Materials Research Bulletin 88 (2017) 188–199

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Fabrication and characterization of graphite-cement composites for microbial fuel cells applications

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ARTICLE INFO

Article history:
Received 13 October 2016
Received in revised form 13 December 2016
Accepted 29 December 2016
Available online 30 December 2016

Keywords:
A. Composites
B. Microstructure
B. Mechanical properties
D. Electrochemical properties
D. Electrical properties

ABSTRACT

Graphite-cement composites, with graphite up to 80% w/w, were prepared and characterized. The key feature of this novel material is its conductive and porous microstructure, due to a synergic effect between cementitious matrix and graphite particles. As graphite content increases, a characteristic percolation threshold exists. The threshold value depends on curing temperature and determines a remarkable change in electrical, physical and mechanical properties. In the proximity of the threshold, conductivity increased from $3.2 \cdot 10^{-5}$ S m^{-1} to 2 S m^{-1} and porosity increased from 48% to 60%. Compressive strength indicates a similar behaviour and thermally cured composites exhibit higher strength. The thermally treated composite with 50% w/w of graphite is chosen for electrochemical analysis. Cyclic voltammetry and kinetic study with linear sweep voltammetry confirmed that these materials can catalyse cathodic reactions with an interesting current density and low overpotential. The graphite-cement composite developed is an eligible material for microbial fuel cell applications.

1. Introduction

Microbial Fuel Cells (MFCs) are bio-catalysed electrochemical systems which can directly convert the chemical energy within an organic substrate to electrical energy through a complex network of redox reactions catalysed by microorganisms [1]. The evolution and reliability of their performance are characterized by a certain degree of randomness and so the power production is not always predictable or conform to a scheduled task [2]. Anyway, the deep understanding of the role of materials used for components is a valuable method to boost performances and to reduce the uncertainty related to bacterial growth as improved charge transfer mechanisms can be realized for MFC scale up and deployment [3,4].

The Oxygen Reduction Reaction (ORR) that occurs at the cathode is difficult to engineer as the electrons, protons and oxygen should react on catalyst surface in the Triple Phase Boundary (TPB) zone. The catalyst must be on a conductive surface, but it must be exposed to both water and air so that protons and electrons in these different phases can reach the same catalytic site [5]. The most used catalyst for ORR is Platinum (Pt) on carbon-based supports in form of clothes, paper, brush or others [6–8]. In the last years, alternative materials to Pt were studied, such as precious metals present in not abundant amount, i.e. Palladium (Pd) or Ruthenium (Ru), or non-precious metals present in abundant quantities, such as Iron (Fe), Cobalt (Co) or Tin (Sn) [9–12]. The most versatile material for the construction of the electrode is definitely carbon, in form of graphite in compact disks, rods, flakes or granules (felt, paper, foams, nanofibers, nanotubes) [4,13,14]. For MFC applications, nanostructured materials derived from graphite must be chemically treated to make them wettable or functionalized in order to be successfully integrated into biological systems. These modified materials have a demonstrated ability to improve the ORR evolution an overall performance of MFCs due to an increased reactivity and porous microstructure [15–17]. In order to reduce the necessity of chemical treatments, the possibility of using graphite/cement composites for the realization of electrodes in MFCs is a facile approach to simplify the preparation of the electrochemically active electrode. In the literature it is reported that, in order to enhance fracture behaviour and mechanical strength, the incorporation of graphite, graphene and carbon nanotubes in cement paste and concrete is an effective way to

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http://dx.doi.org/10.1016/j.materresbull.2016.12.037
0025-5408/

modify the microstructure and to obtain a good dispersion in the cementitious matrix [18–20]. However, the very low amount of graphite or graphene oxide in these materials does not involve substantial changes in other properties of interest for energy applications and therefore the experimental evidences of the civil field cannot be transferred to energy field. This is due to the substantial electrochemical inertia and to the electrical insulator character of cement and concrete. Recently, the development of membrane-cathode assembly for tubular MFCs allowed to reduce issues related to diffusion and electro-drag phenomena at cathode [23]. However, the successful application of graphite/cement composites in MFCs was demonstrated in many different cell configurations [24] and also in extreme conditions of pH and salinity, when food wastes are used as substrate [25]. In this work, a detailed study of fabrication process, together with physical, mechanical, microstructural and electric properties is presented for the first time. The innovation of these materials relies in the consideration that, theoretically, any form of carbon can be used as electrode for MFCs and in the above mentioned literature there are many examples of nanostructured but expensive materials. On the contrary, here a graphite powder and an ordinary portland cement are used in order to give to a basic carbon product that necessary microporous complexity required for MFC applications by using a cementitious matrix and its unique porous structure.

2. Experimental

2.1. Fabrication of graphite/cement composites

Different mixtures based on Graphite Cement (GC) composite were developed and characterized. The cement used was a Portland, category CEM II/A-LL 42.5R, according to the standard EN 197-1 while the graphite used was a commercial product, type UF 2 GK, whose main characteristics are shown in Table 1.

Table 2 shows the chemical composition of cement and graphite used, as indicated in the respective data sheets.

The water content for the preparation of the mixtures was optimized to obtain a good workability of the paste and to ensure a correct mixing between cement and graphite powders. By means of preliminary tests the water/cement ratio (w/c) and the water/graphite (w/g), for all mixtures, were fixed to 0.5 and 1, respectively. The graphite content in the mixtures, by weight on a dry basis, was varied from 5% up to 80%. A reference sample, i.e. graphite-free, was also prepared with a mixture (BIANCO) based only on cement and water. Considering the w/c and the w/g ratios, the overall compositions, by weight on a wet basis, of prepared mixtures are reported in Table 3.

The preparation procedure, for the realization of the GC composites at different content of graphite, is the following:

- Step 1: Paste Graphite + Water (w/g = 1). Mechanically mix for 4 min or until homogeneous.
- Step 2: Paste Cement + Water (w/c = 0.5). Mechanically mix for 4 min or until homogeneous.
- Step 3: Combine the two previous pastes and mechanically mix until homogeneous.
- Step 4: Cast the mixture into moulds and seal.

Table 1
Graphite powder characteristics.

	GK UF 2
d_{90} [μm]	12
d_{50} [μm]	4.5
ρ [g/cm^3]	0.9
σ [S/m]	≈7

Table 2
Chemical composition of raw materials.

% w/w	CEM II/A-LL 42.5R	GK UF 2
CaO	60.84	–
SiO_2	2.66	<0.01
Al_2O_3	4.89	<0.01
Fe_2O_3	3.24	<0.01
MgO	1.94	–
SO_3^{2-}	2.95	<0.1
Na_2O	0.12	–
K_2O	0.84	–
Cl^-	0.94	–
C	–	99.5

Table 3
Overall compositions of prepared mixtures.

Mixture Name	Water (% w/w)	Cement (% w/w)	Graphite (% w/w)
BIANCO	33.33	66.67	0.00
GC05	34.43	62.30	3.28
GC10	35.48	58.06	6.45
GC20	37.50	50.00	12.50
GC30	39.40	42.42	18.18
GC40	41.18	35.29	23.53
GC50	42.86	28.57	28.57
GC60	44.44	22.22	33.33
GC70	45.95	16.22	37.84
GC80	47.37	10.53	42.11

- Step 5: Vibrate for 30 s to remove residual air.
- Step 6: Age the moulds in the conditions of curing for 28 days.
- Step 7: Open the moulds and dry specimens in an oven for 48 h at 110 °C.

Step 5 was necessary in order to obtain specimens free of macroscopic imperfections due to air trapped in the mould or non-correct casting. Two different curing conditions were analysed for Step 6: the first, named TT, was a curing in an oven at a temperature of 40 °C and relative humidity of 100% for 7 days, followed by a curing under room temperature condition (20 ± 3 °C) for 14 days, always at a relative humidity of 100%. Associated specimens are indicated as GCXXT, where XX is the content of graphite on dry basis; the second, named RT, was a complete curing under room temperature (20 ± 3 °C) conditions and 100% of relative humidity for 21 days and the specimens are indicated as GCXXA.

2.2. Characterization techniques

According to the type of analysis and characterization, 3 cylindrical GC specimens for each mixture were prepared using moulds of polyethylene of different sizes. For electrical testing and microstructural characterization, moulds in polyethylene of 2.5 mL with a diameter of 14 mm and 31.5 mm in height were used. For the remaining characterizations cylindrical moulds of 35 mL with a diameter of 31 mm and a height of 74.5 mm were used. All measurements were repeated 3 times and average values calculated.

Density and porosity for GC composites were determined by the Archimedes' method according to the standard ASTM C373-88 using a hydrostatic balance (OHAUS, Pioneer PA), while mechanical strength, i.e. compression, was measured according to EN 12390-4 Standards using a compressive testing machine (CONTROLS, MCC8). Scanning Electron Microscopy (SEM) and Energy