CHAPTER 1

INTRODUCTION

1.1 CHAPTER OVERVIEW

This chapter introduces the basic aspects about the materials used in this study and background for the energy storage properties of the materials. Motivation of the research, problem statement, research objectives and scope of work are also presented in this chapter.

1.2 BACKGROUND AND MOTIVATIONS

Electrochemical capacitors (ECs) are also known as ultracapacitors or supercapacitors. It can be classified into two main categories based on energy storage mechanism, pseudocapacitors (PCs) and electrochemical double–layer capacitors (EDLCs). PCs store electrical energy faradically by electron charge transfer between electrode and electrolyte. Metal oxides and conducting polymers are used as electrode materials for PCs. In EDLCs, a double layer of electrolyte ions is formed on the surface of an electrode material, which arises from the potential–dependence of the surface density of charges stored electrostatically. The electrode materials for EDLCs include all carbon–based materials. Supercapacitors could be used in many applications because of their higher energy output as compared to conventional capacitors and higher power than batteries, in addition to their miniature size. Various types of electrode materials can be used in supercapacitors, including carbon–based materials, conducting polymers and metal oxides. In addition, the electrolyte could be an aqueous, organic or an ionic liquid. In case of an aqueous electrolyte, the operating voltage is limited to 1 V (due to the electrochemical decomposition of water at 1.23 V), whereas an organic electrolyte can achieve a voltage range of 2.5 to 3.5 V (Syzdek et al., 2014). A higher voltage of up to 4.0 V can be achieved for the ionic liquid. Supercapacitors have many advantages, for example, long life cycles, fast charging time, low impedance and high energy and power density, environmental friendly, and also can be operated in a wide temperature range. This study aims to investigate different materials for supercapacitor applications with high power and long life criteria for better energy storage devices. The energy storage properties are directly depending on the structure and morphology of the electrode materials.

In recent years, manganese dioxide (MnO_2) has drawn increasing attention for supercapacitors application, mainly due to the high abundancy of manganese (Jang et al., 2012) that contributes to low material cost as compared to the expensive ruthenium metal. Pang et al. reported high specific capacitance (C_s) (700 F g^{-1}) for MnO_2 thin films in year 2000 and their findings had sparked strong interest among energy research community for its application in supercapacitor electrode (Pang and Anderson, 2000, Pang et al., 2000). Such high capacitance value arises from the ions insertion/desertion within MnO_2 structure and it depends crucially on the particle size, surface area and porosity. Since then, in achieving optimized condition for the aforementioned properties, MnO_2 with different morphologies have been developed, such as nanoflakes (Chou et al., 2006), nanorods (Yousefi et al., 2012a), nanowires (Yousefi et al., 2013), nanopetals (Yang et al., 2012) and nanosheets (Yan et al., 2012). The synthesis route plays a vital role in determining its morphology. The most common synthesis route for MnO_2 is chemical coprecipitation method (Deng et al., 2013, Jiang et al., 2009) involving dissolved Mn^{4+} precursor. However, instability of Mn^{4+} precursor in the aqueous solution as well as the contact resistance between synthesized MnO_2 and current collectors have hindered its wider use in electrochemical applications (Xu et al., 2008, Prasad and Miura, 2004).

Electrochemical deposition is proven to be an effective method to prepare MnO_2 nanostructures (Hu et al., 2014, Yousefi et al., 2013).

On the other hand, carbon–based materials possessing high surface area as the electrode material, and the capacitive originates from the charge accumulation at the interface between electrode and electrolyte (Portet et al., 2005). Pseudocapacitors employ transition metal oxides or conductive polymers (Patil et al., 2013, Song et al., 2013, Xie et al., 2012) as the electrode material. Though the energy densities in pseudocapacitors are higher than that of EDLCs, the faradic reactions within pseudocapacitors could lead to phase changes and limit their life time (Compton and Nguyen, 2010). Graphene with its high surface area and nanosheets morphology and carbon nanoparticles with porous structure are a promising materials from energy storage applications.

1.3 PROBLEM STATEMENT

The need for the development of efficient energy storage systems is paramount in meeting the world's future energy targets, especially when the energy costs are on the increase in addition to the escalating demand. Energy storage technologies can improve efficiencies in supply systems by storing the energy when it is in excess, and then release it timely. Nowadays, batteries are slowly becoming obsolete due to their poor cycleability (limited to a few thousands) and long charge time (tens of minutes) in comparison to supercapacitors. On the other hand, supercapacitors have long life time and fast charging times (Vangari et al., 2013). Nowadays the research focus on developed suitable electrode materials which directly reflect in supercapacitor technology enhancement.

MnO_2 has been identified as a promising pseudocapacitive material to replace toxic and costly materials especially ruthenium oxide. Though manganese source can be found abundantly in nature, it is imperative to stop exploiting nature for the advancement of technology. Instead, recovery of manganese from waste sources could be an alternative to obtain MnO_2. According to United States Environmental Protection Agency (USEPA) analysis, an average of 8 disposable batteries are consumed by an individual annually.