CHAPTER 1

INTRODUCTION TO THE THESIS

1.1 Research Background

Nowadays, the demand for safer and more efficient electrochemical devices has increased due to the growing interest in electronic devices and electric vehicles. Currently, liquid electrolytes are widely used in commercial devices. However, this type of electrolyte tends to make some devices bulky and heavy, thus lowering the specific energy and specific power densities of these devices (Yap, 2012). Besides, the use of liquid electrolyte also bears the high risk of leakage and can cause corrosion during packaging (Osman, Ghazali, Othman, & Isa, 2012). Due to these drawbacks, solid polymer electrolyte (SPE) is a good candidate to replace liquid electrolyte.

Ion conducting polymer electrolytes have become an interesting area in solid state ionics due to their prospective application in solid state electrochemical devices (Tamilselvi & Hema, 2014). Fenton, Parker, and Wright (as cited in Noor, Ahmad, Rahman, & Talib, 2010) were the first to report on polyethylene oxide (PEO)-inorganic salts complexes as SPEs. Later, Armand, Chabagno, and Duclot (as cited in Schaefer et al., 2012) proved the possibility of PEO-alkali metal salt complexes as commercial electrolytes. Since then many polymers have been investigated, mostly synthetic polymers like polyvinyl alcohol (PVA) (Noor, Majid, & Arof, 2013), polyvinyl chloride (PVC) (Subban & Arof, 2004), polyvinyl pyrrolidone (PVP) (Ravi, Kumar, Mohan, &
Rao, 2014) and poly ε-caprolactone (PCL) (Woo, Majid, & Arof, 2011a, 2011b, 2012, 2013). The works are mainly focused on the improvement in ionic conductivity and mechanical strength, as well as chemical, thermal and electrochemical stabilities of polymer electrolytes to realize their potential application in electrochemical devices (Ramesh, Winie, & Arof, 2007; Sim, Majid, & Arof, 2014).

Natural polymers are worth to be investigated due to their natural abundance, low price and environmentally friendly nature (Noor et al., 2012). These polymers are usually used in the pharmaceutical (Ogaji, Nep, & Audu-Peter, 2011; Kulkarni, Butte, & Rathod, 2012), food (Alp, Mutlu, & Mutlu, 2000; Wang, Yang, Brenner, Kikuzaki, & Nishinari, 2014) and biomedical (Mahoney, Mccullough, Sankar, & Bhattachar, 2012) applications. Natural polymers can also be used to prepare SPEs (Aziz, Abidin, & Arof, 2010a, 2010b; Majid & Arof, 2005). Natural polymers are able to be processed as membranes or films with excellent transparency (Noor et al., 2012).

The choice of polymer blend as an electrolyte host is due to the fact that polymer blending is one of the effective techniques to optimize the ionic conductivity (Buraidah & Arof, 2011; Reddy, Kumar, Rao, & Chu, 2006; Xi et al., 2006). Polymer blends have become commercially and technologically more important than the fabrication of homopolymers and copolymers because blending allows one to create a new material with specific properties for the desired application at a low cost (Tamilselvi & Hema, 2014). In this work, the blend of corn starch and chitosan is chosen as the polymer host. Report by Xu, Kim, Hanna, and Nag (2005) suggested that starch and chitosan are compatible and can interact with each other. Starch-chitosan blend has been extensively studied for tissue engineering (Nakamatsu, Torres, Troncoso, Min-Lin, & Boccaccini, 2006),
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biomedical (Baran, Mano, & Reis, 2004) and food packaging (Tripathi et al., 2008) applications.

Ionic source is one of the main constituents in an electrolyte because of its strong influence on the electrolyte’s properties such as conductivity, amorphousness and thermal stability. Alkali metal salts, inorganic acids and ammonium salts are widely used for preparation of SPEs as reported in the literature. Among the alkali metal salts, lithium is the most preferred for polymer electrolyte studies due to the small size of lithium ion (Li$^+$) which provides high gravimetric Coulombic density (Johansson, 1998). Besides, lithium ion conducting electrolytes have a wide potential window (Ghosh, Wang, & Kofinas, 2010). However, due to the safety issue associated with lithium battery, attention has been given to proton conducting electrolytes to serve as electrolyte in device application.

1.2  Objectives of the Present Work

The objectives of this work are as follow:

1. To develop proton conducting starch-chitosan blend based polymer electrolytes by solution cast technique.

2. To characterize the samples using electrochemical impedance spectroscopy (EIS) to identify the highest conducting electrolyte. Further characterization using various techniques will be done to strengthen the EIS results.

3. To optimize the conductivity by adding glycerol as plasticizer.

4. To fabricate and to test an electrochemical double layer capacitor (EDLC) employing the optimized conducting electrolyte.
5. To fabricate and to test proton batteries employing the optimized conducting electrolyte.

1.3 Scope of the Thesis

This thesis is divided into ten chapters. In Chapter 2, a general introduction and literature review on electrolytes, polymers, polymer blend, plasticization, EDLC and proton battery will be discussed. The details of electrolytes preparation and characterization techniques will be the main focus in Chapter 3. The electrochemical devices fabrication and characterization are also presented in this chapter.

Since starch-chitosan blend host is used in this work, the most suitable ratio of the blend to be chosen as the polymer host will be determined. This is because the amorphousness of the polymer host is a crucial factor for ion conduction (Kadir, Aspanut, Yahya, & Arof, 2011; Kadir, Majid, & Arof, 2010). Thus, Chapter 4 will present the X-ray diffraction (XRD) studies on different ratios of starch-chitosan blend to determine the most amorphous blend, thereby selecting the polymer host.

Chapter 5 discusses the interaction of polymer-polymer, polymer-salt, polymer-plasticizer, salt-plasticizer and polymer-salt-plasticizer, resulted from Fourier transform infrared (FTIR) spectroscopy studies. These are necessary as these interactions can affect the ionic conductivity and conductivity mechanism of the ions (Yap, 2012). The conductivity of the electrolytes will be described in detail in Chapter 6. Further in this chapter, transport analysis as well as XRD, scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) results
will be discussed to strengthen the conductivity result. The other electrical properties of
the electrolytes such as dielectric and conduction mechanism will be described in detail
in Chapter 7.

The highest conducting electrolyte in this work will be chosen for fabrication of
an EDLC and proton batteries. The characteristics of the devices are presented in
Chapter 8. Chapter 9 discusses the overall results presented in this thesis and finally
Chapter 10 summarizes the thesis with some suggestions for further works.