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SYNTHESIS, ELECTRICAL AND ELECTOCHEMICAL STUDIES OF BISMUTH ANTIMONY OXIDE FOR ASCORBIC ACID DETECTION

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FS 2017 85

SYNTHESIS, ELECTRICAL AND ELECTOCHEMICAL STUDIES OF BISMUTH ANTIMONY OXIDE FOR ASCORBIC ACID DETECTION

By

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Thesis Submitted to School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Master of Science

May 2017

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the Degree of Master of Science

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Chairman : Tan Yen Ping, PhD
Faculty : Science

Oxide ion conductors have been studied widely for year due to its economic benefit in the application of solid fuel cell and further in chemically modified electrode for ascorbic acid detection. Bismuth oxide was a well-known good oxide ion conductor because of its crystal structure, which has high ratios of oxygen vacancies. Therefore, it was chosen in this studies.

Bismuth antimony oxide ceramics, $Bi_xSb_2O_\delta$ where x=1.0, 1.5, 2.0 have been prepared by solid state method. The single phase of synthesized samples was confirmed by x-ray diffraction (XRD) analysis. The physico-chemical properties of synthesized samples were characterized. The elemental composition of each synthesized samples were in the acceptable range of ±5%. The results showed that the synthesized samples were thermally stable. Bi-O bonds were observed in FTIR for the synthesized samples. The SEM results showed that the porosity of the synthesized samples were reduced with the increasing in composition of bismuth.

The electrical properties of synthesized samples were carried out using AC impedance spectroscopy. The conductivity of the synthesized samples is at the order of 10^{-7}. The activation energy is in the range of 1.23-1.62 eV. The dielectric constant, ε' is in the range of 23-28 and dielectric loss, tan δ is in the range of 10^{-2} at room temperature and frequency 1 MHz.

Furthermore, the synthesized samples were used to study the electrochemical properties of the oxidation of ascorbic acid using cyclic voltammetry (CV). The powder of samples was attached onto the glassy carbon (GC) electrode. The oxidation current of ascorbic acid was enhanced by about 1.52 times by using modified electrode

with 0.1 M potassium chloride as the supporting electrolyte. The optimum oxidation current of ascorbic acid was occurred in pH5. From the temperature studies, the activation energy is found to be 4.68 $kJmol^{-1}$. The scan rate studies showed that a type of surface process was occurred. The calibration curve showed the sensitivity of modified electrode was closed up to 18 $\mu A\ mM^{-1}$. The curve also can applied in the application of detection of vitamin C and commercial fruit juices.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Master Sains

SINTESIS, PENGAJIAN ELEKTRIK DAN ELEKTRIKIMIA OLEH BISMUT ANTIMONI OKSIDA UNTUK PENGESANAN ASID ASKORBIK

Oleh

CHIA CHEW THENG

Mei 2017

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Konduktor ion oksida telah dikaji mendalam dalam beberapa tahun ini disebabkan oleh kemanfaatannya dalam aplikasi bahan api pepejal dan dilanjutkan ke pengubahsuaian elektrod untuk pengesaan asid askorbik. Bismut oksida adalah terkenal dengan conductor ion oksida disebabkan oleh strukturnya yang mempunyai kekosongan oksigen yang tinggi. Jadi, ia dipilih dalam pengajian ini.

Bismut antimoni oksida, $Bi_xSb_2O_\delta$, x=1.0, 1.5, 2.0 telah disediakan dengan menggunakan cara tindak balas keadaan pepejal. Analisis pembelauan serbuk sinar-x (XRD) menunjukkan komposisi dalam sampel yang disintesis adalah phasa tulen. Ciri-ciri fizik dan kimia oleh sampel dikajikan dengan pelbagai alat. Komposisi bahan-bahan dalam sampel adalah ±5%, di mana masih dalam lingkungan. Sampel-sampel yang disintesis adalah stabil dalam analisis terma. Ikatan Bi-O didapati dalam analisis FT-IR. Saiz butir-butiran dan keliangan bagi setiap sampel diperhatikan dengan SEM. Keliangan di antara butiran dikecilkan dengan menambah komposisi bahan bismuth.

Kekonduksian bagi sampel-sampel tulen telah diukur dengan menggunakan spektroskopi impedans. Kekonduksian sampel adalah dalam 10^{-7}. Tenaga aktif adalah dalam lingkungan 1.23-1.62 eV. Pemalar dielektrik, ε' adalah dalam lingkungan 23-28 manakala kehilangan dielektriks, tan δ adalah 10^{-2} pada suhu bilik dan frekuensi 1 MHz.

Sampel disintesis digunakan untuk mengaji pencirian elektrokimia dalam asid askorbik dengan menggunakan kitaran voltametri (CV). Serbuk sampel telah ditampalkan ke atas elektrod karbon berkaca. Arus pengoksidaan oleh asid askorbik

ditingkatkan dengan 1.52 kali dengan menggunakan elektrod diubahsuai dan 0.1 M kalium klorida sebagai penyokong elektrolit. Optimum arus pengoksidaan oleh asid askorbik didapati pada pH 5. Daripada pengajian suhu, tenaga pengaktifan oleh asid askorbik adalah 4.68 $kJmol^{-1}$. Kadar imbasan ujian mununjukkan proses permukaan dilakukan. Graf penentuan menunjukkan sensitiviti oleh pengubaisuai elektrod adalah 18 $\mu A\ mM^{-1}$. Pengajian ini dapat diaplikasikan dalam pengesanan asid askorbik dan jus buah-buahan.

ACKNOWLEDGEMENTS

First of all, I would like to thank my supervisor, Dr. Tan Yen Ping for her guidance, comment, support and suggestions throughout my study. Really appreciate what she has done for me. I would also like to extend my sincere appreciation to my co-supervisor, Associate Professor Dr. Tan Wee Tee. For his guidance and ideas throughout this research work.

I'm grateful for the all the lab assistants in the science faculty for the measurements like FT-IR, DTA, DSC and TGA. I also would like to express my appreciation to the staffs in the Electron Microscopy Unit, UPM for their guidance in the operating instrument. I would like to thank all my lab mates for their supports and encouragement.

Last but not least, my deepest gratitude to my beloved family member for theirs support, encouragement and understanding.

I certify that a Thesis Examination Committee has met on 19 May 2017 to conduct the final examination of Chia Chew Theng on her thesis entitled "Synthesis, Electrical and Electrochemical Studies of Bismuth Antimony Oxide for Ascorbic Acid Detection" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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This thesis was submitted to the Senate of the Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of. Master of Science. The members of the Supervisory Committee were as follows:

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LIST OF ABBREVIATIONS

AC	Alternating current
DTA	Differential thermal analysis
FT-IR	Fourier-transform infrared spectroscopy
ICDD	International Centre for Diffraction Data
SEM	Scanning Electron Microscopy
TGA	Thermogravimetry analysis
a,b,c	Cell parameters
C	Capacitance
C_b	Bulk capacitance
E_a	Activation energy
I	Current
f	Frequency
M’	Real part of electric modulus
M’’	Imaginary part of electric modulus
R	Resistance
V	Voltage
Z	Impedance
Z*	Complex impedance
Z’	Real part of impedance
Z’’	Imaginary part of impedance
ε	Permittivity
θ	Bragg’s angle
λ	Wavelength

CHAPTER 1

INTRODUCTION

1.1 General background

There are many studies had been carried out on the electrical properties of material. This is due to the applications in telecommunication and satellite broadcasting. Since 1960s, the electrical properties of various types of solids had been discovered such as crystalline compound, glasses, composite materials and polymers. Generally, they were known as solid electrolytes or fast ion conductors. Ions can be diffused easily in solid form, aqueous solution or molten salt. They showed the conduction of either cations or anions.

Bismuth oxide has four different phases, which are α, β, ϒ and δ. Each phase has its own characteristics. δ-Bi_2O_3 is only stable at the temperatures in between 730 ˚C and 825 ˚C. Therefore, in order to stabilize the δ-phase to room temperature, various elements were doped into it. Various elements have been reported. The properties of the Bi_2O_3 will be different when different dopants are introduced into it.

The electrical properties of the bismuth-based ceramics had been studied widely. The electrical properties of the bismuth-based ceramics were depended on the dopant and synthesized method. Different dopants and synthesis methods will gave the different properties of the bismuth-based ceramics. Therefore, some dopants are giving dielectric behaviour. They can be used in capacitors and electrical insulators in various applications. The main property of dielectric materials is to support an electrostatic field while the minimum energy dissipated in the form of heat. A decent dielectric material should have high dielectric constant which is the ability of a substance to concentrates the electrostatic lines of flux, and minimum dielectric loss which is the loss of electrical energy.

The dielectric materials can be applied in many devices and components such as varistors, multilayer ceramic capacitors (MLCC), microwave dielectric materials and others. A varistor is an electronic element that has a significant characteristic on non-ohmic current-voltage. Varistors are used to keep the circuits from excessive transient voltage. The varistors will shut down the current induced by the high voltage away from the sensitive components. Example of varistor is Metal Oxide Varistor (MOV). It consists ceramic mass of zinc oxide grains, with other metal oxides such as bismuth. It is place between two metal plates and allows current to flow in one direction only. Therefore, varistors is suitable to use as surge arresters in power transmission and protector of the electronic devices.

Multilayer of ceramic capacitors are made by mixing the ceramic powder in an organic binder and moulding into thin layers. Surface ceramic layer was deposited with metal electrodes, and stacked until a laminated structure was formed. Metal electrodes are arranged in order to have their termination alternate from one edge to another edge of capacitor. A monolithic block was formed when it is sintered at high temperature which able to provide higher capacitance in small mechanical volumes (Levin *et al*., 1989)

Microwave dielectric materials are effective in making smaller devices, and enhance the packaging density of microwave integrated circuit. With these properties, it is used widely in mobile communication components such as hand phones, satellite broadcasting and others devices.

Other than electrical properties and applications, modifying the electrode chemically also had been investigated as an interesting area of research. The chemically modified electrode (CME) study involves the attaching chemical materials or reagents onto the surface of inert electrode. CME is believed that important in increasing of sensitivity and specificity, decreasing the biological matrix interference (Bard *et al.*, 2001).

Electrochemical properties of ascorbic acid (AA) had been studied by using Bi_2O_3 micro-particles modified glassy carbon (GC) electrode. The Bi_2O_3 micro-particles powder was attached onto the glassy carbon electrode mechanically. Bi_2O_3/GC electrode has been reported to improve the sensitivity in the determination of amino acids, vitamins, DNA.

1.2 Problem statement

In recent years, oxide ion conductors have been studied widely due to their high economic benefit in the application of many devices like solid fuel cell (SOFC), oxygen sensors, ceramic membrane separation, and other applications (Fruth *et al*., 2004). Yittria-stabilized zirconia (YSZ) was used as the electrolyte in SOFC, which functions at high temperature, around 1000 ˚C. With this high temperature, it will be costly. Besides, it influences the stability of the material (Ng *et al*., 2009). Therefore, many researches have been carried out in order to search for new oxide ion conductors, which could be function at lower temperatures to reduce the cost.

Bismuth oxide, Bi_2O_3 was a well-known good oxide ion conductor because of its crystal structure, which has high ratios of oxygen vacancies. Bi_2O_3 can be existed in four different polymorphs, which are α, β, ϒ, δ due to its different sintering temperatures. It formed δ-Bi_2O_3 at high temperature, which has an oxygen-deficient structure (West, 1984). Therefore, bismuth-based ceramics have been developed widely.

The electrical properties of bismuth-based ceramics were investigated widely with different dopants. The properties concerned are thermally stable and high conductivity. These bismuth-based ceramics are applied in solid oxide fuel cells and oxygen sensor.

In addition, dielectric materials have been developed to apply in the high frequency and microwave telecommunication and satellite broadcasting. The concerned properties of the materials are thermally stable, dielectric constant and low dielectric loss. With these properties, the materials are considerable to develop as multilayer capacitors or microwave dielectric resonators which used widely in the telecommunication devices (Du *et al.*, 2002).

In order to reduce operating cost, bismuth-based dielectric ceramics are studied widely at low sintering temperature, which is lower than 1000 ˚C. With different values of dielectric constant and low dielectric loss of bismuth-based dielectric ceramics were applied in different devices.

With these good properties of bismuth-based dielectric materials, it can be studied with various materials to improve the performance in applications. Therefore, the studies of the characteristic of bismuth antimony oxide ceramics had been carried out in this research to investigate either is it suitable to be applied in the applications. Antimony oxide was chosen because the Sb^{3+} has a similar outer most orbital with Bi^{3+} ion, which could be an ionic oxide with high polarizability.

Other than that, there is focus on the development of chemically modified electrode recently. It is because of the limitation of current available working electrode like glassy carbon, GC in sensitivity and selectivity. With the chemically modified electrode, it was expected to have detection enhancement compare with GC electrode.

Ascorbic acid was chosen in this studies because of its important in antioxidant property which is essential for our human body. There are only few studies reported on using bismuth oxide as modified electrode in electrochemical studies. Therefore, it was used to modify the GC electrode for ascorbic acid detection with easier way of preparation, hence to improve its sensitivity of detection.

1.3 Objectives

The objectives of this study are:

1. To synthesize and determine the solid solution limit of $Bi_xSb_2O_\delta$ system.
2. To study the electrical properties of synthesized samples.
3. To prepare the chemically modified glassy carbon (GC) electrode with $Bi_2Sb_2O_8$ and study the electrochemical properties of electrode in the oxidation of ascorbic using cyclic voltammetry (CV) in various conditions such as supporting electrolyte, pH, temperature, scan rate and concentration of ascorbic acid.

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