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MICROBIAL FUEL CELLS – AN OPTION FOR WASTEWATER TREATMENT

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Abstract

The Microbial Fuel Cell (MFC) is a promising technology for efficient wastewater treatment and recovering energy as direct electricity for onsite applications. For treatment of biodegradable organic matters in MFCs, removal efficiencies comparable with established treatment methods can be obtained. Even some of the bio-refractory compounds can be effectively removed in MFCs. Power densities higher than 2 W/m^2 and volumetric power of 500 W/m^3 are reported. However the power output varies drastically depending on the MFC configuration, substrate used, type of bacterial culture and operating conditions. The results presented so far demonstrated that electricity can be generated by exploiting microorganisms as biocatalysts, but both technical and biological optimizations are needed to maximize power output. The advantages of using MFCs for wastewater treatment, the organic matter removal efficiency and electricity generation reported recently for different MFC configurations are described in this paper. Factors affecting performance of the MFC are summarized. MFC scale-up issues and further development needs are emphasized. This information on factors affecting MFC performance and scale-up issues would be very useful tool for researchers for shifting this technology from lab-scale to pilot and full-scale applications for sustainable wastewater treatment.

Key words: electricity generation, factors affecting performance, MFC design, scale-up, wastewater treatment

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1. Introduction

The high energy requirements of conventional wastewater treatment systems are demanding for an alternative treatment technology. This treatment technology should be cost effective, requiring less energy for its efficient operation, and should generate energy in such a form that would make overall operation of wastewater treatment self sustainable. Organic matter present in the wastewater can be considered a valuable material acting as a renewable source of energy. The energy available in organic wastewaters can be harvested as electricity by using Microbial Fuel Cell (MFC). Bacteria can be used to catalyze the conversion of organic matter into direct electricity while accomplishing the biodegradation of organic matter to carbon dioxide as an end product (Allen and Bennetto, 1993; Bond, 2003; Kim et al., 2002). Therefore, wastewater treatment and simultaneous direct electricity recovery in MFC allows this device to be used as a power source for onsite appliances (Park and Zeikus, 2000).

Application of MFC for wastewater treatment (Liu et al., 2004) has several advantages, such as a high efficiency for energy conversion of the organic matter into electricity, even working at lower mesophilic temperatures, and the absence of any toxic products. In addition a wide diversity of organic

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EFFECT OF SULFATE CONCENTRATION IN THE WASTEWATER ON MICROBIAL FUEL CELL PERFORMANCE

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Abstract

The effect of presence of sulfate in wastewater on the wastewater treatment efficiency and electricity harvesting capacity of microbial fuel cell (MFC) has been studied in two identical dual chambered MFCs (MFC-1 and MFC-2) at different COD/SO_4^{2-} ratio in synthetic wastewater with sucrose as a carbon source. The MFCs were operated under batch mode at feed cycle time of 48 h. Performance of MFC-1 was evaluated under different COD/SO_4^{2-} ratio of 500, 20, 1, 0.8, 0.5, and 0.3. To understand the reproducibility of the results, experiments with certain COD/SO_4^{2-} ratio in the feed (20, 1, 0.5, and 0.3) were repeated in the MFC-2. Increase in COD removal and power production was observed with decrease in COD/SO_4^{2-} ratio up to 0.8 in the wastewater. Both the MFCs demonstrated similar performances when operated at the similar COD/SO_4^{2-} ratio. Increase in COD removal and power production was observed with decrease in COD/SO_4^{2-} ratio up to 0.8 in the wastewater. MFC-1 demonstrated highest COD removal efficiency of 79% and power density and volumetric power of 97.2 mW/m^2 and 1136.8 mW/m^3, respectively, at the COD/SO_4^{2-} ratio of 0.8. The highest Coulombic efficiency and energetic efficiency were 7.36% and 15.69%, respectively, in MFC-1 at the COD/SO_4^{2-} ratio of 0.8. Deterioration in reactor performance was observed when the COD/SO_4^{2-} ratio was decreased below 0.8.

Key words: COD/SO_4^{2-} ratio, Coulombic efficiency, microbial fuel cell, power density, sulfate reduction

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1. Introduction

Today environmental biotechnology is getting a powerful pull from one of the most pressing needs of human society: sustainability. At the top of the list of sustainability needs, water and energy are the two resources that environmental biotechnology should address directly (Rezaee et al., 2008; Rittmann, 2006). An exciting example where both these goals can be achieved is the recent developments in the microbial fuel cell (MFC) technology, for its application as sustainable wastewater treatment system and generation of direct electricity. Wastewater treatment using MFC is promising since this process can convert the major part of the chemical energy present in the form of organic matter from the wastewater to electricity, and reduces the problem of excess sludge generation during treatment. MFCs offer the opportunity for energy-efficient wastewater treatment (Rabaey et al., 2005).

During the application of anaerobic processes, such as the upflow anaerobic sludge blanket (UASB) reactor, for energy recovery in the form of methane treating low strength wastewater, a major fraction of the produced methane is lost along with the effluent of the reactor. The energy recovery using MFC is expected to be more because of harvesting energy in the form of direct electricity (Aelterman et al., 2008). Using MFC for wastewater treatment has generated considerable interest among the academic researchers in recent years. When MFCs are used for the treatment of wastewaters, the presence of other compounds in the wastewater may interfere with its performance. The knowledge of this aspect is still

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Nitric acid activation of graphite granules to increase the performance of the non-catalyzed oxygen reduction reaction (ORR) for MFC applications

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ABSTRACT

Nitric acid and thermal activation of graphite granules were explored to increase the electrocatalytic performance of dissolved oxygen reduction at neutral pH for microbial fuel cell (MFC) applications. Electrochemical experiments showed an improvement of +400 mV in open circuit potential for graphite granules when they were activated. The improvement of ORR performance observed with activated granules was correlated to the increase of Brunauer–Emmett–Teller (BET) surface of the activated material and the emergence of nitrogen superficial groups revealed by X-ray photoelectron spectroscopy (XPS) analysis on its surface.

The use of activated graphite granules in the cathodic compartment of a dual-chamber MFC led to a high open circuit voltage of 1050 mV, which is among one of the highest reported so far. The stable performance of this cathode material (current density of 96 A m^{-3} at +200 mV/Ag–AgCl) over a period of 10 days demonstrated its applicability as a cathode material without any costly noble metal.

1. Introduction

The cathodic overpotential of oxygen reduction reaction (ORR) at microbial fuel cell (MFC) cathodes based graphite is actually a limiting drawback for the wide development of the technology [1,2]. Basically, the cathode performance can be improved in two ways, either by using a catalyst to reduce the activation energy or by increasing the specific surface area of the graphite material. Many studies reported an increase of the ORR rates involving innovative and cheap catalysts [3,4], and several researchers have used in cathode construction non-catalyzed three-dimensional graphite such as cloth, felt, sponge, or granules [5,6]. The use of activated graphite material for cathode has not been enough explored so far.

Activated carbon and graphite are widely used materials in the industry as catalytic support in industrial reactions mainly because of its inertness, low cost, high surface area, and low deactivation [7]. Their main applications are in the water and wastewater treatment and as adsorbent of heavy metals and organic compounds. Activated carbon has oxygen and nitrogen groups on its surface, which gives many of its chemical properties [8]. Thermal or chemical pretreatments are known to introduce these groups and change the texture of the material surface.

In this work, both chemical and thermal activation of graphite granules were explored to increase the electrocatalytic performance of dissolved oxygen reduction at neutral pH. The new surface properties were analysed coupling BET and XPS analysis. Additionally, activated graphite granules were tested as cathode material in a dual-chamber MFC involving an optimized bioanode prepared under constant potential as described by [9].

2. Experimental procedure

2.1. Activation of graphite granules

Graphite granules were dispersed in a 1000 ml flask of 5% nitric acid. The mixture was refluxed for 12 h at 120 °C. Treated granules were filtered and washed for 15 min with a continuous flow of deionized water, and then dried at 110 °C in an oven for 12 h.

2.2. Electrochemical analysis

ORR performance was investigated at room temperature (20 °C) performing cyclic voltammetries on 50 mL of graphite granules at a scan rate of 1.0 mV/s. Experiments were performed in a 100 mM

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MINI REVIEW

Application of electro-active biofilms

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The concept of an electro-active biofilm (EAB) has recently emerged from a few studies that discovered that certain bacteria which form biofilms on conductive materials can achieve a direct electrochemical connection with the electrode surface using it as electron exchanger, without the aid of mediators. This electro-catalytic property of biofilms has been clearly related to the presence of some specific strains that are able to exchange electrons with solid substrata (eg *Geobacter sulfurreducens* and *Rhodoferax ferrireducens*). EABs can be obtained principally from natural sites such as soils or seawater and freshwater sediments or from samples collected from a wide range of different microbially rich environments (sewage sludge, activated sludge, or industrial and domestic effluents). The capability of some microorganisms to connect their metabolisms directly in an external electrical power supply is very exciting and extensive research is in progress on exploring the possibilities of EABs applications. Indeed, the best known application is probably the microbial fuel cell technology that is capable of turning biomass into electrical energy. Nevertheless, EABs coated onto electrodes have recently become popular in other fields like bioremediation, biosynthesis processes, biosensor design, and biohydrogen production.

Keywords: biocathodes; bioelectrochemical sensors; electro-active biofilms (EABs); electricity generation; microbial fuel cell; wastewater treatment

Introduction

Typically, biofilms have been associated with adverse effects such as biodeterioration of materials or nosocomial infections. But the discovery in the early 2000s of the ability of some biofilms, called electro-active or electrochemically active biofilms (Reimers et al. 2001), to exchange electrons directly with conductive materials, opened new perspectives. Electro-active biofilms (EABs) are the subject of a new area of expanding research involving several disciplines dominated by electrochemistry, microbiology and chemical engineering (Logan et al. 2006; Du et al. 2007). Their applications were explored in many fields, including biotechnology, sustainable energy development or bioremediation. For example, such biofilms are able to reduce heavy metals (eg chromium and uranium) playing a role in bioremediation of groundwater and contaminated soil (Li et al. 2008). EABs can be useful in electrochemical biosensors to monitor the development of biofilms in facilities, where their presence is undesirable. In addition, the EAB has a significant impact in the field of renewable energy including the development of microbial fuel cells (MFCs) and hydrogen production, through which energy production is coupled with the treatment of organic waste (Logan et al. 2008).

Biofilm coated electrodes

Discovery and historic

The conversion of chemical energy into electricity by microorganisms has attracted the attention of a large number of researchers. Due to studies on MFCs the concept of 'Bio-electricity' has really taken its meaning. EAB coated electrodes play vital role in the electron transfer and hence overall performance of the MFC. This EAB concept is being extensively studied in the MFC research in efforts to improve its performance.

Although, the concept of chemical fuel cell was discovered in 1839, it was not until 1910 that Potter discovered that microorganisms can produce electricity. In 1931, this discovery was exploited by Cohen achieving a voltage of 35 V by connecting biological fuel cells in series. This value has still not been exceeded. The development of biological fuel cells was especially enhanced in the 1960s when NASA was interested in processing organic waste into electricity in

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Effect of chemically modified Vulcan XC-72R on the performance of air-breathing cathode in a single-chamber microbial fuel cell

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ABSTRACT

The catalytic activity of modified carbon powder (Vulcan XC-72R) for oxygen reduction reaction (ORR) in an air-breathing cathode of a microbial fuel cell (MFC) has been investigated. Chemical modification was carried out by using various chemicals, namely 5% nitric acid, 0.2 N phosphoric acid, 0.2 N potassium hydroxide and 10% hydrogen peroxide. Electrochemical study was performed for ORR of these modified carbon materials in the buffer solution pH range of 6–7.5 in the anodic compartment. Although, these treatments influenced the surface properties of the carbon material, as evident from the SEM-EDX analysis, treatment with H_2PO_4, KOH, and H_2O_2 did not show significant activity during the electrochemical test. The HNO_3 treated Vulcan demonstrated significant ORR activity and when used in the single-chamber MFC cathode, current densities (1115 mA/m^2, at 5.6 mV) greater than those for a Pt-supported un-treated carbon cathode were achieved. However, the power density for the latter was higher. Such chemically modified carbon material can be a cheaper alternative for expensive platinum catalyst used in MFC cathode construction.

1. Introduction

Treatment and disposal of wastewaters represent one of the major problems of the modern society due to insufficient and inadequate treatment. Present technologies used for wastewater treatment are energy intensive and they are not able to recover valuable products present in different wastewaters. This can be solved by using microbial fuel cell (MFC), due to capacity of specific bacteria to transform organic compounds in electricity and simultaneously achieving wastewater treatment (Rabaey and Verstraete, 2005). The major limitations faced by MFCs towards commercialization is very high cost of the catalysts used for cathode construction to harvest more power.

In order to minimize the operating cost, an air-breathing single-chamber MFCs are being developed by the researchers (Liu et al., 2004); such air-cathode MFC is an efficient and sustainable MFC configuration for recovering electrical energy from organic substances. In a graphite-granule anode and tubular air-cathode MFC, continuous electricity generation was reported at a maximum volumetric power of 50.2 W/m^3 with a current density of 216 A/m^3 from glucose (You et al., 2007). Increased use of single-chamber air-cathode MFC is being observed with simple or modified carbon (pretreated or with metals coating) acting as cathode electrode material (Liu et al., 2004; Wang and Han, 2009). The important characteristics for any catalyst used on the electrodes are: stability, mechanical properties, surface area and chemical composition (Rodriguez-Reinoso, 1998).

Electrode modifications were actively investigated to increase cathodic oxygen reduction. In fuel cells, Pt-coated carbon cathodes yielded higher performance than those with only graphite or carbon cathodes, by increasing their affinity for oxygen and decreasing the activation energy of the oxygen reduction reaction (ORR) occurring on the cathode surface (Freguia et al., 2007). However, its poor kinetics of ORR in neutral pH environment and low temperature, associated with its sulphide poisoning in wastewater applications, has limited its use in MFC cathode investigation (Karyakin et al., 2005; Shukla et al., 2004). Other cheaper catalysts, such as, CoTMPP, Mn(IV), Fe(III), deposited on air-breathing cathode can also increase the power output (Roche and Scott, 2009; Yu et al., 2008). For example, Park and Zeikus reported a 100-times increase in current output of a MFC testing Mn(IV) supported on graphite as cathode instead of graphite alone (Park and Zeikus, 2003, 2002). More recently, Yu et al. demonstrated higher activity

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Original scientific paper

Influence of ceramic separator's characteristics on microbial fuel cell performance

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Abstract

This study aimed at evaluating the influence of clay properties on the performance of microbial fuel cell made using ceramic separators. Performance of two clayware microbial fuel cells (CMFCs) made from red soil (CMFC-1) typically rich in aluminum and silica and black soil (CMFC-2) with calcium, iron and magnesium predominant was evaluated. These MFCs were operated under batch mode using synthetic wastewater. Maximum sustainable volumetric power density of 1.49 W m^{-3} and 1.12 W m^{-3} was generated in CMFC-1 and CMFC-2, respectively. During polarization, the maximum power densities normalized to anode surface area of 51.65 mW m^{-2} and 31.20 mW m^{-2} were obtained for CMFC-1 and CMFC-2, respectively. Exchange current densities at cathodes of CMFC-1 and CMFC-2 are 3.38 and 2.05 times more than that of respective anodes, clearly indicating that the cathodes supported much faster reaction than the anode. Results of laboratory analysis support the presence of more number of exchangeable cations in red soil, representing higher proton exchange capacity of CMFC-1 than CMFC-2. Higher power generation was observed for CMFC-1 with separator made of red soil. Hence, separators made of red soil were more suitable for fabrication of MFC to generate higher power.

Keywords

Cation exchange capacity; Coulombic efficiency; Charge transfer resistance; Charge transfer coefficient; Exchange current density; Power density; Wastewater treatment

Introduction

Recently considerable attention is being paid on the two major problems of the world, which are namely maintaining quality of water body and energy crisis. Solution to these problems could be provided by microbial fuel cell (MFC) to treat organic matter present in wastewater and

Effect of Wastewater Characteristics and Biomass Growth in Cathode Compartment on Performance of Membrane-less Microbial Fuel Cell

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The performance of mediator-less and membrane-less microbial fuel cell (ML-MFC) was evaluated for synthetic wastewater treatment by changing carbon source, alkalinity and total dissolved solids (TDS) concentration in the influent. The ML-MFC, inoculated with pre-heated septic tank sludge, was operated for total 192 days. The chemical oxygen demand (COD) removal efficiency greater than 85% was noticed under different influent characteristics. Higher TDS in the influent, due to sulphate and bicarbonate alkalinity, showed a diminution in power and current density. Built-up of high biomass concentration in the cathode compartment had adverse effect on current and voltage; hence, biomass concentration should be kept under control to get maximum power generation. Close spacing between anode and cathode was considered to be favourable for getting higher power output.

Keywords: Microbial fuel cells; ML-MFC; cathode biofilm; power production; anode surface area; wastewater treatment

The increasing difficulty of sustained supply of fossil fuel and the associated problems of pollution and global warming are acting as major impetus for research of alternative renewable energy technologies [1]. Microbial fuel cell (MFC) offers a possible (and partial) solution to this problem. Although the fuel needed for conventional cells usually is either hydrogen or methanol, some cells which run on other fuels such as wastewater have been developed [2 - 5]. Approaches by which common waste materials and the chemical energy locked within them could be utilized, would offer many benefits. In MFC type fuel cells, the organic contaminants present in the wastewater are oxidized and during this process direct electricity recovery is possible. Thus, simultaneous wastewater treatment and electricity recovery can be achieved. In addition, excess sludge production is very low in MFC, as compared to conventional aerobic wastewater treatment, reducing the cost of further sludge management [6].

A MFC is a device that converts chemical energy to electrical energy with the aid of the catalytic reaction of microorganisms [7]. MFC consists of anode and cathode compartments separated by a cation-specific membrane (proton exchange membrane, PEM). In the anode compartment of MFC, microorganisms oxidize fuel (i.e., organic matter present in the wastewater) generating electrons and protons. Electrons are transferred to the cathode compartment through external circuit, and the protons are transferred to the cathode through the internal membrane. Electrons and protons are consumed in the cathode compartment reducing oxygen to water. Usually oxygen is supplied by aeration in cathode compartment to act as oxidant.

It has recently been shown that certain metal-reducing bacteria, belonging primarily to the family *Geobacteraceae*, can directly transfer electrons to electrodes having electrochemically active redox enzymes, such as cytochromes on their outer membrane [8,9]. These microbial fuel cells do not need mediator for electron transfer to electrodes and are called as mediator-less MFCs. In a mediator-less MFC, the membrane separates the anode from the cathode and functions as an electrolyte that plays the role of an electric insulator and allows protons to move through [10]. Proton transfer through the membrane can be a rate limiting factor, especially with fouling, expected due to presence of suspended solids and soluble contaminants in a large scale wastewater treatment process, requiring replacement. Membranes being expensive may limit acceptance of MFC as a wastewater treatment process.

A membrane-less microbial fuel cell (ML-MFC) was developed [10] and used successfully to enrich electrochemically active microbes that converted organic contaminants to electricity. The chemical oxygen demand (COD) removal rate of 0.526 kg/m^3.day was reported with maximum power production of 1.3 mW/m^2 and current density 6.9 mA/m^2. The present research on MFC is being mainly focused on identifying and enriching electrochemically active microbes and evaluating performance of MFC using different electrode materials, with or without supplementation of external mediator [7,11 - 13]. Few studies have used mixed culture as inoculum to start MFC, *e.g.*, heat treated soil [14], sulphate enriched anaerobic sewage sludge [15], marine sediments [16], activated sludge [10]. Effectiveness of mixed anaerobic sludge as inoculum needs further investigation. If wastewater treatment efficiency and electricity recovery from the ML-MFC could be enhanced, this device has a greater potential for commercial applications due to less production cost.

When any technology is used for wastewater treatment, it should have capability to handle the variation in the characteristics, which is expected in real wastewaters. Hence, further investigations are necessary to study performance of MFC under different alkalinity and total dissolved solids (TDS) concentration present in the wastewater for organic matter removal, as well as effect of these parameters on electricity production. Thus, the objective of this work was to evaluate performance of mediator-less and membrane-less MFC, inoculated with septic tank sludge, for synthetic wastewater treatment and

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The effects of doping on the structural, optical and electric properties of Zn_4Sb_3 material

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Abstract: This paper presents the results of an investigation regarding the synthesis and characterization of the thermoelectric material Zn_4Sb_3 and $(Zn_{1-x}M_x)_4Sb_3$, where M = Ag and/or Sn. The synthesis of the materials was realized by melting high purity precursors in an oven where they were kept isothermally for 12 h at 1173 K. X-Ray diffraction analysis and scanning electron microscopy were used for structural and morphologic characterization. The optical band gap for each sample was determined from absorbance spectra recorded in the visible range 240–400 nm at room temperature. The electrical resistivity as function of temperature was measured and the electrical band gap was estimated for each of the obtained samples. The semiconducting behavior of the materials was reflected in these results.

Keywords: thermoelectric; melting; electrical resistivity; band gap.

INTRODUCTION

The need for permanent discoveries in the domain of resources has influenced this area of research in the latest years. The research has attempted to find alternative sources of energy by either creating them or by regenerating and converting other types of energy. Thermoelectric materials (TE) seem to represent an alternative due to their capacity to convert wasted heat into electrical energy. The performance in the field of this type of materials is represented by the dimensionless *ZT* figure of merit,[1] which could be estimated from the equation:

$$ZT = S^2\sigma T / k \quad (1)$$

where S represents the Seebeck coefficient, σ is the electrical conductivity and k is the thermal conductivity at a certain absolute temperature T.

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Preparation and characterization of the thermoelectric material Zn_4Sb_3

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The thermoelectric materials gained a lot of attention in the last decades, due to their possible applications. The thermoelectric materials can generate electricity from heat and these materials have an efficiency which depends on the dimensionless figure of merit. Zn_4Sb_3 was reported as an excellent thermoelectric material in an intermediate temperature range (473–673 K). In addition to a promising thermoelectric performance, Zn_4Sb_3 has attracted attention for its other features, such as being an environmentally friendly material and with low costs of production. The aims of this paper are to present the results regarding the obtaining and the characterization of the thermoelectric Zn_4Sb_3 material synthesized by melting a precursors mixture at 1173K for 24 hours, using precursors with a high purity. The obtained material was analyzed and characterized through X-ray diffraction and by specific microscopic techniques as: energy-dispersive X-ray spectroscopy, scanning electron microscopy and atomic force microscopy. The X-ray diffraction pattern show that β - Zn_4Sb_3 was formed. The measured particles dimension on the scanned surfaces is between 2.1 and 3.2 μm. Also, the average roughness - S_a and the root mean squared roughness - S_q were determined.

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Keywords: Zinc, Antimony, Thermoelectric materials, Melting, Physical properties

1. Introduction

In the last decades, a lot of attention was gained by research studies with the main goal to find alternative energy resources among the existing ones. One of these directions is to obtain materials which can generate electricity from heat, materials known as thermoelectric materials (TE). The efficiency of the heat conversion of the thermoelectric materials is ensured by a low thermal and a high electrical conductivity of these.

Zn_4Sb_3 was reported as an excellent thermoelectric material in an intermediate temperature range (450–670 K) [1]. Beside the promising performance as a thermoelectric material which could make it commercially viable, Zn_4Sb_3 also possess other attractive features as being environmentally friendly and with low costs of production comparative with other materials with the same properties.

According to the existing studies, Zn_4Sb_3 exists in four crystallographic phases: the α-phase which is stable below 263K, the β-phase from 263 K to 765 K, the γ-phase from 765 K to 805 K [2-4] and the γ' from 805K to 839K [3]. It was reported that only the single β-phase has high thermoelectric properties with a value for the figure of merit (ZT), the main measure of the energy conversion performance of the thermoelectric materials, ZT=1.3 at 670K [1]).

The figure of merit, Z is defined as:

$$ZT=\alpha^2\sigma T/\lambda \quad (1)$$

where α is the Seebeck coefficient, T the absolute temperature, σ the electrical conductivity and λ the thermal conductivity [1].

This high efficiency of Zn_4Sb_3 is coming from the remarkably glass-like thermal conductivity. The low thermal conductivity of Zn_4Sb_3 is coming from the high levels of interstitials and from domains of interstitial ordering, leading to disorder at multiple length scales [5].

A lot of researches regarding methods of obtaining Zn_4Sb_3 with a larger figure of merit were tried. In time, were reported different methods in obtaining Zn_4Sb_3 as: melt and quenching [1, 6-12], solid state reaction [13-14], thin films prepared by co-sputtering [15], zone-melting technique [2, 16], melt-spinning technique [17], melting combined with high-energy ball milling [18-19], melting combined with mechanical grinding [20-22], gradient freeze method [23], low temperature solution route [24], etc.

It was also studied the thermal stability of Zn_4Sb_3 [2, 16, 25-27] because this can affect the practical applications if pure samples cannot be obtained. The thermal stability of Zn_4Sb_3 is poor, ZnSb and Zn is formed after the decomposition of the compound which often appear below the expected range of temperature [2, 26-27]. The thermoelectric Zn_4Sb_3 fabricated by zone-melting technique was appreciated by the researchers to be more thermal stable than simple melting and quenching method because it presents a *limited* degradation, which is considered a huge improvement in the thermal stability [2].

THERMAL BEHAVIOR REGARDING THE THERMOELECTRIC Zn_4Sb_3 OBTAINED BY MELTING AND QUENCHING METHOD

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ABSTRACT: The present paper is focused on studying the thermal behaviour of the Zn_4Sb_3 material. The thermal behavior of Zn_4Sb_3 was investigated using differential thermal analysis which was taken on the temperature range 300 -1073K. The melting point and the solidification temperature of Zn_4Sb_3 were determined. Also, a characterization of the Zn_4Sb_3 material from an electrical point of view was done. It was shown the semiconducting behavior of the material as a function of temperature, and also as function of material electrical resistivity and electrical conductivity. Also, the optical and the electrical band gap were estimated.
KEYWORDS: zinc, antimony, melting, thermoelectric materials, differential thermal analysis, electrical

1. INTRODUCTION

A lot of attention has been focused on the thermoelectric materials in the last decades and lots of researches were dedicated to these for improving their properties and also the mechanical and thermal stability to be more attractive to be used in applications and to replace other types or materials (environmentally non-friendly or expensive). Thermoelectric materials have the property of converting wasted thermalenergy into electrical energy. The efficiency of a thermoelectric material for applications is given by the dimensionless figure of merit (ZT):

$$ZT=\alpha^2\sigma T/k \quad (1)$$

where α is the Seebeck coefficient, σ the electrical conductivity, ($\sigma = 1/\rho$, ρ is the electrical resistivity) and k the total thermal conductivity [1], which means that a good thermoelectric material requires a high thermopower combined with a low electrical resistivity and a low thermal conductivity.

At first, semiconductors have been the materials of choice for the thermoelectric applications. Zn_4Sb_3, thermoelectric material, due to its excellent low thermal conductivity, represents a more environmental friendly material than the oldest categories of other thermoelectric materials which some were more toxic (e.g. PbTe, Bi_2Te_3), and also the obtaining cost for Zn_4Sb_3 are not so high. Using different approaches, experimentally and also theoretically, this material was intensively studied in the last decades for obtaining maximum performance in converting heat into energy [1-10].

For Zn_4Sb_3, three phases are known: α – stable below 263 K, β – stable between 263 and 765 K and γ which is stable above 765 K, respectively [1]. The studies revealed that β-Zn_4Sb_3 is expected to manifest metallic properties and thatthis phase is characterized by the deficiency of zinc atoms [11]. Mikhayluskin and Kim reportedalso that the disordered zinc atoms play the role of electron donors and their concentration determines the gap opening at the Fermi level to give rise to the p-type conduction[12, 13].

Also, the researchers present Zn_4Sb_3 as an excellent thermoelectric material, but with a low mechanical and thermal stability. It was concluded that the low thermal stability of Zn_4Sb_3 is due to the fact that often can appear a decomposition of the material below the expected range of temperature and that an appropriate method of synthesis (e.g. zone-melting technique) which may reduce the decomposition should be used [4, 8, 10, 14, 15]

In the present paper are presented results regarding the investigations of Zn_4Sb_3 using the differential thermal analysis and the temperature dependence for the measured and determined electrical parameters which characterize the material. Based on obtained experimental data we estimated the optical and also electrical band gap.