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Self-powered supercapacitive microbial fuel cell: The ultimate way of boosting and harvesting power

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ABSTRACT

In this work, for the first time, we demonstrate a supercapacitive microbial fuel cell which integrates the energy harvesting function of a microbial fuel cell (MFC) with the high-power operation of an internal supercapacitor. The pursued strategies are: (i) the increase of the cell voltage by the use of high potential cathodes like bilirubin oxidase (BOx) or iron–aminoantipyrine (Fe–AAPyr); (ii) the use of an additional capacitive electrode (additional electrode, AdE) which is short-circuited with the MFC cathode and coupled with the MFC anode (MFC-AdE). The high working potential of BOx cathode and the low impedances of the additional capacitive electrode and the MFC anode permitted to achieve up to 19 mW (84.4 W m^{-2}, 152 W m^{-3}), the highest power value ever reported for MFCs. Exploiting the supercapacitive properties of the MFC electrodes allows the system to be simpler, cheaper and more efficient without additional electronics management added with respect to an MFC/external supercapacitor coupling. The use of the AdE makes it possible to decouple energy and power and to achieve recharge times in the order of few seconds making the system appealing for practical applications.

1. Introduction

Microbial fuel cell (MFC) is a promising biotechnology for multiple applications such as wastewater treatment and energy production from organic compounds (Rinaldi et al., 2008). Enhancement of MFCs performance through anode and cathode electrodes materials development has been the main focus of the past decade for the scientists all over the world (Rinaldi et al., 2008). In general, MFCs can be based on anodes made of carbonaceous (Wei et al., 2011) and not carbonaceous electro-conductive materials (Pocaznoi et al., 2012; Guerrini et al., 2014). Anodes feature high surface area in order to accommodate electroactive bacteria that degrade organics and transfer electrons through an external load. On the other side, cathode catalysts can be from different families of: (i) carbonaceous high surface materials (Watson et al., 2013), (ii) platinum-based materials (Liu et al., 2014), (iii) non-platinum based materials (Antolini, 2015), (iv) enzymatic (Schaetzle et al., 2009; Higgins et al., 2011), and (v) microbial (Jang et al., 2013; Ishii et al., 2014). Such organic/inorganic materials as well as biotic matter work as catalysts or co-catalyst enhancing the oxygen reduction rate and complete the redox reaction of the MFC. It has been previously shown that at neutral working pH, enzymes (bilirubin oxidase and laccase) based catalysis posses the highest open circuit potentials (OCPs) among the existing catalysts for oxygen reduction reaction (ORR) (Mano et al., 2003; Soukharev et al., 2004).

Current/power generated from MFC systems is over 3 orders of magnitude lower compared to traditional hydrogen- or methanol-fuelled FC (Logan and Rabaey, 2012) and therefore a smart design is necessary in order to harvest the low energy produced and for the subsequent delivering of the high power pulses which are required for powering devices. Supercapacitors are electrochemical energy storage systems which deliver high specific power (up to 10 kW kg^{-1}) at required energy levels (Conway, 1999). Electrochemical double layer capacitors (EDLC) use high surface area carbon electrodes that store/deliver charge by an intrinsically fast and highly reversible electrostatic process (Béguin et al., 2014).

Supercapacitors have been externally combined to the MFCs in order to harvest appropriately the energy of the system. The external supercapacitors are recharged by the MFCs and provide high power output during the discharge. This combination has been already investigated by several groups (Wang et al., 2015). The smart design and efficient series/parallel connection of MFCs with external supercapacitors allowed to power small electronics

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devices (Papaharalabos et al., 2013, 2014), sensors (Donovan et al., 2011, 2013; Di Lorenzo et al., 2014; Ewing et al., 2014; Dewan et al., 2014; Park and Ren, 2012), a mobile phone (Ieropoulos et al., 2013), robotics prototypes (Ieropoulos et al., 2005, 2010, 2012) and the pump required to manage the wastewater flow in MFCs (Ledezma et al., 2013).

The size of the supercapacitor to be connected with the MFC is a crucial design point. Indeed, the commercially available EDLCs with capacitance on the order of Farads require a substantial recharging time (on the order of several min or even hours) at the low current regimes of MFCs (on the orders of μA). Every generated high current/power pulse requires a long time before its repetition, and consequently the tool that is powered by the MFC/external EDLC is switched on periodically, with long standby steps.

The capacitive behavior of the MFC anode has been recently investigated (Deeke et al., 2012; Feng et al., 2014). It has been also reported an MFC anode decoration with ruthenium oxide to improve the capacitive response of MFCs (Lv et al., 2012) but its high cost prevents the usage in large scale MFCs.

Designing and improving the capacitive response of the MFC electrodes is a challenging task for creating an integrated MFC-internal supercapacitor system. The capacitive electrodes are expected to accomplish high power discharges, being simultaneously recharged by the MFC redox reactions taking place at the electrode/organics containing solution and electrode/O_2 interfaces.

This approach has been already exploited in the field of biofuel cells where the first use of enzymatic biofuel cells (BFC) as internal supercapacitor was recently demonstrated by Pankratov et al. (2014a, 2014b). In this case, the high surface area, carbonaceous anode and cathode of the BFC operated as the electrodes of the supercapacitor. Higher performances have been recently obtained by Agnès et al. (2014) using a glucose–oxygen enzymatic biofuel cell with maximum open circuit voltage of $\approx$800 mV. The BFC-supercapacitor hybrid system had the highest power achieved of approximately 18 mW (Agnès et al., 2014).

To our best knowledge, for the first time, in this study we report on supercapacitive MFCs where anode and cathode simultaneously harvest energy from wastewater and work as self-powered EDLC. The power delivered by supercapacitors increases with cell voltage and with the decrease of the equivalent series resistance (ESR). We demonstrate how the power output of the MFC can be dramatically improved by two strategies: (i) the use of non-platinum group metal, like iron–aminoantipyrine (Fe–AAPyr) and of bilirubin oxidase (BOx) cathodes to increase cell voltage, and (ii) the usage of a third, capacitive electrode based on high surface area carbon to decrease ESR. The latter is an "additional electrode" (AdE) which is short-circuited with the MFC cathode and is coupled with the MFC anode to give a self-powered supercapacitor (MFC-AdE) This is the first time that the concept of AdC electrode is used. The proof-of-concept is demonstrated using a commercial high surface area carbon brush as the additional electrode and by galvanostatic tests at different currents from 1 mA up to 45 mA.

2. Materials and methods

2.1. MFC configuration and electrolyte composition

Single glass bottle MFC (Cataldo Arbore, Milan, Italy) with 125 mL volume was used. A lateral hole of 2.25 cm^2 allowed the insertion of the cathode that was there screwed using a metallic clamp. Membraneless configuration allowed the exposure of anode and cathode to the same electrolyte. A reference electrode (Ag/AgCl 3 M KCl) was included for the basic electrochemical studies.

The electrolyte was composed of a mixture of 50% volume of activated sludge from Albuquerque Southeast Water Reclamation Facility (New Mexico, USA) and 50% volume of phosphate buffer saline solution (PBS) and KCl 0.1 M. PBS was made using KH_2PO_4 (1.77 g) and K_2HPO_4 (15.16 g). The pH of the electrolyte was 7.5 ± 0.02. An air breathing cathode configuration was used and the tests were run in ambient conditions. The experiments have been carried out in Albuquerque at a constant temperature that was 22 ± 1 °C and at 1600 m above sea level. At that altitude, oxygen concentration is roughly 20% lower compared to sea level due to the lower air pressure. This parameter has to be taken into account when comparing the performance of air-breathing MFCs.

2.2. MFC electrode materials and additional cathode material

Anode electrodes were based on a carbon brush (Millirose, USA) of diameter 3 cm, length of 3 cm and projected area of 9 cm^2. The anodes were pre-colonized by mixed cultures bacteria taken from previous experiments running for over 4 months (Santoro et al., 2015a). Three different cathodes based on activated carbon (AC), iron–aminoantipyrine (Fe–AAPyr) and bilirubin oxidase (BOx) enzymes were used. All the cathodes tested had the same current collector that was metallic stainless steel mesh (McMaster, USA).

AC-based cathode was prepared by mixing 70%wt high surface area AC (Norit SX Ultra, Sigma Aldrich), 10%wt wt% carbon black (CB, Alfa Aesar) and 20%wt wt% PTFE (60% solution, Sigma Aldrich) for 5 min in a coffee grinder. The carbon black was added to enhance the composite electrode conductivity. After mixing, the composite material was pressed at 2 mT into a pellet die for 5 min (Santoro et al., 2014). The composite loading was 35 ± 5 mg cm^{-2}, the geometric area was 2.25 cm^2 and this value was used for the power normalization. The cathode has not been heated as previously shown (Santoro et al., 2014). The volume used for power normalization refers to the chamber volume of 125 mL.

The same procedure was followed to prepare Fe–AAPyr based cathode except that Fe–AAPyr was added into the mixture and mixed vigorously, before pressing at 2 mT. The preparation of Fe–AAPyr has been previously described (Santoro et al., 2015b). The Fe–AAPyr loading was 1.5 ± 0.1 mg cm^{-2}. Synthetic approach for preparation of Fe–AAPyr was based on Sacrificial Support Method developed at University of New Mexico. (Serov et al., 2014a, 2014b)

The preparation of BOx cathode instead was based on AC (70 wt%), 10 wt% CB and 20 wt% PTFE ground for 5 min and then pressed at 2 mT for 5 min. After that, isopropanol (40 μL cm^{-2}) was added on the top to create a hydrophilic/hydrophobic gradient. A multi-walled nanotube paper (MWNTP, Buckeye Composite) was then fused together on the top using pressure 0.25 mT for 5 min. At last, 10 mg of BOx (Amano Enzyme, USA) dissolved in 50 mM PBS solution was then drop-casted onto the MWNTP surface. The cathodes were kept at 4 °C over night for enzyme immobilization. Before the utilization, the liquid was dried and then the cathode was screwed on the lateral hole of the bottle (Santoro et al., 2013).

The additional electrode for the supercapacitor was carbon brush (Millirose, USA) of diameter 2 cm and projected area of 4 cm^2 that was coated with a 95%wt AC- 5%wt Nafion layer (0.3 g total). The carbon brush was immersed into a solution based on Nafion (0.5% alcoholic solution Dupont, 1.0 mL), AC (100 mg) and water–isopropanol solution (1 mL) and then was dried in ambient atmosphere over night. The addition of AC allowed the increase in surface area of the carbon brush and consequently in the capacitance of the overall additional brush. The additional electrode was completely immersed into the electrolyte and short-circuited with the MFC cathode.