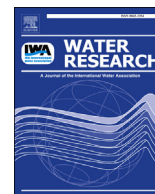




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Electro-osmotic-based catholyte production by Microbial Fuel Cells for carbon capture

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ABSTRACT

In Microbial Fuel Cells (MFCs), the recovery of water can be achieved with the help of both active (electro-osmosis), and passive (osmosis) transport pathways of electrolyte through the semi-permeable selective separator. The electrical current-dependent transport, results in cations and electro-osmotically dragged water molecules reaching the cathode. The present study reports on the production of catholyte on the surface of the cathode, which was achieved as a direct result of electricity generation using MFCs fed with wastewater, and employing Pt-free carbon based cathode electrodes. The highest pH levels (>13) of produced liquid were achieved by the MFCs with the activated carbon cathodes producing the highest power (309 μ W). Caustic catholyte formation is presented in the context of beneficial cathode flooding and transport mechanisms, in an attempt to understand the effects of active and passive diffusion. Active transport was dominant under closed circuit conditions and showed a linear correlation with power performance, whereas osmotic (passive) transport was governing the passive flux of liquid in open circuit conditions. Caustic catholyte was mineralised to a mixture of carbonate and bicarbonate salts (trona) thus demonstrating an active carbon capture mechanism as a result of the MFC energy-generating performance. Carbon capture would be valuable for establishing a carbon negative economy and environmental sustainability of the wastewater treatment process.

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1. Introduction

Addressing water scarcity and sanitation problems requires new methods of purifying water at lower costs and with less energy, whilst at the same time minimising the use of chemicals and their impact on the environment (Shannon et al., 2008). One method is water re-use and reclamation, where water is captured directly from industrial or municipal waste streams. Wastewater treatment is energy intensive, thus capturing part of this energy from waste and reclaiming the water would lower the total energy requirements. Novel technology platforms such as Microbial Fuel

Cells that use bacteria, capable of producing electric current thus recovering energy from wastewater, are particularly attractive. Research in the field of Bioelectrochemical Systems (BES) has focused on utilising compounds found in wastewater for the production of bioelectricity by Microbial Fuel Cells (MFCs), or biosynthesis of various compounds using Microbial Electrolysis Cells (MECs). On the one hand MFCs generate electricity, and on the other hand MECs require external electrical input to facilitate the electrolysis process for valuable product recovery such as hydrogen gas (Call and Logan, 2008), caustic soda (Pikaar et al., 2011; Rabaey et al., 2010) hydrogen peroxide (Rozendal et al., 2009) or acetate (Xafenias and Mapelli, 2014). This is an important area that is already attracting much attention. Regardless of the approach, cost-effective reactor designs and materials are urgently needed for field trials and large-scale implementation. To improve the slow kinetics of the electrochemical oxygen reduction reaction (ORR), various

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catalysts are usually being employed (Wang et al., 2014). Platinum (Pt) for example, has been widely used in chemical fuel cells due to its high catalytic performance at low pH (Erable et al., 2009), however due to its high cost, in addition to relatively fast deactivation in the presence of pollutants such as sulphur, other alternatives are being explored. Some of these approaches include chemical (Haoran et al., 2014), enzymatic (Santoro et al., 2013a), microbial catalysts (Erable et al., 2012) or Non-Pt electrode modification to improve the performance (Ghasemi et al., 2011; Lefebvre et al., 2009; Santoro et al., 2012, 2013b). The electrochemistry of the ORR has been thoroughly studied in the development of chemical fuel cells (Gasteiger et al., 2005; Neyerlin et al., 2007). Complex mechanisms are dependent on the pH conditions, proceeding in the 4-electron or 2-electron (peroxide) pathways forming as a final product H_2O (in acidic conditions) or OH^- (in alkaline conditions), as illustrated in Table 1. Generally, the 4-electron pathway appears to be predominant on noble metal catalysts (Kinoshita, 1988), whilst the peroxide pathway is more common on carbon based electrodes (Kinoshita, 1988).

A similarity between chemical and biological fuel cells is represented by the water fluxes taking place across the membrane. The water distribution in chemical fuel cells is influenced by the tendency of protonic currents to transport water molecules from the anode to the cathode via electro-osmotic drag (Larminie and Dicks, 2003). As a result, an excess of water could cause the decrease of the three phases interface (TPI), flooding the entire electrode and not allowing the oxygen in gas phase to reach the catalytic sites. Therefore the water content in Proton Exchange Membrane fuel cells, is strictly controlled and the water management is a significant aspect to be considered and one of the most important challenges (Larminie and Dicks, 2003; Park and Caton, 2008).

In wastewater-based biological fuel cells, studying water transport is important as electro-osmosis might function as an active filtration process and lead to water recovery from waste.

In open to air cathode MFCs, Kim et al. observed that anolyte loss varies with external resistance due to ionic flux driving the electro-osmotic transport of water and keeping the cathode hydrated (Kim et al., 2009). The transfer of ions through the cation-exchange membrane plays a major role in the charge-balancing ion flux from the anode into the cathodic compartment (Kim et al., 2009). The formation of OH^- at the cathode during the ORR, leads to a pH gradient between the anode and the cathode compartment (Zhao et al., 2006). Whilst the electro-osmotic drag represents an active transport of water from the anode to the cathode, a passive flux through forward osmosis occurs simultaneously, dragging water and other cations to the cathode (in addition to protons). The process of forward osmosis (FO) is natural, where the driving force is the high solute concentration solution (draw solution) that flows along one side of the membrane and low solute concentration (feed

solution) to the other. Water transport occurs passively, hence the FO process is less energy intensive than Reverse Osmosis (RO), despite the fact that it is slower (McCutcheon and Elimelech, 2006). In forward osmosis, the use of catholyte of high salt concentration is acting as a drag solution, passively extracting water from the low to the high concentration (Zhang et al., 2011).

Cathode flooding has been observed in MFCs (Kim et al., 2009; Zhuang et al., 2009) and it can serve as a method for extraction of water, salts and carbon capture (Gajda et al., 2014a, 2015), where the newly produced caustic catholyte is the important by-product of the MFC operation. Therefore, it is important to study the water transport phenomenon in light of the chemical carbon capture opportunities that the process could bring to the microbial fuel cell technology, and in general into a sustainable wastewater treatment processes.

Low-cost and mechanically robust air-cathodes that can achieve good performance, is urgently required for practical MFC applications. Activated carbon and Microporous Layer (MPL) coatings as well as the carbon fibres are cost effective cathode electrodes for MFCs with an added benefit of catholyte recovery (Gajda et al., 2014a,b). In this study, the main water fluxes occurring across the membrane that produced a net liquid catholyte in MFC, are described. This work aims to better understand water transport in a Microbial Fuel Cell system and present the bioelectrosynthesis of alkaline compounds directly onto the cathode surface as a non-limiting and highly beneficial recovery. It follows the previous work describing the production of catholyte on the surface of the cathode electrode, whilst generating electricity, using MFCs fed with wastewater and employing Pt-free carbon-based electrodes (Gajda et al., 2014a).

The current study is investigating the effect of electro-osmotic drag and osmotic pressure on the MFC water transport. Moreover, it is aiming to demonstrate the feasibility of MFC electricity production with simultaneous bioelectrosynthesis of caustic composition. This is particularly important for carbon capture and driving innovation in technologies for stabilising carbon dioxide levels in the atmosphere.

2. Materials and methods

2.1. MFC design and operation

Twelve MFC reactors comprised 25 mL anode and 25 mL cathode chambers were employed, as previously described (Gajda et al., 2013), separated by a CMI-7000 cation exchange membrane (Membranes International, USA). Anode electrodes were made of carbon fibre veil with a carbon loading of 20 g/m^2 (PRF Composite Materials, Dorset, UK) and had a total surface area of 270 cm^2 , folded into 3D rectangular cuboids (geometric surface area of 17 cm^3) in order to fit into the chamber and be fully immersed in

Table 1
Oxygen reduction reaction pathways (adapted from Kinoshita-Ref. (Kinoshita, 1988)).

Conditions	Pathway	Reaction	E_0 (vs. SHE) [V]
Acidic	4-electron pathway	$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	1.229
	2-electron (peroxide pathway)	$\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$	0.67
		Followed by reduction of peroxide: $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$	1.77
		or decomposition: $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$	
Alkaline	4-electron pathway	$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$	0.401
	2-electron (peroxide pathway)	$\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{HO}_2^- + \text{OH}^-$	-0.065
		Followed by reduction of peroxide: $\text{HO}_2^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 3\text{OH}^-$	0.867
		or decomposition: $2\text{HO}_2^- \rightarrow 2\text{OH}^- + \text{O}_2$	

the anolyte fluid. The pre-established anode half cells, initially inoculated with activated sewage sludge at neutral pH (Wessex Water, Saltford, UK), were connected to the 1 L anolyte reservoir to recirculate the feedstock at a constant flow rate of 48 mL/h and to maintain steady state. It was periodically supplemented with fresh sludge mixed with 20 mM sodium acetate used as feedstock. Table 2 describes four types of exposed-to-air cathode electrodes employed in experiments. All cathode electrodes were mechanically pressed against the membrane to maintain good physical contact and enclosed inside the acrylic cathode chamber. The projected contact area was 10 cm². Cathode chambers were kept empty and tightly sealed (in order to limit evaporation losses) but not airtight thus permeable to oxygen. The same folded carbon veil (CV) electrode used as an anode, was also used as the unmodified control for the cathode investigation and was the only 3-dimensional cathode electrode used. Microporous layer on carbon cloth (MPL) and the activated carbon (AC) was prepared as previously described (Santoro et al., 2012, 2014). The cathode chamber had a standard, sealed syringe (5 mL capacity) attached to the bottom, to allow collection of the produced catholyte. All 12 MFCs were divided in 4 experimental triplicates of the cathode electrode tested (Table 2). No metal-based catalysts or buffers were used.

2.2. Analysis of the accumulated catholyte

The catholyte has formed directly on the surface of the electrode and the accumulated liquid was removed by gravitational dripping into sealed collection syringes. Catholyte samples were collected from the cathode collection syringes after 7-day experimental periods, under closed and open circuit conditions.

Conductivity was measured with a 470 Jenway conductivity meter (Camlab, UK) and pH with a Hanna 8424 pH meter (Hanna, UK). Salt crystals were observed under a digital microscope KH-7700 (Hirox, Japan). Samples collected under closed circuit conditions (1 mL) were left to evaporate to determine the elements present in the crystalline salt deposits. Elemental mapping was performed using the energy dispersive X-ray spectroscopic unit (EDX) (Philips XL30 SEM) with detection limits of 0.1–100% wt. The phase composition of crystallised salts was determined using X-ray diffraction (XRD) powder measurements, performed on a Bruker D8 Advance Diffractometer, with the results analysed using an EVA software package (Bruker, UK).

3. Results and discussion

3.1. Power performance and catholyte generation

The MFCs were tested under the same external load (300 Ω) and their performance is shown in Fig. 1. A stable performance was recorded over a period of 7 days, with the average output from three replicates for AC being 309 ± 50 μW (1013 ± 86 μA), for CV MPL 161 ± 53 μW (726 ± 120 μA), for MPL 91 ± 20 μW (551 ± 60 μA) and for CV (control) 81 ± 23 μW (515 ± 102 μA). The results are consistent with previous work (Gajda et al., 2014a) showing the activated carbon cathode to possess superior performance in a

similar configuration. Activated carbon based materials have shown good catalytic properties for ORR in MFCs (Santoro et al., 2013b, 2014). During this stable operation, the formation of water was observed as seen in Fig. 2. The droplets had been dripping into the collection syringes, avoiding accumulation directly onto the electrode surface, therefore the steady state of power generation had not been negatively affected by the catholyte.

3.2. Catholyte volume in relation to power performance

The formation of droplets was observed on the surface of carbon cathodes and further accumulation of the catholyte was collected and analysed. A previous study suggested that the catholyte accumulation is a function of MFC performance (Gajda et al., 2014a) therefore it was attempted to plot the current level vs volume of accumulated liquid (Fig. 3). The cathode flooding has been reported to reduce MFC performance (Zhang et al., 2013) however, here the power (current) performance was (i) stable as shown in Fig. 1 and (ii) directly proportional to the amount of liquid produced (Fig. 3). The catholyte has been removed by gravity and collected in external vessel (syringe), therefore, flooding and further accumulation leading to cathode chamber being filled with liquid were avoided. The design prevented the electrode from drying out, as it was enclosed in the empty chamber, which also avoided salt build-up that was being washed out by the formed droplets. It is suspected that the MFC-generated catholyte provided sufficient hydration for the ORR and allowed effective oxygen exchange.

Fig. 3 shows a relatively strong correlation ($R^2 = 0.8277$) of current performance to the volume of catholyte generated for 9 points (3 different cathodes in triplicates). From this correlation, CV has been considered as an outlier (red points). It has also been observed that the least performing CV was producing relatively more catholyte in comparison to the other 2-dimensional cathodes despite the lower current output. The 3D structure was probably acting like a sponge absorbing the liquid and when pressed, it released excess catholyte. Therefore, it was suspected that the ability of the folded CV “sponge” to absorb the catholyte is causing the osmotic pressure to drive the water transport from the anode (lower salt concentration) to the cathode (higher salt concentration) similar to the forward osmosis in OsMFCs (Zhang et al., 2011).

In order to better understand the mechanisms, the total volume of catholyte has been divided into two main contributors: i) electro-osmotic drag (V_{drag}) and ii) osmotic pressure (V_{osm}). Natural evaporation has been neglected as the cathode chamber was sealed.

$$V_{\text{cath}} = V_{\text{drag}} + V_{\text{osm}} \quad (1)$$

Where:

V_{cath} – The total catholyte produced (under external load)

V_{drag} – Catholyte actively transported by electroosmotic drag and synthesised via ORR.

V_{osm} – Catholyte transported via osmotic pressure (under open circuit)

To evaluate this assumption, MFCs had been left in open circuit (OCP) for another 7 days and the relative amount of catholyte was

Table 2
Types of electrodes in the open to air cathode half cells.

Electrode tested	Electrode material	Cathode type	Cathode projected area
CV	Carbon veil (Control) folded	3D 270 cm ² (folded)	10 cm ²
MPL	Carbon cloth with microporous layer (MPL)	2D 10 cm ²	10 cm ²
CV MPL	Carbon veil with microporous layer (MPL)	2D 10 cm ²	10 cm ²
AC	Carbon cloth with activated carbon layer	2D 10 cm ²	10 cm ²

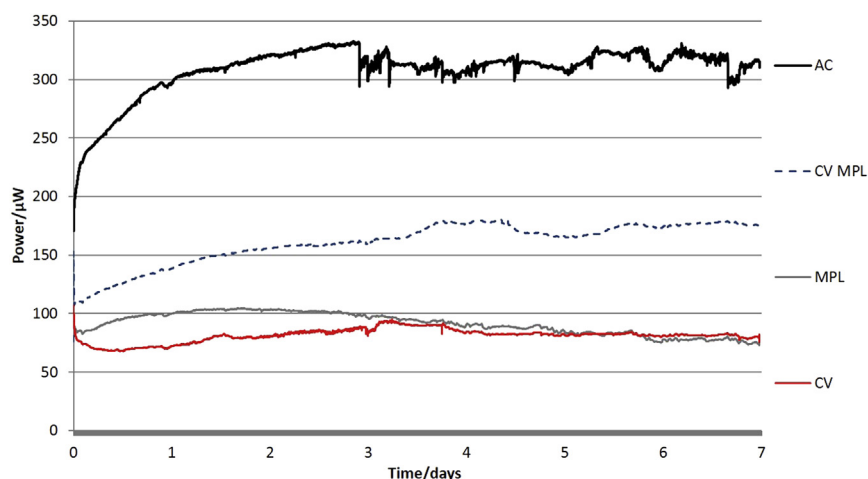


Fig. 1. Power performance of all tested MFCs (mean values).



Fig. 2. Catholyte formation *in situ* as droplets on both the 2D (left) and folded 3D (right) electrodes; catholyte droplets are more visible on the 2D surface.

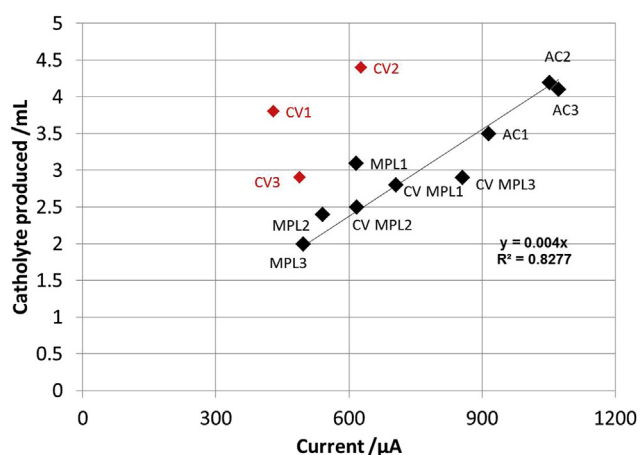


Fig. 3. Catholyte produced under the 300 Ω external resistor over 7 days plotted against MFC current (µA) performance.

collected. This passive movement of electrolyte was governed by the local water concentration gradient and osmotic pressure. The results showed that the 3-dimensional CV “sponge” electrodes produced relatively the most catholyte (Fig. 4a). Values for the volumes of the collected catholyte in OCP were inserted into the rearranged equation (1):

$$V_{\text{drag}} = V_{\text{cath}} - V_{\text{osm}}$$

Fig. 4b shows the relationship between the volume of electro-osmotically transported catholyte, i.e. the difference between the overall catholyte collected and the volume collected due to osmosis, and is shown that it is directly correlated with the current generation. Current would normally be used as a more accurate correlation of electrochemical reactions between the rate of electron transfer and the rate of catholyte formation, however the MFCs are presented herein as energy generators, and therefore correlation with power is equally important. In contrast with Fig. 3, where CV MFCs were considered outliers, in this case, all the conditions were considered and plotted.

It is assumed that the feedstock solution in the anode chamber was making contact with the cathode electrode through the membrane transferring a mixture of ions and water. During MFC operation, ions are being actively transported dragging water molecules with them. Due to the produced catholyte, it is now possible to determine this transport as it only has been reported previously as net water loss (Kim et al., 2009; Zhuang et al., 2009) linking the water loss in open circuit potential to natural evaporation (Kim et al., 2009).

3.3. Catholyte properties

The quality of the formed catholyte had been investigated in terms of pH and conductivity measurements. The pH was very alkaline ranging between 10.61 and 13.23 (Fig. 5). It can be seen that the highest pH levels (>13) were recorded by the cells producing higher current. As previously described, the cathode half reaction resulted in OH⁻ groups that accumulate on the cathode and contribute to increase the pH (Gajda et al., 2014a,b; Popat et al., 2012), especially in the vicinity of the electrode using microelectrodes, to determine the active pathway for oxygen reduction (Babauta et al., 2014, 2013). For this reason, a form of linear correlation can be seen between pH of collected catholyte and generated current (Fig. 5). It was observed that because the cathode chamber is sealed and empty, the catholyte sampling of accumulated liquid in the syringe might affect the pH, therefore it is possible that the 2 samples with a significantly lower pH (the outliers) have had the sampling syringes not fully airtight and the active catholyte would be buffered by atmospheric CO₂. Anodic pH in the feedstock reservoir supplementing all MFCs had increased from initially neutral to 9.21 and it might be related to

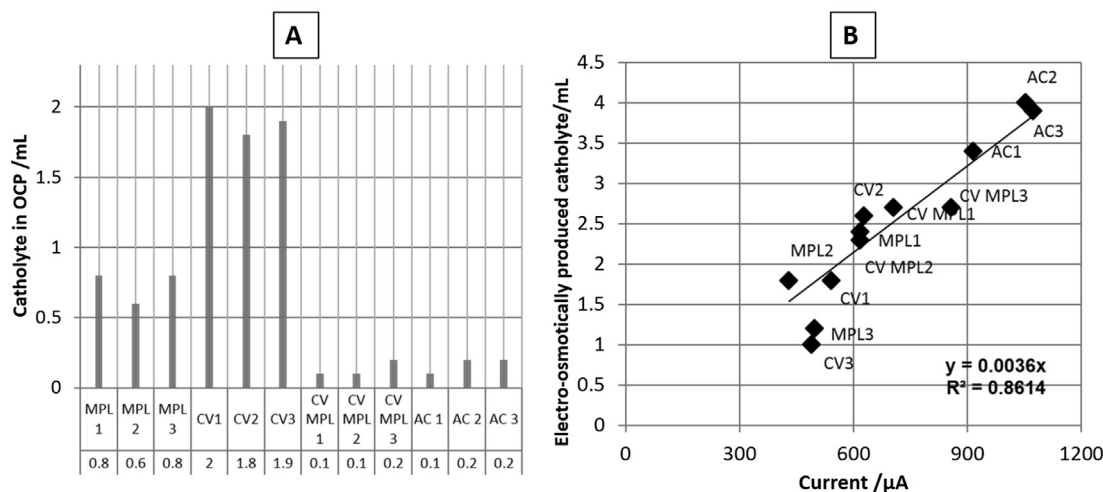


Fig. 4. A) Liquid volume recovered for osmotic pressure under open circuit conditions, B) calculated catholyte volume transported via the electro-osmotic drag in relation to current generation shows a linear relationship.

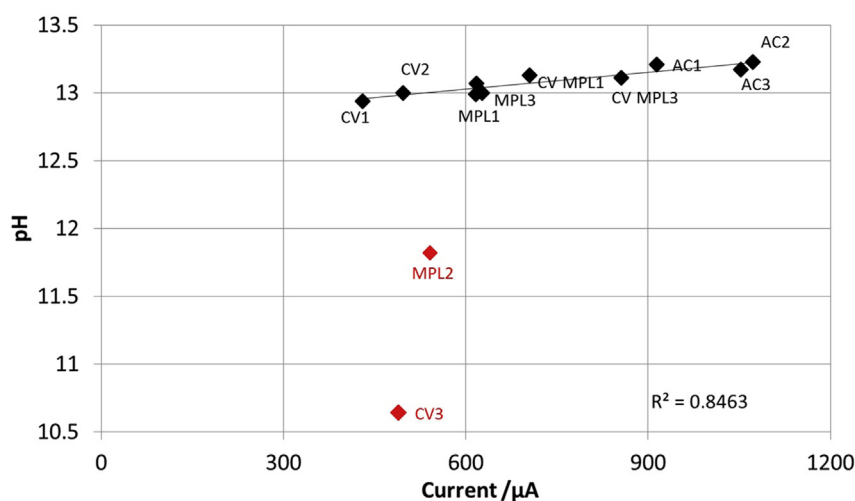


Fig. 5. Correlation between pH of produced catholyte under load showing gradual increase with current generated (outliers marked in red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

electrochemical reactions in the air-cathode changing the electrolyte properties (He et al., 2008).

These alkaline properties have been previously investigated in similar cathode half-cell configurations however with the air inlets open to atmospheric air (Gajda et al., 2014a). Here, as the cathode half-cell was completely closed but not airtight, the pH values were significantly higher than those previously reported (Gajda et al., 2014a). The cationic flux from the anolyte to the cathode has been related to the catholyte pH increase. Rather than combating this pH imbalance, it could be used as an advantage to produce an alkaline solution similar to BES that consume electricity (Rabaey et al., 2010). At present with results from the current study, this may be achieved with the net energy generation, where pH splitting (Harnisch et al., 2008) does not affect the performance.

Active synthesis of hydrogen peroxide was previously shown in MFC and it was dependent on the external resistor used (Fu et al., 2010) however, in alkaline conditions, hydrogen peroxide undergoes decomposition (Navarro et al., 1984; Venkatachalapathy et al., 1999) resulting in the formation of OH^- (Table 1). Alkaline sorbents are used in chemical carbon capture through wet scrubbing (Zeman and Lackner, 2004) and applied at industrial scale in

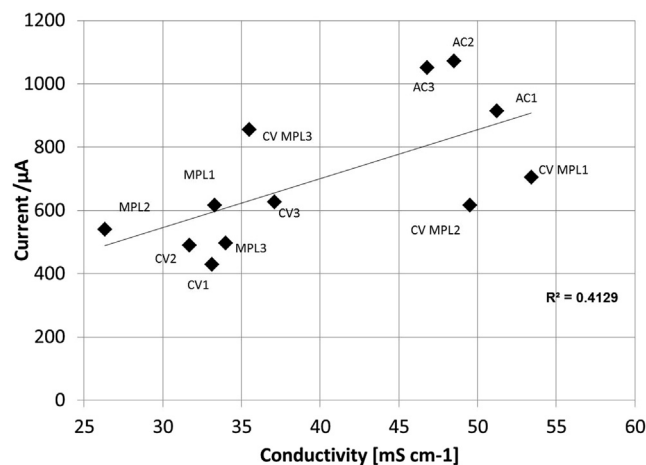


Fig. 6. Conductivity of produced catholyte under load conditions shows linear increase with current.

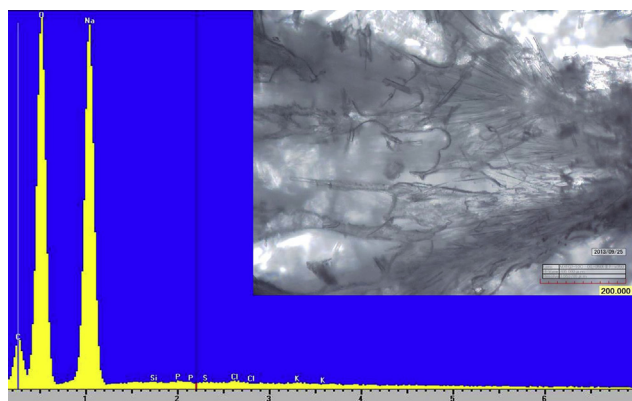


Fig. 7. EDX analysis of crystallised salt and image from digital microscope (inset).

wet scrubbing towers. The method involves the use of an alkaline liquid sorbent such as NaOH and KOH to remove CO₂ from ambient air to produce carbonate salt. It has also been included as an innovative concept idea of artificial trees (Lackner, 2009). MFCs that can cogenerate electricity and active sorbent, are likely to lead to a cost effective way of carbon capture and recycling of waste via artificial photosynthesis (Gajda et al., 2014b). Previous MFC studies that used sodium acetate as feedstock also showed the formation of the precipitates such as sodium and calcium carbonates suggesting that CO₂ produced at the anode prevents pH increase of the MFCs

(Guerrini et al., 2013). The MFC-based extraction of sorbents from wastewater shows to be particularly attractive. Here, it is suspected that due to OH⁻ formation as well as the cationic Na⁺ transport, the sorbent is directly synthesised onto the cathode electrode. The cathode shown here is serving as a sorbent-based air scrubber due to the MFC energy generation.

Increase in catholyte conductivity with power performance indicates that the quality of the catholyte is dependent on current and does not affect the output (Fig. 6). At the same time, anodic conductivity being significantly lower (16.23 mS/cm) suggests that the extracted catholyte is concentrating transported ions. The formed liquid washes the salt deposits off the electrode surface. These catholyte properties can be extremely important in terms of possible uses such as disinfectant, by utilizing the generated hydrogen peroxide *in situ* as an effective way of treating biofouling in cathodes (Babauta et al., 2013). Use of the cathodic chamber for disinfection purposes in MFCs has been previously reported but only with an external supply of disinfectant (Jadhav et al., 2014). In addition, saline solutions in MFCs are advantageous since they naturally decrease the internal resistance, thus resulting in higher power densities without pH control, as previously reported (Ahn and Logan, 2013).

3.4. Evaporate analysis

Each catholyte was left to evaporate in a controlled environment over several days to obtain salt deposits. Initial EDX analysis in the

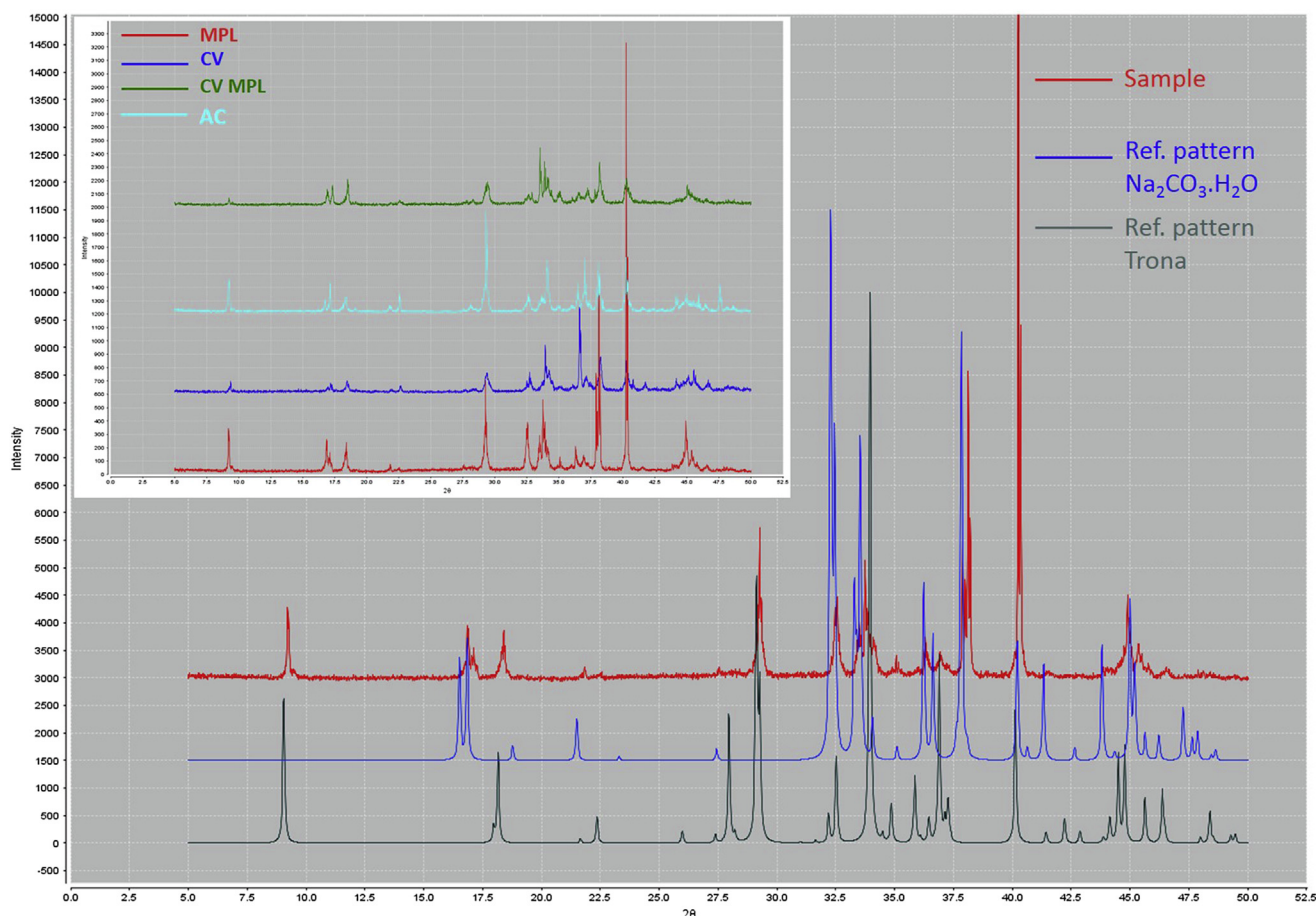


Fig. 8. XRD diffraction pattern comparison showing all 4 samples made up from very similar materials if not the same (inset). The experimental sample shows good comparison with the reference pattern of trona Na₃H(CO₃)₂·H₂O and sodium carbonate monohydrate Na₂CO₃·H₂O.

detection of elements in the evaporite has shown a high atomic content of sodium (excluding carbon). In addition, under a digital microscope the sample clearly show crystalline structures (Fig. 7).

Further analysis through XRD powder diffraction of all four samples showed that they are made of the same material (Fig. 8, inset) and this suggests that it is a mixture of bicarbonates: trona $\text{Na}_3\text{H}(\text{CO}_3)_2 \cdot \text{H}_2\text{O}$ and carbonates: $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$. Comparison of these reference phases with the experimental diffraction pattern is relatively good as shown in Fig. 8.

The evaporite composition suggests that CO_2 is transformed *in situ* into sodium carbonates and bicarbonates, which can be harvested (Vandehey and O'Neil, 2014). Salts were formed using CO_2 derived from anodic wastewater degradation, and as an additional CO_2 capture from air leading towards a carbon negative cycle. In this way, MFCs have the potential to become a technology suitable for practical implementation as a carbon capture and energy regeneration system from waste. It is important to explore further the cathode capabilities depending on application (Harnisch and Schröder, 2010) and use it as the platform for carbon scrubbing (Gajda et al., 2014a,b) or ammonia stripping (Kuntke et al., 2012) with simultaneous energy generation rather than energy consumption.

4. Conclusions

MFCs were shown to produce useful catholyte whilst generating electricity, with plain Pt-free electrodes, thereby representing a promising route for sustainable electricity production and water recycling. Catholyte pH (10.6–13.3 suggesting caustic content) and conductivity, showed gradual increase with power. Cationic transport might present a mechanism of water extraction from the anolyte via electro-osmotic drag (under load) and osmotic pressure (under open-circuit). The total charge transfer in the MFC is related to the electro-osmotic drag of water through the membrane representing the active transport, whereas osmotic pressure gradient between dissimilar solutions is passive and dominant under open-circuit conditions. Caustic catholyte has been collected and mineralised to carbonate/bicarbonate showing an active carbon sequestration method through wet scrubbing with net energy-positive MFC operation.

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