain quality images. TGA is widely used for materials characterization, requires little training and sample preparation, and yields rapid results.

After five weeks in functional MFCs, anodes were removed from the fuel cells and subjected to TGA analysis. A comparison of the mass loss profiles of PEI-anodes versus the unmodified anodes before and after use in the MFCs, revealed significant differences. Only mass loss events above 100 °C were considered significant due to the likely presence of surface adhered water. In the case of the unmodified carbon anodes before and after use in the MFC, a 5% change in mass loss was observed between 100 °C and 200 °C in the TGA weight loss profile (Fig. 5). This is a temperature range where bacterial organic matter is likely to decompose and burn, and thus this difference is attributed to a bacterial biofilm. The TGA data is in agreement with our observations by SEM, as well as our electrochemical data. An active biofilm in direct contact with the carbon foam surface should create a potential difference between the anode and the cathode and generate current, such as observed.

A 5% mass loss correlates to approximately 4 mg of dry bacterial biofilm, in the unmodified MFC. Taking 1.06 g cm^{-3} as an average density of a wet cell [10] and estimating that the dry mass accounts for roughly 30% of the total cell mass, the cumulative cell volume is calculated to be 0.0133 cm^3. If this volume was distributed uniformly over the surface of the unmodified anode (15 cm^2) the biofilm thickness would be about 9 μm. A biofilm of 9 μm is within the range expected given the current and power output of the MFC.

The mass loss profile of the PEI-anode after five weeks in the MFC displayed no new events when compared to the profile before use in the MFC (Fig. 5). The same two mass loss events, centered around 175 °C and 325 °C, were observed in both profiles. No significant change in mass loss was observed between 100 °C and 200 °C as in the unmodified case, suggesting the lack of a substantial biofilm for the PEI-modified case. The overall mass loss was slightly less (1.9%) after use in the MFC than before, which is most likely due to loss of material that was electrostatically adsorbed, but not covalently linked, to the anode surface (e.g. anions to the PEI chains). The buffered anolyte solution is likely to break up such interactions over time.

The lack of MFC voltage and power output, together with the TGA data, seems to indicate that the PEI prevented the formation of a healthy biofilm. Given the previously reported success with PEI coatings for wastewater bacterial biofilm formation [21] this result was surprising. One explanation for the lack of power is that the PEI coating prevented direct contact with the anode surface and consequently prevented electron transfer from the bacteria to the anode. As previously noted, the biofilm must be in electrical contact with an electron sink for current generation. It is inconclusive from the SEM images whether a biofilm had grown on top of the PEI coating, but appears unlikely. The bacteria may have initially adhered and populated the surface of the PEI-anode, but were not in contact with the carbon foam anode and as a result no voltage and power output was generated. Another explanation is that high charge density of the PEI has a toxic effect on the bacteria, however PEI toxicity is generally associated with free polymer in solution, not PEI immobilized on a surface [16]. Another likely possibility for the difference in effect of PEI between our study and Goncalves and Govind's study is that the wastewater bacterial composition was very different from ours and contained strains that flourish on the PEI surface. The bacterial composition of wastewater is likely to be highly variable even between samples collected from the same treatment plant depending on the nutrient composition of the water, the time of year and other factors. In addition, Goncalves and Govind's study involved gold anodes rather than carbon, and the branching density of the polyethyleneimine used in their study was not reported.

To further verify the correlation between TGA data, electrochemical observations, and biofilm formation; we set up an identical fuel cell as in the unmodified carbon case previously described. The cell, JKAD7, was inoculated with the same anaerobic digester bacteria samples collected from wastewater. Fuel cell power output was monitored over 36 days and the anode was subsequently removed from the cell and subjected to TGA analysis.

Similar to the results previously described for the carbon anode, both the voltage and power output of the fuel cell gradually increased over time (Fig. 6). The fuel cell's peak power output after approximately four weeks of biofilm growth was 0.09 mW at 0.46 V, characteristic of metabolically active bacteria. Anodes were removed from the fuel cells and subjected to TGA analysis as previously described (Fig. 7). A 5.4% change in mass loss from before and after use in the MFC was observed between 100 °C and 350 °C, with the majority of this loss occurring between 200 °C and 350 °C. This is in good agreement with the data reported in Fig. 5. The slightly higher mass loss for JKAD7 when compared to the first unmodified carbon MFC correlates to the slightly higher voltage and power output of JKAD7. The mass loss for JKAD7 occurred over a higher

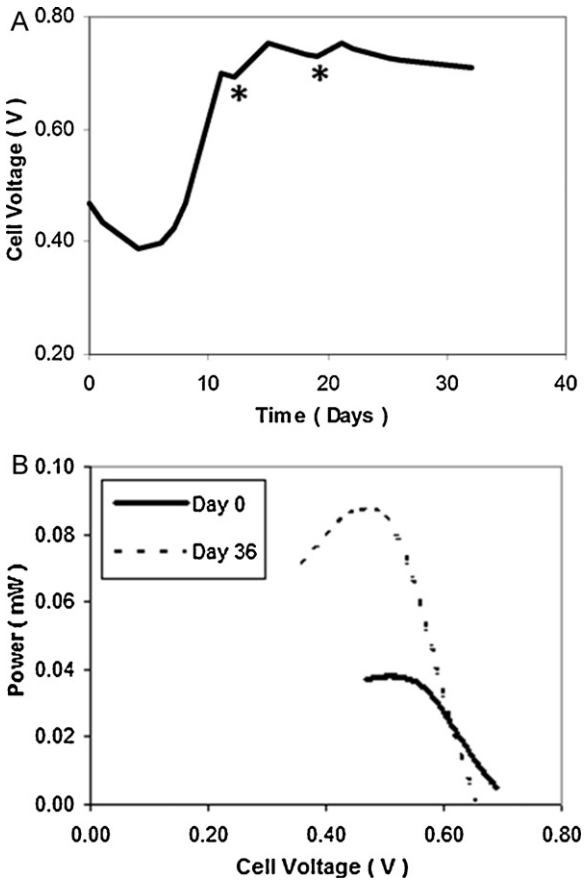


Fig. 6. (A) Fuel cell voltages of MFC JKAD7. A 170 Ω resistor was placed in series with the anode and cathode at day 12. Star (*) indicates dates fresh acetate media was added to the cells. (B) MFC JKAD7 polarization curves. Electron donor: 10 mM acetate. Electron acceptor: 50 mM potassium ferricyanide.

temperature range than for the anode shown in Fig. 5, despite the two anodes being exposed to identical conditions. This difference is likely due to variance in the morphologies of the biofilms on the two anodes. It is known that bacterial biofilms commonly form fibrilar and mushroom like structures [26]. The types of structures composing the biofilm and their densities are likely to affect the temperature that mass losses occur.

Based on our data, TGA appears to be a valid new method for observing trends in biofilm formation on anodes for MFC

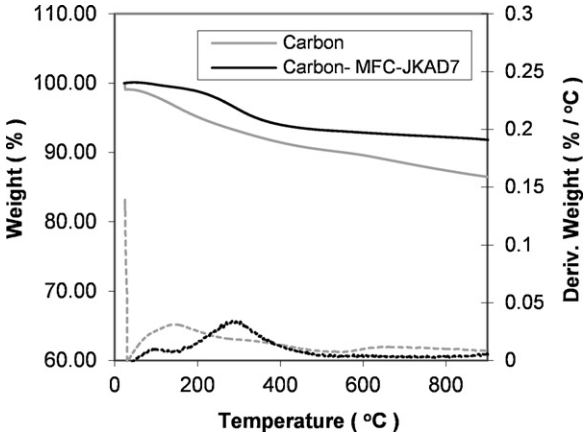


Fig. 7. TGAs of the carbon foam anodes before and after use in an MFC. Solid lines (—) are % weight loss and dashed lines (—) are the derivative of this loss with respect to temperature.

applications. Clear differences were observed between the PEI-modified anode and the two unmodified anodes before and after application in an MFC. Furthermore, the data was in agreement with the SEM images and electrochemical observations. While analysis of the TGA data in PEI-modified case was complicated by electrostatic interactions, the method appears to be useful for a semi-quantitative assessment of biofilms. The method lacks the precision of confocal microscopy, but it is simple, rapid, inexpensive, and demonstrates trends in biofilm formation.

4. Conclusions

In conclusion, we have successfully conjugated PEI unto the surface of carbon foam anodes for MFC applications. We also propose TGA as a useful new tool for observing trends in biofilm thickness. Our PEI conjugation method is rapid, simple, and applicable to surface modification with any compound containing a free amine. We have found that in MFC applications, PEI does not facilitate increased power output. Two possibilities for this observation are that the biofilm formation was retarded by the PEI or that the PEI prevented electron transfer to the anode. Biofilms were characterized by both SEM and TGA, and appeared more dense on the unmodified carbon. Based on our observations, TGA is a useful new tool for simple and rapid observation of trends in biofilm thickness.

Acknowledgments

We thank the following individuals for their contributions to this work: Bob Doty and Joanna Kolodziejska (HRL Laboratories); Professor Kelly Nevin (University of Massachusetts, Amherst); Brad Glassman (Las Virgenes Municipal Water District); Part of this work was supported by the NSF IGERT: Materials Creation Training Program (MCTP) – DGE-0654431, the NSF under award No. DMR 0907453, and the California NanoSystems Institute.

References

[1] B.E. Logan, Nat. Rev. Microbiol. 7 (2009) 375.
[2] D.R. Lovley, Geobiology 6 (2008) 225.
[3] D.R. Lovley, K.P. Nevin, in: C.S. Harwood, A.L. Demain, J.D. Wall (Eds.), Bioenergy, ASM Press, New York, USA, 2008, pp. 295–322.
[4] D.R. Lovley, Curr. Opin. Biotechnol. 19 (2008) 1.
[5] A.E. Franks, K.P. Nevin, Energies 3 (2010) 89.
[6] L.M. Tender, Nat. Biotechnol. 20 (2002) 821.
[7] C.E. Reimers, L.M. Tender, S. Fertig, W. Wang, Enivron. Sci. Technol. 35 (2001) 192.
[8] B.E. Logan, Water Sci. Technol. 52 (2005) 31.
[9] H. Liu, R. Ramnarayanan, B.E. Logan, Enivron. Sci. Technol. 38 (2004) 2281.
[10] B.E. Logan, Microbial Fuel Cells, Wiley, New Jersey, 2008.
[11] A.E. Franks, N. Malvankar, K.P. Nevin, Biofuels 1 (2010) 589.
[12] S. Cheng, H. Liu, B.E. Logan, Enivron. Sci. Technol. 40 (2006) 2426.
[13] A. Rinaldi, B. Mecheri, V. Garavaglia, S. Licoccia, P.D. Nardo, E. Traversa, Enivron. Sci. Technol. 1 (2008) 417.
[14] J.S. Remy, B. Abdallah, M.A. Zanta, O. Boussif, J.P. Behr, B. Demeneix, Adv. Drug Del. Rev. 30 (1998) 85.
[15] J. Zheng, W.S. Manuel, P.J. Hornsby, Biotechnol. Prog. 16 (2000) 254.
[16] A.R. Vancha, S.G. Kishore, V.L. Parsa, M. Jasti, M. González-García, R.P. Ballestero, BMC Biotechnol. 4 (2004) 23.
[17] Y. Bledi, A.J. Domb, M. Linial, Brain Res. Protoc. 3 (2000) 282.
[18] J. Huanga, N. Jin, T. Katsuda, H. Fukuda, H. Yamaji, Biochem. Eng. J. 46 (2009) 65.
[19] J.S. Andrews, V.P. Mason, I.P. Thompson, G.M. Stephens, G.H. Markx, J. Microbiol. Methods 64 (2006) 96.
[20] C.E. Verduzco-Luque, B. Alp, G.M. Stephens, G.H. Markx, Biotechnol. Bioeng. 83 (2003) 1.
[21] J.J. Goncalves, R. Govind, Sens. Actuators B 143 (2009) 341.
[22] M.V. Coppi, C. Leang, S.J. Sandler, D.R. Lovley, Appl. Environ. Microbiol. 67 (2001) 3180.
[23] S. Banerjee, S.S. Wong, Nano Lett. 2 (2002) 195.
[24] H. Kitano, K. Tachimoto, Y. Anraku, J. Colloid Interface Sci. 306 (2007) 28.
[25] J. Li, M.J. Vergne, E.D. Mowles, W.-H. Zhong, D.M. Hercules, C.M. Lukehart, Carbon 43 (2005) 2883.
[26] B. Rittman, in: M. Ghannoum, G.A. O'Toole (Eds.), Biofilms in the Water Industry, Microbial Biofilms, ASM Press, New York, USA, 2004, pp. 359–378.