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Influence of enhanced carbon crystallinity of nanoporous graphite on the cathode performance of microbial fuel cells

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ABSTRACT

We have synthesized a porous graphite with a high degree of local crystallinity by adding copper powder as a catalyst into the magnesiothermic reduction of CO_2. Furthermore, we revealed that the enhanced crystallinity of the carbon cathode catalyst promotes the electrochemical performance of microbial fuel cells under neutral pH conditions, which provides future guidance on the selection of carbon catalysts for microbial fuel cells.

1. Introduction

Microbial fuel cells (MFCs) represent an emerging technology that can directly extract energy from organic materials to generate electricity through microbial activities [1,2]. Exoelectrogenic bacteria oxidize organic compounds and donate electrons to the anode, while the electrons are transferred through the external circuit and consumed by the reduction reactions on the cathode [3,4]. Chemicals, such as $Fe(CN)_6^{3-}$ and permanganate have been used as terminal electron acceptors. However, these chemicals need to be either regenerated or replaced [5,6]. O_2 is a ubiquitous electron acceptor, and air-cathode is the most commonly used cathode [7,8]. Therefore, improving the performance of oxygen reduction reaction (ORR) has been a main focus in MFC cathode development, where the cathode catalyst is the most critical component in determining ORR performance. Metal-based catalysts, such as Pt/C, FePc, and CoTMPP, have demonstrated good performance in MFCs, but their high cost may prevent them from being used for certain practical applications, such as wastewater treatment and remediation [9–11]. Recently, carbon-based materials, such as activated carbon, graphite granules, and graphene, have been demonstrated as promising cathode catalysts because of their comparable performance to metallic catalysts and potentially much lower cost [12–16].

Excellent carbon catalysts have following desirable properties: high specific surface area, suitable surface functional groups, high electronic conductivity and good stability [14,17–23]. However, high specific surface area and superior conductivity typically are not possessed simultaneously by the same carbon structure. For example, graphite is highly conductive but is of very limited surface area; activated carbon could exhibit surface area up to 3000 m^2/g but is hardly a good conductor due to its defective structure and high concentrations of sp^3-bonding kinks [24]. Theoretically, a single layer of graphene will be an ideal candidate considering its high surface area of 2630 m^2/g and its intrinsically high lateral conductivity; however, it is extremely challenging to utilize well-separated layers of graphene as a catalyst material due to its tendency of self-stacking back to graphite [25,26]. Alternatively, most studies in energy storage and conversion sectors have employed reduced graphene oxides (RGO) as active masses, which comprise "wrinkled-paper" like morphology [27–37]. Recently, such RGO materials, sometimes doped by other elements, have been investigated as MFC catalysts in neutral buffer electrolyte [14,38,39]. However, RGO's structures are highly defective like activated carbons, inherited from its intense and corrosive processing by the Hummer's method, thus limiting its conductivity—a key property for an excellent catalyst in MFCs [40]. By far, a direct study on the influence of the carbon crystallinity, which determines the conductivity of carbon materials, on catalytic performance at neural pH is still lacking.

In this contribution, we prepare a porous graphite where both high surface area and highly graphitic structure are realized in a single material, where we reveal that the increased graphitic crystallinity enhances the carbon's catalytic performance in MFCs.

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It is well known that highly graphitic structures are typically only obtainable by annealing graphitizable precursors under high temperatures above 2000 °C. Recently, we reported that magnesiothermic reduction reaction can convert gaseous CO_2 into nanoporous graphite with a high surface area in a controllable manner by flowing CO_2 over hot Mg or Mg/Zn mixture [41]. Reduction by Mg/Zn gives rise to a highly nanoporous graphenic carbon with a surface area above 1900 m^2/g and uniform pore size distribution, which exhibits high-rate electrochemical properties in supercapacitors. With Mg alone as the reductant, the resulting carbon exhibits a good degree of long-range order along the ***c***-axis and *ab* planes, thus being fairly graphitic and graphenic, and exhibits a surface area of 829 m^2/g. A further challenge with respect to this reaction is to further enhance the crystallinity of such CO_2-reduced carbons without compromising its specific surface area.

2. Experimental section

2.1. Preparation of porous graphite

In a typical experiment, 1.5 g of Mg powder well mixed with 4 g of Cu powder (mole ratio 1:1) was placed in an Al_2O_3 boat and heated in a tube furnace at 680 °C under a CO_2 flow at 60 CCM for 60 min. After the reaction, the black product was collected and stirred in 1.0 M HCl solution and 25% $NH_3 \cdot H_2O$ solution at room temperature for 10 h to remove MgO and Cu, respectively. The mixture was then filtered and washed with deionized water several times. Finally, the product is dried at room temperature overnight.

2.2. Characterization methods

X-ray diffraction (XRD) patterns were recorded by using a Rigaku Ultima IV Diffractometer with Cu Kα irradiation ($\lambda = 1.5406$ Å). A 514 nm laser source was employed to collect Raman spectra. The morphology was studied by field emission scanning electron microscopy (FESEM) using an FEI NOVA 230 high resolution SEM with an energy-dispersive X-ray (EDX) attachment. Transmission electron microscopy (TEM) images were recorded by FEI Titan 80–200 TEM. High-angle annular dark field scanning TEM (HAADF-STEM) measurements were carried out on an FEI Titan 80–200 microscope coupled with a HAADF detector and an EDX spectrometer. Nitrogen sorption measurements were performed on Micromeritics TriStar II 3020 analyzer.

2.3. Electrode preparation of ECs

Porous graphite air cathodes for MFCs were fabricated by mixing 40% porous graphite and 60% carbon black with poly(tetrafluoroethylene) (PTFE). The total carbon loading is 8.75 mg/cm^2. PTFE loading is 0.2 mL/g carbon. The carbon/PTFE mixture was stirred and heated (80 °C) in 100% ethanol to form a paste and applied on the carbon cloth substrate with cured (340 °C) PTFE coatings on the air-facing side. These air cathodes were then pressed with a roller compactor.

2.4. Electrochemical measurements

A two-electrode cell configuration was employed to measure the electrochemical performance. Two nearly identical electrodes (by weight and size) were assembled in coin-type cells that use a filter paper (Whatman®) as the separator and a 6.0 M KOH aqueous solution as the electrolyte. A VMP-3 multi-channel workstation was used electrochemical measurements.

Linear sweep voltammetry (LSV) and electrochemical impedance spectra (EIS) tests were conducted in three-electrode cell configuration, using Pt plates (6.5 cm^2) as the counter electrode, the two types of porous graphite cathodes (C-Mg cathode and C-Mg/Cu cathode) (0.7 cm^2) as working electrode, and Ag/AgCl (for LSV) or Pt wire (for EIS) as the reference electrodes. The scan rate of LSV is 0.1 mV/s with voltage window ranging from 0.3 to −0.2 V (vs. Ag/AgCl).

Microbial fuel cells were assembled following previous studies with 7 cm^2 (working area) carbon cloth anode and 14 mL empty bed volume, except for using a small cathode (0.7 cm^2 working area) to ensure the cathode limiting condition. The MFCs were fed with growth medium, which contains KCl, NH_4Cl, 50 mM PBS (pH = 7), minerals, vitamins solution, and 20 mM NaAc as carbon source. Fully grown anodes had been operated with repeatable power output for two months before being assembled with small cathodes in this study.

MFC polarization curves and electrode potential curves were collected by reducing external resistance with an order of 600, 500, 400, 300, 250, 200 Ω at 30 min intervals. The stabilized voltage output and electrode potentials were measured using Ag/AgCl reference electrode. The curves were collected at first batches after switching to a new cathode.

3. Results and discussion

We are inspired by graphene sheet preparation by conducting chemical vapor deposition (CVD) of small organic molecules onto transition metal substrates, such as Ni, Pt, Ru, Ir, and Cu [42–46]. Transition metal substrates play a critical role in nucleating high-quality graphene sheets from the saturated solution with carbon dissolved in metal surface regions. Herein, we utilize one of the most widely employed graphene-forming substrates—copper mixed with Mg powder in the magnesiothermic reaction, attempting to increase the crystallinity of the resulting porous graphite [45]. In a typical experiment, the mixture of Mg and Cu powder with an equal molar ratio is used to reduce gaseous CO_2 under 680 °C for 1 h. After removing MgO by diluted HCl solution (1 M) and then Cu by concentrated $NH_3 \cdot H_2O$, the obtained carbon product is referred to as C-Mg/Cu. As comparison, the carbon product by employing Mg alone is named as C-Mg.

We first characterized the crystalline structures of the resulting carbons by x-ray diffraction (XRD), where the degrees of order along ***c***-axis and ***ab*** planes are revealed. By comparing the XRD patterns of C-Mg and C-Mg/Cu, it is evident that the addition of copper greatly increased the structural crystallinity along both directions. As for C-Mg, there exists a broad shoulder to the left of the (002) XRD peak, which is attributed to its non-graphitic substructures, whereas this shoulder is nearly eliminated in the XRD pattern of C-Mg/Cu (Fig. 1a). In the pattern of C-Mg/Cu, the (002) peak slightly shifts to a larger angle, revealing a smaller d-spacing of 3.41 Å in comparison to 3.43 Å for C-Mg, thus being closer to 3.35 Å of ideal graphite. Graphitic domain size along the ***c***-axis also increases from 6.66 nm in C-Mg to 12.51 nm in C-Mg/Cu, as estimated by the Scherrer equation. The highly graphitic structure of C-Mg/Cu is corroborated by the images of high-resolution transmission electron microscopy (HRTEM), where ordered stacking of graphene layers exists for tens of nanometers in C-Mg/Cu compared to less than 20 nm for C-Mg (Fig. 2c and 2d). However, it is important to note that the resulting structure is not completely homogenous as there are less crystalline areas under TEM with smaller particle sizes. The existence of less dense portions would explain the large surface area of C-Mg/Cu, which will be discussed later on. Furthermore, the graphitic degree can also be empirically characterized by a ratio of the (002) peak intensity and the background at the same diffraction angle, which is referred to as an R-value, first defined by Dahn et al. [47]. A higher R-value suggests a