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Synthesis and application of polypyrrole/carrageenan nano-bio composite as a cathode catalyst in microbial fuel cells

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ABSTRACT

A novel nano-bio composite polypyrrole (PPy)/kappa-carrageenan(KC) was fabricated and characterized for application as a cathode catalyst in a microbial fuel cell (MFC). High resolution SEM and TEM verified the bud-like shape and uniform distribution of the PPy in the KC matrix. X-ray diffraction (XRD) has approved the amorphous structure of the PPy/KC as well. The PPy/KC nano-bio composites were then studied as an electrode material, due to their oxygen reduction reaction (ORR) ability as the cathode catalyst in the MFC and the results were compared with platinum (Pt) as the most common cathode catalyst. The produced power density of the PPy/KC was 72.1 mW/m^2 while it was 46.8 mW/m^2 and 28.8 mW/m^2 for KC and PPy individually. The efficiency of the PPy/KC electrode system is slightly lower than a Pt electrode (79.9 mW/m^2) but due to the high cost of Pt electrodes, the PPy/KC electrode system has potential to be an alternative electrode system for MFCs.

1. Introduction

The increasing demand for fossil fuels coupled with global warming associated with certain environmental concerns has caused a global movement towards the generation of renewable energy. As such, wastewater can be considered a valuable source for the generation of renewable energy in the form of biodegradable organic matters (Ghasemi et al., 2013a). As wastewater treatment plants have high capital costs, energy extraction from wastewater is valuable in the production of renewable energy. Microbial fuel cell (MFC) is a device that generates electricity from organic compounds by using microorganisms as a biocatalyst. It means that a MFC is a device that simultaneously generates electricity while treating wastewater. The advantages of the MFC compared to current technologies such as membrane treatment or anaerobic digestion is its lower costs and potentially high energy efficiency as electricity would be produced directly without any inefficient steps or wastage of materials. A number of factors affect the performance of the MFC such as the microbial inoculums, the proton exchange membrane, internal and external cell resistance, the cathode catalyst and the electrode spacing. Among these factors, the cathode catalyst attracts more attention from researchers. Pt as the common cathode catalyst covers about 50% of the total MFC cost.

Nowadays, intrinsically conducting polymers have attracted a lot of attention in the area of advanced materials, such as polyaniline (PANI), sulfonated PANI (SPAN)-Fe_3O_4 nanocomposites (Reddy, Lee, & Iyengar, 2007), PANi functionalized multi-walled carbon nanotubes with metal nanoparticles (Reddy et al., 2009). Among conducting polymers PPy and its composite exhibit highly attractive for variety of their application because of it is environmentally stable, easy to synthesize and highly conductive as

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well as showing a low electropolymerization of PPy compared to other conductive polymer which allows PPy and its composite stay stable under ambient conditions (Ates, Karazehir, & Sarac, 2012). PPy can be used in biosensors, wires, catalysts and anti-electrostatic coatings (Apetrei & Apetrei, 2013; Safarnavadeh, Zare, & Fakhari, 2013). PPy revealed its biocompatibility through strong interactions with other polymers (Colin & Petit, 2002), and bio molecules (Arora et al., 2006). Thus, polymer composites based on polyconjugated systems create large surface membranes due to the enhancement of conductivity and sensitivity that create stronger catalytic activity. The stabilizing of composites is essential for a variety of applications such as bio (sensor) (Lupu et al., 2013), fuel cell (Ghasemi et al., 2013d), photovoltaic cell (Zhang et al., 2013) and catalysis (Liu et al., 2013). Composite polymers can be synthesized using chemical, electrochemical polymerization and self-assembly process (Reddy, Jeong, Lee, & Raghu, 2010; Reddy, Lee, & Gopalan, 2007). The preparation of well-known composite polymers as catalysts facilitates the modification of a conducting PPy. PPy inorganic composites have been previously used as the cathode or anode electrode in an MFC but in this study PPy, as an inorganic conducting polymer and kappa-carrageenan (KC) biopolymer have been used as the novel nano-bio composite catalyst in a MFC. The composite formations from intrinsically conducting polymers are much different than inorganic conducting polymers. In the other word, composite formation, in conducting polymers is interstitial whereas the composite formation in inorganic conducting polymer is substitution and also, making composite in the conducting polymer is reversible in a way, unlike inorganic polymer, on the other hand, the original polymer can be maintained with no degradation of the polymer backbone (Bakhshi & Bhalla, 2004). The chemical polymerization method has been used due to couple of advantages when compared with the electrochemical method. First, the chemical method is unlimited in terms of the production and collection of composites and second, the chemical method is suitable for the preparation of composite thin films with controlled thickness above 100 nm or of nano size. The composite polymer of KC is not only biodegradable, but is also edible (Alves et al., 2011). KC is known as an acidic hydrophilic polyanion and is also used in the food industry as a gelling and thickening reagent. This polyanion with OSO_3^- (sulphate) functional group makes an intramolecular bridge into the positive charge of the PPy due to the growth of the composites (Colin & Petit, 2002). In addition, KC possesses water retention abilities due to hydrogen bonding and it exhibits high proton conductivity (Fujishima et al., 2008) and KC has not been studied for fuel cell application in till now and in this field seems to be very novel and efficient. The chemical polymerization process is suitable for the synthesizing of PPy/KC composites with controlled thickness and is unlimited in terms of the collection and production of composites.

The electrochemical method has two disadvantages compared to traditional chemical polymerization. One is that the electrochemical method is limited in terms of the mass production of composite electrodes and the other is that the electrochemical method is not suitable for preparing controlled polymer films with thicknesses above 100 mm. However it is proper for preparing very thin films of polymer (Martínez-Huitle & Brillas, 2009).

This method shows that PPy/KC produces as much power and is a simple method utilizing cheaper chemicals than Pt.

The modification of composite polymers by making nanocomposite has attracted a lot of attention due to (Dharuman, Hahn, Jayakumar, & Teng, 2013), improvement of catalytic activity (Nguyet et al., 2013) and production of larger surface area substances.

So for the first time, the nano-bio composite has been used as an alternative for Pt in MFCs to see the effect of that in the MFCs. The results have been compared with Pt as the common cathode catalyst, PPy as the source of polymer and KC as the biopolymer in this paper.

2. Experimental

2.1. Materials

The pyrrole monomer was obtained from Acros Organics. Kappa-carrageenan was purchased from Fluka. Iron(III) chloride ($FeCl_3$) was provided by Sigma Aldrich. The phosphate buffer solution was prepared using K_2HPO_4 and KH_2PO_4 purchased from Merck. Deionised water is used during the experiment.

2.2. Synthesis of PPy and kappa-carrageenan composite

Various amounts of kappa-carrageenan (KC) powder were dissolved in deionised water. KC bio-polymer dissolve in 40 ml of deionized water and then was mixed with the 0.684 g of pyrrole (pre-distilled) by stirring at 40 °C for 10 min continuously. An aqueous solution of the oxidant 10 ml of ($FeCl_3$) in distilled water was added up drop-wise to the mixture. The total volume of the deionized water was used 50 ml. The molar ratio of the $FeCl_3$/pyrrole was always kept at 2:3 (Brezoi, 2010). Formation of black PPy precipitate was clearly observed immediately after the addition of the oxidant. The polymerization process was carried out for 45 min at room temperature by moderate stirring. After optimum condition of KC has been achieved, the KC and PPy were mixed together in 1.46:98.54 wt%.

First, the black precipitate was filtered off, then has been washed it with distilled water, and centrifuged several times in order to isolate the sample. The black kappa-carrageenan–polypyrrole (PPy/KC) powder was then dried in the oven at 60 °C for 5 h. It should be noted that, the electrical properties of the composite are governed by the amount of KC concentration and the results demonstrated that KC properties are affected by changing the temperature employed during concentration of KC solution as well as the KC of dispersant into composite formed.

2.3. MFC configuration

Two cubic shaped chambers were constructed from Plexiglas, with a height of 10 cm, width of 6 cm and length of 10 cm (giving a working volume of 420 ml). They were separated by a Nafion 117 Proton Exchange Membrane (PEM). Oxygen was continuously fed into the cathode by an air pump at a rate of 80 ml/min. Both the cathode and the anode projected surface areas of 12 cm^2. The cathode was carbon paper, coated with 0.5 mg/cm^2 Pt and the anode (as described above) was plain carbon paper (Ghasemi et al., 2011; Rahimnejad et al., 2012).

2.4. Enrichment

Palm Oil Mill Effluent (POME, Indah Water Konsortium) anaerobic sludge was used for the inoculation of the MFCs. The media contained 5 g of glucose, 0.07 g of yeast extract, 0.2 g of KCl, 1 g of $NaH_2PO_4{\cdot}4H_2O$, 2 g of NH_4Cl, 3.5 g of $NaHCO_3$ (all from the Merck company), 10 ml of Wolfe's mineral solution and 10 ml of Wolfe's vitamin solution (added per litre). All experiments were conducted in an incubator at 30 °C. Furthermore, the cathode chamber contained a phosphate buffer solution, which consisted of 2.76 g/l of NaH_2PO_4, 4.26 g/l of Na_2HPO_4, 0.31 g/l of NH_4Cl and 0.13 g/l of KCl (all from the Merck company) (Rahimnejad et al., 2012).