

**UNIVERSITI TEKNOLOGI MARA**

**CHARACTERIZATION OF  
ZnO/MnO<sub>2</sub>-DOPED Li<sub>2</sub>CO<sub>3</sub>-LiI  
BINARY SOLID ELECTROLYTE  
FOR LITHIUM ION PRIMARY CELL**

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## ABSTRACT

The continuity in all-solid-state lithium ion battery development is very important considering the growing demand for a reliable and safety improved energy storage device. In this work, a solid state electrolyte composed of  $\text{Li}_2\text{CO}_3$  and  $\text{LiI}$  was successfully prepared using mechanical milling method followed by low sintering process. The optimized sintering condition of the solid electrolyte was at  $60^\circ\text{C}$  for 24 hours. From the measurement, the  $x\text{Li}_2\text{CO}_3\text{-yLiI}$  ( $x = 80$ ,  $y = 20$ ) solid electrolyte displayed the highest electrical conductivity of  $1.03 \times 10^{-3} \text{ Scm}^{-1}$  at room temperature. The dissociation of  $\text{LiI}$  has provided supplemental charge carriers for ions transport in the solid, which much higher than that of the pure  $\text{Li}_2\text{CO}_3$  sample. A noteworthy increase of ionic conductivity up to  $1.75 \times 10^{-3} \text{ Scm}^{-1}$  was observed at room temperature with the presence of  $\text{ZnO}$  filler. The enhancement in electrical conductivity could be due to the interaction between ionic species and Lewis acid-base group on the filler surface and hence, improve the dissociation rate of ions in solid. Incorporation of 9 wt.%  $\text{MnO}_2$  has successfully amplified the overall conductivity of the sample ( $3.87 \times 10^{-1} \text{ Scm}^{-1}$ ) by increasing the available charge carrier concentration and newly established percolation network for the migration of ions. The interactions between ions and filler's surface groups were also responsible for conductivity enhancement in solid by providing coordination sites for ions transport process. FTIR has revealed the complexation between binary electrolytes and oxide fillers. This could be ascribed to the shift of metal-oxygen absorption band in the samples. Additionally, the increase in absorption intensity of metal-iodine (Li-I) peak signified the increment of charge carrier concentration as a function of fillers. The analysis by XRD technique has confirmed the structural transformation in the solid based on the formation of new peaks and also peak splitting phenomena. The ceramic filler addition has resulted in structural modification of solid in order to accommodate more ions. Subsequently, the increase in defect formations was expected and higher migration rates of ions via Frenkel and Schottky defect were possible. The temperature-dependent analysis demonstrates that the  $\text{Li}_2\text{CO}_3\text{-LiI}$ ,  $\text{Li}_2\text{CO}_3\text{-LiI-ZnO}$  and  $\text{Li}_2\text{CO}_3\text{-LiI-MnO}_2$  samples follow Arrhenius behavior. This was explained by the linear function of conductivity towards temperature suggesting that the systems were thermally activated. Meanwhile, the activation energy was found to be inversely proportional to the total conductivity of the samples. The discharge characteristic of the lithium battery has showed a discharge capacity of  $165 \mu\text{Ah}$  with stable discharge plateau of 4 hours at discharge rate of  $10 \mu\text{A}$ . The incorporation of  $\text{ZnO}$  filler has prolonged the stability of discharge plateau up to 5 hours with discharge capacity of  $234 \mu\text{Ah}$ . The total discharge period was extended from 16 to 23 hours with the presence of  $\text{ZnO}$  filler. Meanwhile, a total discharge period of 25 hours with capacity of  $255 \mu\text{Ah}$  signified that the incorporation of  $\text{MnO}_2$  filler has significantly improved the electrochemical stability of the cell. Additions of ceramic fillers have effectively enhanced the stability of electrochemical cell while providing an additional coordination sites for migration of ions in solid.

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# CHAPTER ONE

## INTRODUCTION

### 1.1 BACKGROUND OF STUDY

Batteries are important for a wide range of applications, including portable electronic devices, automotive thrust and load-levelling for electricity generated from alternating renewable sources. The rapid development of popular devices such as smart phone, wearable devices and smartcard has stimulated the development of flexible batteries that are able to be mounted into these devices with sufficient power output. Among currently popular batteries, lithium ion battery is considered as the most promising cell since its invention by Sony Corporation in 1991 (Gabrielli, Marinaro, Mancini, Axmann, & Mehrens, 2017; Terada et al., 2001). Nowadays, lithium ion battery is one of the main focuses of research with the aim of further improving their mechanical and electrical properties. In order to achieve these goals, considerable efforts have been directed by researchers in improving the performances of lithium ion battery.

In the past decades, energy storage devices such as batteries and capacitors have majorly been powered by liquid electrolyte. However, owing to some of their intrinsic characteristic including thermal stability issues, dendrites growth on interface, poor cycling performance and low ion transport number, it has been impossible to simultaneously attain high energy density in any of the recent popular electrochemical devices (Armand & Tarascon, 2008; Scrosati & Garche, 2010). Therefore, the all-solid-state battery has been recommended and developed as a promising candidate among storage devices for tackling both high energy and power density. Solid state batteries offer the advantage of good thermal stability, wide electrochemical window, high power density and improved safety compared to the conventional liquid electrolytes (Knauth, 2009; Thangadurai & Weppner, 2005). Besides, all-solid-state batteries also demonstrate practically small self-discharge compared to the commonly known energy storage such as capacitors. Technically, solid electrolytes possess high ionic conductivity with good chemical and mechanical stability that do not simply react with the anode or cathode materials of the cell. All-