

**DIELECTRIC PROPERTIES AND ELECTRICAL  
CONDUCTIVITY OF TERNARY ZINC  
MAGNESIUM PHOSPHATE GLASS-DERIVED  
HYDROGEL**

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# **Dielectric Properties and Electrical Conductivity of Ternary Zinc Magnesium Phosphate Glass-Derived Hydrogel**

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## LIST OF ABBREVIATIONS

A	Ampere
Å	Angstrom
B <sub>2</sub> O <sub>3</sub>	Boric oxide
BaO	Barium oxide
BO	Bridging oxygen
cm	Centimeter
C	Celcius
CaO	Calcium oxide
CaCO <sub>3</sub>	Calcium carbonate
CO <sub>2</sub>	Carbon dioxide
CV	Cyclic voltammetry
C <sub>sp</sub>	Specific capacitance
C <sub>d</sub>	Discharged capacitance
DW	Distilled water
EDLC	Electric double layer capacitor
EDX	Energy dispersive X-ray
ESR	Equivalent circuit resistance
F	Farad
FS	Field strength
FTIR	Fourier transform infrared
g	Gram
Hz	Hertz
i.e	Example

IR	Infrared
J	Joule
KBr	Pottassium bromide
K <sub>2</sub> CO <sub>3</sub>	Pottassium carbonate
Li <sub>2</sub> O	Lithium oxide
mA	Miliampere
mF	Milifarad
mJ	MiliJoule
mV	Milivolt
mW	Miliwatt
MAS-NMR	Magic Angle Spinning-Nuclear magnetic resonance
M-O	Metal-oxygen
nm	Nanometre
Na <sub>2</sub> O	Sodium oxide
NBO	Non-bridging oxygen
PbO	Lead (II) oxide
P-O-M	Phosphorus-oxygen-metal
R	Resistance
s	Second
S	Siemen
SiO <sub>2</sub>	Silicate
UV	Ultraviolet
V	Volt
W	Watt
XRD	X-ray diffraction

## LIST OF SYMBOLS

$\vartheta$	Theta
$^{\circ}$	Degree
%	Percent
$\rho$	Density (kg/m <sup>3</sup> )
$\varepsilon'$	Dielectric constant
$\varepsilon''$	Dielectric loss factor
$\sigma$	Conductivity (S/cm)
$f$	Frequency (Hz)
$\omega$	Angular frequency (Hz)
$\Omega$	Resistance (Ohm)

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## Sifat Dielektrik Dan Kekonduksian Elektrik Bagi Kaca Hidrogel Berasal Dari Pertigaan Zink Magnesium Fosfat

### ABSTRAK

Kebocoran dan rintangan permukaan adalah masalah utama yang dihadapi oleh elektrolit berbentuk cecair dan pepejal. Di dalam penyelidikan ini, kaca hidrogel berasal dari pertigaan kaca fosfat dicadangkan sebagai elektrolit dengan kekonduksian proton yang tinggi mungkin boleh mengatasi masalah dan diaplikasikan dalam peranti penyimpanan kuasa. Sebelum proses hidrasi, satu siri kaca hidrogel berasal dari pertigaan zink magnesium fosfat dengan komposisi  $(\text{ZnO})_{30}(\text{MgO})_x(\text{P}_2\text{O}_5)_{70-x}$  dengan  $x = 5, 8, 10, 13, 15, 18,$  dan  $20$  mol % disediakan dengan teknik lindap kejut. Semua sampel kaca disahkan dalam keadaan amorfus oleh Analisis Belauan Sinar-X (XRD). Serbuk kaca dari setiap sampel kaca berjaya berubah kepada produk hidrogel melalui proses hidrasi selepas ditindakbalas dengan air suling dengan nisbah campuran 1:0.5 dan 1:1. Pengukuran ketumpatan, isipadu molar, dan Spektroskopi Inframerah (FTIR) telah digunakan untuk mencirikan sifat fizikal kaca pepejal dan kaca menjadi hidrogel. Keputusan kedua-dua ketumpatan dan isipadu molar dikaitkan dengan rangkaian pempolimeran. Spektra IR untuk kaca pepejal dan hidrogel diukur dalam had nombor gelombang antara  $650 \text{ cm}^{-1}$  sehingga  $4000 \text{ cm}^{-1}$  pada suhu bilik. Adalah didapati bahawa kumpulan serapan fosforus-oksigen-besi (P-O-M) yang hadir dalam struktur debu kaca hilang dalam struktur hidrogel akibat proses hidrasi. Walaubagaimana pun, kation dwivalens mungkin hadir pada rantai fosfat melalui pengkelatan. Sifat dielektrik sampel hidrogel dicirikan oleh analisis impedans dalam julat frekuensi 4 Hz ke 1 MHz. Adalah didapati bahawa sampel hidrogel CZ05 (1:1) mempunyai nilai pemalar dielektrik, kehilangan dielektrik dan kekonduksian elektrik yang tertinggi antara sampel dikaji. Ini mungkin kerana pergerakan cas yang pantas dan mendorong lebih banyak kehilangan tenaga. Hukum kuasa semesta dipadankan dengan spektrum kekonduksian untuk mengekstrak nilai kuasa eksponen  $s$  untuk kesemua sampel. Nilai eksponen  $s$  yang lebih kecil daripada 0.5 menunjukkan sampel hidrogel untuk kedua-dua nisbah campuran 1:0.5 and 1:1 mempunyai laluan kekonduksian berdimensi rendah. Semibulatan pada plot impedan kompleks menunjukkan pengecasan dwilapisan manakala pada frekuensi yang rendah memberi maksud ciri-ciri impedan Warburg. Ujian kitaran voltametri memperlihatkan bentuk hampir segi empat tepat menandakan perilaku kapasiti oleh hidrogel yang diselidiki. Walaupun hidrogel stabil pada tettingkap elektrokimia yang sempit  $\sim 0.35 \text{ V}$ , namun kapasiti spesifik maksimum yang diperoleh adalah  $62 \text{ mF/cm}^2$  oleh sampel hidrogel CZ05 (1:1). Kesemua sampel hidrogel juga dicirikan oleh teknik kronopotentiometri untuk menyiasat perilaku cas dan nyahcas. Hasil kajian menunjukkan sampel hidrogel CZ05 (1:1) menghasilkan tenaga spesifik,  $1.550 \text{ mJ/cm}^2$  dan kuasa spesifik,  $0.865 \text{ mW/cm}^2$  pada ketumpatan arus yang selari,  $0.10 \text{ mA/cm}^2$ . Antara semua sampel yang diuji, didapati bahawa sampel hidrogel CZ05 (1:1) mempunyai sifat terbaik. Sampel ini berpotensi untuk diaplikasikan sebagai elektrolit terkemuka dalam peranti penyimpanan kuasa.



## Dielectric Properties and Electrical Conductivity of Ternary Zinc Magnesium Phosphate Glass-Derived Hydrogel

### ABSTRACT

Leakage problem and contact resistance are the major problems for liquid electrolyte and solid-state electrolyte, respectively. In this research, a highly viscous ternary phosphate glass-derived hydrogel was proposed as high proton-conducting electrolyte that may overcome the problems and applicable to power storage devices. Before hydration, a series of ternary zinc magnesium phosphate glasses having the composition  $(\text{ZnO})_{30}(\text{MgO})_x(\text{P}_2\text{O}_5)_{70-x}$  with  $x = 5, 8, 10, 13, 15, 18,$  and  $20$  mole % were prepared by melt quenching technique. All the samples were confirmed in amorphous phase by X-ray diffraction (XRD) analysis. Glass powder from each glass samples were successfully transformed into hydrogel product via hydration after reaction with distilled water (DW) with ratio mixture 1:0.5 and 1:1. Density, molar volume and Fourier Transform Infrared (FTIR) spectroscopic measurement have been used to characterize the physical properties of solid glass and glass-derived hydrogel. Result of both density and molar volume was correlated with network polymerization. IR spectra of solid glass and hydrogel were measured in the wavenumber range of  $650\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$  at ambient temperature. It was found that the absorption band of phosphorus-oxygen-metal (P-O-M) bonding which present in glass powder structure disappeared in the hydrogel structure due to hydration process. However, the divalent cations may attach to phosphate chain by chelation. The dielectric properties of the hydrogel samples were characterized by impedance analyzer in frequency range of 4 Hz to 1 MHz. It was revealed that CZ05 (1:1) hydrogel sample has highest dielectric constant, dielectric loss and electrical conductivity values among studied samples. This may due to rapid charges mobility and induce more energy losses. Universal power law was applied on fitting to extract the values of power law exponent  $s$  for all the samples from the conductivity spectra. The values  $s$  was smaller than 0.5 revealed that hydrogel samples for both ratio mixture 1:0.5 and 1:1 have low dimensional conduction pathway. Semicircle on the complex impedance plots indicating charging of double layer while at low frequencies imparting Warburg impedance characteristics. Cyclic voltammetric test shows a nearly rectangular shape, which signifies the capacitive behavior of the investigated hydrogel. Even though the hydrogel was stable at narrow electrochemical window  $\sim 0.35\text{ V}$ , the maximum specific capacitance obtained was  $62\text{ mF/cm}^2$  for CZ05 (1:1) hydrogel sample. All the hydrogel samples were also subjected to chronopotentiometric technique to investigate the charge and discharge behavior. The results showed that CZ05 (1:1) hydrogel sample obtained higher specific energy,  $1.550\text{ mJ/cm}^2$  and specific power of  $0.865\text{ mW/cm}^2$  at constant current density of  $0.1\text{ mA/cm}^2$ . Among the studied samples, it was found that CZ05 (1:1) hydrogel sample has the best properties. This sample has potential to be applied as a novel electrolyte in the power storage devices.

# CHAPTER 1

## INTRODUCTION

### 1.1 Research Background

Glasses are disordered amorphous materials with non-periodic arrangements of atoms. Their unique nature has led to the development of many research works in a wide range of technological application such as in medical, engineering, household products, optical, building and construction.

There exist many types of glasses around the world. In large industrial plants, silicate glass is always being used for variety of application by the processing of melt in open air (Shelby, 2005). Other types of inorganic oxides which can readily form a glass without addition of other compound are phosphate and borate glasses. Nowadays, phosphate glasses are becoming an important materials compared to others because they generally have higher thermal expansion coefficient, low melting and softening temperature, higher electrical conductivity and good UV-transmitting materials (Pascuta et al., 2010; Massera et al., 2013). It also has structural versatility where it can accept several cations or anions exchange and hence tailor interest properties for specific technological application (Khor et al., 2009). Recently, there is a founding that this solid phosphate glasses react with water to form a viscous glass-derived hydrogel with higher proton conductivity (Akamatsu et al., 2005). Their high-performance properties have received considerable interest in electrical field. Thus, they may found applications as possible electrolytes in electrochemical devices such as batteries, fuel cells, electrochromic displays, supercapacitors and sensors (Kasuga, 2010).

In addition, energy storage has received a great attention due to application of devices in everyday social and modern usage especially for portable product such as cell

phone and laptop. Development of safer, smaller, and longer lasting energy storage is in demand. Thus far, fast ion conducting materials are important types of electrolyte that could be used to accomplish this need (Christensen, 2012).

Commonly, fast ion conductors or electrolyte may be produced either in liquid or solid type to meet their technological applications. Ionic liquid electrolyte generally represent as aqueous solutions, organic liquid or molten salts. Among all kind of ionic liquid electrolyte, aqueous solution is the most conventional and typical electrolyte (Ito & Nohira, 2000). Although they possess a unique combination of properties, there are quite a few disadvantages when using liquid electrolyte in the devices. Like container filled with liquid, this electrolyte can leak and may corrode the devices. This ultimately decreases the lifespan of the devices (Maharaj, 2012). Moreover, liquid electrolyte is suitable to be used at room temperature only as the boiling point of the organic solvent used limits their thermal stability (Pandey & Hashmi, 2013). Normally, the devices using this electrolyte types may not be portable as it is bulky (Asmara et al., 2011).

Due to concern on the safety issues, further work in overcoming the problems possessed by the liquid electrolyte was conducted. Replacing ionic liquid with solid electrolyte brought a new perspective in building up a better electrolyte performance with safer design. Nafion is among the possible solid electrolyte which has been produced. Nevertheless, this solid electrolyte has not been widely used in energy storage devices due to high cost as well as their unstable properties (Akamatsu et al., 2005). Despite minimizing the size of the devices with higher energy, solid electrolytes are not compatible with all types of electrodes and may suffer high interfacial resistance (Maharaj, 2012). Even though solid electrolyte does not leak, they may crack after a long usage.

Due to the difficulty possess by electrolyte in both liquid and solid forms, a great attention should be pay for hydrogel electrolyte as a new type of electrolyte. Thus, the research and development of phosphate glass-derived hydrogel as fast ion conducting material as an electrolyte is very useful since it possesses excellent processing ability and design flexibility.

## **1.2 Problem Statement**

Phosphate glass is a good dielectric and fast ion conducting material. Addition of zinc and magnesium oxide has been found able to modify the glass structural network and hence improving the glass properties. Ternary zinc magnesium phosphate glass has considerable potential for application as an electrolyte. However, electrolyte in solid form may develop contact resistance meanwhile liquid electrolyte may experience leakage to the system. Therefore, to overcome this shortcoming, the present study developed ternary zinc magnesium phosphate glass-derived hydrogel formulation that has higher proton conductivity. Hence, it will improve efficiency of their performance and may have possibilities for the preparation as a novel electrolyte.

## **1.3 Objective of the study**

The main research objectives of this project are:

1. To fabricate ternary zinc magnesium phosphate glass-derived hydrogel with different magnesium oxide and water content.
2. To analyze the effect of magnesium oxide and water content on the physical properties and structural changes of ternary zinc magnesium phosphate glass of solid glasses and glass-derived hydrogel forms.

3. To analyze the effect of magnesium oxide and water content on the dielectric properties and electrical conductivity of ternary zinc magnesium phosphate glass-derived hydrogel.
4. To investigate the capacitive behaviour and charge-discharge performance of ternary zinc magnesium phosphate glass-derived hydrogel with different magnesium oxide and water content.

#### **1.4 Scope of the study**

In this study, the type of glass is focused on the phosphate glasses with ternary system where the constituents used are zinc oxide, magnesium oxide and phosphoric (v) oxide. The composition of the magnesium oxide in phosphate glass was varied into several series to study the effects of the addition of alkaline earth oxides on the glasses structure and their hydrogelation ability. Besides, the volume of water added to the ternary zinc magnesium phosphate glasses was divided into four ratios (1:0.5, 1:1, 1:1.5 and 1:2) to examine which ratio will form the hydrogel product. Then, several analysis were carry out on the chosen formulation to observe different properties of ternary zinc magnesium phosphate glass-derived hydrogel.

The amorphous natures of prepared samples were analyzed by means of X-ray diffraction measurement (XRD), using powder form. Diffraction patterns were collected in the 2-theta ( $2\theta$ ) range from  $10^\circ$  to  $80^\circ$ , in steps of  $0.02^\circ$  and scan rate  $5^\circ/\text{min}$ .

The IR spectra of ternary zinc magnesium phosphate glass powders were employed by using KBr pellet technique. Meanwhile, the IR absorption spectra of a ternary zinc magnesium phosphate glass-derived hydrogel samples were obtained by placing the hydrogel on the sample holder for mounting in the IR spectrophotometer. All the IR spectra were recorded using a Fourier Transform Infrared Perkin Elmer

spectrometer over the range of wavenumber  $650\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$  at room temperature.

The dielectric properties and electrical conductivity of ternary zinc magnesium phosphate glass-derived hydrogel was measured using impedance analyzer (Hioki IM-3570) with the frequency ranging from 4 Hz to 1 MHz at room temperature.

Meanwhile, the capacitive property of ternary zinc magnesium phosphate glass derived-hydrogel was determined by cyclic voltammetry. The measurement was carried out at three different scan rates (1 mV/s, 25 mV/s and 50 mV/s) in the potential window of 0.35 V up to 100 cycles.

Lastly, the chronopotentiometry was used to determine the specific energy and specific power of ternary zinc magnesium phosphate glass-derived hydrogel. All samples were scan under switching potential of -0.1 V to 0.1 V at different current densities ( $0.10\text{ mA/cm}^2$ ,  $0.25\text{ mA/cm}^2$ , and  $0.50\text{ mA/cm}^2$ ).

## **1.5 Outline of the dissertation**

This dissertation is organized into five chapters. Chapter 1 provides a brief description on the phosphate glasses derived hydrogel, their novel application in electrical field and a brief introduction to this thesis work. General information on materials and the mechanism involved in this work are presented in Chapter 2. Chapter 3 discusses in detail a procedure of samples preparation and the relevant experimental techniques applied in this work. Meanwhile, Chapter 4 discusses the results of the experimental conducted with a detailed explanation. Lastly, Chapter 5 concludes the dissertation with the summary of the presented work and suggestions for future work. At the end of this dissertation, appendices part appears with the additional data, calculations, and relevant publication and award involving this work.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Electrolyte

Electrolyte is any substances that contain free ions which are responsible to conduct electricity (Maharaj, 2012). In general, it may exist in molten state, solid state or aqueous solutions. The main function of electrolyte in energy storage system is to provide a transport medium for ions to travel from one electrode to another electrode. It also acts as a physical barrier between the electrodes to prevent short circuit (Eriksson, 2001).

##### 2.1.1 Classification of electrolyte

Electrolyte can be classified into four types according to their structure and physical properties:

- (1) Frame work crystalline/ polycrystalline materials
- (2) Amorphous glassy electrolytes
- (3) Composite or dispersed phase electrolytes
- (4) Polymer electrolyte

The above classifications refer to their phase structure which it is either ordered or disordered materials. Among these four types of electrolytes, only frame work crystalline materials has ordered phase. Meanwhile, the phase structure of amorphous glassy, polymer and composites electrolytes are arranged in disordered patterns (Agrawal & Gupta, 1999).

## 2.2 Hydrogel

Over the years, researchers have defined hydrogel in many different ways. The most common definition is materials that have ability to swell in the water and can absorb great quantity of water within their structures (Illic-Stojanovic et al., 2013). Another definition is that it is cross-linked materials which absorb large quantities of water without dissolving (Ahmed, 2013). According to Nguyen & Lee (2010), the functionality and the quality of the hydrogel properties depended on their swelling behavior and cross-linked structures. The softness, smartness, and the capacity to store water make hydrogel a great interest to the scientists in discovering their unique property.

The hydrogel is neither completely liquid nor completely solid. As a solvent, water is absorb by hydrophilic functional groups attached to the network backbone of hydrogel structure and allows free diffusion of some solute molecules. Meanwhile, their resistance to dissolution is due to hydrophobic functional groups which cross-links between network chains and connect to each other to form one big molecule (Ahmed, 2013). These half liquid-like and solid-like properties gives a hydrogel its structure, elasticity, stickiness, degree of flexibility and many interesting relaxation behaviors that are not found in either a pure solid or liquid state (Ahmed, 2013). They may exhibit drastic volume changes in response to specific external stimuli such as temperature, solvent quality, pH, and electric field (Dusek & Patterson, 1968; Tanaka, 1978). Interesting behavior of hydrogel received considerable interest in the last three decades and large parts of work have been collected in different reviews (Gerlatch & Arndt, 2009).