UNIVERSITI PUTRA MALAYSIA

PREPARATION AND ELECTRICAL PROPERTIES OF BISMUTH TUNGSTATE SOLID ELECTROLYTES

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By

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

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February 2016

Chairman: Tan Yen Ping, PhD

Faculty: Science

Solid oxide fuel cells (SOFCs) are high efficiency power generators and operated at high temperature (1000 °C). Consequently, this high operating temperature may lead to many technological problems, such as material durability. Bismuth based electrolytes are able to perform higher ion conductivity than the current electrolytes (zirconia based) due to its intrinsic property (a quarter of oxygen sites for ions mobility). However, δ-Bi_2O_3 can exhibit high oxide ion conductivity at limited temperature range (730 °C to 825 °C). Introduction of WO_3 into Bi_2O_3 was conducted in an attempt to stabilize δ-Bi_2O_3 down to room temperature. Unfortunately, the produced WO_3 doped Bi_2O_3 materials with a general formula of (1-x)Bi_2O_3-xWO_3, ($0.22 \leq x \leq 0.255$), were unable to stabilize δ-Bi_2O_3. Eventually, these materials synthesized via conventional solid state method and mechanochemical method, respectively, were fully indexed on the tetragonal system with space group *I41*. Single phase material of $Bi_{6.24}W_{0.88}O_{12}$, can be obtained at lower temperature with shorter durations through mechanochemical method. The tetragonal structure, $Bi_{6.24}W_{0.88}O_{12}$, synthesised through mechanochemical method was obtained at 650 °C for 24 hours, while the conventional solid state method synthesized material required a higher temperature (700 °C) for longer duration (48 hours) to obtain a pure phase material.

It must be highlighted that $Bi_{6.24}W_{0.88}O_{12}$ did not undergo decomposition under the studied temperature range (room temperature to 910 °C) based on the XRD patterns from thermal stability experiment and data from thermogravimetric analysis (TGA). This behavior clearly indicated that $Bi_{6.24}W_{0.88}O_{12}$ was a high stability material. Three vibration bands (ν(W-O-W), Bi-O and ν (W-O)) were noticed in spectra of Fourier-transform infrared (FT-IR) spectroscopy. Scanning Electron Microscopy (SEM) micrographs for pellets sintered at 900 °C illustrated greater grain size compared to pellets sintered at 700 °C. It was inferred that resistance of material could be reduced. X-ray Fluorescence (XRF) analysis recorded data with percentage of error below 5 %,

hence, this validated that compositions material and gave a confidence of the current work results.

$Bi_{6.24}W_{0.88}O_{12}$ exhibited the best ionic conductivity among other solid solutions of (1-x)Bi_2O_3-xWO_3, ($0.22 \leq x \leq 0.255$). $Bi_{6.24}W_{0.88}O_{12}$ fabricated by mechanochemical method demonstrated the highest conductivity of 2.25 x 10^{-2} $ohm^{-1}cm^{-1}$ at 600 °C (average grain size of 12.46 μm to 48.16 μm) than conventional solid state route materials. It was also worthwhile to point out that a pure $Bi_{6.24}W_{0.88}O_{12}$ ion conducting solid electrolyte without any electronic conduction was produced with ionic conductivity of 6 orders higher than the reported YSZ at 600 °C, elucidating a greater potential of $Bi_{6.24}W_{0.88}O_{12}$ to be used as a material utilized in SOFC electrolytes applications.

Doping was carried out on the Bi or W sites in $Bi_{6.24}W_{0.88}O_{12}$ with selected dopants, including monovalent (Li^+), divalent (Ca^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+}), trivalent (Cr^{3+} and Y^{3+}), tetravalent (Sn^{4+}, Ti^{4+} and Zr^{4+}), pentavalent (Sb^{5+}, V^{5+}, Nb^{5+} and Ta^{5+}) and hexavalent (Mo^{6+}) cations in order to investigate their effects on the electrical properties of doped $Bi_{6.24}W_{0.88}O_{12}$ materials. All these dopants can be introduced into $Bi_{6.24}W_{0.88}O_{12}$ with rather limited solid solution ranges. Ion vacancy, ionic potential and unit cell parameters of structure are the main factors that varying the conductivity of the doped materials. $Bi_{6.24}W_{0.68}Nb_{0.20}O_{11.900}$ was developed and achieved the highest oxide ion conductivity (2.96 x 10^{-2} $ohm^{-1}cm^{-1}$ at 600 °C) among other cation dopants. This doped material was 32 % more conductive than the undoped material. Therefore, it is important to point that this doped material could elevated the performance of SOFC. Nb particles (tiny particle) were homogeneously distributed over the surface ceramic of $Bi_{6.24}W_{0.68}Nb_{0.20}O_{11.900}$ as illustrated in SEM image.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PENYEDIAAN DAN SIFAT ELEKTRIK BISMUT TUNGSTAN ELEKTROLIT PEPEJAL

Oleh

YUEN MEI LIAN

Februari 2016

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Sel bahan api pepejal oksida (SOFC) ialah penjana kuasa yang berkecekapan tinggi dan beroperasi pada suhu tinggi (1000 °C). Akibatnya, suhu operasi yang tinggi ini membawa banyak masalah teknologi, contohnya ketahanan bahan. Elektrolit berdasarkan bismut boleh melaksanakan kekonduksian ion yang lebih baik daripada elektrolit semasa (berdasarkan zirkonia) disebabkan oleh sifat intrinsiknya (satu suku ruang oksigen untuk pergerakan ion). Namun demikian, δ-Bi_2O_3 dapat menunjukkan kekonduksian ion yang tinggi pada julat suhu terhad (730 °C ke 825 °C). Pengenalan WO_3 ke dalam Bi_2O_3 dilakukan dengan tujuan untuk menstabilkan δ-Bi_2O_3 hingga ke suhu bilik. Malangnya, bahan WO_3 terdop Bi_2O_3 dengan formula umum (1-x)Bi_2O_3-xWO_3, ($0.22 \leq x \leq 0.255$), yang terhasil ini gagal menstabilkan δ-Bi_2O_3. Akhirnya, bahan tersebut yang disintesiskan dengan tindak balas keadaan pepejal secara konvensional dan mekanokimia secara berasingan, dapat diindekskan pada sistem tetragonal dengan kumpulan ruang *I41*. Bahan berfasa tunggal bagi $Bi_{6.24}W_{0.88}O_{12}$, boleh diperoleh pada suhu yang lebih rendah dengan masa yang lebih singkat yang disintesiskan melalui tindak balas mekanokimia. Struktur tetragonal, $Bi_{6.24}W_{0.88}O_{12}$, yang disintesiskan melalui tindak balas mekanokimia dapat diperolehi pada 650 °C selama 24 jam, manakala bahan bagi tindak balas keadaan pepejal secara konvensional memerlukan lebih tinggi suhu (700 °C) dengan lebih panjang tempoh (48 jam) untuk mendapatkan bahan berfasa tunggal.

Dengan ini, dapat menegaskan bahawa $Bi_{6.24}W_{0.88}O_{12}$ tidak mengalami sebarang penguraian di bawah julat suhu yang dikaji (suhu bilik ke 910 °C) berdasarkan corak XRD daripada eksperimen kestabilan haba dan data daripada from analisis termogravimetri (TGA). Sifat ini jelas menunjukkan bahawa $Bi_{6.24}W_{0.88}O_{12}$ adalah bahan yang berkestabilan tinggi. Tiga jalur getaran (ν(W-O-W), Bi-O and ν (W-O)) dapat diperhatikan dalam spektra spektroskopi inframerah transformasi Fourier (FT-IR). Mikrograf imbasan elektron mikroskopi (SEM) bagi pelet disinter pada suhu 900 °C mempamerkan butiran yang bersaiz besar berbanding dengan pelet disinter pada

suhu 700 °C. Ini boleh dikatakan rintangan bahan dapat dikurangkan. Analisis pendarfluor X-ray (XRF) mencatat data dengan peratusan ralat di bawah 5 %, jadi, ini mengesahkan bahan komposisi dan memberikan satu keyakinan terhadap keputusan kerja ini.

$Bi_{6.24}W_{0.88}O_{12}$ mempamerkan kekonduksian ionik terbaik di kalangan larutan pepejal bagi $(1\text{-}x)Bi_2O_3\text{-}xWO_3$, $(0.22 \leq x \leq 0.255)$. $Bi_{6.24}W_{0.88}O_{12}$ yang diperbuat melalui tindak balas mekanokimia menunjukkan kekonduksian paling tinggi dengan 2.25×10^{-2} $ohm^{-1}cm^{-1}$ pada 600 °C (saiz purata bijirin adalah 12.46 μm ke 48.16 μm) daripada bahan tindak balas keadaan pepejal secara konvensional. Dengan ini adalah berbaloi menunjukkan $Bi_{6.24}W_{0.88}O_{12}$ elektrolit pepejal ionik tulen tanpa kekonduksian elektronik dihasilkan dengan konduksi ionik sebanyak 6 kali lebih tinggi daripada YSZ yang dilaporkan pada 600 °C, menjelaskan $Bi_{6.24}W_{0.88}O_{12}$ berpotensi agung apabila bahan ini digunakan dalam SOFC sebagai elektrolit.

Pendopan dijalankan pada tapak Bi atau W bagi $Bi_{6.24}W_{0.88}O_{12}$ dengan dopan yang terpilih, termasuk kation monovalen (Li^+), divalen (Ca^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+}), trivalen (Cr^{3+} and Y^{3+}), tetravalen (Sn^{4+}, Ti^{4+} and Zr^{4+}), pentavalen (Sb^{5+}, V^{5+}, Nb^{5+} and Ta^{5+}) and heksavalen (Mo^{6+}) bagi mengkaji kesan pendopan pada sifat elektrik pada bahan terdop $Bi_{6.24}W_{0.88}O_{12}$. Semua dopan yang diperkenalkan ke dalam $Bi_{6.24}W_{0.88}O_{12}$ mempunyai julat larutan pepejal terhad. Kekosongan ion, keupayaan ionik dan parameter sel unit struktur merupakan faktor utama yang mempelbagaikan kekonduksian bagi bahan terdop. $Bi_{6.24}W_{0.68}Nb_{0.20}O_{11.900}$ dihasilkan dan mencapai kekonduksian ion yang tertinggi (2.96×10^{-2} ohm^{-1} cm^{-1} pada 600 °C) di kalangan bahan dopan kation. Bahan terdop ini adalah 32 % lebih mengkonduksi daripada bahan tidak terdop. Oleh itu, ini adalah penting mengatakan bahawa bahan terdop ini boleh menaikkan prestasi SOFC. Zarah Nb (zarah kecil) adalah bertaburan secara homogen pada permukaan seramik seperti yang digambarkan di imej SEM.

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I certify that a Thesis Examination Committee has met on 23 February 2016 to conduct the final examination of Yuen Mei Lian on her thesis entitled "Preparation and Electrical Properties of Bismuth Tungstate Solid Electrolytes" 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 Doctor of Philosophy.

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

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Signature: _____
Name of Member of Supervisory Committee: Tan Kar Ban, PhD

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AC	alternating current
dc	direct current
FT-IR	Fourier-transform infrared spectroscopy
ICSD	international centre for diffraction data
SEM	scanning electron microscopy
TGA	thermogravimetry analysis
XRD	X-ray Diffraction
C	capacitance
C_b	bulk capacitance
C_o	vacuum capacitance
C_{dl}	double layer capacitance
C_{gb}	grain boundary capacitance
d	d-spacing
E_a	activation energy
eV	electron volt
f	frequency
h, k, l	miller indices
I	current
k	Boltzmann's constant
K	kelvin
l	thickness
M*	complex electric modulus
M'	real part of electric modulus
M"	imaginary part of electric modulus

R	resistance
R_b	bulk resistance
R_{gb}	grain boundary resistance
RC	resistor-capacitor
T	temperature
V	voltage
Z	impedance
Z*	complex impedance
Z’	real part of impedance
Z”	imaginary part of impedance
Ω	ohm
ρ	resistivity
ε*	complex permittivity
ε_r	relative permittivity
tan δ	dielectric loss
ω	angular frequency
λ	wavelength

CHAPTER 1

INTRODUCTION

1.1 Electroceramics

Ceramic materials can be divided into traditional ceramics and advanced ceramics. In the early civilizations, traditional ceramics are pottery, structural clay products, clay-based refractories, cements, concretes and glasses. Recent year, attention is focused on advanced ceramics, which refer to the ceramics for electrical, magnetic, electronic and optical applications (functional ceramics) and structural ceramics at ambient and elevated temperatures. Traditionally, high electrical resistance ceramic materials are utilized for electrical insulation. In modern days, oxides and oxide compounds employed in the ceramic technology possess high electrical conductivity, either ionic or electronic (Moulson and Herbert, 2003; Rahaman, 2003).

The foundations of electroceramics are the science of ceramic processing, chemistry and solid state physics with its products find applications in diverse fields. Electroceramics is a trans-disciplinary, both in fundamentals and applications aspects. Dielectric ceramics are referred to those linear and non-linear dielectrics. In contrast, conductive ceramics consists of super-conductors, conductors and semiconductors (including ionically and electronically conductive ceramics). In addition, magnetic ceramics and optical ceramics are electroceramics material too (Setter, 2001).

Electroceramics are high technology materials whose properties and applications depend on the close control of structure, composition, ceramic texture, type of dopants and dopant (or defect) distribution. Some ceramics, like 'fast-ion conductors', which could conduct electricity well and predominantly by the transport of ions, thus they contribute crucial roles in fuel cell and sensor technologies. They are present as integral components of the circuit used in computers, signal processing, telecommunications, power transmission and power control technologies due to their wide range of properties such as polarisation, mechanical and optical responses, which may be controlled through composition, chemical substitution, doping and fabrication conditions There are a few examples of the development in electroceramics technology, include ferroelectric research and development, alumina developments for thick-film microelectronics in oxide ceramics and high thermal conductivity ceramics for integrated circuit packaging (Steele, 1991; Levinson, 1987). Table 1.1 lists out some examples of electroceramics.

Table 1.1: Examples of electroceramics

Materials	Properties	Applications
BaTiO-based	High dielectric permittivity	Small plate capacitors, tube capacitors and multilayer capacitors (MLCs)
$Pb(Ti, Zr)O_3$	Piezoelectric	Sensors, actuators, ultrasonic transducer and electro-acoustic
n-doped semiconducting $BaTiO_3$	grain boundaries barrier controlled, positive temperature coefficient (PTC) of the resistivity	self-controlled electrical heating systems
ZrO_2	Ionic conductor	Electrochemical oxygen sensors in cars and high-temperature solid oxide fuel cells (SOFCs)
ZnO	strongly non-linear current-voltage behavior	Overvoltage protection varistors
YBa_2CuO_7	high-temperature superconducting ceramics	power applications as high-voltage energy transmission cables and magnetic energy storage

1.2 Solid Oxide Electrolyte

1.2.1 Overview

Electrical conduction occurs by the long range diffusion of either electrons or ions. Predominant one charge carrier (electron or ion) causes the conduction to occur in a material. Meanwhile, in certain organic materials, mix charge carrier conduction of ionic and electronic is significant.

Solid electrolytes, fast ion conductors and superionic conductors refer to one set of ions that can move easily. They show high conductivity in the absence of a significant electronic contribution. Such materials often have rather special crystal structures with open tunnels or layers through which the mobile ions may move. The conductivity values, example 10^{-3} ohm^{-1} cm^{-1} for Na^+ ion migration in β–alumina at (25 °C) is comparable to those observed for strong liquid electrolytes. It is now apparent from both theoretical and experimental results on a wide variety of materials that ionic conductivities of 0.1 ohm^{-1} cm^{-1} to 10.0 ohm^{-1} cm^{-1} are the maximum that are likely to be obtained for any material. These values are obtained when a large proportion of the ions move at any one time.

Most crystalline materials have low ionic conductivities because the atoms or ion

vibrate at their lattice sites and cannot move freely, escape from their lattice sites. For example, NaCl is an insulator at room temperature (conductivity around 10^{-15} ohm^{-1} cm^{-1}). This phenomenon does not observe for solid electrolytes materials, where cations or anions are free to move throughout the whole structure. Consequently, they are intermediate between normal crystalline solids and liquid electrolytes. Figure 1.1 depicts solid electrolytes as intermediate between normal crystalline solids and liquids. Figure 1.2 shows the electrical conductivities of several common substances.

Solid electrolytes have conductivities that fall between those of a typical semiconductor, silicon and a typical aqueous electrolyte, sodium chloride. They are stable only at high temperatures. Otherwise, they may undergo a phase transition to a polymorph with a low ionic conductivity on cooling. For example, AgI is poor conductor at 25 °C. However, its structure changes to polymorph, α-AgI (phase transition), which has mobile Ag^+ ions on heating, lead to conductivity increases.

There has been many potential applications of solid electrolytes, include fuel cells, sensors, electrochromic materials for both optical display and 'smart window' devices, low-cost electrolysis of water and selective atomic filters. Oxygen detectors for automotive pollution-control systems employ solid O^{2-} conductors and solid-state batteries using Li^+ conducting solid electrolytes are the devices of solid electrolytes.

1.2.2 Conduction Mechanism

In ionic crystal, the individual lattice atoms transfer electrons between each other to form positively charged cations (donate electrons) and negatively charged anions (accept electrons). This strong natural binding force between cations and anions is known as electrostatic. The conductivity of ionic crystals is about twenty two orders of magnitude smaller than the conductivity of typical metallic conductors at room temperature. This could be attributed to the wide band-gap in insulators that allows few electrons to excite from the valance into the conduction bands (Hummel, 1992).

During ionic conduction, ions are charge carriers because the cations or anions are free to move throughout the structure. There are two requirements must be fulfilling either in order for ions to move freely: (i) some lattice sites must be vacant to allow the adjacent ions to hop into the vacancies and leaving their own sites vacant, or (ii) available interstitial sites for ions in interstitial sites hop into the adjacent interstitial sites.

Besides, sufficient energy to pass over an energy barrier is required in order for ions to move through a crystalline solid. Thus, ionic conduction is easier at higher temperatures as ions vibrate more vigorously and defect concentrations are higher. A highly polarized anion framework is needed for significant ionic conduction. Some factors that must be satisfied in order to obtain high ionic conductivity of ceramics are high density of mobile ions, the availability of vacant sites that can be accessed by the

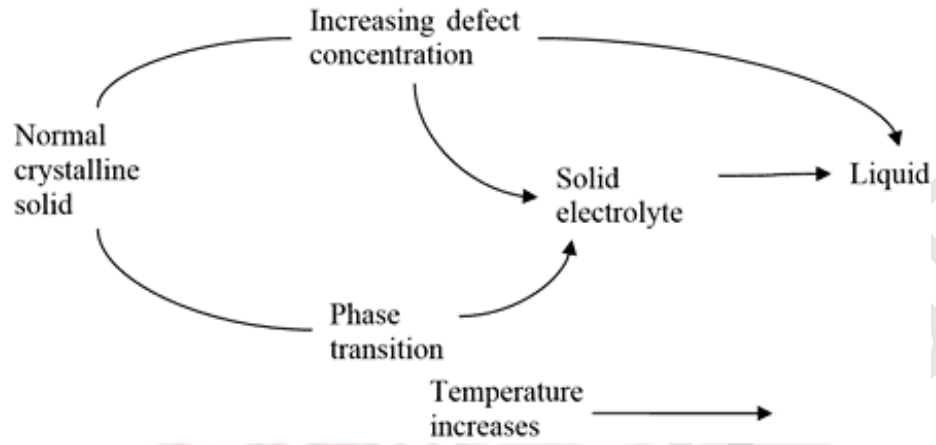

Figure 1.1: Solid electrolytes as intermediate between normal crystalline solids and liquids (West, 1999)

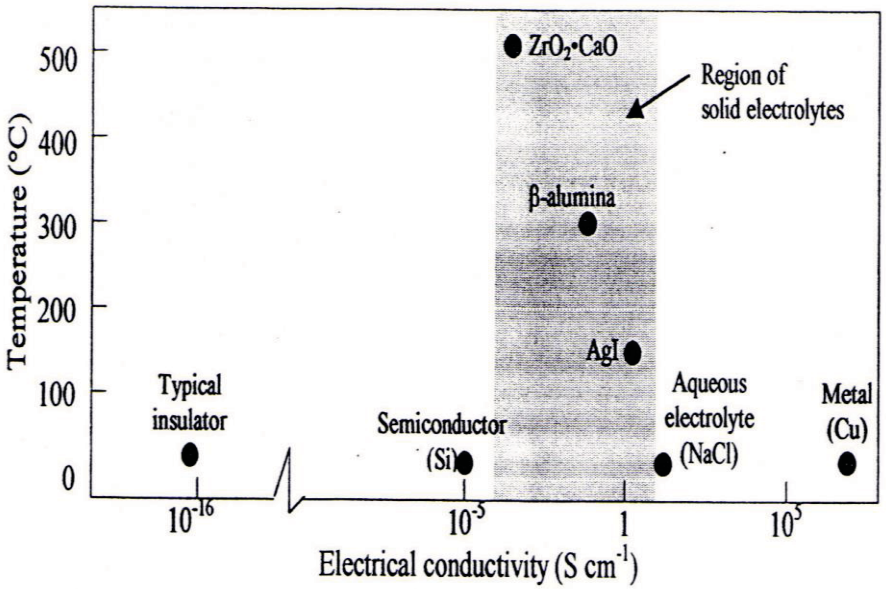

Figure 1.2: Electrical conductivities of selected common substances and representative solid electrolytes (Greenblatt, 1994)

mobile ions and good connectivity among the sites (requiring conduction channels with low free energy (E_a) barriers between the sites).

For any material and charge carrier, the specific conductivity, σ, is given by

$$\sigma = \sum_i n_i e_i \mu_i \quad (1.1)$$

For ionic conductivity, σ,

$$\sigma = N_{ion} e \mu_{ion} \quad (1.2)$$

where N_{ion} is the number of ions which can change their positions under the influence of an electric field, e is elementary charge and μ_{ion} is the mobility of ions.

Arrhenius law shows the correlation between the conductivity and temperature (Corumle et al., 2015). It can be represented by the formula:

$$\sigma = \sigma_o \text{ exponential } (-Ea/kT) \quad (1.3)$$

where σ is oxygen ion conductivity, σ_o is the pre-exponential factor, E_a is the apparent activation energy for oxygen migration, k is the Boltzmann constant and T is the absolute temperature (K).

Oxide ion conductors are ionic conductors as advanced ceramic materials in which oxide ions (anions) act as charge carriers. They are very useful for a number of electrochemical devices, including solid oxide fuel cells (SOFCs) and oxygen sensors.

1.2.3 Application

1.2.3.1 Solid Oxide Fuel Cells (SOFC)

Fuel cells are electrochemical energy conversion devices that generate electricity and heat by converting the chemical energy of fuels without combustion as an intermediate step. It converts gaseous fuels (hydrogen, natural gas and gasified coal) via an electrochemical process directly into electricity. This direct use of hydrocarbon fuels greatly decreases the complexity and cost of the fuel cell system. It does not produce significant amounts of pollutants compared with internal combustion engines. It is environmentally friendly operation, low noise, high efficient and compact in the generation of electricity through chemistry instead of combustion.

Fuel cells and batteries can be connected together in series to produce higher voltages. However, a battery is an energy storage device that stores its fuel internally and that can only supply a fixed amount of energy. In contrast, fuel cell does not need to be recharged and generates electricity as long as fuel and water are supplied externally. Fuel cell has no fixed capacity and can accept almost all kind of fuel, including natural gas, coal gas, gaseous fuels from biomass and liquid fuels (Badwal and Foger, 1995).

Generally, there are four types of fuel cells – solid oxide, proton exchange membrane, molten carbonate and alkaline. Solid oxide fuel cells (SOFCs) are the most attractive because they have the highest efficiencies and the potential of using many fuels, including gasoline and diesel, without expensive external reformers that create more volatile chemicals compare to any conventional fuel cell design. It is significant to environmental benefits. It can operate at high temperatures, producing high-grade exhaust, which can be recovered and used for other applications, such as space heating and cooling, and generating extra electricity by spinning a gas turbine linked to the unit.

As a power generator, it can convert more than 55 % of the energy in its fuel source to electricity. Its efficiency is much higher than that of conventional coal plants (efficiencies around 34 %). When the high-quality exhaust from the electrochemical process is used, overall efficiencies of a SOFC could reach 85 % (Badwal and Foger, 1995).

Besides, solid oxide fuel cells have a wide variety of applications from use as auxiliary power units in vehicles to stationary power generation with outputs from 100 W to 2 MW. A compact SOFC system can supply a maximum power of 64 kW for driving and that the system efficiency is 3 to 4 times higher than an internal combustion engine system. During the past few years, developments in ceramics for solid oxide fuel cells in lowering of the operating temperature from 1000°C to 800°C with improved conductivity characteristics, has been achieved by reducing the thickness and polarisation losses over the cell interfaces, allowing better electrochemical performance (Arespacochaga *et al.*, 2015; Mahato *et al.*, 2015).

SOFCs are made from solid state materials, namely ceramic oxides. Figure 1.3 reveals SOFC consists of three components: a cathode, an anode and an electrolyte (sandwiched between cathode and anode). A dense electrolyte is favourable as a good ion conducting characteristics and low electronic conductivity. Charge carriers in the electrolyte are oxygen species. The electrolyte is a nonporous ceramic material with ion conducting oxide.

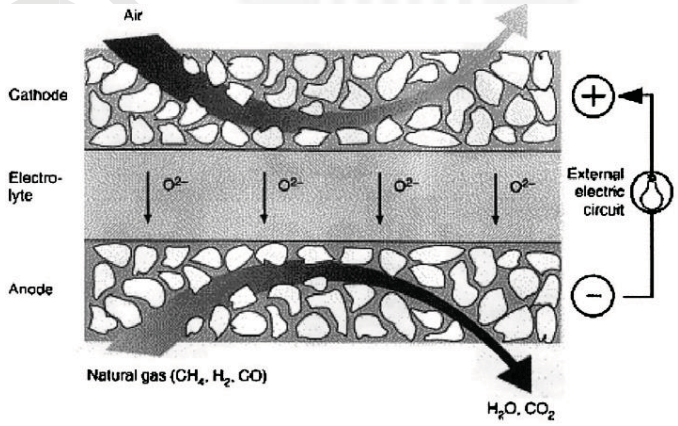

Figure 1.3: Schematic of a ceramic fuel cell or solid oxide fuel cell (SOFC) (Huijsmans, 2001)

At cathode, oxygen (from air) accepts electrons from external circuit and is reduced to negatively charged oxygen ions (O^{2-}). These ions travel through the solid electrolyte to the anode, where they react with fuel at the anode. The fuel is oxidized by the oxygen ions and releases electrons to an external circuit, thereby producing electricity. In other words, electrochemical reduction of oxygen occurs at the cathode and the oxygen passes through the electrolyte membrane via a vacancy mechanism to the anode. At the anode, electrochemical oxidation of hydrogen occurs, where the hydrogen is provided from directly reformed natural gas or other hydrocarbons. The solid electrolyte conducts these ions between the electrodes, thus maintaining overall electrical charge balance and the flow of electrons in the external circuit provides useful power.

Fuel cell stack is the connection of several single cells in series using electrical interconnections to achieve higher voltages. Traditionally, the SOFC electrolyte is yttrium-stabilised zirconia (YSZ) at the extremely high operation temperature (around 1000 °C) over the years because of its oxide ion concentration and its chemical stability in reducing and oxidising atmospheres. This high operating temperature is a major problem which accelerates the degradation of cell components as well as limit choices of cell components. Therefore, the increment cost in fabrication of cell components is unavoidable.

New electrolytes with higher oxygen conductivity and negligible electrical conductivity that could be applied in the SOFC with lower operation temperature compare to YSZ are required in order to reduce materials costs and improve chemical and mechanical stability of the ceramics (Shao *et al.*, 2012; Pelosato *et al.*, 2015).

1.2.3.2 Oxygen Sensor

In solid electrolytes, the conductivity of a solid electrolyte due to the mobility of oxygen ion, O^{2-}, is very low at room temperature and comparable to that of an aqueous electrolyte when temperatures achieve above 600 °C. If the operation temperature is not too high or the oxygen partial pressure is not too low, the conductivity due to the electron mobility can be neglected and pure oxygen ion conduction is assumed. This property is utilized in oxygen concentration cells containing solid electrolytes for the measurement of oxygen partial pressures in gas mixtures or concentrations of gases in liquids.

Oxygen sensors apply in automobiles to control the combustion for the internal combustion engine (air/fuel ratio). However, The main concern of such sensors as oxygen concentration cell are thermal resistance requirement under the exposure to the high temperature exhaust gas up to 1000 °C, gas tightness against the exhaust gas pressure and intensity warranty to endure mechanical shocks. Yttrium stabilize zirconia is currently selected as sensor due to the electrical conduction, mechanical toughness and easily obtainable.

Figure 1.4 depicts the operation principle for oxygen sensor. An oxygen concentration

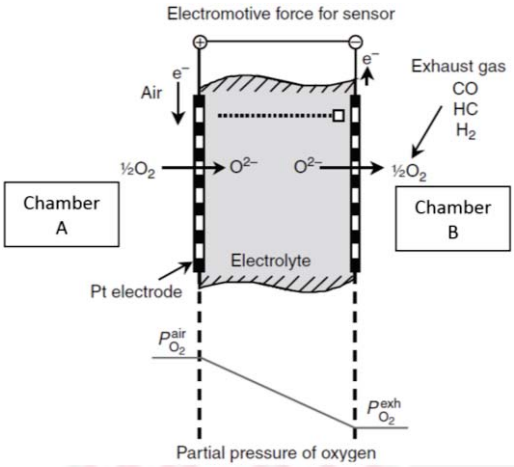

Figure 1.4: The operation principle for oxygen sensor (Yamada, T. 2003)

cell can be constructed by separating two gas chambers (chamber A and B) by an oxygen ion conducting solid electrolyte. Along the border of the solid electrolyte wall, oxide ion is transferred in a direction that reduces the difference of oxygen partial pressure between chamber A and chamber B. Electromotive force is generated and measured. This is known as an oxygen concentration cell. The output will be related to the logarithm of the ratio of the partial pressures of oxygen at each of the electrodes as given by the Nernst equation:

$$\text{Electromotive force} = (RT/4F) \ln (P_a/P_b) \quad (1.4)$$

where R is the gas constant, T is absolute temperature, F is Faraday constant, P_a is oxygen partial pressure in the high oxygen concentration chamber A (oxygen partial pressure in the ambient air/reference material) and P_b is oxygen partial pressure in the low oxygen concentration chamber B (oxygen partial pressure in the exhaust gas/sample). Consequently, when a non-combusting mixture of known oxygen concentration is used as reference (air), the partial pressure of oxygen in the gas mixture of the sample may be determined.

1.3 Solid Solutions

A solid solution is a crystalline phase that can have variable compositions. Simple solid solutions are divided into two types in doped crystals, which are substitutional solid solutions and interstitial solid solutions.

In substitutional solid solutions, the atom or ion that is being introduced directly replaces an atom or ion of the same charge (homovalent) in the parent structure. There are a few requirements to be fulfilled for a range of simple substitutional solid solutions to form. First, the atom or ion must be the same charge as mentioned above. Second, the ions that replace each other must be fairly similar in size. A difference of 15 per

cent in the radii of the metal atoms that replace each other is the most that can be tolerated for the formation of a substantial range of solid solutions.

In non-metallic systems solid solutions, the limit is above than 15 per cent, but it is difficult to quantify this in term of the sizes of the ions and the formation of the solid solutions is very temperature dependent. Consequently, formation of extensive solid solutions often needs high temperatures, whereby the formation of solid solutions at lower temperatures may be more restricted or hardly exist. Ions with similar size may substitute for each other easily and extensive solid solutions that are stable at all temperatures may be formed. For ions that differ in size by 15 to 20 per cent, solid solutions will be formed at high temperatures and with the ionic size differs by more than around 30 per cent, solid solutions are not expected to form. The crystal structure of the two end members of a solid solution is an important factor to consider in the formation of solid solutions. If a complete solid solution series is formed, the end members must be isostructural but conversely, if two phases are isostructural, it is not necessary that a complete solid solution series is formed. Generally, it is common to have partial or limited ranges of solid solutions (West, 1999)

For the formation of interstitial solid solutions, the introduced species occupies a site that is normally empty and no ions or atoms are left out in the formation of interstitial solid solutions. This type of substitution is generally observed in metals in which small atoms such as H, C and N enter empty interstitial sites within the host metal structure.

Besides the simple solid solutions discussed above, there are more complex solid solution formation mechanisms which involved heterovalent or aliovalent substitution (ions are substituted by other ions of different charges). Thus, additional changes involving creation of vacancies or interstitials (ionic compensation) or electrons or holes (electronic compensation) are needed.

For ionic compensation, substitution host cations with higher valence species results in creation of cation vacancies or interstitial anions. Meanwhile, anion vacancies or interstitial cations are created when lower valence species substitute for host cations in a crystal. Thus, cation or anion vacancies can be created to preserve electro-neutrality. Alternatively, interstitial can be created. However, this mechanism is not common because most structures do not have interstitial sites large enough to accommodate extra cations or anions (West, 1999).

There is also another type of substitution called double substitution in which two substitutions take place simultaneously to give solid solutions. The substituting ions may be of difference charge, as long as the overall electro-neutrality is preserved. The mechanism for formation of solid solutions in many metal containing materials and especially in those that have mixed valency involves electronic compensation. This yields products which are semiconducting or metallic, or superconducting at low temperatures. Some examples of this mechanism are generation of cation vacancies by deintercalation, creation of mixed valency cations with insertion of interstitial anions into the structure and creation of interstitial cations of one element and mixed valency

cations of another element which arises from intercalation. This type of phenomena is seen in electrode materials such as $LiMn_2O_4$, $LiCo_2O_4$, $LiWO_3$ and superconductor such as $YBa_2Cu_3O_\delta$ (West, 1999).

1.4 Problem Statements

Fabrication of fuel cells is costly. This is because the currently used electrolyte, yttria-stabilized zirconia (YSZ), only could demonstrates high ionic conductivity at high operating temperature (around 1000 °C) in fuel cell. Durability is another limitation as fuel cell might suffer after the cell repeatedly heats up to high operating temperature and then cools down to room temperature. Moreover, solid oxide systems may have issues with material corrosion, materials aging, undesirable chemical reaction between cell components (like electrolyte, electrodes, and interconnecting material) and precious of the cell components (like platinum) is needed in order to withstand such high operating temperature. In short, precise detailed knowledge of fuel cell electrochemical operations is the main goal that should be obtained in purpose to solve these fuel cell challenges (Mahato *et al.*, 2015).

δ-Bi_2O_3 exhibits higher ionic conductivity than zirconia based electrolytes. However, it has low melting point (824 °C) and can only exist in a narrow stability range (between 730 °C to 825 °C) (Niu *et al.*, 2011). Bi^{3+} in the compounds can be reduced to metallic Bi state in a reducing atmosphere at high temperature (oxygen pressure less than 10^{-7} Pa at 670 °C) (Katayama *et al.*, 2011).Therefore, this unstable of thermodynamic phase change of Bi_2O_3-based materials is a disadvantages for the application as SOFC electrolyte (Lin and Wei, 2011).

Bismuth based tungsten oxide materials with a general formula of $(1-x)Bi_2O_3$-xWO_3, ($0.220 \leq x \leq 0.255$), were studied. WO_3 was chosen as dopant in this present work to introduce into Bi_2O_3. The introduction of more oxygen atoms by doping with high charge valence, W^{6+}, is believed could suppress the phase transition which cause by the present of oxygen vacancies in Bi_2O_3 structure. Two synthesis methods, conventional solid state and mechanochemical method, were selected to evaluate their suitability in synthesizing the desired single phase material at the best synthesis condition (lower temperature and shorter duration). The outcome is believed could provide a useful guideline, specifically for large scale of ceramic production in industrial.

There are few targets of the present work. A material that can present a higher stability at different temperatures with varying oxygen partial pressure and changes of atmospheres is desired as a solid electrolyte in SOFC. In other words, this material does not undergo decomposition to other phase or degradation of ionic conductivity under any conditions in a wide range of temperature (room temperature to 1000 °C). In addition, it will be excellent if a pure oxide ion electrolyte is produced which demonstrates higher ionic conductivity than the current electrolyte (YSZ) at comparable temperature. Therefore, this can accelerate the performance of a fuel cell.

Recent progress in chemical doping is another option to modify the behaviour of a material, specifically the electrical property. Generally, amount of oxide ion vacancy is correlated well with variations in conductivity of doped materials. It is worthy to mention that such phenomenon may or may not be the only one significant criteria in determining the electrical behaviour of a material. Ionic potential cation and unit cell parameters are two other factors that do play a role in determining the variation of electrical conductivity in a material.

1.5 Objectives

The objectives of this study are:

1. To prepare $(1-x)Bi_2O_3$-xWO_3, $(0.220 \leq x \leq 0.255)$, via conventional solid state and mechanochemical methods.

2. To characterize the single phase materials using X-ray powder diffraction (XRD), thermogravimetry analysis (TGA), scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FT-IR) and X-ray fluorescence (XRF) spectroscopy.

3. To study the electrical properties of single phase materials using AC impedance spectroscopy.

4. To prepare and characterize chemically doped materials in $Bi_{6.24}W_{0.88}O_{12}$ by using monovalent (Li^{+}), divalent (Ca^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+}), trivalent (Cr^{3+} and Y^{3+}), tetravalent (Sn^{4+}, Ti^{4+} and Zr^{4+}), pentavalent (Sb^{5+}, V^{5+}, Nb^{5+} and Ta^{5+}) and hexavalent (Mo^{6+}) cations.

5. To correlate electrical properties of prepared materials and other parameters, such as composition and structure.

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