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Short communication

Improvement of activated carbons as oxygen reduction catalysts in neutral solutions by ammonia gas treatment and their performance in microbial fuel cells

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HIGHLIGHTS

- Ammonia treatment improved ORR catalytic activity at pH = 7.
- Oxygen content decreased 29–58% on the surface of treated ACs.
- Nitrogen content was increased up to 1.8% on the surface of treated ACs.
- Treatment increased the basicity of the bituminous, peat, and hardwood ACs.
- Cathode performance improved with all but one ammonia treated AC.

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ABSTRACT

Commercially available activated carbon (AC) powders from different precursor materials (peat, coconut shell, coal, and hardwood) were treated with ammonia gas at 700 °C to improve their performance as oxygen reduction catalysts in neutral pH solutions used in microbial fuel cells (MFCs). The ammonia treated ACs exhibited better catalytic performance in rotating ring–disk electrode tests than their untreated precursors, with the bituminous based AC most improved, with an onset potential of $E_{onset} = 0.12$ V (untreated, $E_{onset} = 0.08$ V) and $n = 3.9$ electrons transferred in oxygen reduction (untreated, $n = 3.6$), and the hardwood based AC (treated, $E_{onset} = 0.03$ V, $n = 3.3$; untreated, $E_{onset} = -0.04$ V, $n = 3.0$). Ammonia treatment decreased oxygen content by 29–58%, increased nitrogen content to 1.8 atomic %, and increased the basicity of the bituminous, peat, and hardwood ACs. The treated coal based AC cathodes had higher maximum power densities in MFCs (2450 ± 40 mW m^{-2}) than the other AC cathodes or a Pt/C cathode (2100 ± 1 mW m^{-2}). These results show that reduced oxygen abundance and increased nitrogen functionalities on the AC surface can increase catalytic performance for oxygen reduction in neutral media.

1. Introduction

Microbial fuel cells (MFCs) are a promising option for reduction of energy costs associated with the treatment of wastewater sources [1]. Power production from MFCs is limited by the overpotential of the oxygen reduction reaction (ORR) at the cathode, which is negatively impacted by the conditions of neutral pH and ambient temperature common in MFCs. Depending on the catalyst properties, the ORR can proceed through either a 4e$^-$ pathway producing water or hydroxide [2], or 2e$^-$ pathway producing hydrogen peroxide as an intermediate [3]. Peroxides can be further reduced through an additional 2e$^-$ reduction step, resulting in a mixed reduction pathway that can approach an apparent four electron transfer to the cathode [3].

In order to achieve commercial viability, low cost materials are essential to the success of MFC technology. Activated carbons (ACs) are inexpensive ORR catalysts that can be made from several biomass waste materials such as coconut shells, wood chips and sawdust. They have a complex surface chemistry that can be tailored to improve their performance for the desired application. AC powder based cathodes have produced power densities in MFCs similar to or slightly higher than those made with a typical platinum catalyst. An MFC with an AC cathode, made using a polytetrafluoroethylene (PTFE) binder and a nickel current collector, produced 1220 mW m^{-2}, compared to 1060 mW m^{-2} with cathodes made with a Pt catalyst and a Nafion binder [4]. MFCs with AC

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and a polydimethylsiloxane (PDMS) diffusion layer reached 1255–1310 mW m^{-2} compared to 1295 mW m^{-2} with a standard Pt and carbon cloth (Pt/C) cathode [5]. Another type of AC air cathode, made by rolling out an AC/PTFE layer on a stainless steel mesh current collector, produced between 1086 and 1355 mW m^{-2} with two different AC powders. Power production compared to a standard Pt/C cathode was not reported [6]. In another study, the power production in MFCs using cathodes made from AC powders with less strong acid ($pK_a < 8$) functional groups was generally higher (1610 ± 100 mW m^{-2} for a peat based AC) than those made from ACs with more strong acid groups (630 ± 10 mW m^{-2} for a hardwood based AC) [7].

Nitrogen incorporation on carbon surfaces has been shown to increase the catalytic activity and selectivity for oxygen reduction through a four electron pathway in both acidic and alkaline environments [3,8,9], but it has not been examined for activity in neutral pH solutions. Several studies have shown that the number of nitrogen functional groups on carbon surfaces can be increased by treatment with ammonia gas at elevated temperatures [3,10–12]. During the process of incorporating the nitrogen into the carbon structure, there is a corresponding reduction in acidic oxygen groups as the oxygen atoms are desorbed from the carbon surface as CO/CO_2. This rearrangement of surface functional groups results in an increase in the basic properties of the carbon surface at the expense of acidic properties [12–17].

In order to improve the performance of AC cathodes in MFCs, ACs made from four different precursor materials were treated with a high temperature, ammonia gas in order to modify the surface chemistry by increasing the number of basic nitrogen groups and decreasing the number of acidic oxygen functional groups. The treated ACs were examined as catalysts for oxygen reduction in neutrally buffered solutions and compared to the untreated precursor ACs. Treated ACs were evaluated in terms of activity and selectivity using a rotating ring–disk electrode (RRDE) and linear sweep voltammetry (LSV). The catalytic activity observed, in conditions relevant to MFC operation (pH 7, 30 °C), was then compared to the change in surface chemistry that included the relative abundance of surface oxygen and nitrogen functional groups. The results of the kinetic and chemical property analyses were compared to the power production produced using the ammonia treated ACs in the cathodes of MFCs, relative to power densities produced with Pt/C cathodes.

2. Experimental

2.1. Activated carbons and ammonia treatment

Four AC powders previously shown to function well as ORR catalysis [7] were chosen that spanned a range of typical physical and chemical characteristics in commercially available AC powders. The four ACs were: a peat based carbon, Norit SXPlus (P, Norit, USA); a coconut shell based carbon, YP50 (C, Kuraray Chemical, Japan); a hardwood carbon, Nuchar SA-1500 (W, MeadWestvaco, USA); and a bituminous coal carbon, CR325B (B, Carbon Resources, USA). The base ACs were treated with ammonia gas (5% in helium) at 700 °C using a vertical cylindrical glass tube reactor in a programmable furnace (model 3210, Applied Test Systems, Inc., Butler, PA). Before heating, the furnace (including sample) was purged with ultrapure nitrogen gas for 30 min. Gas flow was changed to dilute ammonia while temperature was ramped at 5 °C min^{-1}, then held at 700 °C for 1 h. The furnace and sample were purged with ultrapure nitrogen gas while cooling to ambient temperature. The performance of these carbons (denoted as –N) in terms of ORR catalysis was compared to the base AC samples, as well as carbon black XC-72 (CB), and Pt (10%) in carbon black XC-72 (PtC) (Fuel Cell Store, USA) in electrochemical tests.

2.2. Chemical surface analysis

The elements present on the surface of the AC powders were identified by X-ray photoelectron spectroscopy (XPS, Axis Ultra XPS, Kratos Analytical, UK, monochrome AlKα source, 1486.6 eV). A base survey scan was performed first, followed by a detailed scan of C1s (285–289 eV), O1s (531–536 eV), and N1s (398–406 eV) signals [18]. CASA XPS software was used for the elemental and peak fitting analysis.

Potentiometric titrations were performed using a DL53 automatic titrator (Mettler Toledo, USA) in the pH range of 3–11, with volumetric standard NaOH (0.1 M) used as the titrant and NaCl (0.01 M) as the electrolyte. Before titration, 0.2 g of AC was equilibrated with 100 mL of electrolyte adjusted to ~pH 3 using HCl (0.1 M) and degassed with N_2 for 1 h. The experimental data were transformed into proton binding curves (Q, mmol g^{-1}) by subtracting out the blank titration values [19]. The proton binding curves were deconvoluted using the SAIEUS numerical procedure to obtain the distribution of acidity constants [20–22]. This analysis produces separate peaks that denoted different types of functional groups, with the area under the peak corresponding to the quantity of functional groups detected (mmol g^{-1}) based on binding/release of protons during titration.

2.3. Rotating ring–disk electrochemical analysis

Catalyst ink was prepared by adding 30 mg of the powdered sample to 3 mL of DMF and homogenized with a sonifier (S-450A, Branson, USA) fitted with a 1/8 inch micro tip, pulsed at 50% for 15 min, in an ice bath. Nafion (270 μL; 5 wt% solution) was added and the solution was mixed for an additional 15 min. The ink solution (10 μL) was drop coated onto a 5 mm diameter glassy carbon disk (Pine Instruments, USA) and allowed to dry overnight. The disk was prepared before coating by polishing with 5.0 and 0.05 μm alumina paste and cleaned in an ultrasonic bath for 30 min.

All RRDE experiments were run first in nitrogen sparged solution in order to obtain the baseline current, before being switched to an air sparged 100 mM phosphate buffer solution (PBS) (9.13 g L^{-1} Na_2HPO_4, 4.90 g L^{-1} $NaH_2PO_4 \cdot H_2O$, 0.31 g L^{-1} NH_4Cl, and 0.13 g L^{-1} KCl; pH 7). Solutions were sparged for 30 min before LSVs were run, and then the gas was streamed into the headspace for the duration of the experiment. In order to clean the electrode surface of possible contaminants or excess oxygen trapped in the pores of the carbon, the disk potential was cycled between 0.4 and 1.0 V at 100 mV s^{-1} until a consistent current response was observed from one cycle to the next. All potentials are reported vs. 3 M Ag/AgCl reference electrodes (0.197 V vs. SHE). The potential of the disk electrode was then scanned from 0.4 to −1.0 V at 10 mV s^{-1} and rotation rates of 100–2100 rpm, while the potential of the platinum ring was held constant at 0.62 V for H_2O_2 oxidation. The potential sweeps at each rotation rate were repeated three times consecutively to ensure stability of the measurements. The current obtained under nitrogen sparging was subtracted from that obtained under air sparging to obtain the faradaic current attributed to oxygen reduction [23]. Catalyst activity was evaluated by the onset potential (E_{onset}) and limiting current (i_{lim}) [23]. The average number of electrons transferred (n) in the ORR at the disk electrode was calculated based on the amount of H_2O_2 detected using [24]

$$n = \frac{4i_{\mathrm{disk}}}{i_{\mathrm{disk}} + i_{\mathrm{ring}}/N} \qquad (1)$$