

CHAPTER I INTRODUCTION

The disproportionate usage of fossil fuels in order to earn a living and meet energy requirements has grossly affected the globe, causing climatic change due to the dramatic increase in the CO₂ emission (i.e. Global warming). Hence, in order to decrease our current dependence on environmentally harmful fossil fuels, the society has to move toward pursuing sustainable and renewable resources. At the moment, researchers and academia have focused their attentions on renewable energy production from solar energy and wind energy, even though, these natural energies are subject to the climatic conditions. So, it is very imperative to devise a means of storing electricity when it is available and retrieving it when needed (Li & Wei, 2013).

Supercapacitors, also known as ultracapacitors (Hashim & Khair, 2011; Inagaki et al., 2014a) or power capacitors, store electrochemical energy by accumulating the charge from electric double layer, which is caused by electrostatic attraction. In this case, the capacity of the supercapacitor is proportional to the electrode surface, i.e., the electrochemically active surface, where, how much ions are attracted, (Gund et al., 2013; Jiang et al., 2013). Electrochemical Double Layer Capacitors (EDLCs) are possible to be fully charged and discharged in seconds. Although their energy density (about 5–10 Whkg⁻¹) is lower than in batteries or fuel cells, higher power density (10 Whkg⁻¹) can be reached in a short time (Choi et al., 2012). The most attractive advantage of EDLCs is a high power capability (Domingo-Garcia et al., 2010; Ayad et al., 2011; Snook et al., 2011) with the fast charge/discharge rate (Zheng et al., 2012; Choi et al., 2012). Moreover, most of the EDLCs are safer against short circuit than batteries in terms of the possibility of self-ignition. They do not contain any hazardous or toxic

materials (Aravinda et al., 2013a; Aravinda et al., 2013b) and have the durability during long charge-discharge cycle (CD) cycles.

Basically supercapacitors can be represented by two distinct mechanisms describing them: (i) EDLC and (ii) Pseudocapacitor. EDLCs store the charge electrostatically following a reversible adsorption–desorption cycles of electrolyte ions onto active electrode materials. These active materials might not only be electrochemically stable, but also have accessible large surface area and with no any Faradaic reaction at EDLC electrode. The surface storage mechanism allows very fast energy uptake and delivery, and better power performance. However, the physicochemical process and electrode polarization in EDLC are not enough to apply high energy devices. On the other hand, pseudocapacitors, undergoes reversible Faradaic reactions. Chemically modified carbon materials, (Inagaki, 2012; Inagaki et al., 2014b; Inagaki et al., 2014c; Inagaki et al., 2014d; Inagaki et al., 2014e), metal oxide, (Paul et al., 2012) and conducting polymers (Hsieh et al., 2012) are used as electrodes. In case of pseudocapacitors, the stability for CD cycling is relatively poor, though, their energy densities are relatively high compared to EDLCs. Furthermore, the response time is longer than EDLCs, because it takes longer time to move electrons during the redox reaction (Choi et al., 2012). Although supercapacitors can be regarded as “still evolving” into the area of ever more energy containing and powerful devices, they have since been able to address the increasing needs of electronic (cell phones, digital cameras, etc., industrial (uninterruptible power supplies, grid conditioning, windmills, cranes, etc.) (Wu et al., 2012) and in the sectors of transportation/automotive (trains, busses, cars) (Shi et al., 2013; Tran et al., 2013; Wu et al., 2013; Inagaki et al., 2014a). Although supercapacitors have higher capacity than batteries and capacitors, it may present disadvantage of high raw material cost and process difficulty. However the

application of thin film processes to the fabrication of the supercapacitors might overcome the above disadvantage. As a result, supercapacitors in thin film form (and using solid and flexible electrolyte) (Wang et al., 2013b) are gaining increasing interest in the field of lightweight, ultrathin energy management devices for wearable electronics (Dubal et al., 2012). So far most of the current supercapacitors uses liquid electrolyte which could have a side effect on the environment in terms of its hazards, corrosiveness, self-discharge, low density and even the housing of the cell after the sealing of the electrolyte could also be another issue (Wang et al., 2013c). Thus, this research focused on the cell fabrication from a solid polymer electrolytes made from a combination of two different types of polymer electrolytes namely; pure solid polymer electrolyte (PSPE) - using Polyvinyl Alcohol (PVA) and orthophosphoric acid (H_3PO_4) - and hybrid solid polymer electrolyte (HSPE) from a combination of PVA, H_3PO_4 and a filter paper, at different percentage ratio.

Although supercapacitors made from conducting polymers and transition metal oxide provide higher specific capacitance than electrochemical double layer capacitors (EDLCs), their poor rate capability, exorbitant costs and low conductivity, their academic and industrial usages become limited. The excellent chemical and physical properties of carbon materials such as high conductivity, relatively low cost, high surface area, excellent temperature stability, and good corrosion resistance make them valuable candidates for the electrodes of EDLCs, which holds true especially, for graphene and carbon nanotubes (CNTs), which possess the largest theoretical and experimental surface area (Wang et al., 2013a). Also, these CNTs, especially multiwalled CNTs (MWCNTs) have high inherent conductivity, flexibility, chemical and mechanical stability, and larger surface area polarizability (Paul et al., 2012), and can operate within the voltage window of 3 V or more. Furthermore, their predominant

exohedral surface favors the quick accumulation and transport of electrolyte ions so as to increase the performance of quick charge and discharge under high currents (Zheng et al., 2012). Functionalized CNTs are said to be stable for long-term storage, are soluble in aqueous solution, have low toxicity, while increasing more reactivity at their surface walls (Mittal, 2011). Most importantly, when CNTs are functionalized, their pore sizes will be widened up, thereby increasing the chances of ionic penetration at the electrode-electrolyte interface of fabricated supercapacitor (Van Hooijdonk et al., 2013).

In order to reduce the toxic effect to the environment and its inhabitants, two different types of functionalized MWCNTs (Carboxyl and Hydroxyl) were selected for the purpose of fabrication of the supercapacitor. In addition to aforementioned functionalized CNTs, Normal CNTs was also chosen for the fabrication. All the CNTs were obtained commercially. Despite the fact that, there are rapid advancements in supercapacitor fabrications amongst the researchers globally, to the best of this researcher's knowledge, this is the first time comparisons between a functionalized and non-functionalized types of CNTs are made in the fabrication of supercapacitor, and using varied percentage weights (50, 60 and 70 wt%) of cellulose (Hybrid) polymer electrolyte.

1.1 Research Objectives

The aims and objectives of this thesis, which had begun more than three years ago are:

- (a) To devise a means of understanding the ways of increasing the huge potential that supercapacitor possess; such as high power density, longer cycle life, environmental friendliness and energy storage device robustness.

- (b) To investigate the conductivity performances of two different types of polymer electrolytes namely; PSPE - using PVA and H_3PO_4 - and HSPE from the blends of PVA, H_3PO_4 and a cellulose filter paper, at a different percentage ratio so as to come up with the best formation that can be used as a separator in supercapacitor fabrications.
- (c) To fabricate and characterize supercapacitors from electrodes made from three commercially prepared multiwalled CNTs namely; Carboxyl, Hydroxyl and Normal CNTs using the polymer electrolytes with the highest conductivity obtained from (b) above, and make comparison on which among the selected electrode compositions deliver the most outstanding capacitance, energy and power densities.

1.2 Significant of the study

During the period of research which is presented herein, contributions has been made to first, design separators made from solid pure and solid hybrid electrolytes of different percentage ratios. These separators were designed from the blend of PVA and H_3PO_4 for pure solid polymer electrolyte; and PVA, H_3PO_4 with a cellulose (filter paper) for hybrid solid polymer electrolyte. Furthermore, supercapacitors were fabricated from three different types of commercially prepared MWCNTs namely, Carboxyl, Hydroxyl and Normal CNTs. The resulting cells exhibit high capacitance and reasonably lower internal resistance and most importantly, portable in handling compared to other types of capacitors especially made from activated carbon (AC) or those capacitors that uses liquid polymer electrolytes.

As mentioned above, one of the significance of this work is its uniqueness in the way it is conducted. Here is why, even though research on supercapacitor fabrication using CNTs and other material as electrode material received an overwhelming

breakthrough globally, to the best of this researchers knowledge, this is the first time a certain comparisons between a functionalized and non-functionalized types of CNTs are selected for the fabrication of supercapacitor, and using a varied (50, 60 and 70 wt%) cellulose (Hybrid) polymer electrolyte. For this reason, it is thought that this work will answer some questions as regards to the behavior of the capacitance of the capacitor, energy and power density using these types of CNTs and aqueous electrolytes of varying conductivities.

1.3 Limitation of the Study

This work is particularly limited to the fabrication of supercapacitors that were all commercially obtained. However, certain examinations such as field emission scanning electron microscope (FESEM) and Thermogravimetric analysis (TGA) and X-ray diffractometer (XRD) were carried out on the samples in order to re-validate their specifications outlined by the manufacturer. Although a general study on both PSPE and HSPE, the supercapacitor fabrication was limited to hybrid (PVA- H_3PO_4 -filter paper) type of the electrolyte with the highest conductivity only. This is because, in the course of obtaining the highest conductivity, adding up to 70 wt% of H_3PO_4 and 30 wt% PVA, though could form a film but is too flexible to be used as an electrolyte film in the supercapacitor fabrication. In this regard, it was suggested that, incorporating in the PVA a sort of support will make the mechanical strength of the electrolyte to improve remarkably thereby giving room for more weight percentage of acid to be accommodated and this could lead to a higher electrical conductivity of the polymer electrolyte. Hashim & Khiar (2011) used a cellulose to obtain an optimum electrolyte 70 wt% used for the fabrication of EDLC using activated carbon electrode. Hence, it was observed that, at the above optimum percentage concentrations, the highest conductivity of the electrolyte and its desired flexibility was reached.

1.4 Outline

This section will outline, the classification of electrical energy storage devices such as batteries and supercapacitors with respect to their primary characteristics will be presented. Chapter II will give a review of the previous literatures as regards to supercapacitor fabrication, CNTs and polymer electrolytes. The chapter reports some major contributions to the field of CNTs and supercapacitor fabrication based on the carbon nanotube and polymer electrolytes. Chapter III discusses the methodological procedures carried out in order to achieve the stated objectives. Hence the chapter will describe experimental steps taken to produce both electrolytes and electrode that would be used in the fabrication of the supercapacitor. Chapter IV will lay down all the results and discuss them accordingly. Therefore, in this chapter, the resulting fabrications and characterizations of commercially prepared Carboxyl MWCNTs (CPCMWCNTs), Hydroxyl MWCNTs (CPHMWCNTs) and Normal MWCNTs (CPNMWCNTs) using HSPE as separators will be discussed extensively. Chapter V will summarize the contributions of this research. Such contributions may include; the conductivity studies of the solid polymer electrolytes (both PSPE and HSPE) with reference to the percentage ratio of PVA and H_3PO_4 ; the fabrication of high power and energy densities supercapacitors from CPCMWCNTs, CPHMWCNTs, and CPNMWCNTs. Finally, chapter VI will discuss few recommendations that ought to be considered for future challenges.

1.5. Chapter Summary

In this chapter, an overview on the supercapacitor; its definition, a brief mechanism classification and principle of operation was introduced. The chapter also introduces the aims and objectives of carrying out this research, then it highlights the significant and some of the limitations of this study. In the next chapter, a general review of the related

literature detailing much on the principle of operation of the supercapacitor will be presented. It will further review the electrolyte and electrode (especially the CNTs) types used by previous researchers in the fabrication of the supercapacitor.

