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Comparing the short and long term stability of biodegradable, ceramic and cation exchange membranes in microbial fuel cells

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HIGHLIGHTS

- Novel biodegradable bag (BioBag) successfully worked as an MFC membrane.
- BioBag degraded but with stable performance, pointing to missions with expiry dates.
- Ceramic membrane more stable short-term and equal to CEM over long-term.
- CEM exhibited power overshoot and hysteresis during bi-directional polarisation.
- The anolyte of BioBag and ceramic MFCs was less prone to acidification.

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ABSTRACT

The long and short-term stability of two porous dependent ion exchange materials; starch-based compostable bags (BioBag) and ceramic, were compared to commercially available cation exchange membrane (CEM) in microbial fuel cells. Using bi-directional polarisation methods, CEM exhibited power overshoot during the forward sweep followed by significant power decline over the reverse sweep (38%). The porous membranes displayed no power overshoot with comparably smaller drops in power during the reverse sweep (ceramic 8%, BioBag 5.5%). The total internal resistance at maximum power increased by 64% for CEM compared to 4% (ceramic) and 6% (BioBag). Under fixed external resistive loads, CEM exhibited steeper pH reductions than the porous membranes. Despite its limited lifetime, the BioBag proved an efficient material for a stable microbial environment until failing after 8 months, due to natural degradation. These findings highlight porous separators as ideal candidates for advancing MFC technology in terms of cost and operation stability.

1. Introduction

Microbial fuel cells (MFCs) produce electricity via the breakdown of organic matter in a feedstock by bacteria. The liquid feedstock not only acts as the fuel but also undergoes systematic treatment during the process and a large number of substrates have been explored (Pant et al., 2010). In order to transfer the technology from the laboratory to field-use, power output needs to be improved, and the cost of materials reduced. To overcome power limitations multiples can be connected together (Aelterman et al., 2006; Ieropoulos et al., 2008), however due to the biological nature of MFCs, factors such as cell reversal and instability caused by operating parameters can occur in more complex configurations (Oh and Logan, 2007). Furthermore, the fragility of MFCs when subjected to heavy loads was recently demonstrated using a bi-directional polarisation method (Degrenne et al., 2013). In the literature, the majority of data to date are presented based on single polarisation experiments where the external resistance (R_{EXT}) is gradually lowered in a stepwise fashion from the open-circuit voltage (OCV) down to short circuit values. This provides the operator with important data including the maximum power transfer point (MPP), which can be used to derive the sustainable level that the fuel cell can operate and the corresponding R_{EXT}. Furthermore, data can indicate the health of the MFC through polarisation curves which identify where losses may be occurring (Harnisch and Schroeder, 2010), and through power curves where the presence of a power overshoot can indicate underperformance (Ieropoulos et al., 2010b). To provide more of an insight into the stability of the MFCs, a bi-directional characterisation method can be used

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where the MFC is subjected to a second sweep that takes it back up from the low resistances to OCV. Theoretically, in a stable system, the two curves should be identical (Winfield et al., 2011b) but to date the MFC studies that have employed this method have reported significant hysteresis with the second (reverse) inferior to the first (forward) sweep (Aelterman et al., 2006; Degrenne et al., 2013). This is important in terms of the accurate reporting of data and the implications for scale-up when reliable, stable operation will be essential. Furthermore the inferior performance on the return sweep might also be a signal that the microbial community has been temporarily damaged or inhibited because of exposure to heavy loads.

It has been hypothesised that the discrepancy between the two curves is the result of mass transfer limitations imposed on the biofilm after operating at high currents during the forward sweep (Degrenne et al., 2013). While this theory is well founded, the influence of component materials has not been addressed and in particular the choice of proton exchange membranes (PEM). Cation exchange membrane (CEM) was used as the membrane of choice in previous studies that employed the bi-directional characterisation method (Degrenne et al., 2013; Aelterman et al., 2006). Despite being expensive and designed for conventional fuel cells that operate in conditions not suitable for electro-active bacteria (Biffinger et al., 2007), commercially available PEMs are widely used in MFC research. The PEM materials (e.g. CEM) rely on proton/cation conductivity (Li et al., 2011) but recently, novel porous materials that enable non-ion selective charge transfer have being reported that could help advance the technology by lowering the cost; these include j-cloth (Fan et al., 2007), ceramics (Behera et al., 2010) and natural rubber (Winfield et al., 2013b). The current study focuses on two materials that are widely available and could be domestically accessible for application. The first is a ceramic, a material that is highly attractive because of its low cost and ready availability in developing countries (Ajayi and Weigele, 2012) and the second is a plain compostable biodegradable bag (BioBag) of the type that might be found in most domestic food waste systems in homes. Both materials rely on porosity for proton transfer, the ceramic because of its natural structure and the BioBag through biodegradation as has been previously reported with natural rubber membranes (Winfield et al., 2013b). In order to comprehensively evaluate the suitability of new materials as membranes, examination should take place over different time-frames. Therefore in the current study porous materials were compared to commercially available CEM on three levels; (i) short-term analysis (hours) using the bi-directional characterisation method to explore whether hysteresis, and ultimately stability, might be linked to membrane-type, or whether it is the result of microbial exhaustion, (ii) a mid-term analysis (days) to investigate the effects that the membrane type has on anolyte chemistry (pH) and (iii) long-term analysis (months) to evaluate and compare the lifetime of the material.

2. Methods

2.1. Microbial fuel cell design and operation

2.1.1. CEM and BioBag MFCs

Acrylic cuboid MFCs were used for the CEM and BioBag membranes as pictured in Fig. 1a. These were constructed using acrylic anode chambers with an empty chamber volume of 25 mL and electrodes (anodes and cathodes) that were constructed from 270 cm^2 untreated carbon veil with a density of 20 g/m^2 (PRF Composites, Dorset, UK) and folded down to produce 3D rectangular cuboids (with a projected surface area of 17 cm^2). Nickel chrome wire was threaded through the electrodes and used for current collection. CEM samples of dimension 60 × 50 mm of CEM (VWR supplies, Leicestershire, UK) and biodegradable bag composed of fully home compostable material based on starch and compostable polyester (Home compostable caddy liners, Sainsbury's, UK) were prepared as membranes. These were soaked in deionised water for 24 h before being sandwiched between rubber gaskets and employed as separator and/or proton exchange membrane. The thickness of each material was 0.15 mm for BioBag and 0.16 mm for CEM. The anode was housed in the chamber while the open-to-air cathode was held to the other side of the membrane using parafilm.

2.1.2. Ceramic MFC

The ceramic MFC (Fig. 1b) was constructed as follows; a ceramic cuboid chamber, closed all around with a gap of 20 × 50 mm for inserting the electrode, was fashioned using earthenware clay (Standard White Earthenware, CTM Potters Supplies, Exeter) that was air dried and cooked in a kiln at 1150 °C with a resulting anode chamber open volume of 25 mL (Fig. 1b). The chamber walls (with a thickness of 5 mm) were used as structural material and as the medium for proton exchange. The ceramic was soaked for 24 h in deionised water prior to the addition of electrodes. The same anode and cathode dimensions were used as above (270 cm^2 of carbon veil) with the cathode being held securely against the cuboid wall with parafilm.

2.2. MFC operation

Anodes, previously inoculated with primary sludge (Wessex Water, Saltford, UK), were removed from three established MFCs that were selected based on their parity of performance, and used for experimentation. All MFCs were operated under identical conditions and periodically batch-fed with autoclaved TYE solution (10 g tryptone, 5 g yeast extract in 1 L deionised water) with a starting COD of approximately 17.5 g/L, conductivity of approximately 2.5 mS/cm and pH 7. Prior to each new feed the depleted anolyte was removed and analysed. Open to air cathodes were hydrated on a daily basis with tap water. MFCs were operated under 1000 Ω external resistance unless otherwise stated. For pH measurement the feedstock was fed to the MFC at time zero and a sample was removed after 4 h for measurement. Fresh feedstock was then fed to the MFCs (time starts again at zero) and removed after the next feeding time (i.e. 18 h), in this way the feedstock for each reading was only removed and analysed once. The pH data were measured using a pH meter (HANNA pH 209) and presented as the mean based on two 96 h experimental runs.

2.3. Data collection

Electrode output was recorded in volts (V) against time by using an ADC-16 Channel Data Logger (Pico Technology Ltd., Cambridgeshire, UK). Recorded data were processed and analysed using the GraphPad Prism version 6 software package (GraphPad, San Diego, CA, USA). Current (I) in amperes (A) was calculated using Ohm's law, $I = V/R$, where V is the measured voltage in volts (V) and R is the known value of the external load resistor in ohms (Ω). Power (P) in watts (W) was calculated by multiplying voltage with current: $P = I \times V$. Power and current density were calculated using the total empty chamber volume (25 mL). Total internal resistance (R_{INT}) was calculated using the method described by Ieropoulos et al. (2008):

$$R_{INT} = \left(\frac{OCV}{I_L}\right) - R_{EXT}$$

where OCV is the open circuit value of the MFC, I_L is the current under a given load and R_{EXT} is the given load.

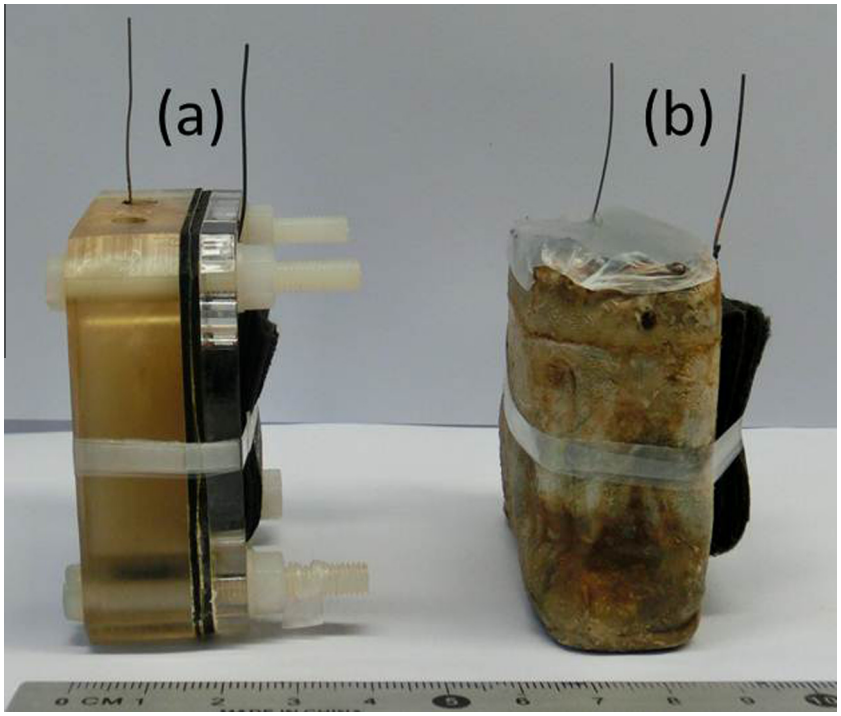

Fig. 1. Photograph of (a) acrylic MFC design used for BioBag and CEM membranes and (b) ceramic MFC.

2.4. Polarisation experiments

Polarisation experiments were performed using an automated computer-controlled variable resistor as previously described (Degrenne et al., 2012). Single (forward) polarisation sweeps were performed by applying 60 resistance values in the range of 1 MΩ down to 3 Ω, and each resistance was connected for 5 min. For the bi-directional sweeps, 60 resistance values were applied from 1 MΩ down to 3 Ω with a sample rate of 5 min for each value before the 60 resistance values were swept back up from 3 Ω to 1 MΩ. There was no 'rest period' between sweeps and so effectively the MFCs were held at 3 Ω for 10 min (5 min forward, 5 min reverse). Each bi-directional test lasted 10 h from start to finish. One day before the polarisation sweeps, the MFCs were drained and fed with fresh feedstock, whilst the cathodes were hydrated immediately before each experiment. All experiments were at least duplicated with the bi-directional sweep hysteresis data calculated as the mean of five runs. For clarity of presentation, power curves presented are based on one representative bi-directional sweep performed at the beginning of month seven.

3. Results and discussion

3.1. Long-term analysis

The biodegradation of a material can transform it from an impermeable barrier to an efficient medium for proton exchange as previously demonstrated using natural rubber (Winfield et al., 2013b). Natural rubber MFCs were able to operate for almost a year but it may be desirable to design reactors to operate for shorter periods of time, perhaps as single-use only sensors before they degrade harmlessly into the environment. Compostable bags were thus trialled not only for their power producing capabilities but also for their degradation characteristics. During the initial 2 weeks of operation negligible working voltage was generated in the BioBag-MFC and the assumption was that in these early stages it was completely impermeable to the movement of protons. After approximately 2 weeks the BioBag MFC began to produce power and so at this stage onwards, protons were able to pass between anode and cathode. From this time single (forward) polarisation experiments were periodically performed. Fig. 2 shows the performance based on the maximum power produced from single (forward) polarisation sweeps over an 8 month period. All MFC types displayed continued improvement up to month six at which point the BioBag MFC peaked in performance. By the end of month seven of operation the BioBag had begun to deteriorate significantly and by month eight, damage was visible to the extent that it was no longer able to provide sufficient separation between electrodes as reflected in the diminished output. CEM and ceramic MFCs continued to perform to a similar level by the eighth month. The good performance exhibited by the ceramic material in the current work supports previous studies that report the suitability of ceramics to operate as PEMs and structural materials in MFCs (Behera et al.,

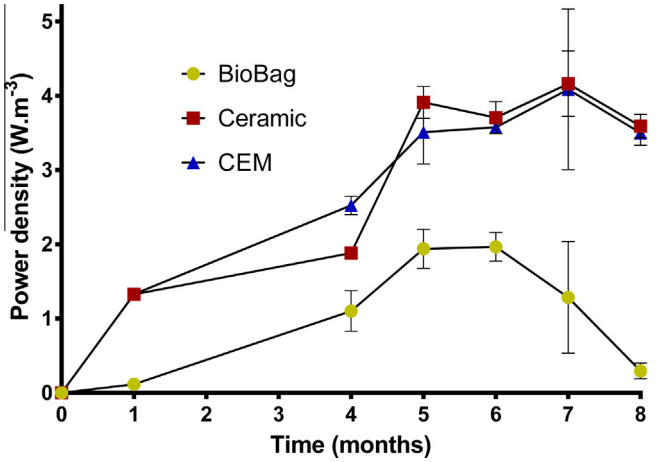

Fig. 2. Comparison of maximum power density produced over time during forward polarisation sweeps for MFCs employing ceramic, compostable bag and CEM as membrane; data presented as mean and range (n = 2).

2010; Ajayi and Weigele 2012; Winfield et al., 2013a). The inferior long-term performance of the BioBag compared to ceramic and CEM-MFCs would initially suggest that it is not an ideal PEM material. However, the very fact that its operation is time-limited by biodegradation processes makes it extremely attractive for short-term and bio-sensitive applications. Furthermore, as will be discussed in the following section, porous membranes could offer greater stability over shorter periods of time.

3.2. Bi-directional characterisation

In order to analyse the stability of membranes over relatively short periods of time (h), bi-directional characterisation analysis was performed. Five bi-directional sweeps were carried out during months five, six and seven. To emphasise curve shape, bi-directional curves are presented in Fig. 3 that were produced from an individual sweep performed at the beginning of month seven. The superior performance of the forward curve over the reverse curve using bi-directional characterisation has been reported before and in both previous studies the membrane used was CEM (Aelterman et al., 2006; Degrenne et al., 2013). In the current study the commercially produced CEM demonstrates the same pattern of hysteresis as described by Degrenne et al. (2013).

This is highlighted in Fig. 3a where the CEM-MFC sweep exhibits a distinct decline in performance during the second (reverse) compared to the forward curve. Furthermore during the majority of experiments, a bending back of the forward CEM curve was observed as indicated by the asterisk (Fig 3a), which is a phenomenon that has previously been termed 'power overshoot' (Ieropoulos et al., 2010b). Power overshoot has been linked to a variety of sub-optimal conditions such as biofilm maturity (Winfield et al., 2011b), insufficient sample rate (Watson and Logan, 2011) and acclimation conditions (Hong et al., 2011; Zhu et al., 2013), but to the authors knowledge the role of materials, and in particular the type of membrane, has not been considered.

The bi-directional power curves produced by reactors using the two less conventional MFC membranes that enable proton transfer via porosity rather than ionic conductivity can be seen in Fig. 3b (BioBag) and Fig. 3c (ceramic). In both cases power overshoot is not observed, despite being inoculated and operated under the same conditions and using identical resistance sweep rates to the CEM-MFC. The CEM-MFC produced significantly higher power density than BioBag-MFC which could be hypothesised as the reason why power overshoot and instability occurred. However, the ceramic MFC exhibits no power overshoot despite generating comparable power densities to the CEM-MFC. Furthermore, power overshoot was observed in CEM-MFCs that, during the early stages of maturation, were producing low power densities similar to the BioBag MFC (data not shown). It is therefore apparent that power overshoot is not produced solely as a result of sub-optimal acclimation or operating conditions, but also as a result of membrane material, which can be integral to providing a stable environment. A similar observation can be made in terms of the extent of hysteresis and membrane type. It has been suggested that the biofilm might be adversely affected by mass-transfer limitations incurred by the operation at high currents (Degrenne et al., 2013). Should this be the case it might be expected that hysteresis would be directly correlated to the amount of current produced i.e. the higher the current the greater the effect on the biofilm as reflected by the inferior power curves on the reverse sweep. The peak current produced by CEM-MFC (32 A m^{-3}) is matched by BioBag-MFC and almost doubled by ceramic-MFC (60 A m^{-3}) yet neither exhibit the same pattern of hysteresis or power overshoot as the CEM-MFC. This suggests that operating MFCs at high currents should not result in reactor failure if the appropriate materials are employed.

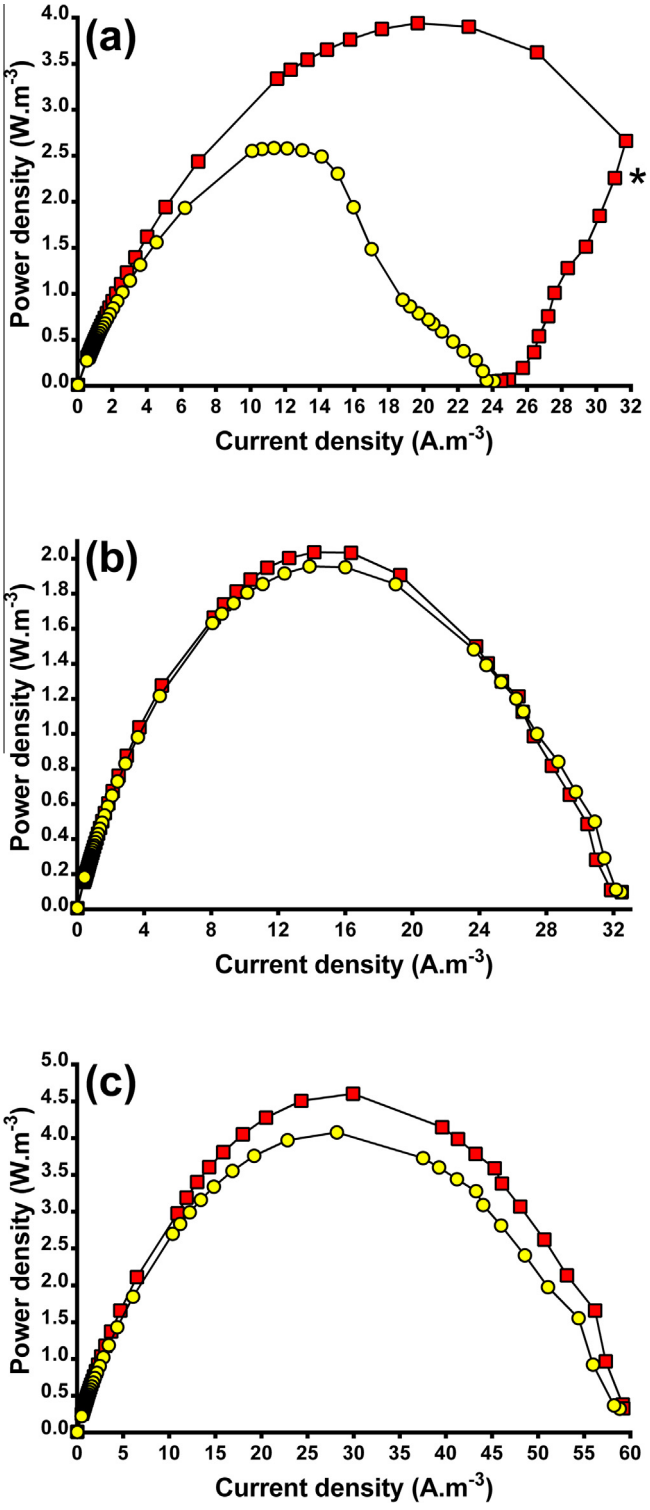

Fig. 3. Bi-directional power density curves for MFCs using (a) CEM, (b) compostable BioBag and (c) ceramic as membrane. Square symbols indicate the forward curve (OCV to short circuit) and closed circles represent the reverse sweep (short circuit to OCV). *Point where power overshoot occurs.

Fig. 4 shows the mean percentage difference (from five runs) between the superior points of maximum power (MPP) generated over the forward sweep compared to the lower MPP produced during the reverse sweep. The CEM-MFC exhibited significant losses compared to the porous membranes with the decline (38%,

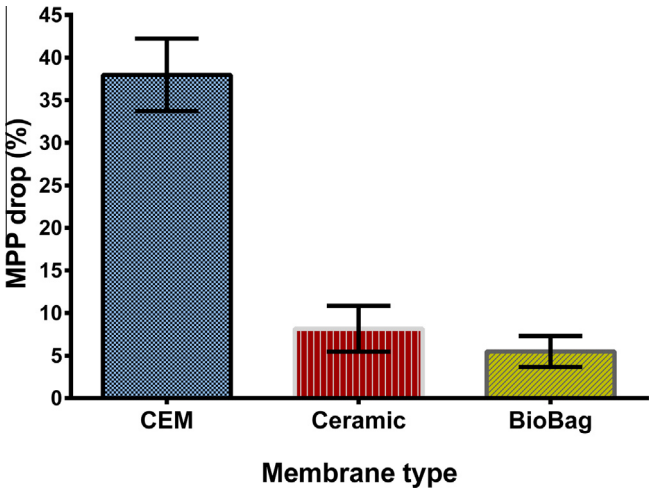

Fig. 4. Percentage drop in maximum power (MPP) between the forward sweep (OCV to short circuit) and the reverse polarisation sweep (short circuit to OCV). Data presented as mean and standard deviation ($n = 5$).

standard deviation: 4.3) being over four times greater than the drop exhibited in either the ceramic (8%, standard deviation: 2.7) or the BioBag (5.5%, standard deviation: 1.8). This short-term deterioration of performance could be vital in terms of operating MFC stacks, where R_{EXT} might vary according to the power demands required. Stability will be equally important when operating in heterogeneous environments such as wastewater treatment where abiotic conditions can quickly fluctuate (Patil et al., 2011). For example pH, COD, temperature, conductivity and fluid chemistry will all affect R_{INT}. The stable performance shown by the porous membranes could help negate problems such as cell reversal in stacks of MFCs where the choice of membrane can exaggerate the phenomenon (Ieropoulos et al., 2010a). This is exemplified in Fig. 5a, which shows that the R_{EXT} responsible for MPP is significantly higher during the second sweep for CEM (73%) compared to BioBag (6%) and ceramic (−8%). Furthermore the total internal resistance of the MFCs as calculated at MPP (Fig. 5b) increases significantly for CEM (64%) with little change observed in the BioBag (6%) or ceramic (4%).

Impedance matching should produce a MPP at an R_{EXT} which equals the reactor's total R_{INT} and this should occur at half OCV (Ieropoulos et al., 2010a). The data presented in Fig. 5 reveal that for all MFCs this was not the case and the MPP occurred at R_{INT} values approximately double those of the R_{EXT} used to produce that value. This phenomenon has been reported before (Winfield et al., 2011a) and could be the result of a dynamic OCV, which inherently changes in response to the operating conditions. For example a porous membrane will naturally allow oxygen to permeate into the anode chamber (Li et al., 2011) a factor that will lower the OCV (and increase R_{INT}) however, once a load is applied, at least some oxygen will be consumed at the cathode keeping the anode chamber more anaerobic. Theoretically, this would result in a higher OCV, and decreased R_{INT}.

3.3. Monitoring pH over fixed resistances

The aforementioned power overshoot in CEM occurred at approximately 100 Ω during the polarisation sweep. Previous reports have demonstrated that the use of CEM can result in a pH splitting where only the dominant ionic species are transferred through the membrane resulting in an accumulation of protons in the anode chamber (Harnisch et al., 2009). This can cause localised acidification, which can be inhibitory to the electroactive members of the anodic microbial community (Torres et al., 2008). Such an increased production of protons at the higher currents during the forward sweep might cause a pH gradient to build up that detrimentally affects the biofilm during the reverse sweeps. Furthermore, the power overshoot on the forward curve and the subsequent hysteresis on the reverse curve suggest that the CEM-MFCs are taking longer to recover perhaps because of the drop in pH. Due to this reason, pH was monitored over longer periods of time (up to 96 h), during which MFCs were operated under 100 Ω loads (i.e. the load that appears to initiate instability in CEM-MFCs during polarisation sweeps) and 1000 Ω loads (the long-term fixed R_{EXT}).

Fig. 6a shows that the anolyte of all MFCs exhibited an immediate drop in pH when operated under 100 Ω loads with the CEM-MFCs dropping to almost double the levels that the porous membranes reached after 4 h. The ceramic and BioBag MFCs recovered to near neutral pH after 18 h but CEM-MFCs were still marginally acidic after 48 h. This illustrates the effect that the membrane type alone can have on internal (electro) chemistry and highlights the importance of material selection. When operating under 1000 Ω load, the CEM-MFCs dropped over half a pH unit after 4 h before recovering to near-neutral levels by 48 h, (Fig. 6b). In contrast ceramic and BioBag did not drop below pH neutral levels at all and were able to maintain efficient proton transfer and balance as soon as fresh feedstock was introduced. The porosity-dependent membranes are not expected to discriminate against any cation species and so a proton build-up at the anode is less likely to take place (Li et al., 2011). Degrenne et al. (2013) hypothesised that hysteresis

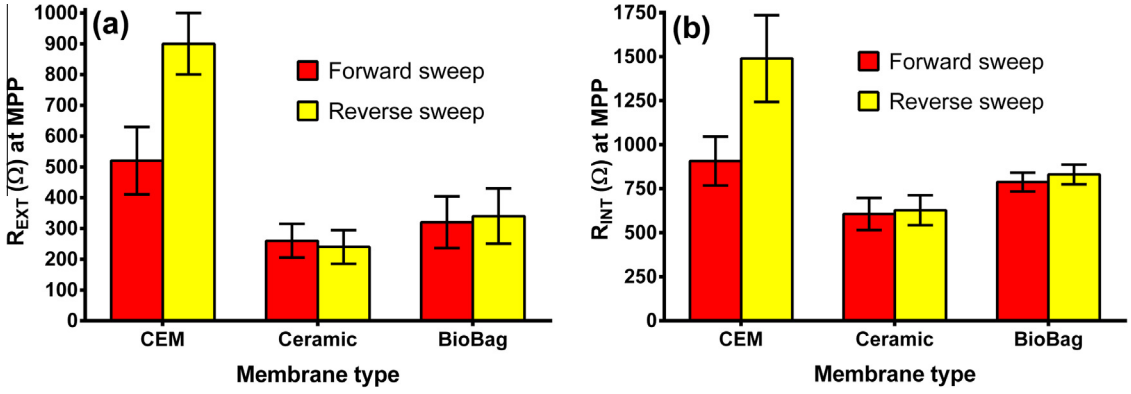

Fig. 5. Comparing the change in (a) external resistance (R_{EXT}) and (b) internal resistance (R_{INT}) at the points of maximum power (MPP) between forward and reverse polarisation sweeps. Data presented as mean and standard deviation ($n = 5$).

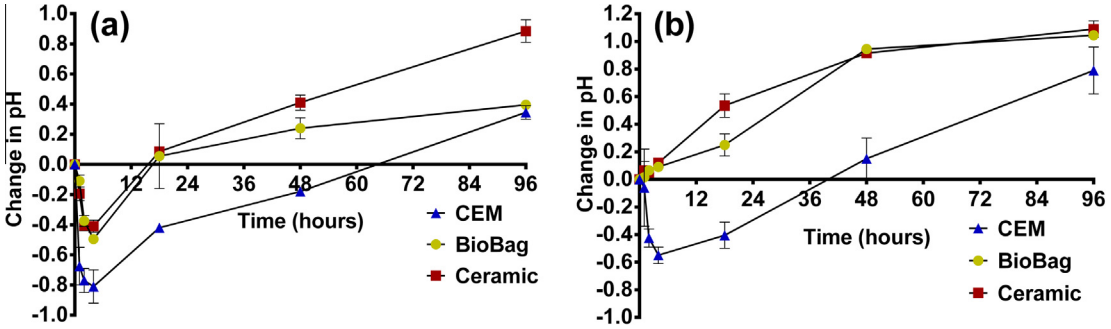

Fig. 6. The change in anolyte pH over time for MFCs operated under either (a) R_{EXT}: 100 Ω or (b) R_{EXT}: 1000 Ω. Data presented as mean and range (n = 2).

might be the result of mass transfer limitations and the current study supports this. However, the pH reduction and slow recovery are a function of the membrane and not the microbial community and the problem might therefore be eliminated through better selection of alternative materials.

For many target applications e.g. wastewater treatment, MFC longevity is essential but other applications, e.g. environmental sensors, might require a pre-set life expectancy. In such a case, short-term stability and reliability will be crucial as was demonstrated through the bi-directional characterisation of the compostable bag membrane. It has been reported that the biodegradation of membrane material could be limiting for operation (Li et al., 2011), yet cheap, disposable MFCs may be an attractive option particularly when potentially any inexpensive, ubiquitous domestic material might be employed. Furthermore, these materials could be incorporated into designs where they serve the dual purpose of ion-exchange membrane and structural material, thus cutting costs and improving spatial requirements. This could also pave the way for novel applications for example in the utilisation of food waste, where the material performs a dual function i.e. compostable bag and proton exchange membrane. The efficient performance of the ceramic membrane both in terms of short and long term stability further confirms the suitability of the material as a viable and inexpensive candidate for accelerating the scale-up and wider use of the MFC technology.

Finally, it should be noted that CEM has been widely used by MFC groups globally without reports of power overshoot or performance degradation, suggesting that it might take a combination of operational parameters, materials and variables to instigate these unwanted phenomena. Despite this, the current study has indicated that porous membranes might be more resilient and future work is needed to further examine whether they are the material of choice for operation in fluctuating or sub-optimal conditions.

4. Conclusions

This preliminary investigation compared porous membranes (ceramic and compostable bag) to cation exchange membranes (CEM) in MFCs. The compostable bag failed after eight months of operation but proved most stable in the short-term. Bi-directional polarisation sweeps highlighted the limitations of CEM which displayed marked performance loss during reverse sweeps, and power overshoot was observed. Porous membranes showed no overshoot and reduced hysteresis. The drop in anolyte pH was higher and recovery significantly longer for CEM-MFCs than their porous counterparts. These findings have implications for scale-up as membrane-type can affect the stability and cost of the system.

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